Noble metal nanowires : synthetic control, morphology induced properties and application in electrochemical catalysis

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**NOBLE METAL NANOWIRES: SYNTHETIC CONTROL,
MORPHOLOGY INDUCED PROPERTIES AND
APPLICATION IN ELECTROCHEMICAL CATALYSIS**

SU DONGMENG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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APPLICATION IN ELECTROCHEMICAL CATALYSIS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2019

Supervisor: Professor Chen Hongyu (no longer in NTU)
Professor Zhao Yanli
Associate Professor Liu Bin

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Abstract

This thesis mostly summarizes the synthetic modification on vertically standing gold nanowire (Au NW) arrays, the alternative substrates to grow Au NW on, the morphology induced catalytic properties, and application brought by these properties. The research focused on synthesis, morphology, property and application of ultrathin Au NW. We started our research on vertically standing ultrathin Au NW by exploring alternative substrate to expand the application range, investigating modified preparation method to achieve more facile synthesis, exhibiting a greatly enhanced operation durability which correlated with morphology and finally proposing a hypothesis regarding mechanistic understanding behind the greatly enhanced durability.

Exploration on alternative metal substrate for preparation of substrate bounded Au NW was discussed in chapter 2. We attempted to tackle with the galvanic replacement problem by approaches like changing surface function group using different silanes, increasing the concentration of thiol ligand used in the Au NW growth step, screening for the proper thiol ligand that might form a layer for capping the metal surface to inhibit galvanic reaction without interfering Au NW growth, adding a ligand or blocker solution pre-treatment procedure before Au NW growth, performing a prior galvanic replacement reaction to consume the surface metal, and finally creating a layer of oxidized surface metal to inhibit the galvanic reaction. Approach that aimed for enhancing the gold reduction rate were also investigated using different reducing agent and increasing the reducing capability by adding sodium hydroxide. Finally, we succeeded in grow bundles of ultrathin Au NW on to the micro-sized dilute dispersed Ag NW on Si substrate. With less surface silver than bulk silver foil, the remaining gold precursor were sufficient for Au NW growth after the galvanic replacement reaction consumed a relatively low portion of gold precursors by surface silver atoms.

In chapter 3, we successfully reported a modified ultrathin Au NW forest preparation method to grow Au NW without the use of gold nanoseed. The modified method used salt adsorption instead of gold nanoseed adsorption. Charge induced nucleation step assisted by adsorbed anions on the pretreated APTES layer was hypothesized to be the key to facilitate the later growth step without the use of seed. The hypothesis on reducing effect of anions were also proposed and preliminarily studied. Finally, Na_2S was the best among all screened salts to obtain as almost the same vertically standing Au NW as what

seeded method could do. A synthetic scheme based on Na_2S was proposed and illustrated.

In chapter 4, we reported the successful preparation of gold in palladium core-shell nanowire (Au@Pd NW) with advantages provided by its morphology induced property to spontaneously enhance both catalytic activity and operation durability that may significantly enhance the performance of anode reaction in DEFCs. The vertically standing nanowire forest with tunable length prepared using modified active site growth method may provide high electrochemical active surface area for high catalytic activity and enhance the electronic charge transport efficiency at the same time. Furthermore, the improved mechanical strength brought by modified salt assisted method together with the highly tunable length and density of vertically standing Au@Pd NW can offer greatly enhanced operation durability at fixed potential for 200,000 s. Nearly 40 percent of the highest anodic performance remained by Au@Pd NW for catalyzing ethanol oxidation reaction could still be achieved even after 200,000 s at a fixed potential.

In chapter 5, we investigated the mechanistic reason behind the high durability we obtained by discussions on correlation between OH^- concentration and performance decrease in pristine Pd plate, inhibition memory effect brought by hydroxide species on short Au@Pd NW, intermediate species identification by in-situ Raman spectroscopy, oxidative state of surface Pd atoms by X-ray photoelectron spectroscopy and product analysis by high performance liquid chromatography. By summarization of the aforementioned discussions, we proposed the OH^- species as the main inhibitor to poison Pd and bring performance decrease during chronoamperometric test. Finally, we would like to propose a dual site hypothesis to explain the high durability of ultrathin Au@Pd NW.

In short, this work based on noble metal nanowire has not only expanded the synthetic parameters of substrate bound vertically standing Au NW from oxide substrate to nanoscale metal nanowire on substrate and from seeded growth to seedless and facile growth, but also greatly extended the range of application for noble metal nanowire. With the greatly enhanced durability for ethanol oxidation reaction achieved by vertically aligned ultrathin Au@Pd NW array and the mechanistic understanding to it, rational design and preparation of novel catalyst would be achieved based on our synthetic controllability in the future work.

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1.Introduction

1.1. Nanomaterials and their applications in catalysis

1.1.1. Unique properties originated from nanomaterials

Nanomaterials, with a most popular definition of solids of any shape and composition with at least one dimension larger than 1 nanometer and smaller than 100 nanometers (1 nanometer = 10^{-9} meter), has attracted great attention from researchers and scientists in chemistry, physics, biology and even medical sciences. ^[1] At this size scale, nanomaterials can exhibit unique physical properties with high application potential due to surface effect and quantum confinement effect, which defer themselves from their respective bulk form. ^[2] The largely decrease from bulk to nanoscale in size of nanomaterials not only affect the surface atom fraction to total atoms, but also cause the increase in portion of low coordinated atoms on the surface. ^[3]

In terms of surface atom fraction, for example in the case of cubic nanoparticles with n atoms on the edge, surface atom fraction factor F would decrease when n increased. When concerning F versus total atoms in a cubic nanoparticle N ($N=n^3$), the curve of F versus n ($=N^{1/3}$) will be illustrated as shown in Figure 1.1.

It was commonly believed that low coordinated atoms on surface of catalyst had higher affinity and activity towards adsorbed species, which is of great importance in catalytic reactions. ^[2] Typically, in cubic nanoparticles, the degree of coordination of surface atoms on the edges is smaller than these on corners and larger than those on sides and inside. In spherical nanoparticles, on the other hand, the degree of coordination of surface atoms are nearly the same. However, the high activity in catalysis of atoms with low coordination number is mostly associated with high destabilization during catalytic reactions. Missing of

atoms on edges especially corners is common even in thermodynamically equilibrated reaction condition.

Figure 1.1 Illustration of the evolution of F (surface atom fraction) for a cubic nanoparticle when plotted against n up to 100 (n refers to number of atoms on one edge, and N is the total number of atoms in one cube). The structure of cube model with $n=2-5$ was displayed as inset. Reprinted with permission from ref. [4]. Copyright © PCCP Owner Societies.

Another unique property of nanostructures high correlated with nanoscale size is lower melting point compared with bulk materials. Due to low coordinated surface atoms of nanomaterials, they are more unstable, which may result in lower lattice energy and decrease in melting point compared to bulk materials. For example, the melting point of bulk gold was reported as 1336 K, a lot higher than melting point of 2.5 nm gold nanoparticles, 930 K. [6] According to both theoretical calculations and experimental data on melting points of nanoparticles with different sizes, trend is clear that nanoparticles with smaller size may have lower melting point. [5]

Figure 1.2. Plotted model predictions of $T_m(D)/T_{m0}$ ($T_m(D)$ is decreased melting temperature of metal nanoparticles with a diameter of D , T_{m0} is melting point of bulk metal) according to theoretical calculations for Indium (magenta line), Tin (navy line), and Bismuth (olive line) nanoparticles respectively. The symbols $\star$, $\diamond$, $\circ$, $\triangle$, and $\square$ show the experimental results. Reprinted with permission from ref. [5]. Copyright © 2012 Elsevier B.V.

Due to the increase in surface to volume ratio of nanostructures, unique physical and chemical properties related to quantum confinement effect, i.e. electron tunneling, [8-10] quantum entanglement, [11-12] ballistic transport, [13-14] electron confinement [15-16] and near-field optical effects [17-19] are found quite different from their bulk counterpart. At the same time, phase transition below melting point, mechanical strength, catalytic activity, and thermal instability are well known examples resulting from size effect of nanostructures. [7, 170]

1.1.2. Applications in catalysis

Small transition metal or metal containing compound clusters and nanoparticles often exhibit phenomenal dependence on size variations not only in their intrinsic physical and electronic properties, but also in their respective catalytic potential resulting from chemical reactivity. ^[169] Unique electronic property of nanomaterials i.e. charge-donating and accepting ability is a key factor in catalysis. For example, electron affinity of gold clusters changed by ca. 2 eV with a variation of cluster sizes. Ionization potential mostly shared the same trend with electron affinity. For platinum, the work function may vary from 9.0 eV for a single atom to 5.3 eV in bulk material. ^[2]

Goodman and coworkers experimentally demonstrated the size correlated electronic factor by establishing casual relationship between size variation of Au nanoclusters supported on TiO₂ and their catalytic performance in CO electro-oxidation reaction. ^[20-22] The Au L_{III} XANES white line of Au clusters of 3 nm, 1 nm and 0.5 nm shows that a smaller Au nanoparticle has larger electron density with a narrower d band located closer to Fermi level. ^[26-31]

Apart from unique electronic property, the highly increased surface-to-volume ratio of nanomaterials compared to their bulk materials is another pronounced factor in catalysis. Almost all chemical reactions in catalytic processes are performed on surface of catalysts. ^[23] Thus nanomaterials, bearing high surface energy and high proportion of low coordinated surface atoms, is of immense significance in catalysis and energy storage industries. ^[24] The variations in fraction of surface atom to all atoms in a nanoparticle, fraction of lower coordinated atoms on edges and corners to all atoms in a nanoparticle and the specific active surface area to per gram of catalyst are all sequentially correlated with variation of nanoparticle size. ^[23] These three key factors could be concluded as surface chemical and structural aspects of catalyst which may determine catalytic performance. To take a closer look at catalytic reactions, catalytic events are well known to initiate on the active catalytic

sites on surfaces of catalysts via surface adsorption process. In Langmuir-Hinshelwood mechanism, reagent molecules, adsorbed species, dissociated species, and catalytic intermediates must interact with atoms on surface active catalytic sites on catalyst topmost surface. Any changes in binding configuration and energy between catalyst surface atoms and above-mentioned species may vary reaction pathways. Thus, the size and shape of nanomaterials with catalytic ability may determine their catalytic performance by varying surface chemical and structural factors of catalytic nanomaterials. [23]

It was once generally believed that particle aggregation only cast the casual effect on the decrease of specific electrochemical surface area. However, according to Maillard etc., surface oxide reduction peak potentials of carbon supported Pt nanoparticles correlated well with the average nanoparticle sizes. This is a clear evidence that particle sizes affect not only the electrochemical surface area but also the electrochemical potentials. Peak potential started to shift from that of bulk polycrystalline Pt foil as the particle sizes decreased below 4 nm. [4]

Figure 1.3. Reduction peak potentials E_d of cyclic voltammetry curves of CO electro-oxidation reaction on glassy carbon supported Pt nanoparticles varied as nanoparticle size changes in 0.1 mol/L H_2SO_4

electrolyte at 100 mV/s in room temperature. Reprinted with permission from ref. [4]. Copyright © PCCP Owner Societies.

In partial electro-oxidation reaction of methanol on Pt nanoparticles, catalytic performance of Pt nanoparticles also shows a dependence of size variation. Pt nanoparticles of 5.8nm, 5.2 nm, 3.4 nm, and 2.7 nm synthesized by microwave assisted polyol synthesis showed an increase in catalytic performance in methanol oxidation reaction with a decrease in Pt nanoparticles size until 3.4 nm. However, there is an unexpected decrease in catalytic performance when size of Pt nanoparticles drops to 2.7 nm. This result is found to be correlated with highly poisoning CO intermediate adsorption ability towards surface atoms on smaller Pt nanoparticles. The smaller Pt nanoparticles are, the higher poisonous to Pt surface CO can be. ^[25]

Figure 1.4. Cyclic voltammety curves of methanol oxidation reaction on Pt/CNTs catalysts prepared by microwave assisted polyol method with different sizes in 2 mol/L methanol and 1 mol/L H₂SO₄ electrolyte

at 20 mV/s in room temperature. The average sizes of Pt nanoparticles supported on CNTs are (a) 5.8 nm, (b) 5.2 nm, (c) 3.4 nm, and (d) 2.7 nm. Reprinted with permission from ref. [25]. Copyright © 2005 Elsevier B.V.

In catalytic reactions, adsorption energy for anchoring reagent molecules on topmost surface of nanomaterials, especially metal nanoparticles, may also be influenced by change in their sizes. [23] The adsorption energy is related to how likely a reactant molecule bond to a metal catalyst atom or a group of metal atoms. If the rate determining step of a catalytic reaction is the break of chemical bond within or between reactant molecules, metal catalyst atoms with low coordinated environment typically may exhibit enhanced catalytic activity. When it comes to nanomaterials, metal catalyst atoms on the surface of nanomaterials is in less self-coordinated environment than their bulk counterpart. This fact may enhance the likelihood of reactant molecule binding, exhibit higher adsorption energy for reactant molecule on metal atoms, and decrease the activation barrier in a catalytic reaction. [23]

Calle-Vallejo etc. established the link between adsorption energy of small H- or O-containing adsorbates and different sizes of Pt nanocrystals using a predicting descriptor, self-coordination number. By using DFT calculations after defining generalized self-coordination number of surface atoms on Pt nanocatalyst, adsorption behaviors of several O-containing species on Pt_n (n=28,201,769) with diameter falls in 0.7-1.7 nm were thoroughly studied. Adsorption energy for adsorbates including *O₂, *OH, *OOH, *O, *H₂O, and *H₂O₂ were found to decrease linearly with the increase of generalized coordination number from 3 to 9. This study provided correlations between surface geometric arrangements and adsorption properties of metal nanocrystals towards typical adsorbates in aqueous solution. [32] Similar trends illustrating correlations between surface coordinating environment and adsorption energy were found in other transition metal nanocatalysts like Au, Co, Rh, Ni, Cu, Ag, Ir and Pd. [33]

In complete oxidation reaction of methane, Pt supported on different oxides (ZrO_2 , $\gamma\text{-Al}_2\text{O}_3$ and $\text{ZrO}_2\text{-CeO}_2$) with different sizes have been extensively studied. It was found that the effect of supporting materials was marginal when diameter of Pt nanocrystals was smaller than 4.5 nm by normalizing CH_4 turnover frequency to the number of surface Pt atoms. Overall, catalytic performance of Pt nanocrystals in complete methane oxidation reaction increases with the decrease in size of Pt nanocrystals. The result and sequential conclusion well aligned with the trend that nanocatalysts with lower surface coordination number may exhibit higher catalytic reactivity in activation of C-H bond, the rate limiting step. [34]

Figure 1.5. Plots of turnover frequencies of main products in complete methane oxidation reaction: CO_2 (a) and H_2O (b) versus dispersion of various oxide supported Pt nanocrystals (▲: Pt/ZrO_2 , ●: $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, ◇: $\text{Pt/ZrO}_2\text{-CeO}_2$, ○: turn-over rate of CO in CO oxidation reaction at 413 K on Pt/ZrO_2). Reprinted with permission from ref. [34]. Copyright © 2004, American Chemical Society.

Au nanoparticles are known to be reactive in catalyzing ethanol dehydrogenation reaction. To extensively study the catalysis reaction and the link between size and Au catalytic performance, a series of Au nanoparticles ranging from 1.7 nm to 15 nm supported on different types of silica was studied on their catalytic performance towards ethanol dehydrogenation to acetaldehyde reaction with and without the presence of oxygen. [35]

Strong size dependence with turnover frequencies was found in direct dehydrogenation reaction without presence of oxygen. The maximum performance was observed on 6nm Au nanoparticles with nearly 100% selectivity towards acetaldehyde below 350 °C. Reason behind the well optimized catalytic performance of 6nm Au nanoparticles might be the maximum existence of surface step sites other than corner sites and terrace sites, which is most favorable to catalyze C-H bond breaking of adsorbed ethoxide. On the surface of Au nanoparticles smaller than 6 nm, corner sites are predominant and step sites are less favorable. On the surface of larger Au nanoparticles, however, terrace sites become preferred than step sites. Enough surface density of catalytic reactive step sites is essential in achieving high catalytic performance in anaerobic dehydrogenation of ethanol towards acetaldehyde reaction. In aerobic dehydrogenation of ethanol to acetaldehyde, however, a different size trend was observed. Much higher catalytic performance was achieved on same catalysts candidate due to the adsorbed oxygen species in aerobic dehydrogenation of ethanol than anaerobic process. It was because the co-adsorbed oxygen species may act as Bronsted base to initiate O-H bond cleavage in the initial reaction step and catalyze the breaking process of C-H bond in subsequent step to form the final product acetaldehyde. The catalytic reactivity of Au nanoparticles larger than 7 nm was enhanced with increase in sizes while that of Au nanoparticles smaller than 7 nm does not change with variation in sizes. Decrease in adsorption energy of oxygen containing adsorbates on Au nanoparticles larger than 7nm was hypothesized to be the reason for the well correlated trend between size and catalytic performance.

Figure 1.6. Plots of turnover frequencies of main in dehydrogenation of ethanol to acetaldehyde in absence (square dots fitted by dash line: ■) and presence (triangular dots fitted by line and dash: ▲) of oxygen versus different sizes of Au nanoparticles supported on silica. Reprinted with permission from ref. [35]. Copyright © 2009, Elsevier. B.V.

Chemical reduction of 4-nitrophenol to 4-aminophenol has been a model study process in preliminarily demonstrating the catalytic potential of Au and Pt based nanomaterials. L-cysteine assisted sodium dodecyl sulfate stabilized growth of Au nanoparticles on α -Fe₂O₃ with various sizes were used to catalyze the reduction of 4-nitrophenol. [36] Strong size to conversion correlation was established in reduction reaction of 4-nitrophenol to 4-aminophenol in presence of sodium borohydride. As is shown in Fig. 1.7, catalytic reaction rate k increased with the decrease in Au nanoparticle sizes. Similar trend was observed in Pt nanoparticles synthesized on wood nanomaterial using mechanical grinding method. [37] Typically, Pt nanoparticles with smaller sizes exhibited higher catalytic activity in chemical reduction reaction of 4-nitrophenol to 4-aminophenol.

Figure 1.7. UV-Vis adsorption spectrum of 4-nitrophenol after sodium borohydride addition with the presence of Au- α -Fe₂O₃ nanoparticles of 2 nm (a, b), 7 nm (c, d), 11 nm (e, f) and the plots of corresponding $\ln(A_t/A_0)$ versus reaction time. Reprinted with permission from ref. [36]. Copyright © 2012, Wiley-VCH.

Oxygen reduction reaction is of high significance in fuel cell related research field and industry. Pt nanoparticles ranging from 2 nm to 5 nm in diameter on carbon supports are regarded as the current best catalyst for oxygen reduction reaction. Yamamoto etc. pushed the

size boundary downwards and reported a dendrimer templated controlled synthesis of smaller Pt nanoparticles. ^[38] Size dependence in smaller Pt nanoparticles with catalytic reactivity was found. Catalytic performance of ultra-small Pt_n (n=12, 28, 60) with various diameters (d=0.9, 1.0, 1.2 nm) was enhanced with the decrease in size of Pt nanoparticles.

In a word, the advantage of nanomaterials in catalysis are size effect, high surface to volume ratio, peculiar electronic properties and ability to tune adsorption energy of reactant molecules. With these advantages, nanomaterials showed quite good catalytic abilities compared with their bulk counterparts. In the future, nanomaterials are expected to have a spectacular prospect in catalyzing electrochemical reactions, photo catalytical reactions and heterogeneous gas-solid interfacial catalytic reactions with all their advantages.

1.2. One dimensional nanomaterials: synthesis, properties and applications

As was discussed above, size effect of nanomaterials is recognized as an important characteristic that may bring enormous potential in catalysis. Morphology effect apart from size should also be considered as one of key factors contributing to enhanced catalytic performance. However, the enhancement in catalytic performance of nanomaterials with various morphologies were mostly attributed to active sites or unique facets on the topmost surface of catalysts, rather than the morphologies they possessed. Though it was usually hard to differentiate that either the morphology as a whole or one or several certain facets should be responsible for the enhancement in catalytic performance. Morphology induced properties, their relevant applications and generality among materials sharing similar morphologies are what we are actually interested in.

We decided to focus our scope of study on one dimensional nanomaterials owing to their unique morphology induced properties and applications in a wide variety of subfields in catalysis. One dimensional nanomaterials, typically referred to rods, wires, belts and tubes, have attracted increasingly copious focus and attention due to their peculiar properties and wide variety of applications in mesoscopic and microscopic physics and fabrication of nanoscale electronic devices. ^[39] One dimensional nanomaterials are mostly defined as materials with only one dimension that are not confined to nanoscale, i.e. the range of 1-100 nm. ^[40] It was generally accepted that one dimensional nanomaterials may be ideal in model study for establishing correlations between electrical and thermal transport or mechanical properties and dimensionality and quantum confinement. ^[39] One dimensional nanomaterials are recognized as a significant candidate in building interconnections and functional units in nanoscale devices in fields of electronics, optoelectronics, electrochemistry and electronic machinery. However, one dimensional nanomaterials were slower in large scale and

industrial development in comparison to zero dimensional nanomaterials like quantum dots until recently due to the lack of proper and well controlled synthetic and fabricating methods for mass production with high phase purity, delicately controlled dimensions, morphologies and chemical composition. Although several kinds of top-down synthetic techniques for one dimensional nanomaterials based advanced nanolithography has been developed such as electron-beam or focused-ion-beam writing, proximal-probe patterning and X-Ray lithography, more generalized and synthesis methodology in larger quantitative scale for one dimensional nanomaterials on a wider variety of materials with lower cost is still in great need. Chemical synthesis among unconventional synthetic methods may offer a promising alternative for large scale synthesis with wider variety of materials, higher purity and lower cost.

1.2.1. Synthetic strategies in nanowire growth

In development of synthetic method for one dimensional nanostructures, the most crucial issue to address is the simultaneous control over dimensions, morphology and uniformity. Among most one dimensional nanostructures formation processes, crystallization is the most essential part, which has been studied for hundreds of years.^[41] Growth from liquid or vapor to solid typically consists of two parts, nucleation and growth. When the concentration of precursor building blocks (atoms, ions, or molecules) reaches a relatively high level over saturation point, they start to aggregate into small nuclei via homogeneous nucleation. As the number of building blocks keeps on increasing, they may either start to form more nuclei or deposit onto existing seed nuclei. To facilitate a controllable nucleation and growth process in formation of perfect crystal, both reversible pathways between building blocks on solids and in liquid, vapor or molten mixture as well as sufficient supply of building blocks at a well-controlled rate are required. The reversible condition and

sufficient supply at certain rate may allow the building blocks to adjust and adopt into most favored position so that as a whole they would form thermodynamically favorable long-range-ordered crystalline nanostructure.

During the past decades, a wide variety of bottom-up synthetic methods for one dimensional nanostructures successfully facilitated the delicate control over dimensions, morphologies and chemical components. They were believed in using the strategies like: i) utilizing intrinsic anisotropic crystallographic structure of solid materials to achieve one dimensional nanomaterial growth (Fig. 1.8.A); ii) creation of liquid-solid interface to reduce the symmetry of seed (Fig. 1.8.B); iii) use a confinement or template with one dimensional morphologies to guide anisotropic growth to form one dimensional nanostructures (Fig. 1.8.C); iv) assist with a proper capping agent to kinetically control the deposition rate of precursors or building blocks (Fig. 1.8.D); v) controlled self-assembly of zero dimensional nanostructures (Fig. 1.8.E); vi) size reduction of one dimensional meso-structures or microstructures (Fig. 1.8.F); vii) supersaturation control to modify seed growth mode.

Figure 1.8. Illustrations of different methods to prepare 1D structure: dictation by the anisotropic crystallographic structure of a solid (A), confinement by a liquid droplet as vapor-liquid-solid process (B), direction growth using a template (C), kinetic control by strong ligands (D), self-assembly of 0D nanomaterials (E) and size reduction of the 1D microstructure (F). Reprinted with permission from ref. [39]. Copyright © 2003, Wiley-VCH.

A number of solid materials grow into one dimensional nanostructures naturally owing to their intrinsic highly anisotropic bonding behavior in their crystalline structure. $(\text{SN})_x$, known as poly (sulfur nitride), an inorganic polymer which attracted extensive attention during 1970s for its applications in metallic property and superconductivity. ^[42,43] Uniform nanowires with a diameter of around 20 nm and a length of several hundreds of micrometers

were easily grown from vapor phase of (SN)_x precursor. Confined and guided by the chain configuration of the building blocks, such as atoms, molecules and ions, these solids would be able to grow into nanowires with diameters kept almost the same as seed and the growth orientation perpendicular to dimensions of seed. Many inorganic minerals, polymeric and biological systems are known exhibit a fibrous growth habit, for example molybdenum chalcogenides ^[44-46], chalcogens ^[47-49], asbestos ^[50], cellulose ^[51] and collagen ^[52].

Apart from the materials that may grow into one dimensional nanostructures driven by intrinsic crystalline property, there are a wider variety of materials with isotropic crystalline nature, for example nearly all metals with face-centered cubic crystal lattice. ^[39] Symmetry breaking is the most critical step in as early as seed nucleation stage. In order to facilitate symmetry breaking in synthetic control, several strategies have been developed during past decades to achieve controlled growth of one dimensional nanomaterials. The vapor-liquid-solid process is known as a versatile method in synthetic approach design by introduction of a flat liquid-solid interface to achieve symmetry breaking. ^[53-65] Template-driven method is another universal method that has been used to synthesize significant number of nanomaterials with different chemical components. ^[66-71] Use of capping ligands to control deposition of building blocks at different orientation provides a different design strategy by facilitating kinetic control over facets. ^[72-78] Purposely design to delicately control supersaturation of a system also offers a powerful approach to efficiently induce and maintain symmetry breaking growth of one dimensional nanomaterials. ^[79-83]

Vapor phase synthesis has been nearly the most developed method in preparation of various kinds of one dimensional materials. ^[84] Technically, it is possible to synthesis one dimensional nanostructure from solid materials by controlling the supersaturation of vaporous building blocks at a low level. It was found in 1921 by Volmer etc. that when mercury vapor started to condense on a glass surface under mercury melting point, mercury nanowire with

around 20 nm width and more than 1 μm length could be formed. ^[85] Sears et al. achieved similar method in synthesis of other metal nanowires and proposed an axial screw dislocation related mechanism. ^[86,87] His hypothesis was that the driving force to form one dimensional nanostructures like nanowires or whiskers was determined by axial screw dislocation causing the freshly adsorbed atoms or other types of building blocks on the entire surface of nanowire migrated towards growing tip. Other than this mechanism, a generally accepted hypothesis is that the degree of supersaturation is the key controlling factor for successful preparation of one dimensional nanomaterials due to the strong correlation between concentration of vaporous precursor and morphology. The major advantage of direct vapor synthesis method is the simplicity and accessibility. Typically, the gaseous precursor was first evaporated, chemical reduced or synthesized via other type of gaseous reaction. Condensation of the gaseous building blocks onto solid substrates at a temperature lower than that of gaseous reactant. Zhu etc. prepared Si_3N_4 , SiC , Ga_2O_3 and ZnO nanowires by simply heating the commercial bulk powder of these materials to gaseous phase and condensing them onto solid substrates. ^[88]

Vapor-liquid-solid method has been the most extensively explored among vapor synthesis methods for preparation of single crystalline nanowires in moderately large quantities. Typically, a vapor-liquid-solid process begins from dissolution of vaporous reactants into liquid nanodroplets of the building block species, then proceeds to nucleation and longitudinal growth into single crystalline nanorods or nanowires. The longitudinal growth is generally accepted to be guided or confined by the nanosized liquid droplets. Normally the dimension and shape of product one dimensional nanomaterial depends on the dimensions of liquid droplets and would remain unchanged during the whole growth process. Thus, the intermediate liquid nanodroplets are usually believed to act as the soft template to confine the growth within dimension of droplets and restrain lateral growth of the

nanomaterial. Yang etc. have confirmed this mechanism by observing Ge nanowire growth on Au and Ge interface using in-situ TEM with a temperature controllable stage. ^[89] With GeI_2 as gaseous Ge source and Au as catalyst, they were able to obtain the TEM image of intermediates during one dimensional growth of Au-Ge nanowire.

Figure 1.9. Scheme for growth process of a nanowire in vapor-liquid-solid mechanism (A), Binary phase diagram between Au and Ge with the estimated composition zones for alloying, nucleation and growth (B). Reprinted with permission from ref. [39]. Copyright © 2003, Wiley-VCH.

Figure 1.10. In-situ TEM image for intermediates of Ge nanowire synthesis in different reaction period: gold nanoparticle by itself (A), gold nanoparticle with tiny amount of Ge, indicated by diameter increase (B), Ge and Au started to melt and formed alloy nanoparticle (C), a liquid-like nanodroplet sharing Au-Ge alloy nanoparticle diameter formed adjacent to alloyed nanoparticle (D), droplet started to grow longitudinally when supersaturation of Ge was reached in the template nanodroplet (E) and Ge nanowire grew longer as time went by (F). Reprinted with permission from ref. [89]. Copyright © 2001, American Chemical Society.

Template directed synthesis is another universal and facile one dimensional nanomaterials preparation method. Template is typically a scaffold within or around which a different material is designed to grow into a nanostructure that is complimentary to shape of template. A wide variety of templates has been explored such as step edges on the surface of

solid substrates, ^[90-96] channels within porous materials, ^[97-108] soft template for mesoporous materials using amphiphilic organic molecules or block copolymers, ^[109-112] biological macromolecules like DNA strand and rod like viruses and existing nanostructures as templates. ^[113-117] Most of the one dimensional nanomaterials derived from templates requires a post treatment step of template removal, usually by chemical etching or calcination.

Capping ligands on specific facets of one dimensional nanomaterials may assist in facilitating a more controllable approach in solution-based methods. For a thermodynamically stable single crystalline nanomaterial, its shape may reflect the intrinsic symmetry of lattice and facets exposed may give a minimal Gibbs total free energy according to Wulff facets theorem. ^[118] At the same time, shape of nanomaterials may also be affected by growth kinetics of different facets. Thus, a versatile strategy for one dimensional nanomaterials growth is to use ligands as capping reagents on certain facets on crystalline solids to change total free energy of the surface and alter the deposition rate of certain facets. The capping reagent approach has been widely used in scalable synthesis of semiconductors and metal nanorods and nanowires. Mixed surfactants as capping reagents to synthesize semiconductor nanorods has been explored by Alivisatos group. ^[119, 120] According to their study, adding hexylphosphonic acid (HPA) and trioctylphosphine oxide (TOPO) may assist in obtaining large quantities of CdSe nanorods with the aspect ratio up to 10. The mixed 2 ligands may promote CdSe growth along c-axis in wurtzite structure during the initial growth stage. Polyol method is known as a facile method to synthesize silver nanowires with uniform size distribution. ^[121-123] The use of poly (vinyl pyrrolidone) (PVP) as capping reagent when reducing silver nitrate by ethylene glycol and introduction of small seed are the key steps to successful synthesis of silver nanowire. When silver nitrate was reduced with the presence of twinned seeds, both homogeneous and heterogeneous nucleation would occur at the same time and nanoparticles with different sizes would form. Later the small nanoparticles would

disappear under an Ostward ripening process and subsequently grow onto big nanoparticles along one dimension with the help of polymeric capping reagent PVP.

Size reduction and self-assembly of nanoparticles are also among common approaches to synthesize one dimensional nanostructures. However, we mostly focus our synthetic methodology to solution approaches. This work is in particular focusing on more of the synthetic control, the morphology and property correlation and the application part than the synthetic methodology part.

1.2.2. Advantages of one dimensional nanomaterials

One dimensional nanomaterials have attracted a lot of interest in the field of electrocatalysis, fuel cell and photocatalysis mostly due to the fact that they have exhibited peculiar properties making them typically outperform in the catalytic process than their zero dimensional counterparts. One of the properties that is beneficial to catalysis is that one dimensional nanostructures may contain less surface defects than zero dimensional nanostructures. ^[39] Defect sites are less favorable in catalysis typically because their difference in surface atom coordination environment may attribute to less catalytic reactivity. Less defects on surface of one dimensional nanomaterials correlates to their morphology. In the preparation step of one dimensional nanomaterials, especially in solution methods, the symmetry breaking process may expose catalytic favorable lattice planes with fewer grain boundaries. Thus, one dimensional nanomaterials may possess higher portion of catalytic favorable facets than zero dimensional nanomaterials.

High electron transport efficiency is another unique property that one dimensional nanomaterials possess. Electron transport is not only crucial and beneficial for catalysis usage but also widely applicable in miniaturization of electronic devices. Miniaturization of electronic devices using traditional top-down methods has reached a critical point where the structural issues may limit the computing speed. Thus, electronic devices built by assembly of nanomaterials prepared by bottom-up method is attracting increasing attentions both for the target of size decrease and the control of fabrication cost. CNTs and metal nanowires is a promising candidate in fabricating nanoscale electronic devices via self-assembly, an efficient bottom up method. The demonstrated prototype nanodevices are p-n junctions, bipolar junction transistors, field-effect transistors, complementary inverters and resonant tunneling diodes. ^[124-128] Apart from applications in electronic nanodevices, the morphology induced high electron transport efficiency resulting from fast charge transport is highly

favorable in electrochemical catalysis. Some of one dimensional nanomaterials like graphene nanoribbons may even exhibit ballistic transport, where charge transport may experience less electron scattering and bring down the resistivity of nanomaterial. ^[129] In a typical heterogeneous electrochemical catalysis, nanomaterials deposited on plate, disk or ring has been widely used. Comparing to stacking of zero dimensional nanomaterials and some one dimensional nanomaterials, vertically standing one dimensional nanomaterials arrays may bring significant benefits in facilitating electron transport from substrates to solid catalysts and electrolyte interface. Schematic illustration is shown in Fig. 1.11. It is clearly shown in Fig. 1.11.a that electron will have to undergo several interparticle charge transport processes in nanoparticle staking mode, which is the cause of contact resistivity. On the other hand, charge transport in standing nanowire array mode shown in Fig. 1.11.b may take shorter distance and less resistivity than stacking mode.

Figure 1.11. Schematic illustration of electron transport mode in nanoparticle dense stacking mode (a) and standing nanowire array mode (b).

Apart from high electron transport and low defects, noble metal nanowires may exhibit a different surface plasmon resonance mode from zero-dimensional noble metal nanomaterials. El-Sayed etc. have spent extensive efforts on surface plasmon resonance (SPR) of Ag and Au nanowires and found two SPR mode corresponding to transverse and longitudinal excitations. ^[130] While wavelength of typical transverse excitation mode is fixed to approximately 410 nm

for Ag and 520 nm for Au, their wavelength of longitudinal mode may be tuned throughout the range from visible to near-infrared by the change of aspect ratios. For semiconductors however, when the diameter falls below the Bohr radius, the energy level of nanowires will change accordingly. ^[131-133] Hardness of polycrystalline one dimensional nanostructures may be observed increased as the decrease of grain size on micrometer scale, which is known as Hall-Petch effect. ^[134, 135] For single crystalline SiC nanorods, the Young's modulus was estimated to be 610-660 GPa according to Lieber group's study using Atom Force Microscopy. ^[136] Additionally, one dimensional nanomaterials, especially nanowires, were harder to become closely packed three dimensional nanostructures, even though some of the nanowires prepared by solution method were easily aggregated upon removal of surfactants or stabilizer molecules. In the case of typical nanoparticles, when they were suspended and concentrated in solution and drop-casted onto the electrode surface, most of nanoparticles may become aggregated and closely packed, which may lose the beneficial high surface to volume ratio as well as catalytic reactive sites as a result. For standing nanowire or nanotube arrays, the loss of active sites due to aggregation may be avoided. Even simply drop casted the concentrated nanowire solution, nanowires may hardly form a less catalytically favorable close packing.

With all the advantages above, one dimensional nanomaterials are highly appreciated in both sensing and electrochemical catalysis. Cu nanowire arrays was demonstrated by Tao etc. first to be organic molecule sensor. ^[137] When organic molecules adsorbed onto Cu nanowires, the conductivity of the device will decrease due to the scattering of electrons by adsorbates on Cu nanowires. By modifying Si nanowire based nanoscale field effect transistor with 3-aminopropyltriethoxysilane (APTES), a nanosensor for pH was prepared functioning with the conductivity change with surface charge change during protonation and deprotonation process. ^[138]

Figure 1.12. Schematic illustration of preparation from nanoFET to APTES modified nanosensor for pH sensing (A), zoom-in scheme showed nanowire surface change with the change of pH value. Real-time conductance of nanosensor by change of pH from 2 to 9. Inset bottom is FESEM image of Si nanowire device. (B) Plots of conductance versus pH on typical APTES functionalized Si nanowire device (C) and pristine Si nanowire device (D, red). The dashed green line is a plot of surface charge density for silica as a function of pH. Reprinted with permission from ref. [138]. Copyright © 2001, The American Association for the Advancement of Science.

Silver is known as catalyst for four-electron reduction pathway in oxygen reduction reaction. ^[139] Kwak etc. compared cathodic performance of silver nanowire and silver nanoparticle in lithium oxygen batteries. ^[140] One dimensional structure of nanowires may supply facile electron transport and large contact area to enhance the efficiency of oxygen reduction reaction on cathode side.

Figure 1.13. Cyclic voltammetry of Li_2O_2 batteries using AgNP and AgNW as cathode from 2.0 V to 4.3 V at 100 mV/s. Reprinted with permission from ref [140] Copyright © 2016 Elsevier B.V.

Platinum, bearing the highest activity in dissociative adsorption of methanol, is the most promising candidate for methanol oxidation reaction. However, pristine Pt may suffer from poisoning during catalysis reaction due to some carbonaceous intermediates like CO. The poisoning would cause a decrease in catalytic performance of Pt based catalysts. Highly ordered three-dimensional Pt nanowire network was prepared by hard templated method, using a laser irradiated and etched polymer foil as template and electroless deposition method to synthesize nanowires according to Rauber etc. ^[141] For per surface area of Pt, the peak current of nanowire network is higher than both commercial Pt black and Pt on carbon, as shown in Fig. 1.14 b. It was suggested that the high electron and reactant transport efficiency

to active sites of highly ordered three-dimensional nanowire networks may bring benefit to both catalytic performance and stability.

Ethanol oxidation reaction is the model anodic reaction in direct alcohol fuel cell, which is a promising candidate for portable energy supply applications. Ethanol have more advantages than methanol in higher energy density, lower toxicity and easier in transport and storage due to higher boiling point. For complete oxidation of ethanol, Pt and Pt based nanocatalysts are promising alternatives owing to their high efficiency in facilitating C-C bond breakage at low overpotentials. Zhang etc. compared pristine and porous Pt nanowire arrays with Pt film electrode in their performance in ethanol oxidation reaction. ^[142] Both pristine and porous Pt nanowire arrays outperformed Pt film in cyclic voltammetry anodic peak current density and chronoamperometry test. More active sites brought by morphological characteristics in nanowire arrays was concluded to be the reason for high performance in catalytic activity and stability.

Figure 1.14. (a) SEM image of a piece cut from freestanding Pt three-dimensional nanowire network with an inset showing a closer look of nanowire network in high resolution. (b) Cyclic voltammetry of methanol oxidation reaction catalyzed by Pt nanowire network, Pt black and Pt/C catalyst in 0.5 mol/L H_2SO_4 + 0.5 mol/L CH_3OH solution. The insets in (b) showed peak current density j_a (top) and peak mass activity j_m (bottom) of forward peak in MOR for above 3 catalysts. Reprinted with permission from ref [141] Copyright © 2011 American Chemical Society.

Figure 1.15. Cyclic voltammetry curve in (a) 1mol/L NaOH solution and (b) 1mol/L NaOH and 1mol/L ethanol solution by (i) Pt film electrode, (ii) Pt nanowire array electrode, (iii) porous Pt nanowire array electrode at scan rate of 20 mV/s. Reprinted with permission from ref [142] Copyright © 2009 The Royal Society of Chemistry.

CO₂ reduction to hydrocarbons on Cu based catalysts is a complex process. Wilson group reported Cu nanowires derived from Cu(OH)₂ nanowires for their length related hydrocarbon products distribution. [143] As shown in Fig. 1.16, H₂ production always competed with CO₂ reduction at the same time. With the increase in Cu nanowire array length and density, the portion of H₂ decreased and products for CO₂ reduction reaction increased. While C₂H₄, HCOOH and CO formation were observed at all lengths of nanowires, n-propanol started to form when length increased to 2.4μm. With further increasing of Cu nanowire length, ethanol and C₂H₆ was formed until nanowire length reached 7.3μm. They attributed this trend of length vs selectivity to nanowire array morphology induced local pH effect. With the increase of Cu nanowire array length and density, the concentration decay of HCO₃⁻, the soluble form of CO₂, and local pH increase promoted further reduction of CO₂ on Cu nanowire catalysts.

Figure 1.16. Faradic efficiency for products C₂H₄, C₂H₆, CO, HCOOH, ethanol, n-propanol, and H₂ of CO₂ reduction reaction on Cu nanowire arrays with different lengths at -1.1V versus RHE in CO₂ saturated 0.1mol/L KHCO₃ (pH = 6.83) solution (0μm refers to Cu foil). Reprinted with permission from ref [143] Copyright © 2016 Wiley-VCH Verlag GmbH &Co. KGaA, Weinheim.

Core-shell nanowire may combine the unique properties and advantages of two elements and enhance the chemical and electrochemical stability in their applications. Lee et. al. prepared a highly stretchable and transparent supercapacitor by using Ag-Au core-shell nanowire network.^[144] As a promising candidate for wearable electrochemical device, the application of transparent and stretchable Ag nanowire network was sometimes restrained by its chemical and electrochemical instability. With a uniform gold coating on pristine Ag nanowire, the Ag-Au core-shell nanowire would survive hydrogen peroxide corrosive working condition and remain little morphology change after up to 500 cycles of charge-discharge process. No significant IR drop was noticed when Ag-Au core-shell nanowire network was 60% elongated.

In summary, one dimensional nanomaterials, including but not limited to, nanowires, nanorods, nanopipes, nanotubes, hollow nanorods, nanobelts, nanoribbons and nanosprings, typically outperform their zero dimensional counterparts owing to various unique properties. Their high surface to volume ratio, high electron transfer efficiency, less defects, excellent mechanical and optical properties has made them competitive candidates for applications in electrochemical catalysis, photochemical catalysis and sensing devices.

1.3. Ultrathin Au NW arrays

Gold has been known for its nobility as bulk since its first written record in around 1900 BC. Nanoscale gold-based materials, however, sacrificed part of its nobility due to downsize in all dimensions, which has made gold nanomaterials useful in electrochemical catalysis and co-catalytic activities in photocatalysis. Apart from zero dimensional gold nanomaterials, one dimensional gold based nanomaterials, especially vertically standing Au NW arrays, has also demonstrated themselves as attractive candidates in sensing and detection applications. Au NW array can be stable field emitters ^[145] and also used for surface enhancement Raman scattering (SERS) detection ^[146, 147]. Gold based nanowire arrays can be used as glucose sensor ^[148], tumor diagnosis ^[146] and light sensitive retina substitute in vision recovery for blind mice ^[149].

1.3.1. Synthesis of Au NW arrays

Among all the synthesis methods of Au NW array or forest, electrochemical deposition of gold within porous anodic aluminum oxide (AAO) ^[150, 151] or porous polycarbonate polymer ^[152] as template was the most commonly used mature method. However, like other template assisted methods, the synthesis method suffers from the risk of contamination to the nanowire arrays brought by templates and also the risk of breaking the morphology of designated nanowire arrays in the template removing step. The diameter of template assisted Au NW arrays was controlled by templates, which was mostly tens or hundreds of nanometers in size. Ultrathin Au NW arrays, especially those can vertically stand on substrates had not been studied extensively.

Figure 1.17. (a) SEM image of vertically standing Au NW arrays on a Si substrate. Reprinted with permission from ref [153] Copyright © 2013 American Chemical Society.

Recently He J. etc. reported a highly unconventional solution growth method of Au NW forest under ambient condition. ^[153] Using this method, Au NW arrays can be grown from one side of substrate-bound seeds in aqueous solution using a strong ligand. Previously, only a tiny number of seeded growth method for ultrathin metal nanowires has been reported. ^{[154,}
^{155]} Apart from that, mostly weak ligands such as oleyamine ^[156-158], hexadecyltrimethylammonium bromide (CTAB) ^[159, 160] and polyvinylpyrrolidone (PVP) ^{[161,}
^{162]} has been used in solution growth method, making this strong ligand assisted method very unique.

Figure 1.18. Scheme image of (a) synthesis procedure of vertically standing Au NW arrays on substrate and (b) due to strong ligand effect, growth would only be able to start from the interface between seed and substrate. Reprinted with permission from ref [153] Copyright © 2013 American Chemical Society.

Scheme in Fig. 1.18 showed the synthesis procedure of vertically standing Au NW forest. ^[153] An oxide substrate was treated with 3-aminopropyltriethoxysilane (APTES) in ethanol and water mixed solution and washed before soaked in Au seeds solutions to facilitate immobilization of Au seeds onto the oxide substrate. Later with the presence of a strong ligand, 4-mercaptobenzoic acid (4-MBA), the gold precursor, hydro chlorauric acid (HAuCl_4), was reduced by L-ascorbic acid and grow into AuNW arrays. This method looked similar to the conventional vapor-liquid-solid (VLS) growth method in chemical vapor deposition condition. However, careful studies were carried out on the detailed mechanism and found out that they were quite distinct.

In terms of mechanism, this method is drastically different from conventional VLS growth method. In a typical VLS method, the growth material first fused into the molten seed and then nucleated along the nanowire at the seed-nanowire interface. This meant 3 things: the freshly grown segment was always formed next to the seed, the dimensions of freshly grown segment was mostly decided by dimensions of seed, and the binding of ligand (if any) should not affect the dimensions of nanowire. In this strong ligand assisted solution growth method, how fast the strong ligands bind to the fresh growth interface between nanowire and substrate and how fast could the gold precursor be reduced and provided gold supply were the determining factor. When strong ligand like 4-MBA bind on the gold seed, the subsequent reduced gold precursor would not be able to deposit onto the seed. They would deposit at the seed-substrate interface to facilitate nanowire growth, as this should be the only place where strong ligands like 4-MBA cannot bind efficiently shortly after the formation of Au NW on the interface. The newly grown Au NW surface would be covered by 4-MBA soon after fresh gold deposition. How fast the strong ligands bind and how fast the gold precursors get reduced would control the diameter of the nanowire arrays.

There were several key characteristics of the Au NW forest prepared by J. He etc. First, in this method, nanowire can only be grown on substrates instead of in solutions. This may be because there should be a gold-substrate interface to create a difference in binding condition for strong ligands. In colloidal conditions, seeds are usually heterogeneous nucleation center and would simply grow larger instead of growing into nanowires. Second, growth of nanowire only started from one side of seeds, with the diameter of nanowires independent on the diameter of seeds. On the contrary, the dimension of nanowires was strongly dependent on the concentration of strong ligands. When the concentration of strong ligand increased, the diameter of nanowires synthesized would be decreased regardless the size of seeds. In this way, this method showed its controllability in nanowire dimensions. Last, the nanowires

synthesized using this method was not perfectly straight like the conventional single crystalline metal nanowires. This characteristic showed that in this method, the chosen strong ligands were not designed to cover certain facets in order to assist nanowire growth.

With these unique characteristics, this unconventional Au NW growth method distinguished itself from other solution-based synthesis methods, in which seeds were often recognized as nucleation centers in colloidal synthesis. In traditional VLS method, as the entire molten seed and precursor acted as the catalyst as a whole, the diameter of resulting nanowire was usually similar to or slightly larger than the size of seed.^[89] The high tunability of the resulting nanowire using this reported method according to the authors has showed its difference from the conventional solution-based synthesis methods. In VLS synthesis method, high temperature and molten seeds were necessary for vapor phase supply of designated building blocks, whereas in this solution-based method, proper mixing ratio of precursors, room temperature and ambient conditions is enough for nanowire arrays to grow.^[89,153] Apart from this, growth was originated from the interface between seed and nanowire, thus seeds were pushed away from grown nanowire by newly grown segment in VLS method.^[89] On the contrary, seeds were always pushed away from the substrate by freshly grown segments from the interface between nanowire and substrate at the bottom.

Besides the facile preparation procedure and high tunability in dimensions of resulting nanowire arrays, this method distinguished itself from other solution-based methods by the flexibility in terms of substrate choices. According to the authors, a variety of oxide surfaces, even including natural snail shell surface, could be used as substrate for nanowire array growth.^[153] Au NW may also be grown on glass fibers and used as fixed-bed catalysts for reduction of 4-nitrophenol to 4-aminophenol.^[163] Au NW could also be grown onto fluorine doped tin oxide (FTO) glass substrate. This has brought a possibility for this type of ultrathin Au NW array to be used as electrochemical catalyst. Besides the flexibility in substrate

choice, some other noble metal nanowire arrays other than gold, such as silver and palladium, may also be synthesized using this facile method.^[164] With a slight modification in synthesis procedure, Au-Pd di-block nanowires can also be prepared using this method.^[164]

The strong synthetic controllability of this facile solution-based method to prepare substrate-bound vertically standing nanowire array has been applied to various scenarios. Qian et al. have prepared a monolithic gold aerogel with ultralow density by simply prepared the Au NW using this method at gram scale, made them into suspension and freeze-dried into a gold aerogel.^[165] Zhai and coworkers prepared Au NW forest via aforementioned seeded mediated method and then immobilized them onto PDMS to prepare a stretchable and wearable electrode for biosensing of hydrogen peroxide.^[166] Zhu et al grew Au NW on a PDMS pyramid microarray-based hierarchical structure as pressure sensor for preparation of wireless heart rate device.^[167] Gong and coworkers utilized a modified stepwise nanowire coverage and growth method to prepare staircase-like nanowire patches.^[168] It was called electronic skin for its property of location and sharpness sensitive to fingertip touch.

Apart from the various applications of Au NW mentioned above, when Au NW was coated with other noble metal such as Pd and Pt, the application can be extended to electrochemical sensing and catalysis. The flexibility of substrate choices, the tunability of nanowire length and diameter, the facile preparation procedure and the variety of candidate noble metals had made this method an ideal system in electrochemical catalysis study, which will be explored in Chapter 5. Before that, the exploration of more substrate choices and an improved method without seed usage would be discussed in Chapter 3 and Chapter 4. The nanowire structure related catalytic properties and relative mechanistic discussion in ethanol oxidation would be discussed in Chapter 5.

1.4. Research motivation and summary

This thesis mostly summarizes the synthetic modification on vertically standing Au NW arrays, the alternative substrates to grow Au NW on, the morphology induced catalytic properties, and application brought by these properties. The research was focused on synthesis, morphology, property and application of ultrathin Au NW. We started our research on vertically standing ultrathin Au NW by exploring alternative substrate to expand the application range, investigating modified preparation method to achieve more facile synthesis, exhibiting a greatly enhanced operation durability which correlated with morphology and finally proposing a hypothesis regarding mechanistic understanding behind the greatly enhanced durability.

Exploration on alternative metal substrate for preparation of substrate bounded Au NW was discussed in chapter 2. We attempted to tackle with the galvanic replacement problem by approaches like changing surface function group using different silanes, increasing the concentration of thiol ligand used in the Au NW growth step, screening for the proper thiol ligand that might form a layer for capping the metal surface to inhibit galvanic reaction without interfering Au NW growth, adding a ligand or blocker solution pre-treatment procedure before Au NW growth, performing a prior galvanic replacement reaction to consume the surface metal, and finally creating a layer of oxidized surface metal to inhibit the galvanic reaction. Approach that aimed for enhancing the gold reduction rate were also investigated using different reducing agent and increasing the reducing capability by adding sodium hydroxide. Finally, we succeeded in growing bundles of ultrathin Au NW on to the micro-sized Ag NW with the concentration that could undergo further treatment and form transparent conductive film. With less surface silver to consume than bulk silver foil, gold precursor remained just enough for Au NW growth after the galvanic reaction consumed a relatively low portion of gold precursors by surface silver atoms.

In chapter 3, we successfully reported a modified ultrathin Au NW forest preparation method to grow Au NW without the use of gold nanoseed. The modified method used salt adsorption instead of gold nanoseed adsorption. Charge induced nucleation step by adsorbed anions on the pretreated APTES layer is the key to facilitate the growth step without the use of seed. Reducing effect of anions were also studied. Finally, Na₂S was the best among all screened salts to obtain as almost the same vertically standing Au NW as seeded method could do. Finally, a synthetic scheme based on Na₂S was proposed and illustrated.

In chapter 4, we reported the modified preparation of Au@Pd NW with advantages offered by its morphology induced property to spontaneously enhance both catalytic activity and operation durability that may significantly enhance the performance of anode reaction in DEFCs. The vertically standing nanowire forest with tunable length prepared using active site growth method may provide high electrochemical active surface area for high catalytic activity and enhance the electronic charge transport efficiency at the same time. Furthermore, the improved mechanical strength brought by modified salt assisted method together with the highly tunable length and density of vertically standing Au@Pd NW can offer greatly enhanced operation durability at fixed potential for 200,000 s. Nearly 40% of the highest anodic performance remained by Au@Pd NW for catalyzing ethanol oxidation reaction could still be achieved even after 200,000 s at a fixed potential.

In chapter 5, we investigated the mechanistic reason behind the high durability we obtained by discussions on correlation between OH⁻ concentration and performance decrease in pristine Pd plate, inhibition memory effect brought by hydroxide species on short Au@Pd NW, intermediate species identification by in-situ Raman spectroscopy and product analysis by high performance liquid chromatography. By summarization of the aforementioned discussions, we proposed the OH⁻ species as the main inhibitor to poison Pd and bring

performance decrease during chronoamperometric test. Finally, we would like to propose a dual site hypothesis to explain the high durability of ultrathin Au@Pd NW.

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2. Exploration of alternative substrates for ultrathin Au NW forest growth

2.1. Introduction

Metal nanowires, especially noble metal nanowires, has attracted increasing attention during recent decades owing to their unique properties like high anisotropy and both heat and electronic conductivity which make them ideal candidates as linkage and substrate in nano-sized electronic devices. ^[1-3] With comparable working effect, noble metal nanowires have demonstrated their dominating role in applications like sensors and catalytic reactions by significantly decreasing the usage amount comparing to their bulk counterparts. ^[4-5] Gold and silver nanowires, the nanowires that have been studied the most among noble metal nanowires, have enjoyed the most attentions on both their preparation method and their variety of applications. ^[6-11]

In the first chapter, unique synthetic approach reported by J. He for preparation of ultrathin Au NWs forest on substrate surface has been discussed briefly. ^[12] The preparation method was quite unconventional because the novel vertically aligned Au NW initiated their growth from the ultra small gold seed nanoparticles that were bound to the substrate surface. The unique Au NW forest preparation method distinguished itself from several other synthetic method for substrate bound nanowires by its controllability in up to tens of μm in length of nanowires and up to tens of cm^2 large scale in surface area in ambient conditions, unlike the traditional VLS method normally at harsh condition and high temperature.

Additionally, the diameter of the Au NW array forest could be controlled within a relatively wide range when tuning the concentration of 4-MBA, regardless of the shape or diameter of the gold seed used. Besides that, the length of the synthesized Au NW array could be tuned simply by variation of the preparation time. All of the useful characteristics of ultrathin Au NW forest mentioned above could make it an outstanding candidate in a wide variety of applications as fixed-bed sensor or electrochemical catalyst. Apart from that, when using active site growth method to grow substrate bounded ultrathin Au NW forest, substrate could be varied from oxide substrates like surface partial oxidized silicon wafer, trumpet shell, ^[12] glassy fiber, ^[13] ordered zinc oxide pillar arrays, ^[14] plastic, paint and even on the surface of colloidal silica nanoparticles. The ability to grow Au NW forest on semi-conductive substrates makes it easier to explore potential applications in the field of electrochemical sensing and electrocatalysis.

However, before the substrate bounded ultrathin Au NW forest could be used as electrocatalyst, there were still some problems to solve. First of all, the choice of substrate which Au NW stands on during electrocatalysis may be a crucial factor. It's not enough to be only conductive or semi-conductive. The candidate substrate should be of large surface area in order to utilize the potential in substrate bounded Au NW nano forest. Besides that, the mechanical strength and mechanical stability of substrate bounded ultrathin Au NW forest might also be a challenging aspect. When prepared on oxide based semi-conductive substrates or carbon-based conductive substrates, there were usually no binding between gold seed nanoparticles and the substrate outer surface. In this way, although the ultrathin Au NW forest on oxide-based substrates showed impressive mechanical stability after completely dried, they still might experience a major peeling off when scratched on wet surface with as prepared ultrathin Au NW forest. Thus, the appropriate approach to enhance the bonding

between the substrate surface and the vertically standing ultrathin Au NW forest should be also of high importance.

With the discussed criterion above, metal substrate, either noble metals or transition metals could be taken into consideration as potential candidates. First of all, metal foils and metal-based substrates could be of higher conductivity than traditional oxide based semi conductive substrates like silicon wafer, fluorine doped tin oxide (FTO) and Indium doped tin oxide (ITO). Higher conductivity could be essentially beneficial to a wider variety of applications in electrochemical sensing and electro catalysis. Among conductive metal-based substrates, Ag was widely used as an ideal candidate for transparent conductive film. Cu could be used as conductive board as well as soft substrates for conductive wearable devices. Ni has a wide variety of applications in solar cell, fuel cell and lithium batteries as conductive counterparts. Exploration of potential possibilities for substrates of ultrathin Au NW forest among the 3 above mentioned metals could expand their existing applications without compromising unique features of ultrathin Au NW forest. Apart from that, if the Au NW could grow nicely on flat metal substrates, the metal-metal (M-M) bond might strongly enhance the mechanical strength as well as the mechanical stability of the substrate bounded ultrathin Au NW on the designated metal substrate.

The main obstacle to achieve Au NW growth on bulk Ag and Cu was galvanic replacement. In this chapter, we struggled to tackle with the galvanic replacement problem that sabotaging the gold reduction process by approaches like changing surface function group using different silanes, increasing the concentration of thiol ligand used in the Au NW growth step, screening for the proper thiol ligand that might form a layer for capping the metal surface to inhibit galvanic reaction without interfering Au NW growth, adding a ligand or blocker solution pre-treatment procedure before Au NW growth, performing a prior galvanic replacement reaction to consume the surface metal, and finally creating a layer of oxidized

surface metal to inhibit the galvanic reaction. While almost all trials on bulk Ag and Cu were not enough for Au NW growth, it was demonstrated that while bulk Ag and Cu with multiple facets were not easy to be consumed those atoms on the surface by galvanic replacement, nanosized Ag and Cu would possess less surface atom in total number to consume gold precursor via galvanic replacement, which might result in an alloy surface adjacent to the gold nanowire array part. In other words, an alloyed nanoparticle or nanowire head and nanowire tail heterogeneous nanostructure could be prepared and may shine light on more complicated applications based on heterogeneous nanostructures.

Here, we would like to share our trials to explore the alternative substrates that were ideal for facilitating substrate bounded ultrathin Au NW forest growth. Although the goal of selecting an ideal metal substrate was only achieved on Ni while the strong galvanic replacement effect cannot be compromised by ligand modification in the case of Ag and Cu, the problems and experiences we gained in the trial might be useful for future work.

2.2. Materials and methods

2.2.1. Materials

All the aqueous solutions used in the following experiments were prepared using deionized water (resistivity $> 18 \text{ M}\Omega\cdot\text{cm}^{-1}$). Hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49.9% on metals basis, Sigma Aldrich), copper foil (thickness 0.25 mm, 99.999% trace metal basis, Sigma Aldrich), brass foil (Cu 63% / Zn 37%, thickness 0.5 mm, Sigma Aldrich), silver foil (thickness 0.25 mm, 99.999% trace metal basis, Sigma Aldrich), copper(II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2\cdot 5\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), silver nitrate (AgNO_3 , $>99.0\%$, Sigma Aldrich), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), iron(II) nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $>99\%$, Sigma Aldrich), 4-mercaptobenzoic acid (4-MBA, 90%, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), 3-cyanopropyltriethoxysilane (CPTES, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), sodium borohydride (98%, Sigma Aldrich), hydroquinone (1,4-benzenediol, $>99.0\%$, Sigma Aldrich), ethanol for AuNW growth (99.85% technical grade) were used as received. Copper specimen grids (200 meshes) with carbon support film were purchased from Beijing XXBR Technology Co. Silicon wafer (6" Si (100) wafer, prime grade, 1-10 Ω/cm). Fluorine doped tin oxide (FTO) glasses (15mm x 10mm x 0.5mm) were purchased from Sigma Aldrich. Nickel foams with 1.0mm thickness were purchased from Suzhou JSD Co. Ltd.

2.2.2. Methods

Characterization methods. All transmission electron microscopy (TEM) images were obtained on a JEM-1400 (JEOL) operated at 100 kV. All field emission scanning electron microscopy (SEM) images were obtained on JSM-6700F (JEOL).

Preparation of TEM Samples. TEM copper grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 30 s to improve the surface hydrophilicity. Then the sample solution was dropped onto the hydrophilic face of TEM copper grids placed on the filter paper in less than 30 min. The filter paper below TEM copper grids was used to wick off the excess sample solution around the TEM grid, which was then dried in air for 1 h.

Synthesis method of 3-5 nm gold nanoseed (Au NS). A 50 mL round bottom flask was filled with 20 mL deionized water. 160 μ L sodium citrate (1 wt%) aqueous solution and 100 μ L HAuCl₄ (50 mmol/L) aqueous solution was added into the flask and kept stirring for 1 min. Then 620 μ L NaBH₄ (0.1 mol/L) aqueous solution prepared by ice water was added in one shot with vigorous stirring. The solution turned from light yellow to reddish orange, indicating the successful formation of Au NS. The solution was kept stirring for 30 min and stood still for at least overnight for the consumption of unreacted NaBH₄.

Synthesis of AuNW on Si wafer substrate. Before growing AuNW forest on Si wafer, the as-purchased Si wafer was first cut into 1 x 1 cm² piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the Si wafer was continuously sonicated in deionized water for 15 min for 3 times. The clean Si wafer was left to dry on filter paper before use. Later the Si wafer was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated nickel foam was washed with ethanol twice and with water twice to remove the excess silane in the Si wafer. After each washing step, the excess ethanol or water on the Si wafer was removed by filter paper. After functionalized by CPTES, the Si wafer was soaked in citrate stabilized Au NS (diameter 3-5 nm) solution for 1 h to complete the adsorption step of Au NS. Then the Si wafer was washed with water twice to remove the excess unabsorbed Au NS. The Au NS-adsorbed Si wafer was then immersed in the thoroughly mixed reaction solution containing 890 μ L ethanol and 522 μ L water as solvent,

110 μL 10 mmol/L 4-MBA in ethanol as ligand, 68 μL 50 mmol/L HAuCl_4 in water as gold precursor and 410 μL 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the Si wafer with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Typical synthesis of AuNW on nickel foam substrate. Before growing AuNW forest on nickel foam, the as-purchased nickel foam was first cut into $0.5 \times 1 \text{ cm}^2$ piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the nickel foam was continuously sonicated in deionized water for 15 min for 3 times. The clean nickel foam was left to dry on filter paper before use. The nickel foam was functionalized with cyano or amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated nickel foam was washed with ethanol twice and with water twice to remove the excess silane in the nickel foam. After each washing step, the excess ethanol or water in the nickel foam was removed by filter paper. After functionalized by APTES, the nickel foam was soaked in citrate-stabilized Au NS (diameter 3-5 nm) solution for 1 h to complete the adsorption step of Au NS. Then the nickel foam was washed with water twice to remove the excess unabsorbed Au NS. The Au NS-adsorbed nickel foam was then immersed in the thoroughly mixed reaction solution containing 890 μL ethanol and 522 μL water as solvent, 110 μL 10 mmol/L 4-MBA in ethanol as ligand, 68 μL 50 mmol/L HAuCl_4 in water as gold precursor and 410 μL 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the nickel foam was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Synthesis method of AuNW on nickel foam substrate with stirring. To grow AuNW on nickel foam with stirring, all reaction conditions were unchanged except that during APTES functionalization step, Au NS adsorption step and AuNW growing step, a stir bar was added in the solution and kept stirring.

Synthesis method of AuNW on nickel foam substrate with a different silane. To grow AuNW on nickel foam with CPTES, all reaction conditions remained unchanged except the replacement of APTES with CPTES. The stirring condition can be stirring or not stirring.

Synthesis method of AuNW on nickel foam substrate without Au NS. After the nickel foam was functionalized with silanes and washed, the nickel foam was directly placed into the gold growing solution and stand still for 30 min. Then AuNW can be grown on nickel foam.

Synthesis method of AuNW on Cu/brass/Ag foil substrate. Before growing AuNW forest on Cu/brass/Ag foil, the as-purchased Cu/brass/Ag foil was first cut into 1 x 1 cm² piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the Cu/brass/Ag foil was continuously sonicated in deionized water for 15 min for 3 times. The clean Cu/brass/Ag foil was left to dry on filter paper before use. Later the Cu/brass/Ag foil was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated Cu/brass/Ag foil was washed with ethanol twice and with water twice to remove the excess silane on the noble metal foil. After each washing step, the excess ethanol or water on the Cu/brass/Ag foil was removed by filter paper. After functionalized by APTES, the Cu/brass/Ag foil was soaked in citrate stabilized Au NS (diameter 3-5 nm) solution for 1 h to complete the adsorption step of Au NS. Then the Cu/brass/Ag foil was washed with water twice to remove the excess unabsorbed Au NS. The Au NS-adsorbed Cu/brass/Ag foil was then immersed in the thoroughly mixed reaction solution containing 890 μ L ethanol and 522 μ L water as solvent, 110 μ L 10 mmol/L 4-MBA in ethanol as ligand, 68 μ L 50 mmol/L HAuCl₄ in water as gold precursor and 410 μ L 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the Cu/brass/Ag foil with Au was rinsed thoroughly with ethanol twice and with water twice and dried on filter paper.

Synthesis method of AuNW on Cu/brass/Ag foil substrate with stirring. To grow AuNW on nickel foam with stirring, all reaction conditions were unchanged except that during APTES functionalization step, Au NS adsorption step and AuNW growing step, a stirring bar was added in the solution and kept stirring.

Synthesis method of AuNW on Cu/brass/Ag foil substrate with a different silane. To grow AuNW on nickel foam with CPTES, all reaction conditions remained unchanged except the replacement of APTES with CPTES. The stirring condition can be stirring or not stirring.

Synthesis method of AuNW on Cu/brass/Ag foil substrate without Au NS. After the nickel foam was functionalized with silane and washed, the nickel foam was directly placed into the gold growing solution and stand still for 30 min. Then AuNW can be grown on nickel foam.

Trial substrate	Silane	With seed / seedless	Other variable condition	Successful or not
Si wafer	APTES	seed	-	Yes
Ni foam	APTES / CPTES	seed	-	both Yes
Cu / Brass / Ag	APTES / CPTES / MPTMS / MPTES	seed	-	all No
Cu / Ag	APTES	seed	Ligand concentration	all No
Cu / Ag	APTES	seed	Blocker treatment	all No
Cu / Ag	APTES	seed	Acid wash	all No
Cu / Ag	APTES	seed	Pre-galvanic replacement	all No
Si / Cu / Ag	APTES	seed	Enhance reducing rate by adding NaOH	Yes / No / No
Ag NW	APTES	seed	-	Yes

Table 2.1. Experimental parameters for control experiments in this chapter

2.3. Results and discussion

As was briefly discussed in introduction part, the standard preparation method of ultrathin AuNW forest on oxide substrate was thoroughly investigated by J. He et al.^[12] As was clearly stated in the experimental part, the unconventional active site preparation method consisted of prior substrate cleaning, subsequent substrate treatment, substrate surface functionalization, gold nanoseed adsorption, and finally the substrate bounded ultrathin Au NW forest growth. The selected substrate was first washed thoroughly with both organic solvent like acetone or ethanol and water to remove the surface organic residue. An oxygen plasma or vacuum plasma treatment should be followed afterwards to facilitate further surface cleaning and improve the hydrophilicity on the substrate surface. Then thoroughly cleaned substrate surface was functionalized by amino group provided by APTES solution. Gold seed colloidal solution was later used to carry out seed adsorption procedure on as treated substrate surface so that the anchoring points for following gold deposition could be able to bound on the substrate surface owing to the affinity between amino group and gold seeds. Finally, the gold precursor was reduced onto the fresh active sites between substrate bounded gold nanoseed with top portion covered by thiolate ligand and surface. With more and more gold precursor get reduced, substrate bounded ultrathin Au NW forest was prepared finally.

However, the drawbacks of the as reported unconventional method might be obvious. Although the growth of substrate bounded ultrathin Au NW forest could significantly enhance the conductivity of even nonconductive substrates like trumpet shells and glass fibers, the conductivity after enhancement was still limited and insufficient to carry out electro catalysis and electrochemical sensing. Apart from that, the mechanical strength and stability of substrate bounded ultrathin Au NW forest was quite weak for the purpose of carrying out solution based electrochemical catalytic reactions. All these disadvantages urged

the further exploration of more conductive substrates with enhanced binding between gold and substrate materials. Among the conductive candidates, metals should be the first several options to start with as metal and gold was more likely to form stronger binding than carbon.

To start with surface bounded ultrathin Au NW forest growth on metal substrates, the standard preparation method has to be amended to tackle with the problem brought by the metal nature of galvanic replacement. There were quite a few successful works to grow gold over copper and silver into core shell multi counterpart nanostructures without sabotaging the original copper and silver nanostructures. The key points they made in their successful preparation methods were mainly focused on the controllability over both galvanic replacement reaction rate and reduction rate of gold precursor by reducing agent. With the knowledge and trends provided by these works, it was principally decided that our design principle should focus on reducing the galvanic replacement reaction rate, spontaneously promoting the reduction rate of gold precursor and controlling fresh gold deposition selectively on the active site on the bottom of vertically standing Au NW.

We first carried out the preparation of substrate bounded vertically standing ultrathin Au NW on copper foil, brass foil, silver foil, nickel foam and silicon wafer using the standard method reported by J. He. The metal substrates together with silicon wafer for control experiments were washed thoroughly before stood still for oxygen plasma in 15min. Later they were treated with APTES solution for 15min before washed and soaked in colloidal solution of gold nanoseed with diameter of 3-5 nm. Finally, they were put in the Au NW growth solution containing gold precursor, 4-MBA as thiolate ligand and L-ascorbic acid as reducing agent for 15min. According to Fig. 2.1 and Fig. 2.2, judging by the color change before and after Au NW growth, at least gold was successfully grown onto these metal substrates. However, when they were characterized under SEM, we found from Fig. 2.3 that Au NW growth only partially succeeded on nickel foam while there was not a single standing

nanowire on resulting Cu, brass and Ag foil. Even partially succeeded on Ni foam, from Fig. 2.3 we could still see relatively large portion of short nanowires and nanoparticles that were not likely to be pre-adsorbed gold nanoseeds apart from the bundles of vertically standing Au NW on the surface of Ni foam. On copper and brass foil, there seemed no significant change on the nanoscale morphology judging from Fig. 2.3 b) and Fig. 2.3 c). If there were no color change judging from Fig. 2.1 and Fig. 2.2, it was difficult to tell whether there was gold grown onto the copper and brass substrate or not. On silver foil, however, there were significant nanoscale surface morphological changes took place when gold was reduced onto silver foil. Tiny standing nano sheets or spikes were identified on the as synthesized silver surface.

Fig. 2.1. Photo of selected bulk metal substrates after thoroughly washed and before Au NW growth.

Fig. 2.2. Photo of selected bulk metal substrates after Au NW growth.

Fig. 2.3. SEM images of Au growth on nickel foam (a), copper foil (b), brass foil (c) and silver foil (d) by using as reported growth method for vertically standing ultrathin Au NW forest. (Scale bar: 1 μm)

A piece of silicon wafer undergoing the same synthetic procedure with the four bulk metal substrates was placed together in the same reaction pot during the Au NW growth to ensure that the reproducibility of the as reported unconventional growth method. Judging from Fig. 2.4, there were uniform vertically standing ultrathin Au NW on the silicon wafer. This control result showed that there was still sufficient gold source in the growth solution. When no galvanic replacement effect near the surface of silicon wafer, the relatively inert substrate, vertically standing ultrathin Au NW would be able to grow normally as reported. It seemed that the sufficient gold source remaining in growth solution could not reach the active site between pre-adsorbed gold seed and bulk metal substrate and was reduced and

accumulated elsewhere instead. It could be concluded that the reaction rate of galvanic replacement might be all higher than gold reduction rate in the three respective failed cases while the remaining gold source in bulk solution was still enough for successful and partially successful growth on silicon wafer and nickel foam.

Fig. 2.4. SEM images of Au NW growth on Si wafer by using as reported growth method for vertically standing ultrathin Au NW forest as a control result. (Scale bar: 100 nm)

According to our design principle discussed previously, we first decide to focus on approaches to hinder or suppress galvanic replacement reaction rate between reduced gold precursor and bulk metal foil. As was reported in the standard preparation method, the substrate surface was functionalized by APTES to provide amino group which was known helpful for adsorption of gold nanoseed onto the as treated substrate. The layer formed by slightly hydrolyzed APTES assembly should be a layer that might benefit in prohibiting galvanic replacement. However, the slightly positive charge on amino group owing to low degree of water hydrolysis might brought extra chances for gold nucleation onto the substrate instead of onto the active site between the substrate and the pre-adsorbed gold nanoseed.

With this hypothesis, we decided to try different silane such as CPTES, MPTMS and MPTES to decrease the amino group assisted gold nucleation effect.

From Fig. 2.5, it was showed clearly that changing surface function group from amino group to cyano and thiol group failed to solve the problem that gold may nucleate on the Cu foil surface instead of deposit at the active site between metal substrate and pre-adsorbed gold nanoseed. Aggregated bulky micro sized particles and clusters could be seen on CPTES treated Au on Cu foil, which implied the excessive gold nucleation and aggregation on the top of copper foil might be the cause for exhaustive consumption of gold precursor. When MPTMS and MPTES were used to replace APTES, the resulting Au on Cu foil also tend to have nanoparticle aggregations. What's more was that on thiol group treated Cu foil, the surface of the resulting Au on Cu seemed to have nanostructures with different layer, indicating that incomplete coverage of the silane layer may be the reason for failure to suppress galvanic reaction. In the case of brass foil showed in Fig. 2.6, similar situation happened when changing the surface function group from amino group to cyano and thiol group. As brass was copper and zinc alloy, making it difficult to distinguish the influence between respective metals, we would focus more on pure copper foil as substrate.

Fig. 2.5. SEM images of Au growth on Cu foil by using modified growth method in which APTES was replaced by CPTES (a), MPTMS (b), and MPTES (c) for vertically standing ultrathin Au NW forest as a control result. (Scale bar: 1 μ m)

Fig. 2.6. SEM images of Au growth on brass foil by using modified growth method in which APTES was replaced by CPTES (a), MPTMS (b), and MPTES (c) for vertically standing ultrathin Au NW forest as a control result. (Scale bar: 1 μm)

From Fig. 2.7, it was clearly presented that changing surface function group from amino group to cyano and thiol group also failed to solve the problem that gold may nucleate on the Ag foil surface instead of deposit at the active site between metal substrate and pre-adsorbed gold nanoseed. When cyano group was used in the modified preparation method, more severe aggregates of bulky silver and gold bimetallic cubes than the Au on Ag foil using amino group. It could be indicated that the potential problem of amino group causing nucleation and aggregation might have become more severe when cyano group was used. In the thiol group cases, however, the resulting Au on Ag foil has similar nanoscale surface structure to the one using amino group. The tiny standing bimetallic nanosheets or spikes could be seen almost everywhere while no NWs could be identified. Unlike the behaviors on Cu and brass foil, there were no multilayer of Au and Ag bimetallic nanostructures on the topmost surface, indicating that there might be no clear evidence for incomplete coverage by MPTMS and MPTES on Ag foil. It could be concluded that the changing of molecules for surface functionalization was not able to hinder or suppress galvanic replacement reaction from sabotaging the reducing process of gold onto the active site between the metal substrate and pre-adsorbed gold seed.

Fig. 2.7. SEM images of Au growth on Ag foil by using modified growth method in which APTES was replaced by CPTES (a), MPTMS (b), and MPTES (c) for vertically standing ultrathin Au NW forest as a control result. (Scale bar: 1 μm)

Besides surface functionalization step, increasing ligand concentration to form binding between thiol group on thiolate ligand and surface metal atoms on substrate surface could be used as an alternative approach to suppress the galvanic replacement reaction.

Fig. 2.8. SEM images of Au growth on Cu foil by using modified growth method in which concentration of 4-MBA was changed to 10 mM (a), 50 mM (b), and 100 mM (c) for vertically standing ultrathin Au NW forest as a control result.

Fig. 2.9. SEM images of Au growth on Ag foil by using modified growth method in which concentration of 4-MBA was changed to 10 mM (a), 50 mM (b), and 100 mM (c) for vertically standing ultrathin Au NW forest.

Besides only increasing concentration of the ligand 4-MBA that was used in standard ultrathin Au NW growth, introduction of some other thiol ligand to be used to as mixed thiolate ligand solution in order to form a shield or coverage on surface metal atoms on substrate surface could be treated as a promising approach to suppress the galvanic replacement reaction without sacrificing the ultrathin Au NW growth. It was discussed by Y. Wang et. al. that thiol ligand with rigid bone structure and straight line configuration such as some aromatic ligand could form nice packing on the existing gold seed and be used as capping ligand for vertically standing ultrathin Au NW growth while the soft wavy aliphatic thiol ligand and some aromatic ligand having the configuration that could not form closely packing might lead to failure in preparation of Au NW. We decided to pick 2-naphthalenethiol and 6-mercaptopyridine-3-carboxylic acid as alternative candidates to test on Si wafer first before diving into gold growth on copper and silver surface.

Fig. 2.10. SEM images of ultrathin Au NW growth on Si wafer by using modified growth method in which surface was changed to 4-MBA as a control result (a), 2-naphthalenethiol (b), and 6-mercaptopyridine-3-carboxylic acid (c) for vertically standing ultrathin Au NW forest.

From Fig. 2.10, among the results of screening aromatic thiol ligand on Si wafer for Au NW growth, only the sample prepared using 2-naphthalenethiol as thiol ligand was found having at least some Au NW growth. According to experimental observation, the growth solution containing 6-mercaptopyridine-3-carboxylic acid turned to dark instantaneously after the addition of L-ascorbic acid as reducing agent. The reason for such immediate solution color change might be that either 6-mercaptopyridine-3-carboxylic acid was not an appropriate ligand that may form closely packing on gold surface, or it could not form a Au(III)-thiol ligand intermediate with gold precursor to control the deposition rate of gold, facilitating the formation of freestanding colloidal gold nuclei by the reduced gold precursor in the solution.

With the only two choices of ligand capping trial, two pieces of copper foil were soaked in 10 mM 4-MBA and 10 mM 2-naphthalenethiol ethanol solution respectively for 1 hour after they washed and functionalized by APTES solution before the adsorption of gold nanoseeds and gold growth step. However, we could tell from Fig. 2.11 that both gold on copper samples didn't have Au NW on copper foil surface. The copper foil treated with 4-MBA had bumps of gold and copper bimetallic clusters and aggregates. The copper foil treated with 2-naphthalenethiol had vertically standing sheet like spiky nanostructures as well

as bumps of gold and copper bimetallic aggregates on the bottom of the spiky nanostructures. Despite the fact that new nanostructures containing Au-Cu was prepared, the trial on preparation of Au NW on Cu substrate was still unsuccessful.

Fig. 2.11. SEM images of Au growth on Cu foil by using modified growth method in which a step of 1 hour substrate incubation in 10 mM 4-MBA (a) and 10 mM 2-naphthalenethiol (b) before the ligand capped Cu substrate were put into gold growth solution for preparing vertically standing ultrathin Au NW forest.

A series of molecules could be used as surface blocker to lower the contact between gold growth solution and metal substrates. To start with the exploration of effect of surface blocker chemicals, the Cu substrate was incubated for 1 hour in 1 mM polyethylene glycol 35000 (Fig. 2. 12. a), 1 mM N-[N α ,N α -Bis(carboxymethyl)-L-lysine]-12-mercaptododecanamide (Fig. 2. 12. b), 10 mM polyacrylic acid (Fig. 2.12. c) and 10 mM poly(ethylene glycol) methyl ether thiol (Fig. 2. 12. d) before the blocker capped Cu substrate were put into gold growth solution. As was shown in Fig. 2.12, no successful Au NW preparation was achieved on blocker molecule capped Cu substrate surface.

Fig. 2.12. SEM images of Au growth on Cu foil by using modified growth method in which a step of 1 hour substrate incubation in 1 mM polyethylene glycol 35000 (a), 1 mM N-[Nα,Nα-Bis(carboxymethyl)]-L-lysine]-12-mercaptododecanamide (b), 10 mM polyacrylic acid (c) and 10 mM poly(ethylene glycol) methyl ether thiol (d) before the blocker capped Cu substrate were put into gold growth solution for preparing vertically standing ultrathin Au NW forest.

After we had tried three kinds of approaches to introduce surface hindrance on bulk metal foil and failed, what was planned next was purposely performing a galvanic replacement before the whole preparation procedure. The planned galvanic replacement was designed to consume surface copper / silver atoms with the equivalent amount of gold precursor in the solution. The modified method with the addition of prior galvanic replacement reaction was almost the same with as reported standard preparation method

except that the washed metal substrate was soaked in gold growth solution for 15min before even APTES treatment. After the prior galvanic replacement reaction, the copper foil and silver foil all could be identified with significant color change. They were washed with water for 2 times and treated with APTES, gold seed and finally gold growth solution.

From Fig. 2.13, a significant nanoscale morphological change on copper foil (b) compared to normal copper foil with gold nanoseeds (a) could be identified with the presence of large amount of triangular nanosheets strings that were highly possible to be gold and copper bimetallic nanostructure. It's interesting to know that gold-copper bimetallic triangular nanosheets could be prepared simply by galvanic replacement reaction probably with the help of 4-MBA. Also, a significant change from gold on copper foil after prior galvanic replacement (b) to gold on copper foil (c) prepared by standard active site growth method after (b) could be identified with surprise. There was some relatively large triangular frame like residue on the top of gold-copper bimetallic clusters and aggregates on the copper substrate surface. It could be concluded that in copper foil case, purposely designed prior galvanic replacement before Au NW growth could not solve the problem of galvanic replacement interfering normal Au NW growth.

Fig. 2.13. A modified growth method was used that a step of prior galvanic replacement using the growth solution without reducing agent was added to consume the surface galvanic reactive copper. SEM images of morphology of nanoscale bulk Cu foil with pre-adsorbed gold nanoseed (a), Au on Cu foil after the first galvanic replacement (b) and Au on Cu foil after the first galvanic replacement and the standard gold growth procedure (c).

From Fig. 2.14, a significant nanoscale morphological change on silver foil (b) compared to normal silver foil with pre-adsorbed gold nanoseeds (a) could be identified with the presence of large amount of both irregular micrometer-sized polyhedrons and nanometer-sized particles and clusters that were highly possible to be gold and silver bimetallic nanomaterial on the top of probably silver foil substrate. The irregular micrometer-sized gold and silver bimetallic polyhedrons were not seen in any of the previous results. As the only thing that was different between prior galvanic reaction and standard Au NW preparation method was the addition of reducing agent L-ascorbic acid, it could be indicated that the presence of L-ascorbic acid might accelerate the accumulation of reduced gold species during the initial stage of gold reduction. This fact might bring up a hypothesis that any approach that only by altering reducing rate acceleration without effective inhibition to spontaneous galvanic replacement reaction might not be able to work well. Also, a significant change from gold on silver foil after prior galvanic replacement (b) to gold on silver foil (c) prepared by standard active site growth method after (b) could be identified. There was vertically standing gold silver bimetallic nanosheets and spikes standing on the previous irregular polyhedron surface. In addition, we could see that the polyhedron nanostructures on which nanosheets stood (c) were shorter than those grown in prior galvanic replacement reaction (b), indicating the consumption of material of the polyhedrons and the gold silver bimetallic nature of the micrometer sized polyhedrons. It could be also concluded that in silver foil case, purposely designed prior galvanic replacement before Au NW growth could not solve the problem of galvanic replacement interfering normal Au NW growth.

Fig. 2.14. A modified growth method was used that a step of prior galvanic replacement using the growth solution without reducing agent was added to consume the surface galvanic reactive silver. SEM images of morphology of nanoscale bulk Ag foil with pre-adsorbed gold nanoseed (a), Au on Ag foil after the first galvanic replacement (b) and Au on Ag foil after the first galvanic replacement and the standard gold growth procedure (c).

Creating a thin oxide layer on topmost of Cu and Ag surface layer could also be a potential approach to work on. To easily create a thin oxidized metal layer on the thoroughly washed bulk metal foil, oxygen plasma for a longer time were used to try in the first place. From Fig 2.15, the approaches using dilute acid to clean Cu surface only (a), dilute acid washed and plasma (b) and only plasma (c) exhibited the morphological change with washing rather than with plasma. In the two Cu bulk substrates that were washed with dilute acid, long and large bumps of aggregated nanostructures could be identified while in the case without any wash only plasma treatment, the as prepared Cu surface was piled with small aggregates of nanostructures. It could be concluded that oxygen plasma was not useful in inhibiting galvanic replacement.

Fig. 2.15. SEM images of Au growth on Cu foil by using modified growth method in which a step of surface pre-treatment approach using dilute acid wash (a), dilute acid wash plus plasma (b), and plasma without dilute acid wash (c) on Cu foil substrate before proceeded to the rest of preparation steps for vertically standing ultrathin Au NW forest.

From Fig 2.16, the approaches using dilute acid to clean Ag surface only (a), dilute acid washed and plasma (b) and only plasma (c) exhibited the no abnormal morphological changes. There were no significant differences among the 3 as prepared bulk Ag substrate. Hence it could be concluded that oxygen plasma was not useful in inhibiting galvanic replacement in both Ag and Cu cases.

Fig. 2.16. SEM images of Au growth on Ag foil by using modified growth method in which a step of surface pre-treatment approach using dilute acid wash (a), dilute acid wash plus plasma (b), and plasma without dilute acid wash (c) on Ag foil substrate before proceeded to the rest of preparation steps for vertically standing ultrathin Au NW forest.

Long time wash in concentrated nitric acid could be another facile approach to create oxidized metal layer on bulk Cu and Ag foil substrate. From Fig 2.17, the approaches using

dilute acid to wash Cu surface only (a) and concentrated acid to create surface oxidation on Cu surface (b) exhibited similar morphological characteristics. There were only slight differences between the 2 resulting nanostructures of Au on Cu substrate. Hence it could be concluded that concentrated acid wash was not meant to creating densely packed oxide layer on metal substrate surface in inhibiting galvanic replacement in Cu case.

Fig. 2.17. SEM images of Au growth on Ag foil by using modified growth method in which a step of surface pre-treatment approach using dilute acid wash to only clean the surface (a) and concentrated acid wash to create a thin oxide layer (b) on Ag foil substrate before proceeded to the rest of preparation steps for vertically standing ultrathin Au NW forest.

From Fig 2.18, the approaches using dilute acid to wash Ag surface only (a) and concentrated acid to create surface oxidation on Ag surface (b) exhibited almost no abnormal morphological changes. There were no significant differences among the two resulting nanostructures of Au on Ag substrate. Hence it could be concluded that concentrated acid wash was not meant to creating densely packed oxide layer on metal substrate surface in inhibiting galvanic replacement in both Ag and Cu cases.

Fig. 2.18. SEM images of Au growth on Ag foil by using modified growth method in which a step of surface pre-treatment approach using dilute acid wash to only clean the surface (a) and concentrated acid wash to create a thin oxide layer (b) on Ag foil substrate before proceeded to the rest of preparation steps for vertically standing ultrathin Au NW forest.

In the reported active site growth method for preparation of vertically standing ultrathin Au NW, L-ascorbic acid was used as reducing agent. L-ascorbic acid was used widely in ambient condition as a reducing agent with slower reducing rate than sodium citrate at high temperature, hydroquinone, hydrazine, hydroxylamine, and sodium borohydride at room temperature. High temperature is not welcome in the active site method as it would sabotage the packing of thiolate ligand on the existing gold surface, making more potential active sites instead of only one at the bottom of the gold seed. On the other hand, sodium borohydride is much more reactive and would instantaneously cause the formation of large number of gold nuclei in growth solution instead of steady deposition at only the active site between substrate and existing gold seed. As a result, to enhance the reducing rate of reducing agent, the limited choice had to fall on hydroquinone, hydrazine, formaldehyde and hydroxylamine. From Fig 2.19, the only two successful Au NW growth on Si wafer for preliminary screening on reducing agents were prepared by L-ascorbic acid and hydroquinone.

Fig. 2.19. SEM images of ultrathin Au NW growth on Si wafer by using modified growth method in which different reducing agents, such as L-ascorbic acid as a control result (a), formaldehyde (b), hydrazine (c), hydroxylamine (d), hydroxylamine hydrochloride (e) and hydroquinone (f) with the same concentration of 20 mM were used at the gold reducing step for vertically standing ultrathin Au NW forest.

As only hydroquinone except for L-ascorbic acid could be used to synthesize vertically standing ultrathin Au NW on Si wafer, hydroquinone was used as reducing agent at the same concentration in the standard Au NW growth procedure. It could be seen from Fig. 2.20 that no Au NW could grow on copper foil and silver foil when using hydroquinone sharing the same concentration with L-ascorbic acid in standard Au NW growth procedure.

Fig. 2.20. SEM images of ultrathin Au NW growth on Si wafer (a), Cu foil (b) and silver foil (c) by using modified growth method in which 20 mM hydroquinone were used instead of 20 mM L-ascorbic acid at the gold reducing step for vertically standing ultrathin Au NW forest.

As only hydroquinone other than L-ascorbic acid could be used to synthesize vertically standing ultrathin Au NW on Si wafer, another approach using dilute NaOH as catalyst to promote the reducing rate of both L-ascorbic acid and hydroquinone could be used. To start with the trials on NaOH addition, L-ascorbic acid with NaOH was used as reducing agent at the same concentration in the standard Au NW growth procedure. It could be seen from Fig. 2.21. that Au NW could not be grown on copper foil and silver foil when using the same concentration of L-ascorbic acid with the help of NaOH in standard Au NW growth procedure.

Fig. 2.21. SEM images of ultrathin Au NW growth on Si wafer (a), Cu foil (b) and silver foil (c) by using modified growth method in which 20 mM L-ascorbic acid and 2 mM NaOH mixed solution were used instead of 20 mM L-ascorbic acid alone at the gold reducing step for vertically standing ultrathin Au NW forest.

Hydroquinone with NaOH was used as reducing agent at the same concentration in the standard Au NW growth procedure. It could be seen from Fig. 2.22. that Au NW could not be grown on copper foil and silver foil when using 20 mM hydroquinone with the help of 2 mM NaOH in standard Au NW growth procedure.

Fig. 2.22. SEM images of ultrathin Au NW growth on Si wafer (a), Cu foil (b) and silver foil (c) by using modified growth method in which 20 mM hydroquinone and 2 mM NaOH mixed solution were used instead of 20 mM L-ascorbic acid alone at the gold reducing step for vertically standing ultrathin Au NW forest.

Finally, after thoroughly investigated the previous results, it was decided that a last option that growth of Au NW on Ag NW before they were made into transparent conductive film could be tried. According to previous results, oxides were either fail to be formed or fail to hinder the exposure of surface metal atom. Small molecules like thiolate ligands and relatively larger molecules that might act as monolayer on the bulk metal surface could not create a layer between bulk metal surface atoms and gold precursor in solution. The addition of prior galvanic replacement reaction approach to solve the gold consumed by galvanic reaction problem was not working. Options aimed at increasing the reducing rate of gold precursor to seek for chances to form Au NW before got reduced by bulk metal atoms were not working as well. The last aspect to tackle the problem was to decrease the amount of surface metal atoms to suppress galvanic replacement reaction rate by using less silver

substrate. Silver nanowire were reported as a good candidate for preparation of transparent conductive film. In the traditional preparation recipe, silver nanowire prepared in colloidal synthesis were used in dilute colloidal solution, which might be able to meet the requirement of less silver surface atoms on any substrate.

Fig. 2.23. SEM images of micro scale Ag NW on Si wafer (a) and successful ultrathin Au NW growth on micro scale Ag NW on Si wafer (b) by using as reported ultrathin Au NW forest growth method.

2.4. Conclusion

We have tried our best to explore the possibilities among conventional bulk metal substrates as alternatives for semi conductive silicon wafer and oxide based semi conductive substrates. During the initial screening part, we would be able to change the substrate from silicon wafer in the as reported ultrathin Au NW array growth method to nickel foam. Later, we struggled to tackle with the galvanic replacement problem that sabotaging the gold reduction process by approaches like changing surface function group using different silanes, increasing the concentration of thiol ligand used in the Au NW growth step, screening for the proper thiol ligand that might for a layer for capping the metal surface to inhibit galvanic reaction without interfering Au NW growth, adding a ligand or blocker solution pre-treatment procedure before Au NW growth, performing a prior galvanic replacement reaction to consume the surface metal, and finally creating a layer of oxidized surface metal to inhibit the galvanic reaction. Approaches that aimed for enhancing the gold reduction rate were also investigated using different reducing agent and increasing the reducing capability by adding sodium hydroxide. Finally, we succeeded in grow bundles of ultrathin Au NW on to the micro-sized Ag NW with the concentration that could undergo further treatment and form transparent conductive film. With less surface silver to consume than bulk silver foil, gold precursor remained just enough for Au NW growth after the galvanic reaction consumed a relatively low portion of gold precursors by surface silver atoms.

2.5. Reference

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3. Modified Na_2S assisted Au NW growth method without the use of seed

3.1. Introduction

Recently, using nanomaterial as catalysts for chemical reaction and electrochemical reaction has gained more and more interests due to its quantum size effect ^[1] and high surface area. Metal nanowire among them is especially attracting tremendous attention and efforts to develop their potential applications in catalysis owing to their unique physical and electronic properties. The ability to achieve morphological control over the growth of designated metal nanowire was of fundamental significance. In particular, to further explore the boundaries of synthetic capability for preparation of substrate bounded Au NW (Au NW) may not only expand the understanding of how different parameters affect the growth procedure but also provide a wider variety of application scenarios of the substrate bounded Au NW and its active surface growth method.

In the first chapter, a unique synthetic approach reported by J. He for preparation of ultrathin Au NW forest on substrate surface has been discussed briefly. ^[2] The preparation method was quite unconventional because the novel vertically aligned Au NW initiated their growth from the ultra small gold seed nanoparticle that were bound to the substrate surface. A follow-up work by Y. Wang initiated the preliminary exploration on synthetic parameters including ligand candidates and correlation between ligand molecular structure and ligand packing for substrate bound vertically standing Au NW growth. ^[3] Some other parameters

like alternative substrates screening and reducing agent screening was discussed in the previous chapter 2. However, with the inspiration of one trial to grow Au NW on silver and silver sulfide (Ag_2S) octahedral respectively (as shown in Fig 3.1), an idea came to light that the residue sulfide anion in Ag_2S octahedral colloidal solution might be the reason for the difference in Au NW density at the background other than bundles of Au NW originated from gold wrapped silver octahedral nanoparticles.

Fig. 3.1. SEM images of Au NW growth on Si wafer substrate by using Ag (a) and Ag_2S (b) octahedral nanoparticle as seed to grow Au NW. (Scale bar: 1 μm)

Here, we reported a modified vertically standing ultrathin Au NW forest preparation method to grow Au NW without the use of gold nanoseed. The modified method used salt adsorption instead of gold nanoseed adsorption. Charge induced nucleation step by adsorbed anions on the pretreated APTES layer is the key to facilitate the growth step without the use of seed. Reducing effect of anions were also studied. Na_2S was the best among all screened salts to obtain as almost the same vertically standing Au NW as seeded method could do. The standing nature of Na_2S assisted growth of Au NW in solution was demonstrated by using PDMS coating on Si wafer surface with Au NW to 'freeze' the standing posture of Au NW. Finally, a synthetic scheme based on Na_2S was proposed and illustrated.

3.2. Materials and methods

3.2.1. Materials

All the aqueous solutions used in the following experiments were prepared using deionized water (resistivity $> 18 \text{ M}\Omega\cdot\text{cm}^{-1}$). Hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49.9% on metals basis, Sigma Aldrich), sodium nitrate hydrate ($\text{NaNO}_3\cdot 5\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$, ACS reagent $>99\%$, Sigma Aldrich), 4-mercaptobenzoic acid (4-MBA, 90%, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), 3-cyanopropyltriethoxysilane (CPTES, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), sodium borohydride (98%, Sigma Aldrich), hydroquinone (1,4-benzenediol, $>99.0\%$, Sigma Aldrich), ethanol for AuNW growth (99.85% technical grade) were used as received. Copper specimen grids (200 meshes) with carbon support film were purchased from Beijing XXBR Technology Co. Silicon wafer (6" Si (100) wafer, prime grade, 1-10 Ω/cm).

3.2.2. Methods

Characterization methods. All transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 kV. All field emission scanning electron microscopy (SEM) images were collected on a JSM-6700F (JEOL). All electrochemistry data were collected on a CHI-760e electrochemical workstation.

Synthesis method of 3-5 nm gold nanoseed (Au NS). A 50 mL round bottom flask was filled with 20 mL deionized water. Then 160 μL sodium citrate (1 wt%) aqueous solution and 100 μL HAuCl_4 (50 mM) aqueous solution was added into the flask and kept stirring for 1

min. Then 620 μL ice-cold NaBH_4 (0.1 M) aqueous solution was added in one shot with vigorous stirring. The solution turned from light yellow to reddish orange, indicating the formation of Au NS. The solution was kept stirring for 10 min and collected to use after overnight for the consumption of unreacted NaBH_4 .

Synthesis of Au NW using seeded method on Si wafer substrate. Before growing Au NW forest on Si wafer, the as-purchased Si wafer was first cut into $1 \times 1 \text{ cm}^2$ piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the Si wafer was continuously sonicated in deionized water for 15 min for 3 times. The clean Si wafer was left to dry on filter paper before use. Later the Si wafer was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated Si wafer was washed with ethanol twice and with water twice to remove the excess silane in the Si wafer. After each washing step, the excess ethanol or water on the Si wafer was removed by filter paper. After functionalized by APTES, the Si wafer was soaked in citrate stabilized Au NS (diameter 3-5 nm) solution for 1 h to complete the adsorption step of Au NS. Then the Si wafer was washed with water twice to remove the excess unabsorbed Au NS. The Au NS-adsorbed Si wafer was then immersed in the thoroughly mixed reaction solution containing 890 μL ethanol and 522 μL water as solvent, 110 μL 10 mmol/L 4-MBA in ethanol as ligand, 68 μL 50 mmol/L HAuCl_4 in water as gold precursor and 410 μL 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the Si wafer with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Synthesis of Au NW using salt assisted method on Si wafer substrate. Before growing Au NW forest on Si wafer, the as-purchased Si wafer was first cut into $1 \times 1 \text{ cm}^2$ piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the Si wafer was continuously sonicated in deionized

water for 15 min for 3 times. The clean Si wafer was left to dry on filter paper before use. Later the Si wafer was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated Si wafer was washed with ethanol twice and with water twice to remove the excess silane in the Si wafer. After each washing step, the excess ethanol or water on the Si wafer was removed by filter paper. After functionalized by APTES, the Si wafer was soaked in respective salt solution for 1 h to complete the adsorption step of salt anion. Then the Si wafer was washed with water twice to remove the excess unabsorbed salt. The salt adsorbed Si wafer was then immersed in the thoroughly mixed reaction solution containing 890 μL ethanol and 522 μL water as solvent, 110 μL 10 mmol/L 4-MBA in ethanol as ligand, 68 μL 50 mmol/L HAuCl_4 in water as gold precursor and 410 μL 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the Si wafer with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Synthesis of Au NW using seed-adsorption and salt assisted method on Si wafer substrate. Before growing Au NW forest on Si wafer, the as-purchased Si wafer was first cut into 1 x 1 cm^2 piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the Si wafer was continuously sonicated in deionized water for 15 min for 3 times. The clean Si wafer was left to dry on filter paper before use. Later the Si wafer was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated Si wafer was washed with ethanol twice and with water twice to remove the excess silane in the Si wafer. After each washing step, the excess ethanol or water on the Si wafer was removed by filter paper. After functionalized by APTES, the Si wafer was soaked in citrate stabilized Au NS (diameter 3-5 nm) solution for 1 h to complete the adsorption step of Au NS. Then the Si wafer was washed with water twice to remove the excess unabsorbed Au NS. After that, the

Si wafer was soaked in 0.02 mM Na_2S solution for 1 h to complete the adsorption step of S^{2-} anion. Then the Si wafer was washed with water twice to remove the excess unabsorbed S^{2-} . The Au NS- Na_2S -adsorbed Si wafer was then immersed in the thoroughly mixed reaction solution containing 890 μL ethanol and 522 μL water as solvent, 110 μL 10 mmol/L 4-MBA in ethanol as ligand, 68 μL 50 mmol/L HAuCl_4 in water as gold precursor and 410 μL 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the Si wafer with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Synthesis of Au NW using Na_2S assisted method on Si wafer substrate. Before growing Au NW forest on Si wafer, the as-purchased Si wafer was first cut into 1 x 1 cm^2 piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the Si wafer was continuously sonicated in deionized water for 15 min for 3 times. The clean Si wafer was left to dry on filter paper before use. Later the Si wafer was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 30 min. Then the pretreated Si wafer was washed with ethanol twice and with water twice to remove the excess silane in the Si wafer. After each washing step, the excess ethanol or water on the Si wafer was removed by filter paper. After functionalized by APTES, the Si wafer was soaked in Na_2S solution with the concentration of 0.4 μM , 0.02 mM, 1 mM, 50 mM for 1 h to complete the adsorption step of salt anion. Then the Si wafer was washed with water twice to remove the excess unabsorbed Na_2S . The salt adsorbed Si wafer was then immersed in the thoroughly mixed reaction solution containing 890 μL ethanol and 522 μL water as solvent, 110 μL 10 mmol/L 4-MBA in ethanol as ligand, 68 μL 50 mmol/L HAuCl_4 in water as gold precursor and 410 μL 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the Si wafer with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

seeded / salt	seeded	HCl / NaOH	NaCl / NaNO ₃ / acetate	Na ₂ SO ₄ / Na ₂ CO ₃ / Na ₂ HPO ₄ / sodium tartrate	Na ₂ S / NaI
density	dense	sparse	sparse	sparse	dense
bundle	no	big / small	small	small / small / small / big	no

Table 3.1. Experimental parameters for control experiments in this chapter

3.3. Results and discussion

In a typical synthesis of substrate bound vertically aligned Au NW array, a Si wafer was thoroughly washed before putting into chamber of oxygen plasma to enhance the surface hydrophilicity. Later, the Si wafer would be put into APTES in ethanol and water mixed solution for functionalization of amino group by APTES assembly into a nice even layer. There followed the gold nanoseed (Au NS) adsorption step before the as treated Si wafer with Au NS was put into the Au NW growth solution with gold precursor, 4-MBA as ligand and L-ascorbic acid as reducing agent. It was in the seed adsorption step that sulfide anion might be involved in Au NW growth in the Ag₂S seed case in introduction part. Therefore, it could be interesting to know what it would be like when the whole preparation procedure for Au NW was carried out without the use of Au NS.

To start with exploration of alternative choices to facilitate Au NW growth instead of Au NS, a pair of control experiment with (Fig. 3.2.b) and without (Fig. 3.2.a) the use of Au NS was performed prior to exploitation of alternative anions. Comparing to a typical synthesis of substrate bound vertically aligned ultrathin Au NW arrays, the morphology of as prepared Au NW was significantly different in the way that there were bundles of Au NW with small head on one end of every bundle. The length of bundles of Au NW were approximately the same among bundles, indicating that the initial nucleation of Au on Si wafer probably started at the same time. The length of Au NW using typical seeded growth method, however, was only slightly shorter than that of Au NW bundles without Au NS involved during synthesis. Ideally if initial nucleation of the Au NW bundles happened at the same time of initial deposition on active surface at the bottom of Au NS, the Au NW bundles would be longer than typical Au NW owing to less nucleation sites originated in the initial nucleation step. The fact that Au NW and Au NW bundles had length with slightly difference might indicated that the initial nucleation step might take some time. In this case, the growth method without seed or any

other anion adsorption would sacrifice a bit of length. Besides that, bundles of Au NW with a small head on top could not stand on its own and be packed nicely like the typical Au NW. Therefore, it could be concluded that simply remove the Au NS adsorption step in preparation of standing nanowire arrays would not be able to achieve similar Au NW morphology with the typical preparation method.

Fig. 3.2. SEM images of Au NW growth on Si wafer substrate by using a modified ultrathin Au NW forest growth method without (a) and with (b) the use of gold nanoseeds. (Scale bar: 1 μm)

In the introduction part in this chapter we found that anion or salt residue on Ag octahedral or in colloidal Ag octahedral nanoparticle solution might be the reason for formation of densely lying Au NW originated from self nucleation. To exploit anion effect, pH effect should also be considered. In Fig 3.3, Au NW were prepared with the APTES functionalized substrate treatment in 0.02 mM HCl (Fig. 3.3.a) and 0.02 mM NaOH (Fig. 3.3.b). In acidic condition with pH of 4.7, the Au NW were in larger bundles with a increased diameter and decreased bundle number than Au NW bundles without the use of Au NS. In alkaline condition with pH of 9.3, the Au NW were in smaller bundles with a decreased diameter and increased bundle number than Au NW bundles without Au NS used. The trend in acidic condition and basic condition was distinctly and strangely different. Typically, if it was anion effect working, both anions were of the same concentration. Even if the relatively

fast diffusion rate of OH^- and H^+ in aqueous solution was in the way, the anion in acidic condition might vary so little even though H^+ concentration might vary a lot. Then ideally if Cl^- was distributed well on APTES functionalized Si wafer, the bundle number in acidic condition would be larger than that in alkaline condition. Thus, the high probable explanation to the decreased number of Au NW bundles in acidic condition should be that H^+ may neutralize the partially hydrolyzed APTES functionalized Si wafer surface, suppressing the anion adsorption effect. Although the number of Au NW bundles on Si wafer treated in alkaline condition was larger than that without Au NS treatment, it was still smaller than our initial sulfide anion treated data. The slight bump in the middle of Au NW bundles in both conditions might be caused by some unexpected change of growth solution during the preparation procedure. Therefore, it could be concluded that in order to facilitate vertically standing Au NW growth, either HCl or NaOH should not be ideal chemicals for APTES functionalized Si wafer to be treated with.

Fig. 3.3. SEM images of Au NW growth on Si wafer substrate by using an acid (a) and base (b) treated modified ultrathin Au NW forest growth method without the use of gold nanoseeds. (Scale bar: 1 μm)

Further screening among salts were started from anions with 1-negative charge. Sodium chloride (NaCl), sodium nitrate (NaNO_3) and sodium acetate were picked and used in 0.02

mM respectively. The resulting Au NW prepared on APTES functionalized Si wafer substrate treated by NaNO_3 (Fig. 3.4.a), NaCl (Fig. 3.4.b) and sodium acetate (Fig. 3.4.c) shared similar morphology, which was that some small bundles of Au NW and a large number of single Au NW lying down on the substrate as the low density between NWs failed to hold themselves up. Despite the difference between bundle sizes from several tens of NWs to one, almost all NWs had small heads on top of them. Their Au NW bundles was way smaller than those of no seed and alkaline treated ones. However, the three screened 1-negative charged anions were all no better than sulfide anion or Au NS in facilitating nicely distributed Au NW growth.

Fig. 3.4. SEM images of Au NW growth on Si wafer substrate by using a series of 1-negative anions NaNO_3 (a), NaCl (b) and sodium acetate (c) treated modified ultrathin Au NW forest growth method without the use of gold nanoseeds. (Scale bar: 1 μm)

Anions with 2-negative charge were also screened accordingly. By treated in Na_2SO_4 (Fig. 3.5.a), Na_2CO_3 (Fig. 3.5.b), Na_2HPO_4 (Fig. 3.5.c) and sodium tartrate (Fig. 3.5.d) after APTES functionalized step before Au NW growth, the resulting morphology of Au NW were slightly different from each other. The Au NW using Na_2SO_4 , Na_2CO_3 and Na_2HPO_4 could achieve similar density while the Au NW using sodium tartrate were bundles of Au NW lying down on the Si wafer. It might be the larger size of the anion in the case of sodium tartrate that it might be adsorbed on APTES surface with a larger spatial distribution than smaller anions like sulfate, carbonate and hydrogen phosphate. The Au NW using Na_2SO_4 , Na_2CO_3

and Na_2HPO_4 were slightly better than Au NW using NaNO_3 , NaCl and sodium acetate in the way that even smaller bundles and heads on NW top could be found. It could be indicated that 2-negative charged anions behaved themselves better than 1-negative charged anions by facilitating gold initial nucleation on substrate surface. Therefore, the initial gold nucleation on APTES treated substrate surface should be most likely induced by charge of anions adsorbed on substrate surface.

Fig. 3.5. SEM images of Au NW growth on Si wafer susbstrate by using a series of 2-negative anions Na_2SO_4 (a), Na_2CO_3 (b), Na_2HPO_4 (c) and sodium tartrate (d) treated modified ultrathin Au NW forest growth method without the use of gold nanoseeds. (Scale bar: 1 μm)

In the case of 3-negative charged anion, however, as shown in Fig. 3.6, when sodium citrate was used to assist initial gold nucleation, bundles of Au NW similar to Fig. 3.5.d could

be identified. It might still because of the fact that the size of 3-negative charged anion citrate was larger than typical inorganic anions, causing the spatial distribution of citrate anions sparser. Sparser anion distribution would lead to less potential charge induced nucleation points, resulting in less Au NW bundles with larger diameter.

Fig. 3.6. SEM images of Au NW growth on Si wafer substrate by using a sodium citrate treated modified ultrathin Au NW forest growth method without the use of gold nanoseeds. (Scale bar: 1 μ m)

In our preliminary trial discussed in introduction part, the sulfide anion could lead to similar nanowire growth with those by typical Au NS method. However, none of the previously screened anions could achieve anything similar. It was hypothesized that perhaps not only the charge offered by anions on APTES surface could provide potential nucleation points, but also reducing ability offered by some anions could facilitate faster gold nucleation. With the help of reducing ability and charge, anions might be able to facilitate gold nucleation in a faster and larger scale.

To test this working hypothesis, four anions with different charge and different reducing ability were chosen. As shown in Fig. 3.7., NaBr (Fig. 3.7.a), NaI (Fig. 3.7.b), Na₂S (Fig. 3.7.c) and Na₂Se (Fig. 3.7.d) were used to treat the APTES functionalized Si wafer before the substrates were put into Au NW growth solution. Before the discussion of morphological

characteristics of respective resulting Au NW, the reducing ability sequence of the four anions from strong to weak was as following, Na_2S , NaI , Na_2Se and NaBr . Thus, NaBr was predicted to facilitate Au NW preparation with more Au NW bundles and less standing Au NW while Na_2S would benefit more of standing Au NW growth than bundles formation. In the SEM image of Au NW using NaBr (Fig. 3.7.a), we could see similar bundles of Au NW in accordance with our prediction. In the case of Na_2S and NaI , independently standing Au NW could be identified in their respective SEM images. Therefore, it would be fairly conclusive that reducing ability together with the possessed charge of anions used in treatment after APTES functionalization may decide the resulting Au NW morphology.

Fig. 3.7. SEM images of Au NW growth on Si wafer substrate by using a series of reducing anions NaBr (a), NaI (b), Na_2S (c) and Na_2Se (d) treated modified ultrathin Au NW forest growth method without the use of gold nanoseeds. (Scale bar: 1 μm)

Among the two best anions demonstrated to assist Au NW growth, S^{2-} possessed higher charge and higher reducing ability at the same time. To further optimize the active surface growth method without the use of Au NS, the effect of different Na_2S concentration on Au NW growth should be investigated. Na_2S aqueous solution with a series of concentration of 0.4 μM (Fig. 3.8.a), 0.02 mM (Fig. 3.8.b), 1 mM (Fig. 3.8.c) and 50 mM (Fig. 3.8.d) were used to treat the APTES functionalized Si wafer before putting into the Au NW growth solution. From the SEM images, it could be identified that with the increase of salt concentration, the density of Au NW on Si wafer increased significantly. In the most dilute salt concentration, bundles of Au NW could be often recognized. In the most concentrated salt solution, however, it could be indicated that most Au NW were vertically aligned Au NW standing on the Si wafer instead of lying down and entangled with each other. Hence it could be concluded that by optimization of Na_2S concentration used on APTES functionalized Si wafer substrate, the density of resulting Au NW could be adjusted within a wide range from NWs that may lie down owing to sparse Au NW spatial distribution to NWs that may be perfectly vertically aligned and hard to distinguish a single NW from the others.

Fig. 3.8. SEM images of Au NW growth on Si wafer substrate by using a series of 0.4 μM (a), 0.02 mM (b), 1 mM (c) and 50 mM (d) Na_2S treated modified ultrathin Au NW forest growth method without the use of gold nanoseeds. (Scale bar: 1 μm)

Apart from exploration of controllability of Na_2S assisted Au NW growth method, another fact that we were interested in was that if Au NW in sparse spatial distribution on Si wafer was standing in solution. In previous discussion on Na_2S concentration, when 0.02 mM Na_2S was used to treat APTES functionalized Si wafer, the resulting Au NW possessed a morphology that head on Au NW top was rare while Au NW cannot collectively maintain a standing posture. If we wanted to know if the resulting Au NW would remain standing posture in solution, a modification procedure should be casted to chemically or thermally freeze the Au NW when they were still in solution. A PDMS coating over Au NW could be

utilized to chemically freeze the Au NW in the layer of PDMS. PDMS precursor A was soaked in organic solvent together with as synthesized 1 hour (Fig. 3.9.b) and 2 hours (Fig. 3.9.c) Au NW before the addition of PDMS precursor B. The substrate in solution was then kept in oven at 65 degree Celsius for overnight annealing. The resulting optical spectroscopic image was showed in Fig. 3.9.a. As PDMS was transparent under optical microscope, the layer that was pointed at by microscopic needle was the layer of as prepared Au NW. When the two substrates with respective length of Au NW bearing PDMS coating was characterized under SEM, not only the Au NW could be seen apparently standing on the substrate surface, but also the length of Au NW on two samples could be easily identified as 4.49 μm and 11.34 μm respectively. It could be therefore concluded that for Au NW with sparse spatial distribution, as long as they were independent of each other instead of forming bundles, they would be able to stand vertically and independently in solution.

Fig. 3.9. Optical spectroscopic image of PDMS coated 0.02 mM Na_2S assisted Au NW (a) and SEM images of 0.02 mM Na_2S assisted Au NW growth for 1 hour (b) and 2 hours (c) on Si wafer substrate with PDMS coating. Their estimated respective length of two Au NW samples were 4.49 μm and 11.34 μm . (Scale bar: 1 μm)

Besides the exploration of salt candidates, determination of proper salt concentration and confirmation of standing posture of Na_2S assisted Au NW, comparison between Na_2S and Au NS on their respective effect on Au NW should also be discussed. A treatment combination of Na_2S and Au NS was also included in the comparison to check if the presence of Na_2S may

further enhance the density of as prepared Au NW. From Fig. 3.10, SEM images of different Au NW density obtained by using 0.02 mM Na₂S (Fig. 3.10. a & d), Au NS (Fig. 3.10. b & e), 0.02 mM Na₂S + Au NS (Fig. 3.10. c & f) treatment prior to Au NW growth was characterized and analyzed. In the short Au NW batch, it could be easily distinguished that the density of as prepared Au NW was correlated to the surface treatment approach used. 0.02 mM Na₂S together with Au NS treatment on Si wafer would result in more densely packed short Au NW than only Au NS and only 0.02 mM Na₂S on Si wafer. In long Au NW batch with a preparation time of 15 minutes, loosely packing in 0.02 mM Na₂S case, typical close packing in Au NS case and densely packing in 0.02 mM Na₂S + Au NS case of Au NW shared the same phenomenon with short Au NW batch. Additionally, not only density but also length of 2.5 μm was improved in 0.02 mM Na₂S + Au NS case from the use of Au NS only case with the length of 1.5 μm. Typically in different preparation reactions with the same reduction rate, the more dense the Au NW was, the shorter the Au NW length could be. This unexpected fact further indicated that the reducing ability of sulfide anion might be responsible for the increase in length rather than the typical decrease.

Fig. 3.10. SEM images of Au NW growth on Si wafer substrate by using 0.02 mM Na_2S (a), Au NS (b), 0.02 mM Na_2S + Au NS (c) to treat Si wafer after APTES treatment before a 2 minute ultrathin Au NW forest growth and using 0.02 mM Na_2S (d), Au NS (e) and 0.02 mM Na_2S + Au NS (f) to treat Si wafer before a 15 minute ultrathin Au NW forest growth. (Scale bar: 1 μm)

Overall, it could be primarily hypothesized the role of anion that was used to treat the APTES functionalized substrate before Au NW growth could be originated from the charge possessed and reducing ability of anion. Among the anions that were discussed above, Na_2S possessed the 2-negative charge as well as the relatively strong reducing ability was recognized to be the best choice to be used instead of Au NS treatment before Au NW growth. As was shown in Fig 3.11, the schematic illustration exhibited the comparison in experimental procedures between the as reported active surface growth method with the use of Au NS and the modified Na_2S assisted Au NW growth method. Although from the schematic illustration we could see that the only difference lied between the Au NS or Na_2S adsorption step to facilitate Au deposition or nucleation on the treated substrate, the quality of APTES layer could be of higher significance to anion adsorption than Au NS adsorption.

As-reported seeded growth method

Na_2S assisted Au NWs growth method

Fig. 3.11. Schematic illustration of synthetic procedure of Au NS based and salt assisted ultrathin Au NW forest growth method.

3.4. Conclusion

In this chapter, we successfully reported a modified vertically standing ultrathin Au NW forest preparation method to grow Au NW without the use of gold nanoseed. The modified method used salt adsorption instead of gold nanoseed adsorption. The preparation of gold nanoseed may consumed more time than a simple salt solution preparation. Charge induced nucleation step by adsorbed anions on the pretreated APTES layer was hypothesized to be the key to facilitate the growth step without the use of seed. Reducing ability of anions on the resulting Au NW morphology were also discussed. While both charge and reducibility of anions may rely on the formation of APTES layer, the adsorption of salt on APTES layer was hypothesized to be the key step to a nice vertically aligned Au NW array growth. Finally, Na_2S was the best among all screened salts to obtain as almost the same vertically standing Au NW as seeded method could do. The standing nature of Na_2S assisted growth of Au NW in solution was demonstrated by using PDMS coating on Si wafer surface with Au NW to "freeze" the standing posture of Au NW. Finally, a synthetic scheme exhibiting the compared synthetic procedure between the use of Au NS and Na_2S was proposed and illustrated.

3.5. Reference

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4. Enhanced operational durability of Au@Pd NW for electro-oxidation of ethanol in alkaline solution

4.1. Introduction

Direct alcohol fuel cells (DAFCs) ^[1-3] are attracting increasing attention and interest as a new kind of renewable and portable power sources, as there are some irreplaceable and distinguished advantages comparing to the hydrogen fuel cell. Alcohols, such as methanol, ethanol, ethylene glycol, and glycerol, exhibit relatively high volumetric energy density compared to hydrogen gas. Apart from that, as liquid is easier to handle than combustible gas, the storage and transport of alcohol is much safer than the case of hydrogen. DAFCs has been already on the highway of commercialization and become a promising alternative in energy providing future applications. Increasing research works are therefore being focused on design and development of more efficient anode electrocatalyst for DAFCs.

Among all these kinds of alcohols, ethanol showed unique properties compared with other alcohols. First, ethanol is the least toxic alcohol compared to other common liquid alcohols like methanol and isopropanol. A large portion of the culture on the world even values the wine, certain concentration of ethanol aqueous solution, as popular drink. Second, ethanol is among the renewable energy, ^[4] which makes it an ideal candidate fuel to be utilized in alignment with the principle of sustainable development. Large amount of the sugar can be refined from the crops like corn. The sugar can be easily distilled into ethanol, which can be used as fuel in mobile vehicles. After the combustion of the ethanol, the release

of carbon dioxide can be reused by crops during their growth again. Besides that, the energy density of the ethanol is almost comparable with the gasoline, which is a kind of one-off fossil fuel. The energy density of methanol is only 6.1 kWh/kg while that of ethanol increases to 8.0 kWh/kg, which is similar with the gasoline, around 10 kWh/kg. All these advantages of ethanol could make direct ethanol fuel cells (DEFCs) a relatively good choice to study among all kinds of DAFCs. ^[5]

The performance of fuel cells mostly relies on reduction and oxidation electrochemical reactions catalyzed by proper functioned and efficient electrochemical catalysts on both cathode and anode side. In the case of DEFCs, both reactions based on ethanol as fuel at the anode and oxygen as oxidant at the cathode requires ideal electrochemical catalysts with high efficiency to lower the electrochemical overpotential for high energy conversion efficiency and high durability to enhance operation time for long term power supply. ^[6] Until recently, platinum (Pt) and Pt based electrochemical catalysts is still among the best candidates for catalyzing anode reaction of DEFCs. However, Pt is facing limitation by its relatively high cost and low availability, hindering itself from industrial mass production. ^[7-8] With a higher abundance comparing to Pt, palladium (Pd) could serve as a promising alternative for catalyzing ethanol oxidation reaction, the anode reaction of DEFCs. Pd could function well as catalyst for ethanol oxidation reaction in alkaline conditions which increased the amenability of device fabrication with slightly lower performance than Pt. ^[3, 9] Apart from catalytic activity, low durability is another enduring obstacle standing in the way of catalyst commercialization, especially for Pd based catalysts. ^[10-13] Therefore, how to increase both the catalytic activity and the operation durability of Pd for ethanol oxidation reaction to match or overshoot that of Pt is attracting increasing attention and effort.

There have been a number of studies aiming at both catalytic activity and operation durability enhancement of Pd based catalysts for ethanol oxidation reaction in alkaline media.

Among these valuable works, different beneficial approaches towards both catalytic activity and operation durability enhancement together with efforts in expanding understanding have been reported. Li Y. etc believed that CO might be the key factor of performance decrease over time. ^[14] According to their claim, Ni(OH)₂ was used to provide OH⁻ supply to enhance CO electro-oxidation ability of Pd nanocrystals and achieved promoted durability. Chen W. etc used bimetallic approach to achieve rational design of durable catalyst Pd_xCu_{100-x} networks. ^[15] According to their hypothesis with supporting evidence, the beneficial aspect of bimetallic catalyst is to enhance tolerance against CO-like inhibitors formed during the ethanol oxidation reaction period. Wang L. etc found that when shorten Pd-Ni active site distance in Pd-Ni-P ternary NP, both catalytic activity and durability will be increased due to enhanced production of OH radical to promote the efficient removal of carbonaceous inhibitors. ^[16] Santos M. etc achieved impressive durability by using Au-Pd bimetallic nanomaterial supported on carbon to enhance tolerance to inhibitor. ^[17] Though they found no 1C product in bimetallic system, they didn't talk about the exact inhibitor species. Despite these valuable works focusing on enhancement in both catalytic activity and operation durability, there are still room for improvement as some of them were making marginal improvements.

Electrocatalyst	Electrolyte	Specific peak current	Cyclic stability	Chronoamperometric stability
Au@Pd NW	1.0 M NaOH + 1.0 M ethanol	8500 mA·mg ⁻¹	NA	~86% activity retention after 3600 s; ~38% activity retention after 200,000 s
PdAg NDs ^[18]	1.0 M KOH + 1.0 M ethanol	2630 mA·mg ⁻¹	50% activity retention after 10000 cycles	52% activity retention after 10000 s
Pd/Ni(OH) ₂ /rGO ^[14]	1.0 M KOH + 1.0 M ethanol	1546 mA·mg ⁻¹	95% activity retention after 40000 cycles	76% activity retention after 3600 s; 55 % activity retention after 20000 s
Pd _x Cu _{100-x} Networks ^[15]	1.0 M KOH + 1.0 M ethanol	5 mA·mg ⁻¹	NA	42 % activity retention 7200 s
Au@Pd NRs ^[19]	1.0 M KOH + 1.0 M ethanol	2920 mA·mg ⁻¹	NA	33% activity retention after 3600 s
Pd/RGO ^[20]	1.0 M KOH + 1.0 M ethanol	1500 mA·mg ⁻¹	86 % activity retention after 100 cycles	33 % activity retention 3600 s
Pd-Au/C ^[21]	1.0 M NaOH + 1.0 M ethanol	25 mA·mg ⁻¹	NA	Dropped to zero after 3600 s

Our Au@Pd NW has exhibited advantages offered by its morphology induced property to spontaneously enhance both catalytic activity and operation durability that may significantly enhance the performance of anode reaction in DEFCs. The vertically standing nanowire forest with tunable length prepared using active site growth method may provide high electrochemical active surface area for high catalytic activity and enhance the electronic charge transport efficiency at the same time. Furthermore, the improved mechanical strength brought by modified salt assisted method together with the highly tunable length and density of vertically standing Au@Pd NW can offer greatly enhanced operation durability at fixed potential for 200,000 s. Nearly 40% of the highest anodic performance remained by Au@Pd NW for catalyzing ethanol oxidation reaction could still be achieved even after 200,000 s at a fixed operation potential.

4.2. Materials and methods

4.2.1. Materials

All the aqueous solutions used in the following experiments were prepared using deionized water (resistivity $> 18 \text{ M}\Omega \cdot \text{cm}^{-1}$). Hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49.9% on metals basis, Sigma Aldrich), sodium nitrate hydrate ($\text{NaNO}_3 \cdot 5\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, ACS reagent $>99\%$, Sigma Aldrich), 4-mercaptobenzoic acid (4-MBA, 90%, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), 3-cyanopropyltriethoxysilane (CPTES, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), sodium borohydride (98%, Sigma Aldrich), hydroquinone (1,4-benzenediol, $>99.0\%$, Sigma Aldrich), ethanol for AuNW growth (99.85% technical grade) were used as received. Copper specimen grids (200 meshes) with carbon support film were purchased from Beijing XXBR Technology Co. Silicon wafer (6" Si (100) wafer, prime grade, 1-10 Ω/cm).

4.2.2. Methods

Characterization methods. All transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 kV. All field emission scanning electron microscopy (SEM) images were collected on a JSM-6700F (JEOL). All electrochemistry data were collected on a CHI-760e electrochemical workstation.

Synthesis of Au NW using salt assisted method on FTO substrate. Before growing Au NW forest on FTO glass, the as-purchased FTO glass was first cut into $1.5 \times 1 \text{ cm}^2$ piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the FTO glass was continuously sonicated in deionized water for

15 min for 3 times. The clean FTO glass was left to dry on filter paper before use. Later the FTO glass was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 15 min. Then the pretreated FTO glass was washed with ethanol twice and with water twice to remove the excess silane in the FTO glass. After each washing step, the excess ethanol or water on the FTO glass was removed by filter paper. After functionalized by APTES, the FTO glass was soaked in Na₂S solution for 1 h to complete the adsorption step of salt anion. Then the FTO glass was washed with water twice to remove the excess unabsorbed Na₂S. The Na₂S treated FTO glass was then immersed in the thoroughly mixed reaction solution containing 890 μ L ethanol and 522 μ L water as solvent, 110 μ L 10 mmol/L 4-MBA in ethanol as ligand, 68 μ L 50 mmol/L HAuCl₄ in water as gold precursor and 410 μ L 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the FTO glass with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Core shell deposition of Pd on Au NW on FTO glass. Before deposition of Pd onto Au NW on FTO, the FTO with Au NW was soaked into 0.1% (v/v) mercaptoacetic acid in DMF solution. The petri dish in sealed plastic bag with Au NW on FTO was then sit in oven with a fixed temperature of 65 °C for 2 hours. This was a ligand exchange process to remove 4-MBA, the stubborn thiol ligand used in Au NW preparation. Then the FTO with Au NW was washed in water thoroughly before soaked into growth solution with PVP, PdCl₂ and L-ascorbic acid for 1-12 hours to complete the palladium growth onto Au NW.

Electrochemical test for ethanol oxidation reaction. The electrochemical properties of our different catalysts were studied in the standard three-electrode cell. The cyclic voltammetry, stability tests and some other electrochemical tests were done by using a CHI-760e electrochemical workstation. The counter electrode we used was platinum foil (1 x 2 cm²). The reference electrode we used was saturated calomel electrode (SCE). The working

electrode we used was nickel foam with AuNW or FTO with AuNW. The electrolyte we used to do the ethanol oxidation reaction was 1.0 M NaOH, 1.0 M ethanol aqueous solution saturated with N₂. The stirring speed during the purging N₂ gas and electrochemical test was 500 rpm all the time. The scan rate of cyclic voltammetry test was 50 mV/s. The stability test was carried out at -0.2 V vs. SCE. The entire electrochemical test was carried out at 25 °C.

4.3. Results and discussion

Before the start of any electrochemical catalytic measurements, the selection of proper catalyst together with suitable substrate, if the chosen catalyst was not freestanding, should be of top priority. In the previous chapters, we already achieved modification of preparation method of vertically standing ultrathin Au NW on a variety of substrates. Within the candidate substrates that were known to facilitate successful Au NW growth, conductive or semi conductive ones like fluorine doped tin oxide (FTO), indium doped tin oxide (ITO), carbon-based materials like glassy carbon electrode, carbon cloth, and Si wafer were suitable candidates for achieving electrochemical catalytic reaction. However, due to the nature of our modified growth method, the designated substrate might not be thoroughly cleaned or easily reused. With this concern, electrodes that was expensive and meant to be reused like glassy carbon electrode should not be considered. Mechanical strength of the substrate should also be considered as there might be frequent binding between electrode substrate, electronic wires and electrochemical cell. Thus, cheap disposable and relative robust conductive support like FTO might be a good option to start with. There might still be room for optimization, however, as three-dimensional substrates like nickel foam or carbon paper might bring enhanced catalytic activity of Au@Pd NW in future device performance.

For the choice of catalyst, as was previously discussed, Pd was a better catalyst candidate than Au due to their catalytic activity and overpotential difference in ethanol oxidation reaction. Since we already promoted the synthetic controllability on ultrathin Au NW forest with potential high electrochemical surface area, we should start with Pd coating on Au NW. An optimized Pd chemical coating method was used in Pd coating on Au NW with the L-ascorbic acid as reducing agent. Since the as-prepared Au NW by active surface growth method were covered with 4-MBA on the Au NW surface, it was almost impossible to achieve an even layer of Pd coating with the presence of 4-MBA. It was because that in the

active surface growth method, 4-MBA was believed to form closely packing on the Au surface owing to its π - π intermolecular interaction. In this way, to achieve successful Pd layer growth, the 4-MBA on Au NW surface should be removed or replaced. Apart from that, as there is less than 5% lattice mismatch between Au and Pd, it would be easier for Pd to form an even layer of coating over Au if the reduction of Pd is in slow and thermodynamically favored manner. Based on the selection criterion discussed above, a ligand exchange between water soluble mercaptoacetic acid (MAA) and 4-MBA and a reducing agent with relatively low reducing rate L-ascorbic acid were decided to facilitate even layered growth of Pd on Au NW surface. A piece of substrate with as prepared Au NW was placed in MAA in DMF solution at 65 degree Celsius for two hours to achieve successful ligand exchange between 4-MBA and MAA. DMF was chosen to allow the dissolution of both ethanol soluble 4-MBA and water soluble MAA at the same time to facilitate ligand exchange. After the ligand exchange step, the substrate was washed thoroughly in water to remove MAA and then placed in Pd growth solution with L-ascorbic acid and Pd precursor. Finally, a consistently reproducible Pd coating on Au NW to prepare Au@Pd NW could be achieved.

Physical characterization of morphological characteristics on Au@Pd NW was performed to confirm the core-shell coating as well as elemental distribution after the modification of preparation method of both Au NW growth and Pd coating. A schematic illustration from Fig. 4.1. a showed the complete coverage of Pd over Au in Au@Pd NW. A large area scanning electron microscopic image exhibited the approximate length and large area morphological characteristics of Au@Pd NW in a typical Au@Pd NW growth. The vertically standing posture of Au@Pd NW and an approximate length of 11.43 μm could be indicated from the large area SEM image. From the electron energy loss spectroscopy (EELS) mapping of a single Au@Pd NW of Fig. 4.1 c, a clear nanoscale view of a single Au@Pd NW was presented. For a single Au@Pd NW, the diameter of Au NW before coating was around 7

- 9 nm and diameter of Au@Pd NW after Pd coating was 11 - 14 nm. The layer thickness of Pd coating over Au NW was approximately 2 nm. From the energy dispersive X-ray spectroscopy (EDX) line scan along the cross-section of a single Au@Pd NW shown in Fig. 4.1 d - g, the clearly illustrated elemental distribution of Au (blue dots in d, f and line in g) and Pd (magenta dots in e, f and line in g) showed that a nice and even Pd coating over Au was achieved in a single Au@Pd NW. It could be therefore concluded that the preparation of core-shell Au@Pd NW was successfully achieved with nicely distributed Pd coating over Au surface.

Fig. 4.1. Physical characterization of morphological and structural exhibition of Na₂S assisted Au@Pd NW: schematic illustration (a), large area SEM image of Au@Pd NW with the estimated length of 11.43 μm (b), electron energy loss spectroscopy (EELS) mapping of a single Au@Pd NW (c), energy dispersive X-ray spectroscopy (EDX) line scan along the cross-section of a single Au@Pd NW showing elemental distribution of Au (d), Pd (e), Au Pd overlap (f) and elemental distribution curve (g).

After achieving the nice core-shell coating of Pd on Au NW, the electrochemical

measurement on as prepared FTO substrate with vertically standing ultrathin Au@Pd NW forest for ethanol oxidation reaction would be carried out. First, cyclic voltammetry (CV) curve of Au@Pd NW (red line in Fig. 4.2 a) and commercially available palladium on carbon (blue line in Fig. 4.2 a) for their respective electrochemical surface area (ECSA) were measured in N₂-saturated 0.5 M H₂SO₄ aqueous solution at a scan rate of 50 mV / s. Typically a ECSA measurement is carried out in electrolyte containing either 1 M H⁺ or 1 M OH⁻ to characterize the oxidation and reduction behavior of a catalyst with a known and simple counter reaction in three electrode electrochemical system. As there might be OH⁻ adsorption and desorption on Pd peak getting in the way with the determination of Pd reduction peak, the measurement for ECSA on target and control electrodes were made in acidic aqueous solution as previously stated. The ECSA for Au@Pd NW and Pd on carbon after normalized to per gram of Pd was 122.8 and 22.7 m² / g respectively. It was indicated that the electrochemically active site on Au@Pd NW was more than 5 times more than that on state-of-art commercial Pd on carbon catalyst. More importantly, CV curve of Au@Pd NW (red line in Fig. 4.2 b) and commercially available palladium on carbon (blue line in Fig. 4.2 b) for their catalytic activity in ethanol oxidation reaction (EOR) were measured in N₂-saturated 1M ethanol and 1 M NaOH mixed aqueous solution at a scan rate of 50 mV / s. At the same time, chronoamperometric (I-t) curve of Au@Pd NW (red line in Fig. 4.2 c) and commercially available palladium on carbon (blue line in Fig. 4.2 c) were also measured in the same electrolyte. All current densities in CV scans and I-t measurements was normalized to the Pd loading amount, i.e. gram of Pd. As indicated in Fig. 4.2 b, the catalytic performance of Au@Pd NW for ethanol oxidation reaction was 2.5 times of Pd on carbon at 0 V vs SCE in alkaline media. Although the anodic peak in the forward scan of Au@Pd NW was at 4.3 V with an astonishing current density of approximately 8500 A / g_{Pd}, the fair comparison has to be made at a same voltage where both scans would reach. The anodic peak

at 4.3 V in the CV of Au@Pd NW and the anodic peak at 0 V in the CV of Pd on carbon should both be attributed to the oxidation peak of ethanol to acetic acid on respective catalysts while the drop of peak should be assigned to the temporary inhibition caused by the inhibiting species. Most importantly when it comes to chronoamperometric test showed in Fig. 4. 2. c, it was explicitly displayed that the performance decay in Au@Pd NW (red line in Fig. 4. 2. c) was far less than that in Pd on carbon (blue line in Fig. 4. 2. c). The remaining current density in Au@Pd NW measurement was 85.68% after 3,600 s of chronoamperometric measurement at -0.2 V vs SCE in N₂-saturated 1M ethanol and 1 M NaOH mixed aqueous electrolyte while in Pd / C only 11.07% of current density was left. Inspired by this astonishing improvement in catalytic performance, an extremely long chronoamperometric measurement was carried out as shown in Fig. 4. 2. d. It surprised us even more than its performance in an hour that, after 200,000 s I-t test at -0.2 V in N₂-saturated 1 M ethanol and 1 M NaOH mixed aqueous electrolyte, our Au@Pd NW retained 37.92% of initial current density. In Pd on carbon, however, it would only take around 900s, 0.45% of the time used by Au@Pd NW, to drop to 37.92% of its initial current density. The greatly enhanced durability that our Au@Pd NW has achieved would definitely shine light on development of highly durable direct ethanol fuel cell applications.

Fig. 4.2. Electrochemical characterization of Na₂S assisted Au@Pd NW comparing to commercialized Pd on carbon: CV scans of 11.43 μm Au@Pd NW and Pd on carbon with equivalent amount of Pd in 1.0 M NaOH solution for electrochemical active surface area characterization (a), CV scans (b) and chronoamperometric I-t test (c) of 11.43 μm Au@Pd NW and Pd on carbon with equivalent amount of Pd in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH for catalytic activity characterization for ethanol oxidation reaction, and an extreme 200,000 s chronoamperometric I-t test of 11.43 μm Au@Pd NW in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH for catalytic activity characterization for ethanol oxidation reaction (d). Scan rate of CV scans were kept at 50 mV / s.

With the greatly enhanced operation durability of ultrathin Au@Pd NW forest achieved, the exploitation of the origin behind this fact became outstandingly crucial to facilitate further optimization and potential rational design towards better catalysts. As the controllability on preparation of Au@Pd NW was strong enough for establishing length and density variation by simply control the preparation time and density of seeds or concentration of salt, we could start to resolve the exploitation procedure by focusing on length variation of Au@Pd NW.

A series of Au@Pd NW with a variation in length of 0.61 μm, 0.76 μm, 1.33 μm, 2.02 μm, 3.52 μm, 5.02 μm, 7.22 μm and 11.43 μm was prepared by using Na₂S assisted active surface growth method and previously discussed Pd coating method on FTO substrates. CV and I-t measurement of Au@Pd NW of different length for their catalytic activity and

durability in ethanol oxidation reaction were measured in N₂-saturated 1M ethanol and 1 M NaOH mixed aqueous solution at a scan rate of 50 mV / s. It was presented in Fig. 4. 3. a, that with the increase of Au@Pd NW length, the anodic peak which was attributed to the reaction of ethanol oxidation to acetate shifted positively and increased significantly in peak current density. At the same time, the drop of anodic peaks also shifted positively with the increase of Au@Pd NW length. The drop of anodic peak should be assigned to the temporary inhibition caused by the inhibiting species, indicating that as Au@Pd NW length increased, the resistance against temporarily inhibiting species would be increased accordingly. In Fig. 4.3.b, the percentage of remaining current density after 28,800 s (8 hours) also increased together with the increase in length. Apart from that, there was another characteristic of the I-t curves of the series of Au@Pd NW with different length. Unlike the I-t curve of commercially available Pd on carbon shown in Fig 4.2.c, the series of I-t curves of Au@Pd NW with different length exhibited a two-stage drop in their respective catalytic performance decrease. This trend shared the same feature with the greatly enhanced operation durability that was discussed above in Fig. 4.2.d.

Fig. 4.3. Electrochemical characterization of Na₂S assisted Au@Pd NW: CV scans (a) and chronoamperometric I-t tests (b) of Au@Pd NW with different length of 0.61 μm, 0.61 μm, 0.76 μm, 1.33 μm, 2.02 μm, 3.52 μm, 5.02 μm, 7.22 μm and 11.43 μm in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH for catalytic activity characterization for ethanol oxidation reaction. Scan rate of CV scans were kept at 50 mV / s.

Besides the variety of Au@Pd NW length, the density of vertically standing Au@Pd NW was also within the controllability of our modified active surface growth method. By either tuning the concentration of pre-adsorbed Au nanoseeds (Au NS) or salt solution, the density of resulting Au@Pd NW could be easily tuned and controlled. To facilitate high reproducibility of the results, the dilution of pre-adsorbed Au NS was used as the modified synthetic approach towards the preparation of Au@Pd NW with various density. Concentration of Au NS used was described by the diluting percentage of the as prepared Au NS. Additionally, the Au@Pd NW prepared with different Au NS density were kept at almost the same nanowire length in order to avoid interference with the previously demonstrated length effect on stability. The CV and I-t measurement of Au@Pd NW of different density with the use of 0.01%, 0.1%, 1% and 10% diluting percentage of the as prepared Au NS for their catalytic activity and stability within 1,800 s in ethanol oxidation reaction were measured respectively in N₂-saturated 1M ethanol and 1 M NaOH mixed aqueous solution at a scan rate of 50 mV / s. It was presented in Fig. 4. 4. a, that with the increase of Au@Pd NW density, the anodic peak in forward scan which was attributed to the reaction of ethanol oxidation to acetate shifted positively and increased in peak current density. However, the increase in peak current density as the increase in density of Au@Pd NW was not recognized when compared at a selected voltage due to their almost same length. The anodic peak in backward scan which was annotated as ethanol oxidation to acetate after the release of temporarily inhibiting species, however, changed little with the increase of Au@Pd NW density, which might also because of their almost the same length. At the same time, the drop of anodic peaks also shifted positively with the increase of Au@Pd NW density. The drop of anodic peak should be assigned to the temporary inhibition caused by the inhibiting species, indicating that as Au@Pd NW density increased, the resistance against temporarily inhibiting species would be increased accordingly. In Fig. 4.4.b, the percentage of remaining current

density after 1,800 s also increased together with the increase in density. Apart from that, there was another characteristic of the I-t curves of the series of Au@Pd NW with different density. Unlike the I-t curve of commercially available Pd on carbon shown in Fig 4.2.c, the series of I-t curves of Au@Pd NW with different density exhibited a two-stage drop in their respective catalytic performance decrease. This trend shared the same feature with the greatly enhanced operation durability and the trend of different length that was discussed above in Fig. 4.2.d and Fig 4.3.b.

Fig. 4.4. Electrochemical characterization of Au@Pd NW: CV scans (a) and chronoamperometric I-t tests (b) of Au@Pd NW with different surface gold nanoseed density of 0.01%, 0.1%, 1% and 10% in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH for catalytic activity characterization for ethanol oxidation reaction. Scan rate of CV scans were kept at 50 mV / s.

Additionally, when different Pd coating time was used in optimization of Pd coating method, an unexpected trend that decrease in Pd coating time resulted in enhancement in stability was discovered. In a typical Au@Pd NW synthesis, the time for Pd coating was originally 12 hours in order to ensure the complete core shell coating. To optimize Pd coating step and save preparation time, we tried to shorten the coating time. CV and I-t measurement of Au@Pd NW with different Pd coating time, 1 hour, 3 hours, 5 hours and 12 hours, for their catalytic activity and stability within 3,600 s in ethanol oxidation reaction were measured respectively in N₂-saturated 1 M ethanol and 1 M NaOH mixed aqueous solution at a scan

rate of 50 mV / s. As was shown in Fig. 4.5.a, with the increase of Pd coating time, the anodic peak in forward scan which was attributed to the reaction of ethanol oxidation to acetate shifted positively and increased in peak current density. However, due to the same batch of Au NW with same length, the increase in peak current density as the increase in Au@Pd NW Pd coating time was not recognized when compared at a selected voltage. The anodic peak in backward scan which was annotated as ethanol oxidation to acetate after the release of temporarily inhibiting species, however, changed little with the increase of Pd coating time, which may also due to the fact that Au@Pd NW with different Pd coating time were technically the same in length. At the same time, the drop of anodic peaks also shifted positively with the increase of Pd coating time on NWs, except that the 5 hours and 12 hours coating of Au@Pd NW overlapped with each other. The drop of anodic peak should be assigned to the temporary inhibition caused by the inhibiting species, indicating that as Pd coating increased, the resistance against temporarily inhibiting species would be increased accordingly. Strangely however, in Fig. 4.5.b, the percentage of remaining current density after 3,600 s increased with the decrease of Pd coating time. In the case of 5 hours and 12 hours coating, despite the fact that their CV curves overlapped, their respective retained current density differed significantly from each other in a reproducible manner. That is to say, the Au@Pd NW with the thinnest Pd coating layer retained the most current density after a 3,600 s chronoamperometric measurement while it seemed to be the least resistant against temporary inhibition in its CV curve.

Fig. 4.5. Electrochemical characterization of Au@Pd NW: CV scans (a) and chronoamperometric I-t tests (b) of Au@Pd NW with different palladium coating time of 1 hour, 3 hours, 5 hours and 12 hours in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH for catalytic activity characterization for ethanol oxidation reaction. Scan rate of CV scans were kept at 50 mV / s.

The abnormality of this set of data may be originated from the fact that the reason behind the performance decay during chronoamperometric measurement and the temporary inhibiting species that was responsible for the drop of forward scan anodic peak was two different stories. It was reported that in the oxygen reduction reaction catalyzed by Au@Pd nanoparticle with different Pd thickness and pure Pd nanoparticle, the reduction peaks of Pd oxide on Au@Pd nanoparticle constantly shifted negatively with the increase in Pd thickness until reached to the peak on pure Pd nanoparticle. ^[22] With aforementioned understanding together with our data of different Pd thickness, we might have a preliminary guess on the reason behind the performance decay on Au@Pd NW in I-t test for ethanol oxidation reaction that Pd oxide, or oxidized Pd species, or Pd-O* might be the main inhibitor during I-t measurement. The detailed discussion would be expanded in chapter 5.

Since the stability related trends of length, density and Pd coating time were shared by both Au NS adsorbed and Na₂S assisted Au@Pd NW, a more optimized durability might be achieved using Au NS assisted Au@Pd NW. It was the drawback of Au@Pd NW on FTO, however, to prevent further optimization of durability on Au@Pd NW. In a typical CV curve

of long Au@Pd NW, the forward scan wouldn't drop until a relatively high voltage was reached. This relatively high voltage was mostly above 0.4 V vs SCE. As long as the forward scan would end and drop of peak at anywhere higher than 0.4 V, there would be bubbles seen on the electrode substrate with Au@Pd NW during backward scan. The bubbles were believed to be oxygen bubbles, as oxygen evolution reaction might already happen during the backward scan. Owing to the fact that there was little additional binding between Au@Pd NW and FTO substrate other than the APTES layer in the initial stage of preparation, Au@Pd NW on FTO prepared with high density by Au NS pre-adsorption would be badly peeled off during CV scans as showed in Fig. 4.6.a. With a slightly lowered density, however, Au@Pd NW prepared by Na₂S assisted method as showed in Fig. 4.6.b could survive most of the large potential range ethanol oxidation CV measurements. They could be long lasting in electrochemical catalytic reactions even after long chronoamperometric measurements.

Fig. 4.6. Photos of relatively long Au NS treated (a) and Na₂S treated (b) Au@Pd NW in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH for catalytic activity characterization for ethanol oxidation reaction. (a) was obtained after only one CV scan while (b) was obtained after long chronoamperometric test.

4.4. Conclusion

Here we reported the modified preparation of Au@Pd NW with advantages offered by its morphology induced property to spontaneously enhance both catalytic activity and operation durability that may significantly enhance the performance of anode reaction in DEFCs. The vertically standing nanowire forest with tunable length prepared using active site growth method may provide high electrochemical active surface area for high catalytic activity and enhance the electronic charge transport efficiency at the same time. Furthermore, the improved mechanical strength brought by modified salt assisted method together with the highly tunable length and density of vertically standing Au@Pd NW can offer greatly enhanced operation durability at fixed potential for 200,000 s. Nearly 40% of the highest anodic performance remained of Au@Pd NW for catalyzing ethanol oxidation reaction could still be achieved even after 200,000 s at a fixed operation potential.

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5. Study of the origin of enhanced operation durability of Au@Pd NW in ethanol oxidation reaction in alkaline media

5.1. Introduction

DEFCs has been already on the expressway of commercialization and become a promising alternative in energy providing devices and future applications. ^[1] Increasing research works are therefore being focused on design and development of more efficient anode and cathode electrocatalyst for DEFCs. As was discussed in previous chapter, the performance of fuel cells mostly relies on reduction and oxidation electrochemical reactions catalyzed by proper functioned and efficient electrochemical catalysts on both cathode and anode side. In the case of DEFCs, both reactions based on ethanol as fuel at the anode and oxygen as oxidant at the cathode requires ideal electrochemical catalysts with high efficiency to lower the electrochemical overpotential for high energy conversion efficiency and high durability to enhance operation time for long term power supply. ^[2] Low or insufficient operation durability has always been an obstacle standing in the way of catalyst commercialization. On the cathode side, the detailed reaction mechanism, beneficial catalysts and approaches to achieve impressive durability on catalysts for oxygen reduction reaction was extensively studied during the past decades. On anode side, however, the mechanistic study of ethanol oxidation reaction has been carried out for a long time, yet conclusive and

detailed studies with molecular level identification of intermediate species are far less than expected. In the previous chapter, given the fact that we have demonstrated an outstanding performance by using our Au@Pd NW as anode catalyst, the reason behind such high durability together with high catalytic activity should be worthy of our attention. Therefore, how to know the reason behind such impressive operation durability of ultrathin Au@Pd NW for ethanol oxidation reaction deserves our curiosity and effort.

In the previous chapter, it was concluded that the operation durability of Au@Pd NW for ethanol oxidation reaction (EOR) was associated with the length, density and coating time of Pd. But how such trends confirmed by experiments could be associated with the greatly enhanced durability was still unknown. Apart from that, indeed we could gain specific knowledge on how to improve the operation durability of one specific catalyst. In order to purposely design a theoretically ideal catalyst, however, to have knowledge within only one or two specific kind of catalyst might be far not enough. The study on ethanol oxidation reaction mechanism and the catalytic processes by pristine Pd catalyst could possibly offer a new aspect in understanding the origin of greatly enhanced operation durability of Au@Pd NW for ethanol oxidation reaction.

There have been a number of studies aiming at operation durability enhancement of Pd based catalysts for ethanol oxidation reaction in alkaline media. Among these valuable works, different beneficial approaches towards both catalytic activity and operation durability enhancement together with efforts in expanding understanding have been reported. Li Y. etc believed that CO might be the key reason for the decreased performance over time. ^[3] According to their claim, Ni(OH)₂ was used to provide OH⁻ supply to enhance CO electro-oxidation ability of Pd nanocrystals and achieved promoted durability. Chen W. etc used bimetallic approach to achieve rational design of durable catalyst Pd_xCu_{100-x} networks. ^[4] The designated Pd_xCu_{100-x} network finally could achieve a 42 % activity retention after 7200 s

chronoamperometric test. According to their hypothesis, the beneficial aspect of bimetallic catalyst is to enhance tolerance against CO-like inhibitors formed during the ethanol oxidation reaction period. Wang L. etc found that when shorten Pd-Ni active site distance in Pd-Ni-P ternary NP, operation durability will be increased due to enhanced production of OH radical to promote the efficient removal of carbonaceous inhibitors.^[5] Santos M. etc achieved impressive durability by using Au-Pd bimetallic nanomaterial supported on carbon to enhance tolerance to inhibitor.^[6] Though they found no 1C product in bimetallic system, they didn't talk about the exact inhibitor species. Despite these valuable works focusing on enhancement in operation durability, the lack of understanding the underlined mechanism of ethanol oxidation reaction still remained problematic.

There were two main ideas on the chemical nature of the inhibiting species on molecular level, one is hydroxide species, the other is carbonaceous species. However, whether there is C-C bond cleavage was claimed to be dependent on the concentration of ethanol.^[7] When ethanol concentration in the alkaline electrolyte was around 0.1 M, C-C bond cleavage on Pd would be more likely to happen than that in higher ethanol concentration. In the normal working condition of direct ethanol fuel cell, however, the alkaline electrolyte consisted of at least 1 M ethanol and 1 M or 2M sodium or potassium hydroxide is widely used. Therefore, in real life application scenario, C-C bond cleavage during the oxidation reaction of ethanol would be less likely to happen.

However, how hydroxide species may affect the catalytic performance of Pd based electrochemical catalyst in fixed potential chronoamperometric (I-t) test still remained unclear. Efforts and works on solving the durability problem by exploring structure-property correlation to achieve rational design of catalysts was crucial yet sufficient in Pd-EOR system.

In this chapter, we investigated the mechanistic reason behind the high durability we obtained by discussions on correlation between OH⁻ concentration and performance decrease

in pristine Pd plate, inhibition memory effect brought by hydroxide species on short Au@Pd NW, intermediate species identification by in-situ Raman spectroscopy and product analysis by high performance liquid chromatography (HPLC). By summarization of the aforementioned discussions, we proposed the OH^- species as the main inhibitor to poison Pd and bring performance decrease during chronoamperometric test. Finally, we would like to propose a dual site hypothesis to explain the high durability of ultrathin Au@Pd NW.

5.2. Materials and methods

5.2.1. Materials

All the aqueous solutions used in the following experiments were prepared using deionized water (resistivity $> 18 \text{ M}\Omega \cdot \text{cm}^{-1}$). Hydrogen tetrachloroaurate(III) (HAuCl_4 , 99.9%, Au 49.9% on metals basis, Sigma Aldrich), sodium nitrate hydrate ($\text{NaNO}_3 \cdot 5\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 99.999% trace metals basis, Sigma Aldrich), sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, ACS reagent $>99\%$, Sigma Aldrich), 4-mercaptobenzoic acid (4-MBA, 90%, Sigma Aldrich), 3-aminopropyltriethoxysilane (APTES, Sigma Aldrich), 3-cyanopropyltriethoxysilane (CPTES, Sigma Aldrich), sodium citrate tribasic dihydrate (99.0%, Sigma Aldrich), L-ascorbic acid (Sigma Aldrich), sodium borohydride (98%, Sigma Aldrich), hydroquinone (1,4-benzenediol, $>99.0\%$, Sigma Aldrich), ethanol for AuNW growth (99.85% technical grade) were used as received. Copper specimen grids (200 meshes) with carbon support film were purchased from Beijing XXBR Technology Co. Silicon wafer (6" Si (100) wafer, prime grade, 1-10 Ω/cm).

5.2.2. Methods

Characterization methods. All transmission electron microscopy (TEM) images were collected on a JEM-1400 (JEOL) operated at 100 kV. All field emission scanning electron microscopy (SEM) images were collected on a JSM-6700F (JEOL). All electrochemistry data were collected on a CHI-760e electrochemical workstation.

Synthesis of Au NW using salt assisted method on FTO substrate. Before growing Au NW forest on FTO glass, the as-purchased FTO glass was first cut into $1.5 \times 1 \text{ cm}^2$ piece and sonicated in ethanol/acetone 1:1 solution for 15 min for 3 times to remove the surface organic residual. After that, the FTO glass was continuously sonicated in deionized water for

15 min for 3 times. The clean FTO glass was left to dry on filter paper before use. Later the FTO glass was functionalized with amino group and was immersed in APTES water/ethanol 1:1 solution (0.1% v/v) for 15 min. Then the pretreated FTO glass was washed with ethanol twice and with water twice to remove the excess silane in the FTO glass. After each washing step, the excess ethanol or water on the FTO glass was removed by filter paper. After functionalized by APTES, the FTO glass was soaked in Na₂S solution for 1 h to complete the adsorption step of salt anion. Then the FTO glass was washed with water twice to remove the excess unabsorbed Na₂S. The Na₂S treated FTO glass was then immersed in the thoroughly mixed reaction solution containing 890 μ L ethanol and 522 μ L water as solvent, 110 μ L 10 mmol/L 4-MBA in ethanol as ligand, 68 μ L 50 mmol/L HAuCl₄ in water as gold precursor and 410 μ L 20 mmol/L L-ascorbic acid in water as reducing agent for 15 mins. Finally, the FTO glass with Au NW was rinsed thoroughly with ethanol twice and water twice and dried on filter paper.

Core shell deposition of Pd on Au NW on FTO glass. Before deposition of Pd onto Au NW on FTO, the FTO with Au NW was soaked into 0.1% (v/v) mercaptoacetic acid in DMF solution. The petri dish in sealed plastic bag with Au NW on FTO was then sit in oven with a fixed temperature of 65 °C for 2 hours. This was a ligand exchange process to remove 4-MBA, the stubborn thiol ligand used in Au NW preparation. Then the FTO with Au NW was washed in water thoroughly before soaked into growth solution with PVP, PdCl₂ and L-ascorbic acid for 1-12 hours to complete the palladium growth onto Au NW.

Electrochemical test for ethanol oxidation reaction. The electrochemical properties of our different catalysts were studied in the standard three-electrode cell. The cyclic voltammetry, stability tests and some other electrochemical tests were done by using a CHI-760e electrochemical workstation. The counter electrode we used was platinum foil (1 x 2 cm²). The reference electrode we used was saturated calomel electrode (SCE). The working

electrode we used was nickel foam with AuNW or FTO with AuNW. The electrolyte we used to do the ethanol oxidation reaction was 1.0 M NaOH, 1.0 M ethanol aqueous solution saturated with N₂. The stirring speed during the purging N₂ gas and electrochemical test was 500 rpm all the time. The scan rate of cyclic voltammetry test was 50 mV/s. The stability test was carried out at -0.2 V vs. SCE. The entire electrochemical test was carried out at 25 °C.

5.3. Results and discussion

Before our discussion on the origin of the high operation durability of Au@Pd NW was initiated, to determine what should be the reason behind the drop in performance, that is, the main inhibitor that poison the Pd during chronoamperometric ethanol oxidation reaction. Hopefully with increasing understanding on the chemical nature of the main inhibitor, we would be more efficient and experienced in designing catalysts for EOR with higher catalytic performance and operation durability. To break down the problem, we might start analyzing how the concentration variation of two main components in the working electrolyte may affect the catalytic performance of catalyst in a simple system. As there were only two main components in the working electrolyte, the main inhibitor should be originated from either component or be formed during the interactions between 2 reactants and Pd. During the interaction between 2 reactants and Pd, carbonaceous species (or ethoxi species) and hydroxide species (or hydroxi species) should be the two main intermediate species that may be candidates for inhibitor. By altering the NaOH and ethanol concentration respectively, we might be able to determine which species was more likely to be responsible for the performance decay of Pd.

As a starting point, to explore the nature of key inhibitor in electrochemical catalytic ethanol oxidation reaction on Pd, we used pristine Pd plate as the model study catalyst. First, its cyclic voltammetry (CV) curve was measured in N₂-saturated NaOH with concentration varying from 0.1 M to 4 M containing 1 M ethanol which was shown in Fig. 5.1. Current density was normalized to the surface area of pristine Pd plate electrode. At the same time, its chronoamperometric (I-t) curve was also measured in the same respective electrolytes. Current density was normalized to electrode surface area (Fig. 5.2 a) and to the maximum current (Fig. 5.2 b) of pristine Pd plate electrode. As indicated in Fig. 5.1, pristine Pd plate in electrolytes with various NaOH concentration and constant amount of ethanol exhibited a

negative shift of anodic peak in the forward scan between -0.25 and 0.2 V as NaOH concentration increased, and a negative shift of relatively smaller anodic peak in the backward scan between -0.4 and -0.2 V. The former was usually recognized as the oxidation of ethanol to acetic acid while the drop of peak should be assigned to the temporary inhibition caused by the inhibiting species. The latter one was normally claimed to be the oxidation of ethanol after the release of inhibiting species from active sites on Pd surface. [8] When it comes to chronoamperometric test showed in Fig. 5.2 a, pristine Pd plate in electrolytes with various NaOH concentration experienced increasing rate of performance decay as NaOH concentration increased. The trend was more clearly displayed in Fig. 5.2 b whereas normalized current was used to eliminate the difference in starting current density in prospective chronoamperometric measurements.

Fig. 5.1. CV scans graph of ethanol oxidation reaction on pristine Pd plate in electrolytes with different NaOH concentration from 0.1 M to 4.0 M and same ethanol concentration 1.0 M. Scan rate was kept at 50 mV / s.

Fig. 5.2. Chronoamperometric I-t graph (a) and normalized chronoamperometric I-t graph (b) of ethanol oxidation reaction on pristine Pd plate in electrolytes with different NaOH concentration from 0.1 M to 4.0 M and same ethanol concentration 1.0 M.

The second set of CV and chronoamperometric curves were measured on pristine Pd plate in presence of 1M NaOH containing ethanol with its concentration varying from 0.1 M to 4 M. Current density was normalized to electrode surface area (Fig. 5.3) of pristine Pd plate electrode and to the maximum current in chronoamperometric measurement. As presented in Fig. 5.3, pristine Pd plate in electrolytes with constant amount of NaOH and various ethanol concentration exhibited a positive shift of anodic peak in forward scan between -0.3 and 0 V as ethanol concentration increased, and a positive shift of smaller anodic peak in backward scan between -0.4 and -0.2 V. Peak assignment was the same with CV curves above. In chronoamperometric measurements showed in Fig. 5.4 a, pristine Pd plate exhibited a slower decay when ethanol concentration increased and NaOH concentration remained the same. The trend was more explicitly presented in Fig. 5.4 b, when CV curves were normalized to the maximum current respectively.

Fig. 5.3. CV scans graph of ethanol oxidation reaction on pristine Pd plate in electrolytes with different ethanol concentration from 0.1 M to 4.0 M and same NaOH concentration 1.0 M. Scan rate was kept at 50 mV / s.

Fig. 5.4. Chronoamperometric I-t graph (a) and normalized chronoamperometric I-t graph (b) of ethanol oxidation reaction on pristine Pd plate in electrolytes with different ethanol concentration from 0.1 M to 4.0 M and same NaOH concentration 1.0 M.

From the two set of CV and I-t data showing how ethanol and NaOH concentration variation affect the temporary inhibition in CV scan and performance decay in I-t

measurement, we can see that more negative the temporary inhibition voltage was in CV and faster the performance decayed as the OH⁻ concentration increased and ethanol concentration decreased. Especially in increasing ethanol concentration batch, when ethanol concentration reached 1 M and higher, upgoing slope of forward scan in CV curves overlapped while only the anodic peak position shifted positive. This may indicate that there was competition between NaOH and ethanol adsorption to Pd. When there was more ethanol than 1 M in the electrolyte solution, there would be more ethanol for OH⁻ to consume and eventually form temporary inhibition at the anodic peak potential. In this point of view, we could conclude that OH⁻, hydroxide species on Pd or hydroxi species on Pd should be the main inhibiting species in the case of pristine Pd plate.

Similar trend in CV scans were identified from Fig. 5.5 when CV scans of EOR for one sample of short Au@Pd NW in different NaOH concentration. First, its cyclic voltammetry (CV) curve was measured in N₂-saturated NaOH with concentration varying from 0.1 M to 2 M containing 1 M ethanol which was shown in Fig. 5.5. As indicated in Fig. 5.5, short Au@Pd NW in electrolytes with various NaOH concentration and constant amount of ethanol exhibited a negative shift of anodic peak in the forward scan between -0.2 and 0.1 V as NaOH concentration increased, and a negative shift of relatively smaller anodic peak in the backward scan between -0.4 and -0.15 V. The former was usually recognized as the oxidation of ethanol to acetic acid while the drop of peak should be assigned to the temporary inhibition caused by the inhibiting species. The latter one was normally claimed to be the oxidation of ethanol after the release of inhibiting species from active sites on Pd surface.^[8] Since the confirmed trend in Au@Pd NW was almost the same with the trends in Pd plate case, we could conclude that OH⁻, hydroxide species on Pd or hydroxi species on Pd should also be the main inhibiting species in the case of Au@Pd NW.

Fig. 5.5. CV scans graph of ethanol oxidation reaction on short Au@Pd NW in electrolytes with different NaOH concentration from 0.1 M to 2.0 M and same ethanol concentration 1.0 M. Scan rate was kept at 50 mV / s.

From the previous discussion, it was concluded that OH^- , Pd-hydroxide or oxidized Pd species should be the main inhibitor that poison Pd during ethanol oxidation reaction on both pristine Pd plate and Au@Pd NW. The drop of peak in CV curves was dependent not only on ethanol and hydroxide concentration, but also on length and density of Au@Pd NW as was discussed in chapter 4. This phenomenon was called CV hysteresis. It was normally attributed to mass transport when change of scan rate in CV might cause CV hysteresis. However, in our case, CV hysteresis was too significant to ignore (Fig 4.2-4.5). A hypothesis was proposed that hydroxide as inhibitor may consume Au@Pd NW catalyst surface.

Apart from concentration variation experiment, there was another set of experiment that might also demonstrate OH^- related species as the main inhibitor. On short Au@Pd NW, there was a phenomenon called inhibition memory effect. In a typical fixed potential

chronoamperometric I-t test, the experiment usually started right after a complete CV scan. When CV scan was stopped halfway and I-t measurement was followed right after that, in pristine Pd plate and long Au@Pd NW case, there would be almost no difference from a typical I-t measurement. In short Au@Pd NW, however, when I-t measurement was started right after a CV scan stopped at 0.3 V, which was the highest voltage scanned in a full CV, the current would unexpectedly become zero or near zero. The zero current on the electrode substrate with Au@Pd NW could not be changed even the electrode was taken out of the electrolyte solution and washed with water. When the electrode substrate with Au@Pd NW was put back into the electrolyte solution and scanned a full CV before put to I-t measurement, the starting current as well as the trend of performance decay with time remained the same with the previous I-t measurement after a typical full CV. The zero-current memory effect on short Au@Pd NW was called inhibition memory effect.

Fig. 5.6. CV scan (a) and I-t test (b) graph of ethanol oxidation reaction on 0.61 μm Au@Pd NW in electrolytes with 1.0 M NaOH and 1.0 M ethanol. In graph (b), green line was started right after CV stopped at -0.6 V and blue line was started right after CV stopped at 0.3V. Scan rate of CV was kept at 50 mV / s.

It could be indicated that zero or nearly zero in current was equivalent to complete poisoned Pd surface on short Au@Pd NW. The chemical nature of the species that Pd was complete poisoned by should be different from temporary inhibition at anodic peak voltage in CV scans. On the other hand, the inhibiting species with memory effect could be removed

from poisoned Pd surface on short Au@Pd NW by full CV scans. CV scans typically would involve an oxidation reaction in anodic scan and a reduction reaction in reverse scan. That is to say, the formation of inhibiting species that required either oxidation or reduction to remove might also involve an oxidation or a reduction reaction. Therefore, to study the chemical nature of the inhibitor to cause inhibition memory effect, a series of chemicals in aqueous solution could be used to treat the poisoned Pd surface. If the result of one solution was positive, the current of I-t measurement after candidate solution washed should recover to a current approximately the same with the current of I-t measurement right after a full CV scan, as was shown in Fig. 5.7. If the result of one solution was negative, the current of I-t measurement after candidate solution washed should remain zero, as was shown in Fig. 5.8.

Fig. 5.7. Chronoamperometric I-t test graph of ethanol oxidation reaction on 0.61 μm Au@Pd NW in electrolytes with 1.0 M NaOH and 1.0 M ethanol. In the I-t graph, red line was started right after CV stopped at 0.3V, light blue line was started after the electrode substrate was taken out of and back into electrolyte solution, and navy line was started right after the electrode substrate was washed in candidate solutions with positive result of successful recovery.

Fig. 5.8. Chronoamperometric I-t test graph of ethanol oxidation reaction on 0.61 μm Au@Pd NW in electrolytes with 1.0 M NaOH and 1.0 M ethanol. In the I-t graph, red line was started right after CV stopped at 0.3V, light blue line was started after the electrode substrate was taken out of and back into electrolyte solution, and navy line was started right after the electrode substrate was washed in candidate solutions with negative result of no recovery.

From table 5.1, after the complete poisoned electrode substrate with Au@Pd NW was washed each candidate solution, the candidate solution would be marked as "+" when the current recovered to the current equivalent to the result of typical I-t measurement. If the current remained zero, the candidate solution would be marked as "-".

Wash with	Name & concentration (all % is v/v)	Result performance recovery: + fail to recover:-	Wash with	Name & concentration (all % is v/v)	Result performance recovery: + fail to recover:-
Acid	0.5 M HCl	+	Water	Room temperature	-
	0.1 M H ₂ SO ₄	+		40°C	-
	0.5 M HNO ₃	+		100°C	-
	1% H ₃ PO ₄	+	Base	2 M NaOH	-
	5% HCOOH	+		ammonia	-
	1% CH ₃ COOH	+	Salt	2 mM Na ₂ S	-
	1% CF ₃ COOH	+		acetate buffer	-
	1% CH ₃ CH ₂ COOH	-		0.1% sodium citrate	-
	1% lactic acid	+	Oxidant	1% H ₂ O ₂	-
	1% acrylic acid	+		1 mM HAuCl ₄	-
	1% 2-bromo-2-methylpropionic acid	+		1 mM H ₂ PdCl ₄	-
	1% D-gluconic acid	-	Ligand	0.1% MAA	-
	1% octanoic acid in ethanol	-		0.1% MPA	-
	1% oxalic acid	+		10 mM 4-MBA	-
	1% 1,3-acetonedicarboxylic acid	-		50mg/mL PVP (M _w = 40,000)	-
	1% citric acid	-	Organic Solvent	methanol	-
	1% benzoic acid	-		ethanol	-
Reducing agent	1% NaBH ₄	+		isopropanol	-
	20 mM L-ascorbic acid	+		ethyl acetate	-
Aldehyde	1% HCHO	+		acetone	-
	1% CH ₃ CHO	+		hexane	-
	1% glutaraldehyde	+		cyclohexane	-
	50 mM D-glucose	+		THF	-
	1% benzaldehyde	+		DMF	-
	1% 4-formylbenzoic acid	+		DMSO	-

Table 5.1. An experimental result summary of all the candidate chemical solutions to be used to wash off the inhibition memory effect and assist the performance recovery of short Au@Pd NW. The solutions that can be used to wash the substrate with short Au@Pd NW and regain the current were marked as "+". The solutions that cannot help the substrate regain the current were marked as "-".

Among all the candidate solutions, all the organic solvents, all the alkaline, salt, oxidant and ligand aqueous solutions could not remove the inhibiting species responsible for inhibition memory effect. Some acids, all reducing agents and aldehydes could detoxicate the inhibited Pd surface. Among all the working acids, strong acids were able to function better than weak acids in removing inhibiting species on Pd.

It could be concluded that the inhibiting species responsible for inhibition memory effect on short Au@Pd NW was a product or intermediate of some oxidative reaction. In the ethanol oxidation reaction, not only ethanol but also Pd surface atom on Au@Pd NW may get oxidized. As acid could also wash away the inhibiting species with memory effect, among two main kind of oxidized intermediates, CH_3CHO^* / $^*\text{CH}_2\text{CHOH}$ / CH_3CO^* and Pd-OH^* / Pd-O^* , only Pd-OH^* and Pd-O^* could be both reduced and neutralized. Therefore we could conclude that this set of data may provide evidence for existence of Pd-OH^* or Pd-O^* .

Apart from the quick and dirty method of washing away the inhibiting species, more direct determination on the chemical nature of inhibiting species responsible for performance decay of Au@Pd NW was still of great significance. In-situ Raman spectroscopy should be an effective approach to identify electrochemical intermediates online.

In the in-situ Raman spectroscopy measurement, the electrode substrate with $11.43\ \mu\text{m}$ Au@Pd NW was soaked in working electrolyte solution together with the saturated calomel electrode and carbon stick counter electrode, connected to CHI electrochemical workstation and faced upwards. Laser beam was focused via camera onto the topmost Au@Pd NW surface before a full range scan from $200\ \text{cm}^{-1}$ to $4600\ \text{cm}^{-1}$ was started. When the constant voltage was altered, it should be paused for some time and restart until the current in chronoamperometric measurement remained constant. In-situ Raman spectra on the topmost of Au@Pd NW at $-0.8\ \text{V}$, $-0.2\ \text{V}$ and $0.8\ \text{V}$ was recorded and plotted accordingly. From Fig. 6.9, several significant peaks together with several relatively small peaks could be identified

in four different conditions. The largest peak among them at approximately 3350 cm^{-1} should be attributed to O-H stretching vibration peak in water. While this peak appeared on the spectra collected under all four conditions, the peak intensity decreased with the increase of potential applied. The peak at around 1620 cm^{-1} was attributed to O-H bending vibration peak in water, which share the same trend with the largest peak. These two trends might indicate that OH adsorption is competitive to ethanol oxidation reaction according to the fact that the OH peak was weaker at the voltages which ethanol oxidation reaction happened. The peak at approximately 615 cm^{-1} - 620 cm^{-1} should be attributed to Pd-O* or Pd, which were quite significant in constant potential 0.8 V condition and no voltage condition. It could be predicted that when no voltage was applied to the Au@Pd NW in ethanol and NaOH mixed electrolyte solution, OH⁻ might have higher affinity to surface Pd atoms on Au@Pd NW than ethanol, making it easier to form Pd-oxygen bond. When 0.8 V vs SCE was applied to Au@Pd NW in working electrolyte consisted of ethanol and NaOH, OH⁻ could be accumulated and poison the electrochemical active sites of Au@Pd NW in a short time, facilitating the further oxidation of Pd and formation of Pd-O* species. At low voltage range, however, there were almost no peak within the range of Pd-O binding at -0.8 V and -0.2 V vs SCE. It could be indicated that Pd-O binding and Pd-ethanol binding might be competitive against each other at lower potential range and Pd-O binding might become dominant at high potential range.

Fig. 5.9. In-situ Raman spectra on 11.43 μm Au@Pd NW in working electrolyte consisted of 1.0 M NaOH and 1.0 M ethanol when -0.8 V, -0.2 V, 0.8 V (all voltage was relative voltage to saturated calomel electrode) and no voltage were applied to the electrode substrate with Au@Pd NW on top.

After significant peaks were attributed, a closer look to small peaks was necessary to identify other adsorbed and intermediate species. First, the Raman peak range for CO linear adsorption on Pd was 2050 cm^{-1} - 2090 cm^{-1} and that for CO bridge bond adsorption on Pd was 1940 cm^{-1} - 1980 cm^{-1} . However, from Fig. 6.10, no peak could be identified within 1900 cm^{-1} - 2100 cm^{-1} in any of the four conditions. It could be concluded that no CO adsorption could be identified.

Fig. 5.10. Zoom-in image from 1900 cm^{-1} to 2100 cm^{-1} in-situ Raman spectra on 11.43 μm Au@Pd NW in working electrolyte consisted of 1.0 M NaOH and 1.0 M ethanol when -0.8 V, -0.2 V, 0.8 V (all voltage was relative voltage to saturated calomel electrode) and no voltage were applied to the electrode substrate with Au@Pd NW on top.

From Fig. 5.11, the peak at approximately 2935 cm^{-1} could be attributed to $\text{CH}_3\text{-C}$ on Pd. This peak could be seen in all four conditions, indicating that there was always no C-C bond breaking at the chosen potential.

Fig. 5.11. Zoom-in image from 2800 cm^{-1} to 3000 cm^{-1} in-situ Raman spectra on 11.43 μm Au@Pd NW in working electrolyte consisted of 1.0 M NaOH and 1.0 M ethanol when -0.8 V, -0.2 V, 0.8 V (all voltage was relative voltage to saturated calomel electrode) and no voltage were applied to the electrode substrate with Au@Pd NW on top.

According to Fig. 5.12, 3 peaks in zoom-in Raman spectra with the range of 800 cm^{-1} - 1500 cm^{-1} were attributed accordingly on the Figure. The peak attributed to C-C in ethanol on Pd could be seen with almost same peak intensity in four conditions. The peak attributed to C-C in acetate on Pd rose at -0.2 V and 0.8 V when ethanol oxidation reaction happened on Au@Pd NW surface. At -0.8 V, the peak attributed to C-O in ethanol on Pd, in other words, ethanol adsorption on Pd, was high owing to the fact that Pd could adsorb ethanol at a relatively low voltage. At -0.2 V and 0.8 V, however, ethanol on Pd peak dropped significantly as acetate peak rise.

Fig. 5.12. Zoom-in image from 800 cm^{-1} to 1500 cm^{-1} in-situ Raman spectra on 11.43 μm Au@Pd NW in working electrolyte consisted of 1.0 M NaOH and 1.0 M ethanol when -0.8 V, -0.2 V, 0.8 V (all voltage was relative voltage to saturated calomel electrode) and no voltage were applied to the electrode substrate with Au@Pd NW on top.

In short, the 3 key information that in-situ Raman data provided were that neither CO adsorbed on Pd nor C-C bond cleavage could be observed, ethanol and hydroxide adsorption on Pd should be competitive processes, and acetate was the main intermediate species other than $\text{ethanol}_{\text{ads}}$, OH_{ads} (Pd-OH^*) and Pd-O^* . Therefore, the inhibitor cannot be carbonaceous species, no matter 1C or 2C. It could be indicated that Pd-O^* or Pd-OH^* should be the main inhibitor of Au@Pd NW for ethanol oxidation reaction.

High performance liquid chromatography (HPLC) could be another indirect approach to address the inhibitor problem by analysis of liquid products after long time ethanol oxidation reaction on durable Au@Pd NW. From Fig. 6.13, there were 3 peaks observed from both 0.1 M and 1 M products after 75,000s electrolysis. The first peak was most likely from sodium

sulfate (Na_2SO_4), which was formed when the electrolysis product containing sodium hydroxide (NaOH) was neutralized with sulfuric acid (H_2SO_4) in the liquid flow phase before injected into HPLC column. The second peak, with a retention time of approximately 27 minutes, should be attributed to the existence of acetate as compared to acetate control (red line). The third peak with a retain time of 31-32 minutes should be annotated to ethanol. No peak at 24.8 minutes was identified, indicating that in the remaining electrolyte after electrolysis, the only product of ethanol oxidation reaction is sodium acetate in alkaline media.

Fig. 5.13. HPLC data of product obtained from electrolysis on Au@Pd NW in working electrolyte consisted of 0.1 M NaOH and 0.1 M ethanol (purple line) and 1.0 M NaOH and 1.0 M ethanol (blue line) at -0.2 V vs SCE. The liquid phase used was 0.1 M H_2SO_4 , the flow rate of liquid phase was 1 mL / min and the column temperature was 40 °C.

From all the above discussions, we could conclude that the main inhibitor that was responsible for performance decrease of durable Au@Pd NW should be hydroxide species. Upon knowing the chemical nature of main inhibitor to poison Au@Pd NW and bring performance decay during chronoamperometric measurement, the next question we need to answer should be why the 11.43 μm Au@Pd NW may retain high durability after 200,000 s

I-t test. As hydroxide species became known to cause performance decay, we could translate the question into that why the Au@Pd NW was hydroxide resistant.

In the previous chapter, high durability of 11.43 μm Au@Pd NW together with structure-property correlations like increase in length and density closely associated with increase of durability were discussed. In the CV scans using Au@Pd NW with different length, the anodic peak almost never dropped to zero except the shortest one. When CV for EOR has to scan to a more positive potential than 0.4V vs SCE (like red line in Fig. 6. 14) in order to see peak drop, during the backward scan there is always a curve of which anodic current is not zero, like blue line in Fig. 6.14. There was a notable fact that, almost all Au@Pd NW with length more than 2 μm in the Fig. 5.3 shared the fact that their anodic forward scan stopped at a potential that higher than 0.4V and their backward scan started with current above zero. Apart from the set of length and durability correlation data, there could be other CV scans sharing the characteristic mentioned above. It was widely known that oxygen evolution reaction (OER) may start to occur on noble metal catalyst in alkaline solution from around 0.4V vs SCE. Therefore, we can call the potential range larger than 0.4V vs SCE the OER range. In OER in alkaline electrolyte, as the forward scan started from negative to positive voltage, the OH^- accumulation on anodic electrode surface increased spontaneously with voltage. As long as the accumulation of OH^- saturated on the electrode surface, further oxidation steps would occur, Pd-OH^* would be oxidized to Pd-O^* or Pd-OOH^* and finally oxygen formed. (as shown in Fig. 6.15) In ethanol oxidation reaction, similarly, as forward scan started from negative to positive, OH^- accumulation on catalytic surface increased spontaneously with voltage. Ethanol concentration within the close region around catalyst on the other hand, didn't change with the increase of voltage. As ethanol and OH^- adsorption on Pd was competitive reactions and OH^- accumulated as voltage increased, ethanol adsorption on Pd would be decreased with voltage increase and finally all active sites would be occupied

by hydroxide species. When the end voltage of forward scan was in OER range, there might be a part of Pd-OH* that was further oxidized to Pd-O*, which might be the reason why anodic peak near the end of forward scan in Fig. 6. 14 cannot drop to zero. Those sites that get oxidized to Pd-O* in forward scan and form O₂ and Pd during backward scan should be named B site. The area under forward scan curve in OER range should be named A site, as these sites would be consumed by competition between ethanol and hydroxide adsorptions and get released after acetate formed. When the CV scan didn't go beyond the normal OER onset potential, like that of 0.61 μm Au@Pd NW, their A and B site were all in operations catalyzing ethanol oxidation reaction, rather than distinguished from one another.

Fig. 5.14. CV scan of ethanol oxidation reaction on 2.02 μm Au@Pd NW in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH at a scan rate of 50 mV/s. The CV curve was divided into 2 parts which represented the 2 working sites in A-B dual site hypothesis: Part A referred to the whole forward scan and backward scan below OER range and Part B referred to backward scan in OER range.

To justify the idea to use OER to explain abnormal EOR CV curve in Au@Pd NW, CV in EOR working electrolyte and CV in 1.0 M NaOH solution in the same potential range with

the same scan rate of 10 mV / s were overlapped to see the correlation between EOR and OER. The both CV curve, especially backward scan curve, overlapped perfectly. Therefore, it was justifiable to use OER reaction mechanism to assist in solving EOR mechanistic problem.

Fig. 5.15. CV scan of ethanol oxidation reaction on 2.02 μm Au@Pd NW in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH at a scan rate of 10 mV/s. The CV curve was divided into 2 parts which represented the 2 working sites in A-B dual site hypothesis: Part A referred to the whole forward scan and backward scan below OER range and Part B referred to backward scan in OER range.

Hence, we proposed a hypothesis that may possibly explain the mechanistic reason to high durability of our Au@Pd NW. There could be two sites on the Au@Pd NW electrode on which CV scan may reach voltages beyond onset potential of respective OER. One is named A site, mostly used in catalyzing ethanol oxidation reaction. The other is named B site, on

which hydroxide species would be further oxidized and finally form oxygen. A and B site was not supposed to have chemical composition difference. The only difference was that when scanning voltage was beyond OER onset potential, hydroxide species on B site might be able to get further oxidized while hydroxide species on some A site would form acetate together with ethanol on other A site. As Pd-O* could not react with ethanol_{ads} to free the occupied sites, occupied B site could only be freed when oxygen released at backward scan.

Fig. 5.16. Schematic flow chart of A-B dual site hypothesis

In the extremely long durability test, the A-B dual site hypothesis may be able to explain why there would always be a turning point and a long and flat platform after that. In the 11.43 μ m Au@Pd NW, electrochemical active sites consisted of A and B were in such a large number that when it came to the end of CV scan before durability I-t measurement at -0.8 V vs SCE, large amount of active sites were occupied by ethanol. When the I-t started at -0.2 V, the pre-adsorbed ethanol got consumed by OH⁻ attracted by -0.2 V and freed the site by acetate formation. Then the freed site may be occupied by ethanol or OH⁻ respectively. As the ethanol oxidation reaction went on, the A and B sites that was occupied by ethanol recycled and used over time until pre-adsorbed ethanol all got consumed and only the cycle of adsorption and release would provide ethanol adsorption and following oxidation reaction on A site. Later, the OH⁻ accumulation would induce the further oxidation of Pd-OH* on B site.

As the relatively low OH⁻ accumulation at -0.2 V compared to 4.8 V in 11.43 μm Au@Pd NW case, the B site get consumed much slower than A site.

Fig. 5.17. Graph of 200,000 s chronoamperometric I-t test of ethanol oxidation reaction on 11.43 μm Au@Pd NW in working electrolyte consisted of 1.0 M ethanol and 1.0 M NaOH. The area under I-t curve was divided into 2 parts which represented the 2 working sites in A-B dual site hypothesis: Part A referred to electrochemical active sites that may catalyze EOR and Part B referred to electrochemical active sites that may only be slowly saturated with Pd-O*.

5.4. Conclusion

In this chapter, we investigated the mechanistic reason behind the high durability we obtained by discussions on correlation between OH^- concentration and performance decrease in pristine Pd plate, inhibition memory effect brought by hydroxide species on short Au@Pd NW, intermediate species identification by in-situ Raman spectroscopy and product analysis by high performance liquid chromatography. By summarization of the aforementioned discussions, we proposed the OH^- species as the main inhibitor to poison Pd and bring performance decrease during chronoamperometric test. Finally, we would like to propose a dual site hypothesis to explain the high durability of ultrathin Au@Pd NW.

5.5. Reference

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6. Summary and outlook

6.1. Summary

This thesis mostly summarizes the synthetic modification on vertically standing Au NW arrays, the alternative substrates to grow Au NW on, the morphology induced catalytic properties, and application brought by these properties. The research was focused on synthesis, morphology, property and application of ultrathin Au NW. We started our research on vertically standing ultrathin Au NW by exploring alternative substrate to expand the application range, investigating modified preparation method to achieve more facile synthesis, exhibiting a greatly enhanced operation durability which correlated with morphology and finally proposing a hypothesis regarding mechanistic understanding behind the greatly enhanced durability.

Exploration on alternative metal substrate for preparation of substrate bounded Au NW was discussed in chapter 2. We attempted to tackle with the galvanic replacement problem by approaches like changing surface function group using different silanes, increasing the concentration of thiol ligand used in the Au NW growth step, screening for the proper thiol ligand that might form a layer for capping the metal surface to inhibit galvanic reaction without interfering Au NW growth, adding a ligand or blocker solution pre-treatment procedure before Au NW growth, performing a prior galvanic replacement reaction to consume the surface metal, and finally creating a layer of oxidized surface metal to inhibit the galvanic reaction. Approach that aimed for enhancing the gold reduction rate were also investigated using different reducing agent and increasing the reducing capability by adding sodium hydroxide. Finally, we succeeded in grow bundles of ultrathin Au NW on to the micro-sized Ag NW with the concentration that could undergo further treatment and form transparent conductive film. With less surface silver to consume than bulk silver foil, gold precursor

remained just enough for Au NW growth after the galvanic reaction consumed a relatively low portion of gold precursors by surface silver atoms.

In chapter 3, we successfully reported a modified ultrathin Au NW forest preparation method to grow Au NW without the use of gold nanoseed. The modified method used salt adsorption instead of gold nanoseed adsorption. While gold nanoseed preparation required extra time and effort, the improved salt assisted Au NW growth method may bring higher efficiency in vertically aligned ultrathin Au NW preparation. Charge induced nucleation step by adsorbed anions on the pretreated APTES layer was hypothesized to be the key to facilitate the growth step without the use of seed. Reducing effect of anions were also discussed briefly. While the charge and reducibility factor both correlated to APTES layer formation, the molecular-level discussion of salt in this modified Au NW preparation method still remained in the form of hypothesis. Finally, Na₂S was the best among all screened salts to obtain as almost the same vertically standing Au NW as seeded method could do. A synthetic scheme based on Na₂S was proposed and illustrated.

In chapter 4, we reported the modified preparation of Au@Pd NW with advantages offered by its morphology induced property to spontaneously enhance both catalytic activity and operation durability that may significantly enhance the performance of anode reaction in DEFCs. The vertically standing nanowire forest with tunable length prepared using active site growth method may provide high electrochemical active surface area for high catalytic activity and enhance the electronic charge transport efficiency at the same time. Furthermore, the improved mechanical strength brought by modified salt assisted method together with the highly tunable length and density of vertically standing Au@Pd NW can offer greatly enhanced operation durability at fixed potential for 200,000 s. Nearly 40% of the highest anodic performance remained by Au@Pd NW for catalyzing ethanol oxidation reaction could still be achieved even after 200,000 s at a fixed potential.

In chapter 5, we investigated the mechanistic reason behind the high durability we obtained by discussions on correlation between OH^- concentration and performance decrease in pristine Pd plate, inhibition memory effect brought by hydroxide species on short Au@Pd NW, intermediate species identification by in-situ Raman spectroscopy and product analysis by high performance liquid chromatography. By summarization of the aforementioned discussions, we proposed the OH^- species as the main inhibitor to poison Pd and bring performance decrease during chronoamperometric test. Finally, we would like to propose a dual site hypothesis to explain the high durability of ultrathin Au@Pd NW.

6.2. Outlook

With the summarized and accumulated synthetic controllability, established structure-property correlations and mechanistic understanding in one dimensional nanostructures synthesis and electrochemical catalytic reactions and applications, several future directions could be proposed.

First in efforts to achieve Au NW growth on metal substrate, despite the fact that we failed to achieve Au NW growth on bulk Cu and Ag substrates within the variation range of our experimental parameters, several novel substrate bound bimetallic nanostructures has been achieved with the change of synthetic parameters. The stacked Au-Cu bimetallic triangular nanosheets might be used in catalyzing carbon dioxide reduction reaction if proper Cu to Au ratio could be achieved while maintained the morphology of stacking nanosheets. The ligand effect on preparation of vertically standing Au-Ag bimetallic nanosheets which was prepared using high concentration of 4-MBA could be further explored as the nanostructure itself might be novel. If Au was removed by CN^- assisted chemical etching from the vertically standing bimetallic nanosheets structure, the Ag surface with high porosity and high surface area could be prepared and used in potential catalytic reactions for which Ag could be good catalyst.

In the following development of modified S^{2-} anion assisted Au NW preparation method, a wider variety screening of salts could be done to expand the boundary of preparation parameters. Furthermore, the effect of oxidative together with reductive anions could be studied to achieve more systematically mechanistic understanding on the oxidative and reductive anion effect. Additionally, effect of cations could also be explored in order to enhance the understanding to the hypothesis of charge induced gold nucleation process.

With the achievement in successful preparation of Au@Pd NW bearing greatly enhanced operation durability on FTO, a further optimization Au@Pd NW preparation on

three dimensional conductive substrates like carbon paper and nickel foam should be of high priority. Initial successful Au NW growth on carbon paper and nickel foam was achieved previously. The optimization on both synthetic approaches and morphological characteristics to further enhance the catalytic activity and operation durability should be achieved and hopefully put into more application scenarios like an anode electrode of fuel cell that leveled with industry standards.

Finally, on the understanding of the origin of high durability of our Au@Pd NW, what we already achieved was the discussion and expansion of understanding on the hydroxi resistance property of our core shell Au@Pd NW. With this understanding, we should be able to accomplish more discussions and understandings in nanowire array system and even nanoparticle system for ethanol oxidation reaction. With the comprehensive understanding on the mechanistic nature in various aspects of ethanol oxidation reaction, we could achieve rational morphological and compositional design and preparation of novel catalyst based on our powerful knowledge in synthetic controllability.