Assembly and application of metal and metal oxide nanowires

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**ASSEMBLY AND APPLICATION OF METAL AND
METAL OXIDE NANOWIRES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCE

2013

Assembly and Application of Metal and Metal Oxide Nanowires

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Abstract

This thesis contains three parts. In the first part, highly SERS active 3D multi-layered wood pile like silver nanowires (AgNW) substrate was prepared using Langmuir Blodgett (LB) via a layer by layer approach. The assembled 3D nanowire substrate has higher and more homogenous SERS enhancement than the 2D monolayer of AgNW due to the increased in hot spots created by vertical stacking of the nanowires layers as shown by Raman mapping results. However, when the number of nanowire layers was increased beyond three layers of AgNW, the increased in SERS signal plateaued off. This can be attributed to the laser penetration depth. In addition, the multilayer AgNW substrate showed an angle independent SERS intensity and had a larger SERS depth cross section, allowing the multilayer AgNW to be more reliable and versatile for future sensing applications. In the second part, highly SERS active free standing silver nanowires (FS AgNW) film was prepared using vacuum filtration technique. The high SERS enhancement effect is due to the increase in SERS hot spots formed at the junctions of the overlapping AgNW within the free standing networks. A lack of correlation between thickness of the prepared free standing Ag NW and the SERS intensity measured was observed. This could be due to the excessive thickness of the FS AgNW. In the final part, we fabricated anatase TiO₂ nanowires via hydrothermal method. Acid washing of the initial synthesized sodium titanate nanowires played an important role in determining the final crystal structure of the synthesized nanowires. Incomplete ion exchanged of sodium ions with hydrogen ions during the acid washing

process led to the formation of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanowire instead of the desired anatase nanowire after calcination. Calcination of the synthesized nanowire will increased their photocatalytic rate and the anatase nanowire had the highest photocatalytic rate among all the synthesized nanowires.

Chapter 1 Introduction

1.1 Introduction to fabrication of 3D woodpile-like silver nanowires as highly active SERS platform

1.1.1 Introduction to Raman

Raman scattering was discovered by Chandrasekhara Venkata Raman in 1921 in India.¹ This discovery won him the Nobel prize in physics in 1930.² Raman scattering is the inelastic scattering of light by atoms or molecules. When a photon of light interacts with a molecule, polarisation of the electron cloud and excitation of the electron to a “virtual” energy state may occur. When the molecule relaxes back to its ground state, a photon is released in any direction, resulting in scattering. There are 3 main types of scattering: Rayleigh scattering, Stokes and Anti-Stokes scattering as shown in Figure 1.1. After the excitation, if the molecule relaxes back to the same energy state without losing or gaining energy, (the energy of the initial photon is the same as the energy of scattered photon), it is known as Rayleigh scattering. If the scattered photon loses or gains energy during the scattering process, it is known as Raman scattering, which is an inelastic scattering process. There are two types of Raman scattering: Stokes scattering and Anti-Stokes scattering. If the molecule is excited from the ground to virtual state and subsequently relaxes down to a higher energy vibrational state, the scattered photon will lose energy. Hence, the scattered photon is red shifted to a longer wavelength and this

process is known as Stokes scattering. If the molecule is excited from a higher energy vibrational state to virtual state and relaxes back to ground state, the scattered photon will gain energy and be blue shifted to shorter wavelength. This process is known as Anti-Stokes scattering.

Figure 1.1. Diagram showing types of light scattering: Rayleigh scattering (elastic scattering), Stokes scattering (molecule absorb energy) and Anti-Stokes scattering (molecules lose energy).

The change in photon energy during the scattering process is known as Raman shift. Since, the measured Raman shift is dependent on the vibrational states of the molecule which is specific to the chemical bonds and symmetry of molecules, Raman spectroscopy can be used for structural analysis and as a molecular detection tool.

However, the main disadvantage of Raman spectroscopy is its inefficiency due to the small scattering cross-sections which is about 15 orders of magnitude lower than fluorescence excitation.³ Hence, Raman spectroscopy was not commonly used until the discovery of surface enhanced Raman spectroscopy (SERS) in the 1970s.

1.1.2 Introduction to SERS

Since the discovery of surfaced enhanced Raman spectroscopy (SERS) in the 1970s,⁴⁻⁶ many potential applications have been unveiled; detection of molecules^{7,8} and biological molecules^{9,10} with ultrahigh sensitivity such that detection of a single molecule is also possible.^{11,12}

SERS was first discovered in 1974 when Fleischmann and co-workers observed intense Raman scattering from pyridine absorbed onto a roughened silver electrode surface.⁴ However, they failed to recognise the major enhancement effect and attributed the large signal observed to the increased number of molecules that were scattered on the electrode surface. Three years later, Van Duyne group⁵ and Creighton group⁶ reported independently that the large intensity observed could not be simply accounted for by the increase in the number of molecules present and proposed that an enhancement of the scattered intensity occurred in the absorbed state.

The large increase in Raman intensity is mainly due to the electromagnetic enhancement effect caused by the resonant interaction between surface plasmon in metal and incident light.³ The plasmon resonance and SERS

enhancement effect are dependent on the size, shape, nature and external environment of the metal nanoparticles. Studies have shown that when two nanoparticles are in extremely close proximity, the electromagnetic field (EM) at the gap region between the two nanoparticles increases dramatically.¹³⁻¹⁵ This region of highly concentrated electromagnetic field (EM) is also known as a “hot spot” which increases the SERS intensity significantly. Hence, effort is put in to create reproducible and controlled hot spot structures to fabricate a highly sensitive SERS substrate.

Wang et al. fabricated highly ordered 2D CTAB- stabilized Au nanoparticles arrays with very small inter-particle spacing of 8 nm that had high SERS enhancement factor of up to 10^8 .¹⁶ Several groups had managed to assemble gold nanorods,¹⁷ gold nanoparticles,¹⁸⁻²⁰ silver nanoparticles¹⁷ and silver nanorods²¹ into multilayer structure and studied their SERS properties. In general, results indicated that assembled multilayer had much higher SERS intensity as compared to monolayer assembly of nanoparticles. However, the spatial distribution of Raman intensity across a large area of 3D SERS substrate has yet to be discussed. In most literatures, assembled 3D nanoparticles that had been reported were highly disordered in nature which limits homogeneity of the SERS enhancement effect.

1.1.3 Use of silver nanowire as SERS substrate

Large scale synthesis of high aspect ratio silver nanowires (AgNW) with length up to $\sim 50 \mu\text{m}$ had been reported by Sun et al.²²⁻²⁵ These nanowires have large surface areas and high crystallinity which make them a useful potential

SERS substrate for ultra-sensitive sensing. However, the enhancement effect of trunk single smooth nanowire is low as the longitudinal surface of the nanowire couples weakly to light due to the mismatch between photon and nanowire plasmon dispersion.²⁶ In order to overcome this challenge, many studies have been done to increase the amount of hot spots found on the nanowires.

Figure 1.2. Methods to create hotspots on silver nanowires: (A) chemical etching,¹ (B) assembling nanoparticles onto silver nanowire,² (C) using of manipulator to create nanowires pair,³ (D) assembling the nanowires into closely packed structures using LB technique.⁴

For single nanowire, the number of hot spots can be increased by either the use of chemical etching to roughen the surface of the AgNW²⁷ or by

assembly of nanoparticles onto silver nanowire to create more inter-particle gaps.²⁸ Two different groups, Kang et al.²⁹ and Du et al.³⁰ reported the use of manipulator to create nanowires pair. They reported that the hot spots were the dimeric part which had the strongest SERS effect. Hot spots can also be created by assembling the nanowires into closely packed structures.³¹ Jeong et al. reported the fabrication of a raft of aligned silver nanowires electrochemically using anodic alumina templates.³² They reported that the EM field was large enough to allow single molecule detection by SERS. Tao et al. had assembled closely packed monolayer of AgNW using Langmuir- Blodgett (LB) technique and reported large electromagnetic field enhancement factor of 2×10^9 for resonant dye, Rhodamine 6G, and 2×10^5 for non-resonant dyes, thiol and 2,4-dinitrotoluene.³³ They also reported that the SERS intensity was dependent on the direction of polarisation of the incident light.³⁴ However, currently, the SERS studies of highly crystalline, ordered nanowires were currently limited to 2D structures. There is a lack of study on orderly assembled multi layered 3D nanowires which should have much higher SERS enhancement effect than 2D assembled nanowires.

1.1.4 Our Objective

In this paper, we report a method to increase the SERS hot spots of nanowires. The nanowires were assembled into a closely packed 2D and 3D multilayer structure in order to harvest the plasmonic coupling effect between nanowires which will increase the detected SERS signal. Langmuir- Blodgett technique was used to assemble the nanowire using a layer by layer approach to

create closely pack multi-layer wood pile like structure. As the number of layer increases (the nanowires are assembled from 2D to become 3D), more hot spots are created by vertical stacking of the closely packed nanowires which can overcome the low SERS enhancement effect of the body of smooth nanowires.

The assembled 2D and 3D silver nanowires substrates were used for systematic studies of Raman intensities in all X, Y and Z directions using atomic force microscopy (AFM) Raman mapping. In addition, angle dependent studies were conducted on the assembled one, two, three, four and five layers of AgNW using AFM Raman. Throughout this research, AFM Raman mapping was used as it can show the distribution and homogeneity of SERS enhancement effect of the substrate over a large area. Hence, by assembling the nanowires into closely pack 3D structure, we aimed to create a highly sensitive SERS platform with SERS enhancement that is greater than that of the previously reported 2D assembled nanowires.

1.2 Introduction to free standing silver nanowires film as a potential sensitive SERS substrate

1.2.1 Introduction to vacuum filtration technique

Vacuum filtration is a simple technique used to assemble nanofibrous materials to create a free-standing film.³⁵⁻³⁸ After the filtration process, the nanowires overlap to form a stable free-standing network structure. Unlike conventional nanoparticles, which need to be deposited on substrate such as Silicon wafer for characterisation and application, these free-standing films do not need any additional substrate for support and can be directly analysed and used for various applications. As compared to other assembly methods such as the layer by layer method,³⁹⁻⁴² the filtration method does not require specified chemical interactions between substrate, thus increasing the simplicity of the assembly process. However, this method is only suitable for materials with very high aspect ratio in addition to the ability to disperse well in the solvent, and must display sufficient rigidity to withstand suction filtration.³⁵

Wang and co-workers utilised the vacuum filtration method to synthesize nanostructured sheets of Ti–O nanobelts for gas sensing and antibacterial applications.⁴³ Three types of Ti–O-compound-based nanobelts ($\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{H}_2\text{Ti}_3\text{O}_7$, and TiO_2) are prepared from commercial TiO_2 powders using an alkaline hydrothermal process. These nanostructured sheets were prepared using vacuum filtration technique. They reported that the nanostructured sheets are favourable for absorption and photodegradation of

various pollutants, and can be used as filter membranes for water or air purification.

De et al. reported the preparation of a thin, transparent and conductive film from silver nanowires.⁴⁴ These silver nanowire films were prepared using the vacuum filtration technique. They reported the prepared films had optical transmittance and sheet resistance highly similar to that displayed by commercially available indium tin oxide. In addition, such films hold great promise as flexible, transparent electrodes.

1.2.2 Our objective

As mentioned in chapter 1.1.3, despite having a large surface area, the SERS enhancement effect of single smooth silver nanowire (AgNW) is low due to the weak coupling of the longitudinal surface of the nanowire to light. This is attributed to the mismatch between photon and nanowire plasmon dispersion.²⁶ In order to overcome this challenge, many studies have been done to increase the amount of hot spots found on the nanowires.

Here, we increase the SERS hot spots and overall SERS sensitivity of nanowires via using vacuum filtration technique to fabricate free standing silver nanowires (FS AgNW) film. Vacuum filtration is a simple and easy method to make large-scale free-standing films.^{37,38,45,46} As mentioned previously in chapter 1.2.1, this method is only suitable for materials with very high aspect ratio, with the ability to disperse well in the solvent and possess adequate rigidity to withstand suction filtration.³⁵ Silver nanowires synthesized using the

polyol method^{24,25,47} met all the requirements for the above filtration method and can be assembled using this method.

While making of free standing nanowires film have been extensively reported, the SERS enhancement effect of free standing silver nanowires (FS AgNW) remains unexplored. Here, we focus on increasing the number of SERS hot spots on AgNW via the filtration technique. The AgNW will deposit onto the filter membrane and overlap randomly resulting in the formation of a stable network structure. Within the network structure, when two AgNW overlap, strong electromagnetic coupling occurs at the junction of the nanowire pair. This creates high density of hot spots throughout the FS AgNW network by harvesting collective electromagnetic enhancement at the nanowire junctions throughout the FS AgNW film.

1.3 Introduction to photocatalysis and fabrication of TiO₂ nanowires

1.3.1. Introduction to photocatalysis

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst.⁴⁸ In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on a TiO₂ electrode under ultraviolet (UV) light.⁴⁹ Thereafter, heterogeneous photocatalysis has been widely researched on in the field of environmental toxins removal as it offers a good substitute for the current energy-intensive conventional treatment methods with the capacity for using renewable and pollution-free solar energy. Currently, many environmental toxin such as rhodamine 6G (R6G) dye,⁵⁰ phenol,⁵¹ organoarsenic species,⁵² brevetoxins (PbTx)⁵³ and many other photocatalytically degradable pollutants have been studied.^{54,55}

This toxin removal process is based on advanced oxidation processes (AOPs). When photon energy ($h\nu$) greater than the band gap energy of TiO₂ is illuminated onto its surface, a TiO₂ electron will be photoexcited to the empty conduction band. This photonic excitation will form an empty unfilled valence band and thus an electron-hole pair is formed. This can cause series of chain oxidative - reductive reactions and the in situ generation of highly reactive transitory species (i.e. H₂O₂, OH·, O₂^{·-}, O₃) that can cause the mineralization of organic compounds, degradation of dyes, destruction of water pathogens, virus and highly toxic inorganic compounds such as cyanides.^{49,56-59} Unlike the conventional treatment methods which transfer pollutants from one medium to

another, photocatalysis leads to the formation of non-toxic products. In addition, the secondary waste generation is minimal.⁶⁰

1.3.2 Introduction to titanium dioxide

Titanium dioxide (TiO_2) has received the greatest interest in R&D of photocatalytic technology as it has many advantages such as relatively inexpensive, non-toxic, highly photoactive and photostable.⁶⁰⁻⁶² TiO_2 occurs in nature in three crystallographic phases: rutile, anatase and brookite. Rutile and anatase can be described in terms of chains of TiO_6 octahedral, where each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions.

Titanate nanowires can be formed by using a hydrothermal approach.⁶³⁻⁶⁸ These nanowires have an advantage over commercially available TiO_2 nanoparticles as the nanowires can be separated by filtration or sedimentation, making them a more ideal candidate for practical photocatalytic process. Hydrothermal method is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperatures and/or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determines the internal pressure produced.⁶⁹

In a typical reaction, titanate nanowires are obtained by treating TiO_2 white powders in a 10 - 15 M NaOH aqueous solution at 150 - 200 °C for 24 - 72 hours without stirring within an autoclave. From literature, this will lead to

the formation of sodium titanate nanowire.⁷⁰ However, the photocatalytic activities of these sodium titanate nanowires are generally slow. Research had shown that the photocatalytic activity was dependent on the crystal structure of the synthesized nanowires, with anatase TiO_2 nanowire showing the highest photocatalytic efficiency.^{71,72} Hence, post treatments are needed to convert these sodium titanate nanowires to anatase phase to increase their photocatalytic efficiency.

Figure 1.3. (A) TEM image, (B) HR TEM image and (C) SEM image of anatase TiO_2 nanowires.⁵

The synthesized sodium titanate nanowires were washed with 0.1 M HCl followed by water until the pH value reached ~ 7 . This decreases the sodium content in the titanate nanowire because hydrogen ions replace the sodium ions to form the hydrogen titanate ($\text{H}_2\text{Ti}_6\text{O}_{13}$) structure.⁷⁰ After centrifuging and drying the sample in air, the products can be calcinated at 700°C for conversion to anatase phase to improve their photocatalytic activity.^{38,71} If the hydrogen titanate nanowires were calcinated at lower temperature (from 400°C to 600°C), the hydrogen titanate nanowires may be converted to the titanium dioxide polymorph, TiO_2 (B), nanowires instead.^{63,71}

However, another research group reported that calcinations at 550 °C will convert the hydrogen titanate nanowires into pure anatase TiO₂, which contradicts with the above findings.

Some groups had reported that when the hydrogen titanate nanowires were calcinated at high temperature (at around 600 °C), fragmentation of the nanowires will occur to form a mixture of nanowire and irregularly shaped particles.⁷¹ On the other hand, other groups reported structure stability up until 800 °C and heating beyond 800 °C results in the conversion of the hydrogen titanate nanowire to titanium dioxide rutile phase.⁷³

1.3.3 Our objective

Currently, the exact conditions for fabrication of TiO₂ anatase nanowire are still ambiguous. In this project, we will investigate the experimental conditions to fabricate TiO₂ anatase nanowires. In addition, we will investigate the photocatalytic activity of the synthesized nanowires by monitoring the photocatalytic degradation of methyl orange in the presence of the synthesized nanowires under UV irradiation.

Chapter 2 Fabrication of 3D woodpile-like silver nanowires as highly active SERS platform

2.1 Experimental Section

Materials. Poly(vinyl pyrrolidone) (PVP, average MW = 360,000), anhydrous ethylene glycol (EG, 99.8 %) were purchased from Sigma Aldrich; NaCl (99.5 %) was purchased from Goodrich Chemical Enterprise; AgNO₃ (99+ %) was purchased from Alfa Aesar. All chemicals were used without further purification. Milli-Q water (> 18.0 MΩ.cm) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of AgNW. AgNW were synthesized based on a modified literature procedure.⁴⁷ In a typical synthesis, 10 ml of EG was added to a round bottom flask containing 7 mg of NaCl and 0.5015 g of PVP and the mixture was heated at 160 °C. Using a syringe pump, 0.12 M AgNO₃ solution in 5 mL EG was added dropwise at a rate of 5 mL/h into the PVP solution while stirring at 1000 rpm. After the addition of AgNO₃, the nanowire solution was further heated for 30 min at 160 °C and then cooled to room temperature. The nanowire solution was washed several times using acetone and ethanol until the supernatant became colourless to remove the small colloidal particles. The final product was dispersed in ethanol and was left to sediment stand overnight in the fridge. The top suspension was

transferred into a new vial while the sediment was discarded to remove large colloidal particles. The final product was dispersed in ethanol.

Langmuir-Blodgett (LB) assembly of AgNW. To 1 ml of AgNW, 1.5 ml of chloroform solution was added and mixed to form a suspension. The chloroform suspension of nanowires was added dropwise to the air–water interface of the LB trough (KSV NIMA KN1002). After the chloroform had evaporated, the nanowires monolayer was compressed at a constant speed of 3 mm min^{-1} . After compressed to the predefined target pressure (13 mN m^{-1})., Subsequently, the monolayer was vertically deposited onto the clean silicon substrates at a dipping speed of 1 mm min^{-1} to achieved a monolayer AgNW assembly.

To assemble 2 layers of silver nanowires, the silicon substrate containing the monolayer AgNW as turned 90° and was used in the LB process instead of the clean silicon substrate. Hence, another layer of AgNW was assembled on the monolayer substrate and a two layer AgNW substrate was formed using LB. This process was repeated using the silicon substrate containing two, three and four layers of AgNW to get three, four and five layers of AgNW respectively.

Figure 2.1. Illustration of the LB assembly of multilayer AgNW process.

Raman spectroscopy. The AgNW were ligand-exchanged with 1 mM 4-methylbenzenethiol (4-MBT) in ethanol with stirring at room temperature for at least 12 h. These samples were rinsed with ethanol and subsequently dried under N_2 gas. Raman measurements were performed using Raman measurements were performed using a Witec alpha 300S with confocal Raman Imaging. Raman system with an excitation wavelength of 532 nm (measurement power = 0.36 mW, unless otherwise stated) supplied by a YAG laser (Power output = 50 mW) was used. All mapping experiments were performed using a $100\times$ objective lens (NA = 0.9) with 0.02 s accumulation time with a piezo-scanning stage, unless otherwise stated. Samples were scanned at different angle to obtain orientation dependent Raman map. AFM module is integrated with the Witec alpha 300S system and attached to a $20\times$ objective (Zeiss). AFM measurement was done with AC mode (non-contact

mode) using a BudgetSensors AFM probe with Aluminium aluminium coated back-reflected coating (model TAP300G-Al). Free amplitude set-point was set around $A_0 = 1.5$ V. AFM and Raman modes were interchanged to correlate the nanowire morphology with Raman mapping.

Characterization. Scanning electron micrographs were obtained using JEOL-JEM-1400 electron microscope. Images were obtained with an operating voltage of 5 kV. UV – vis spectra were recorded using a Cary 60 UV – vis spectrophotometer. Instead of using silicon substrate, the monolayer Ag nanowire film assembled on a quartz glass slide using LB and the UV – vis absorption spectra was were recorded.

2.2 Results and discussion

Figure 2.2. (A) Low magnification SEM images of the synthesized AgNW, (B) high magnification SEM images of the synthesized AgNW. Histogram of (C) length distribution and (D) diameter distribution of the Ag nanowires.

The high aspect ratio AgNW was synthesized using a modified polyol process as reported by literature.⁴⁷ In short, the silver nitrate was added dropwise into a mixture of ethylene glycol (EG) and poly(vinylpyrrolidone) (PVP) at 160 °C to form high aspect ratio AgNW. The products were characterized using scanning electron microscope (SEM) (Figure 2.2) and UV-Vis spectroscopy (Figure 2.5 (A)).

From the SEM image in Figure 2.2, the synthesized Ag nanowires had the average length of $13\ \mu\text{m} \pm 5\ \mu\text{m}$ and average diameter of $77\ \text{nm} \pm 13\ \text{nm}$.

First, a drop of diluted silver nanowires was drop casted onto silicon substrate to study the SERS effect of different parts of AgNW pairs. Throughout this chapter, we used non-resonant Raman probe molecules, 4-MBT, instead of other probe molecules that have non-specific adsorption because 4-MBT is known to form a self-assembled monolayer on the surfaces of Ag nanowires via a strong Ag-S coordination bond.⁴⁸ The formation of homogenous monolayer of probe molecules on SERS substrate is essential for reliable and quantitative comparison in the Raman analysis. First, a pair of cross AgNW and parallel AgNW was located using optical microscope as shown in Figure 2.3 (A) and (B). Next, Raman mapping was performed over a large area and the Raman spectra in Figure 2.3 (E) corresponds to 4 different areas of the substrate that were identified in Figure 2.3 (C) and (D) : (1) body of nanowire, (2) tip of nanowire, (3) junction of parallel nanowires pair, (4) junction of crossed nanowires pair.

Figure 2.3. (A, B) Optical microscope image and (C, D) AFM image of crossed and parallel AgNW respectively. (E) AFM Raman spectra recorded at various location of the substrate: (1) body of nanowire, (2) tip of nanowire, (3) junction of parallel nanowires pair, (4) junction of crossed nanowires pair.

A typical Raman spectral of 4-MBT is shown in Figure 2.3 (E). 4-MBT molecules have two characteristic Raman peaks which are located at $1,075\text{ cm}^{-1}$ and $1,578\text{ cm}^{-1}$.^{74,75} The peak at 1075 cm^{-1} is due to a combination of the phenyl ring-breathing mode, CH in-plane bending, and CS stretching, while the peak at 1578 cm^{-1} can be assigned to phenyl stretching motion.¹⁴ The 4-MBT Raman peak at 1075 cm^{-1} was chosen to be used for comparison of SERS intensity throughout this whole paper because the 1578 cm^{-1} peak overlaps with the Raman signals produced by the PVP molecules which occur within the region of $1400 - 1600\text{ cm}^{-1}$.

As shown in Figure 2.3 (E), the SERS intensity measured at Raman shift of 1075 cm^{-1} for tip of nanowire, junction of parallel nanowires pair and junction of crossed nanowires pair were 8 counts, 182 counts and 202 counts respectively while for the body of nanowire, negligible SERS enhancement was observed. The

Raman intensity of mapping measured at the area of the tip of single nanowire was very weak possibly due to the short acquisitions time of 0.2 seconds that was used during the measurement. The lack of SERS enhancement at the bodies of the nanowires may be due to a mismatch between photon and nanowire plasmon dispersion which results in weak coupling of the nanowire surface to light.²⁶

The Raman intensity measured at the junctions of cross and parallel AgNW pair was much stronger than that measured at the area of the tip of nanowire. This is due to the plasmonic coupling at the junction of the 2 nanowires that produced highly intense localized electromagnetic field which had been shown in previous studies.^{29,76} The highly intense localized electromagnetic field significantly increased the SERS signal measured at both the junctions of cross and parallel AgNW pair. This result is in agreement previously reported literature which also concluded that SERS intensity of dimer was greater than that of single nanowire.³⁰

To the best of our knowledge, current literature on SERS studies of AgNW assembled using LB technique have only been performed on 2D assembled AgNW which consisted only parallel gaps. From the results obtained, in addition to parallel gap, vertical gap can also create strong SERS enhancement. Hence, we can harvest the plasmonic coupling effect and overcome the low SERS enhancement of single nanowires by assembling the nanowires into a multilayer structure to produce a highly active SERS platform.

The intensity for cross nanowires pair is slightly higher than that of parallel. This may be because the parallel AgNW pair is formed by interparticle attractive forces between particles while for the crossed AgNW, the two nanowires are

placed directly on top of each other. This causes the gap between the parallel AgNW to be wider than that of the cross AgNW, leading to the lower SERS intensity detected.

In order to conduct a systematic study on the SERS enhancement effect of the assembled 2D and 3D AgNW, closely packed monolayer, two layers, three layers, four layers and five layers of silver nanowires were assembled using Langmuir-Blodgett technique (LB). The monolayer of silver nanowires was assembled on silicon substrate using LB technique, a method that was previously reported by Tao *et al.*³³ The silicon substrate containing the monolayer silver nanowires was turned 90° and another layer of silver nanowires was assembled by vertically stacked on top of the existing monolayer of AgNW by using LB technique to fabricate two layers of silver nanowires. This process was repeated using the silicon substrate containing two, three and four layers of silver nanowires to get three, four and five layers of silver nanowires respectively. The assembled nanowires were characterised using SEM. Closely packed monolayer, two layers, three layers, four layers and five layers of silver nanowires were obtained as shown in Figure 2.4 (A – E) respectively.

Figure 2.4. (A - E) SEM image of 1 layer, 2 layers, 3 layers, 4 layers and 5 layers of silver nanowires respectively, scale bar = 1 μm . The inset is the zoom in SEM image, scale bar = 100nm. (F) AFM cross sectional height profiles of 1 layer, 2 layers, 3 layers, 4 layers and 5 layers of silver nanowires.

During the LB assembly, the nanowires could not be perfectly aligned due to the differences in nanowire length. This led to the formation of crevices and prevented the close packing of the AgNW as shown in Figure 2.4 (A). From these gaps, we can observe two layers and three layers of silver nanowires structures in the SEM image. However, it was difficult to observe the fourth and fifth layers as they were blocked by the closely packed layers above. Hence, AFM cross sectional height profile was done to characterize and determine the presence of the fourth and fifth layers as shown in Figure 2.4 (F).

A graph showing the AFM cross sectional height profiles of monolayer, two layers, three layers, four layers and five layers of silver nanowires is shown in Figure 2.4 (F). The measured AFM height profiles of monolayer, two layers, three

layers, four layers and five layers of silver nanowires were ~ 70 nm, ~ 155 nm, ~ 241 nm, ~ 320 nm and ~ 390 nm respectively. The linear increased in the height profile confirm the formation of the fourth and fifth layers of AgNW.

Figure 2.5. (A) UV-Vis spectra of the Ag nanowire in solution and (B) assembled monolayer Ag nanowire film (C) Dark field images of single Ag nanowire prepared by dropcasting of Ag nanowire solution and (D) assembled monolayer film of Ag nanowire, respectively.

Figure 2.5 (A) shows the UV-Vis spectra of the synthesized silver nanowire in ethanol solution. From Figure 2.5 (A), a weak shoulder peak at 350 nm and a main peak at 385 nm were observed. This result is in agreement with previous

literature work on AgNW with five-fold symmetry.²⁵ These peaks can be assigned to the transversal modes of the nanowires, corresponding to the out-of-plane quadrupole resonance at 350 nm and out-of-plane resonance at 385 nm.²⁵ After being assembled into closely pack monolayer on a quartz glass slide using LB technique, these modes are broaden and red-shift to 500 - 600 nm in the assembled monolayer film as shown in Figure 2.5 (B). The 500 - 600 nm extinction peak can be attributed to the excitation of longitudinal plasmon formed within the monolayer of closely packed AgNW.³³ we have included the dark field images of the single Ag nanowire (made from colloidal Ag nanowires directly drop casted on substrate).

Figure 2.6. (A - E) Confocal Raman mapping image in the x-y axis, (G - K) histograms of distribution of SERS intensity and (L) Plots of average SERS intensity and enhancement factor vs the number of Ag nanowire layers

The assembled monolayer, two layers, three layers, four layers and five layers of silver nanowires were ligand exchanged with 4-MBT. Raman area mapping in the x-y axis of $10 \times 10 \mu\text{m}^2$ and a total of 1600 measurement points were carried out and the average intensity of the peak at 1080 cm^{-1} is shown in Figure 2.6. The Raman mapping images corresponding to monolayer, two layers, three layers, four layers and five layers of AgNW is shown in Figure 2.6 (A - E) and the intensity of white pixel correlates with the intensity of 4-MBT Raman peak at 1075 cm^{-1} . The Raman image showed that the assembled nanowires were SERS active across the whole substrate.

The histogram in Figure 2.6 (G – K) shows the distribution of the Raman mapping intensities measured during the Raman mapping for monolayer, two layers, three layers, four layers and five layers of silver nanowires respectively. The Raman mapping intensities for each sample were in the same order of magnitude, indicating that the homogeneity of SERS enhancement effect in the assembled AgNW.

From Figure 2.6 (G), the histogram shows that more than 57 % of the 1600 measurement points of the monolayer Ag nanowire substrate have zero or undetectable SERS signal. Hence, despite having an average signal of ~ 20 counts as shown in Figure 2.6 (L), more than half of the monolayer AgNW array experiences either zero and/or an undetectable SERS signal. This might be due to the lack of perfect close packing of nanowires arising from the differences in AgNW length and the gaps formed within the AgNW monolayer array during the assembly process. This causes an increase in gap distance in certain parts of the

AgNW array and weakens the plasmonic coupling between AgNW, leading to a decrease in SERS intensity and undetectable SERS signal.

When the AgNW was assembled to form three layers, four layers and five layers 3D SERS substrate, zero intensity was no longer observed as shown in Figure 2.6 (H-K). As the number of layers increase, the Raman intensity increases and the spatial distribution of Raman signal becomes more homogeneous across the assembled AgNW substrate. This might be due to the increase in the number of hot spots produced when the AgNW layers were vertically stacked on top of each other.

From Figure 2.6 (L), it shows an average Raman count of ~20 Raman counts for monolayer, ~120 Raman counts for two layers, ~520 Raman counts for three layers, ~370 Raman counts for four layers, ~440 Raman counts for five layers. The intensity of Raman peaks increased significantly by 26 fold as the layers increased from monolayer to three layers of AgNW which then plateaued off as the numbers of layers of AgNW increased from three to five. The large increase in the SERS intensity as number of layers increased from monolayer to three layers was due to the increase in the number of hot spots produced when the layers were stacked on top of each other.

In the monolayer assembly of AgNW, plasmonic coupling occurs between the closely packed parallel nanowires creating hot spots between them. However, when the nanowires were assembled to form two layers, gaps were also formed between the two layers of nanowires in addition to the gaps existing between the parallel nanowires in each layer. This caused more hot spots to be formed and

explained the 6 fold increase in the SERS intensity as the number of layers increased from one to two layers of AgNW.

However, Figure 2.6 (L) showed that the SERS intensity reached saturation when the number of layers of AgNW increased beyond three layers. The saturation of the SERS intensity may be due to the inability of the laser to penetrate through the multiple layers of the closely packed AgNW to reach the bottom layers. Hence, even though more than three layers 4-MBT capped AgNW are present, we may be analysing only the 4-MBT molecules on the top three layers of AgNW. This is in agreement with a conclusion made by a previous SERS study on multilayer silver nanorod.²¹

For further investigation of the SERS performance of the assembled Ag nanowire layers, the enhancement factor (EF) is calculated according to the equation $EF = (I_{SERS} / N_{SERS}) / (I_{solution} / N_{solution})$, where I_{SERS} and N_{SERS} refer to the SERS intensity and the number of 4-MBT molecules excited by the laser when attached onto Ag nanowires.

Calculation of enhancement factor (EF)

$$EF = \frac{I_{SERS}}{I_{solution}} \times \frac{N_{solution}}{N_{SERS}}$$

$$I_{\text{surface}} = 20 \text{ counts}$$

(0.02 s acquisition time, for monolayer Ag nanowires, measured using 100
× objective lens)

$$I_{\text{solution}} = 0.066 \text{ counts}$$

(normalized using 33 counts measured at 10 s acquisition time, based on 1
M benzenethiol solution, 100 × objective lens)

Laser beam x- and y-axis resolution = 500 nm (100 × objective lens)

Laser beam z-axis resolution = 1.0 μm (100 × objective lens)

N_{solution} = number of molecules in solution within the measured laser spot

= V solution × Concentration of molecules × Avogadro's number

$$V_{\text{solution}} = \pi \times r^2 \times h$$

$$= 3.142 \times (500 \text{ nm}/2)^2 \times 1 \text{ μm}$$

$$= 1.96 \times 10^{-19} \text{ m}^3$$

$$\begin{aligned} N_{\text{solution}} &= 1.96 \times 10^{-19} \text{ m}^3 \times 1 \text{ M} (= 1000 \text{ mol/m}^3) \times 6.022 \times 10^{23} \\ &= 1.18 \times 10^8 \end{aligned}$$

N_{Surface} = number of molecules on the surface of Ag nanowire within the measured laser spot

Individual Ag nanowire length = 13 μm

Diameter of Ag nanowire = 77 nm

Laser beam x- and y-axis resolution = 500 nm (100 $\times$ objective lens)

$$\begin{aligned} \text{Surface area of laser spot} &= \pi \times r^2 \\ &= 3.142 \times (500 \text{ nm}/2)^2 \\ &= 1.96 \times 10^5 \text{ nm}^2 \end{aligned}$$

$$\begin{aligned} \text{Total surface area of a single nanowire} &= 2\pi rh \\ &= 2 \times 3.142 \times (77/2 \text{ nm}) \times 500 \text{ nm} \\ &= 1.2 \times 10^6 \text{ nm}^2 \end{aligned}$$

$$\begin{aligned} \text{Projected surface area of a single nanowire} &= 2rh \\ &= 3.85 \times 10^4 \text{ nm}^2 \end{aligned}$$

= 5 – for monolayer of Ag nanowire film

= 10 – for 2L Ag nanowire film

= 15 – for 3L Ag nanowire film

= 20 – for 4L Ag nanowire film

= 25 – for 5L Ag nanowire film

Surface area of a methylbenzenethiol molecule = $2.3 \times 2.3 \text{ \AA}^2/\text{molecule}$
= $0.0529 \text{ nm}^2/\text{molecule}$

$$N_{\text{Surface}} = \text{Total surface area of a single nanowire} \times \text{Total number of nanowires within measured}$$

$$\begin{aligned} & \text{laser spot / Surface area of a methylbenzethiol molecule} \\ &= 1.2 \times 10^6 \text{ nm}^2 \times 5 / 0.0529 \text{ nm}^2/\text{molecule} \\ &= 1.17 \times 10^7 \text{ molecules} \end{aligned}$$

$$\mathbf{F} = [20/1.17 \times 10^7]/[0.066/1.18 \times 10^8]$$

$$= 3.1 \times 10^3 \text{ (for monolayer of Ag nanowires)}$$

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nanowire layers demonstrate enhancement factors of 1.4×10^4 and 1.3×10^4 , respectively. Even though the increment in enhancement factor for 3L Ag nanowires may seem little, the homogeneity of the SERS signals is improved as compared to the 1L Ag nanowires. For 1L Ag nanowires, the SERS enhancement was originated from the parallel nanowire gaps. However, for multilayer Ag nanowires, two types of hot spots were created at each assembly cycle (i.e., the vertical gaps in between first and second layers of Ag nanowires and the parallel gaps between adjacent Ag nanowires during the second assembly). Hence, as Ag nanowires were assembled from 2D (monolayer) to 3D (≥ 2 layers) configuration, both vertical gaps and parallel gaps were generated, resulting in a drastic increase in the number of SERS hot spots and homogeneous SERS signal from the woodpile layers.

Figure 2.7. (A - C) AFM Raman z axis mapping image of monolayer, three layers and five layers of AgNW respectively. (D) Plot of z axis depth cross section vs Raman intensity.

In order to determine if the hot spots are distributed within the multilayer AgNW layers and verify the SERS active depth of the assembled AgNW, Raman mapping of the monolayer, three layers and five layers of AgNW were conducted. First, a Raman line scan is performed in the x -direction at a specific laser focal point in the z -plane, typically 10 μm above the top surface of a nanowire array. Then, the confocal laser is shifted in the z -direction by a piezo stage, where another line scan is performed. The process is repeated until a Raman map ($40 \times 20 \mu\text{m}$) in the x - z direction is obtained.

From the Raman mapping images in Figure 2.7 (A - C), distinctive white horizontal lines were observed for all samples which can indicate that the assembled AgNW shows strong SERS signals across the x-axis. The surrounding areas are dark which indicated no SERS signal.

The x-z SERS intensity was plotted against the depth cross section to facilitate a quantitative comparison of the measured SERS intensity among the monolayer, three layers and five layers of assembled AgNW as shown in Figure 2.7 (D). The results showed that the SERS active depth of monolayer was much lesser than of three layers and SERS active depth of three layers was similar to that of five layers. For monolayer of AgNW, the full width half maximum (FWHM) depth cross section length was $\sim 1\ \mu\text{m}$ and the maximum Raman intensity was ~ 100 counts. For three layers and five layers of AgNW, the FWHM depth cross section length are $\sim 1.5\ \mu\text{m}$ and the maximum Raman intensities were ~ 1508 counts and ~ 1246 counts respectively.

A higher FWHM depth cross section length is more desirable as it can provide a more accurate SERS measurement. This is because when the laser beam is slightly out of focus, a more accurate SERS measurement will be obtained if the laser is focused in the SERS active depth than if it is not focused in the SERS active depth. The z axis confocality of the Raman instrument is $\sim 1\ \mu\text{m}$ and the three layers and five layers of AgNW samples which had a higher FWHM depth cross section length can get a more accurate result than monolayer AgNW when the laser is out of focus.

The Raman intensity and FWHM depth cross section length were similar for three layers and five layers of AgNW. This result further confirms the possibility that illumination by the laser source is limited to the top three layers of AgNW (top ~241 nm of the assembled AgNW). Hence, the saturation of the SERS signal when the AgNW is assembled beyond three layers is attributed to the limited depth of penetration by the laser.

Figure 2.8. (A - E) AFM Raman studies mapping image of monolayer, two layers, three layers, four layers and five layers of AgNW respectively. (F) Polar plots of integral SERS intensity of monolayer, two layers, three layers, four layers and five layers of assembled Ag nanowire at various angles.

AFM Raman angle dependent experiment was performed to study the relationship between SERS intensity and the angle of the excitation source used. A linear polarized laser beam was used and the assembled AgNW samples were rotated at various angles to study the effect on the SERS intensity as shown in Figure 2.8. The results showed that the SERS intensities were angle independent for all monolayer, two layers, three layers, four layers and five layers of AgNW. However, this contradicts results of previous literature.^{26,32} A direct comparison between our results and that of literature is not valid due to the difference in AgNW morphology and packing density. The AgNW reported in the literature had a diameter of 45 nm and a length of 1.6 μm which was different from our work.

Figure 2.9. (A) and (B) Polar plots of SERS intensity measured at various angle of loosely packed monolayer of Ag nanowires compressed to the predefined target pressure of 6.5 mN m^{-1} and 10.5 mN m^{-1} respectively. (C) and (D) SEM image of a loosely packed monolayer of Ag nanowires. (E) and (F) Raman angle-dependent x-y mapping of 3L Ag nanowires at 0° , 30° , 45° , 60° , 90° , 120° , 135° , 150° , and 180° , respectively.

In order to verify the effect of packing density of the AgNW on SERS intensity at various angles, Raman angle dependent studies was performed with

less compact monolayer assembly of AgNW as shown in Figure 2.9. The less compact monolayer assembly of AgNW was fabricated by reducing the LB target pressure to 6.5 and 10.5 mN. The results showed that the SERS intensities were angle independent for the less compact monolayer assembled nanowires. This shows that the Raman signal intensity would not be affected by the variation of the sample's orientation, making it useful for industrial applications.

2.3 Conclusions

We have successfully prepared highly SERS active multi-layered woodpile-like silver nanowires using LB technique. Currently, to the best of our knowledge, the SERS effect of highly ordered multi-layer AgNW has not been investigated. This systematic study allows a better understanding of 3D SERS substrate. Current SERS studies of AgNW are limited to 1D (single nanowire) and 2D (monolayer) assemblies and there is a lack of understanding between the ordered 3D nanowires assembly and its impact on SERS. The understanding of this 3D effect is important for future designing of SERS substrates. The 3D nanowire substrate has higher SERS enhancement that was brought about by the increased in hot spots created by vertical stacking of the nanowires as compared to the 2D monolayer of AgNW. However, there is a limit to the enhancement effect brought about by the increased in number of layers of AgNW with a maximum enhancement effect observed in three layers of AgNW. Hence, a relatively thin SERS substrate is sufficient to fabricate a highly sensitive SERS platform. In addition, the SERS intensity obtained from assembled multi-layered silver nanowires substrate was angle

independent, indicating that it is SERS active regardless of sample orientation. It may be useful for sensing application in areas such as life science and environmental science.

Chapter 3 Fabrication of free standing silver nanowires film as a sensitive SERS substrate

3.1 Experimental Section

Materials. Poly(vinyl pyrrolidone) (PVP, average MW = 360,000), anhydrous ethylene glycol (EG, 99.8 %), 4-methylbenzenethiol (MBT), rhodamine 6G (R6G) and Durapore ® PVDF filter membranes of pore size 5 µm were purchased from Sigma Aldrich; NaCl (99.5 %) was purchased from Goodrich Chemical Enterprise; AgNO₃ (99+ %) was purchased from Alfa Aesar. All chemicals were used without further purification. Milli-Q water (> 18.0 MΩ.cm) was purified with a Sartoriusarum® 611 UV ultrapure water system.

Synthesis of AgNW. AgNW were synthesized based on a literature procedure.⁴⁷ In a typical synthesis, 7 mg of NaCl and 0.4995 mg of PVP were dissolved in 10 mL of EG and the mixture was heated at 160 °C. Using a syringe pump, 0.12 M AgNO₃ solution in 5 mL EG was added dropwise at a rate of 5 mL/h into the PVP mixture while stirring at 1000 rpm. After the addition of AgNO₃ the nanowire solution was further heated for 30 min at 160 °C and cooled to room temperature. The nanowire solution was washed several times using acetone and ethanol until the supernatant became colorless to ensure small colloidal particles were removed. The final product was dispersed in ethanol.

Preparation of free-standing AgNW (FS AgNW). Various volume of 1.85 mg/mL of AgNW in ethanol was filtered using a PVDF filter membrane with pores of 5 μm . The filtration was usually completed within 5 min. Subsequently, the AgNW were dried in nitrogen box and peeled off from the filter membrane using a pair of tweezers.

Raman spectroscopy. The assembled nanowires were placed in 1 mM 4-methylbenzenethiol (4-MBT) or 1 mM rhodamine 6G (R6G) in ethanol and stirred at room temperature for at least 12 h. These samples were rinsed with ethanol to remove the excess Raman probe to ensure that only a monolayer of Raman probe was detected. The samples were subsequently dried under N_2 gas. For the FS AgNW, Raman measurements were performed using a Horiba JY LabRAM HR Raman system with an excitation wavelength of 514.5 nm (Laser power = 0.44 mW). All Raman measurements were performed using a 100 $\times$ objective lens (NA = 0.9) and the acquisition time used was 2 s (unless stated otherwise).

Characterization. Scanning electron micrographs were obtained using JEOL-JEM-1400 electron microscope. Images were obtained with an operating voltage of 5 kV.

3.2 Results and discussion

Firstly, high aspect ratio AgNW was synthesized using a modified polyol process⁴⁷, the method reported in chapter 2. The AgNW was then assembled using

the vacuum filtration method. 25 mL of 1.85 mg/mL AgNW solution was filtered using a PVDF filter membrane with pores of 5 μm . After drying the AgNW in nitrogen box, the AgNW peeled off from the filter membrane using a pair of tweezers and the morphology and thickness was characterized using SEM.

Figure 3.1. Photo images of (A) front view and (B) side view of the FS AgNW that was peeled off from the filter membrane using a pair of tweezers.

As shown in Figure 3.1, the AgNW was able to be peeled off from the filter paper using tweezers and did not need any additional substrate for support. The diameter of each batch of prepared FS AgNW is 1.7 cm. The mass of the dried FS AgNW film prepared from 25 mL of AgNW was 0.0452 g and the thickness of was ~ 150 μm as shown by the cross section SEM image in Figure 3.2. From SEM

image, we observed that the AgNW were indeed randomly oriented and a network structure containing many overlapping AgNW was obtained.

Figure 3.2. SEM images of (A) front view and (B) cross-section of the FS AgNW.

The FS AgNW was cut into smaller pieces using a scalpel and placed in 8 ml of 1 mM 4- methylbenzenethiol (4-MBT) solution for ligand exchange to take place. As mentioned in chapter 2, non-resonant Raman probe molecules, 4-MBT, was chosen over other probe molecules that have non-specific adsorption because 4-MBT is known to form a self-assembled monolayer on the surfaces of Ag nanowires via a strong Ag-S coordination bond.⁴⁸ The formation of homogenous monolayer of probe molecules on SERS substrate is essential for reliable and quantitative comparison in the Raman analysis. These samples were rinsed with ethanol to remove any excess 4-MBT molecules and subsequently dried under N₂

gas. The setup of the SERS measurement of 4-MBT molecules that were present on the FS AgNW is illustrated in Figure 3.3 below.

Figure 3.3. Illustration of the setup of the SERS measurement of 4-MBT ligand exchanged Ag nanowire.

Ten Raman spectra were obtained at random points on the FS AgNW and the average spectrum is shown in Figure 3.4 below.

Figure 3.4. Average Raman spectra of the free standing AgNW after ligand exchange with 4-methylbenzenethiol. (4-MBT)

The average Raman spectra of 4-MBT is shown in Figure 3.4. The peak at 1077 cm^{-1} is due to a combination of the phenyl ring-breathing mode, CH in-plane bending, and CS stretching, while the peak at 1582 cm^{-1} can be assigned to the phenyl stretching motion.¹⁴ The intensity of 4-MBT peak at 1077 cm^{-1} was chosen for comparison of SERS intensity throughout this whole paper because the 1582 cm^{-1} peak overlaps with the Raman signals produced by the PVP capping agent which occur within the region of $1400 - 1600\text{ cm}^{-1}$. The average intensity of the peak at 1077 cm^{-1} for 10 random points measured was 3525 ± 816 counts.

A 50 nm thick Ag film was prepared on silicon wafer using thermal evaporation method to serve as a control for the Raman measurements. The Ag film was placed in 4-MBT solution for at least 12 h for the self-assembly of Raman probes to take place. Subsequently, it was taken out of the solution and rinsed with ethanol to remove the unbound 4-MBT molecules. Finally, it was dried under nitrogen gas. The Raman spectrum of the 4-MBT capped 50 nm thick Ag film was shown in Figure 3.5 below.

Figure 3.5. Raman spectrum of 4-MBT capped 50 nm thick Ag film.

As compared that of FS AgNW, the Raman peak intensity of 1077 cm^{-1} peak obtained from Ag film was significantly lower and was only ~ 100 counts. The

high SERS enhancement for the FS AgNW is attributed to the increase in the number of hot spots formed in the AgNW network. When two nanoparticles are in close proximity, it can give rise to highly intense and localized electromagnetic fields when excited by incident light, causing large SERS enhancement.⁷⁶ After filtration, the AgNW formed a randomly orientated network structure and allowed the formation many close gaps and junctions between two adjacent AgNW in the network. Hence, more SERS hot spots were formed and overall SERS sensitivity of the FS AgNW increased.

Next, we investigate the relationship between the thickness of FS AgNW and the SERS enhancement effect. The thickness of the FS AgNW can be tuned by varying the amount of AgNW filtered. Instead of using 25 mL, 45 mL of AgNW was filtered and the thickness was characterized using SEM (Figure 3.6).

Figure 3.6. SEM image of (A) front view and (B) cross section image of the thicker FS AgNW.

The mass of the dried FS AgNW was 0.0802 g and the cross sectional thickness was $\sim 265 \mu\text{m}$. The sample was ligand exchanged with 4-MBT and the average Raman spectrum of 10 points measured is shown in Figure 3.7 below.

Figure 3.7. Average Raman spectrum of 150 μm and 265 μm thick FS AgNW film.

Initially, we expected the average Raman intensity to increase with the increasing thickness of FS AgNW due to the greater number of hot spots present in the AgNW and greater number of 4-MBT molecules present. However, the average Raman intensity of the 1077 cm^{-1} peak for the 265 μm thick FS AgNW film was 2430 ± 498 counts. Despite the increased thickness of FS AgNW film

from 150 μm to 265 μm , the Raman intensity did not increase. This experiment was repeated and the average intensity of the 1077 cm^{-1} peak was 3634 ± 1105 counts. This shows that the thickness of the free standing Ag nanowire does not have an effect on the measured SERS intensity.

In order to gain a better understanding of the relationship between the thickness of the assembled Ag nanowire and their SERS enhancement effect, we refer to chapter 2 Figure 2.5 and Figure 2.6, which shows a saturation of the SERS intensity as the thickness of assembled AgNW increase beyond 3 layers. This may be due to the inability of the laser beam to penetrate the multiple layers of closely packed AgNW and hence failure to reach the bottom layers. Hence, with greater than three layers of 4-MBT capped Ag nanowires present, the SERS intensity did not increase as the analysis may be limited only to the 4-MBT molecules presenting on the top three layers of AgNW.

Even though direct comparison of results cannot be made due to the different packing densities of between LB assembled Ag nanowires and FS AgNW, we can conclude SERS intensity will reach saturation when the substrate is beyond a certain thickness. This explains the similarity of the SERS intensity observed for the FS AgNW prepared using 25 mL and 45 mL of AgNW. The FS AgNW prepared was too thick (more than 150 μm) and only the 4-MBT on the surface of the FS AgNW could be analyzed.

Hence, we tried to reduce the thickness of the FS AgNW by reducing the volume of AgNW filtered. Instead of using 20 ml of AgNW as reported previously,

500 μl , 1 mL, 1.5 mL, 2 mL, 2.5 mL, 3 mL, 3.5 mL, 4 mL and 4.5 mL of AgNW were filtered. However, the FS AgNW formed were too thin to be peeled off from the filter paper. A minimum of 5 ml of filtered AgNW was required to produce FS AgNW that could be completely peeled off from the filter paper. The mass of the dried filtered FS AgNW is 0.0092 g and the thickness is 29 μm as shown in Figure 3.8.

Figure 3.8. SEM image of (A) front view and (B) cross section image of the FS AgNW prepared from 5 mL of AgNW. The inset is the zoom in cross section SEM image.

The FS AgNW was cut into smaller pieces using a scalpel and was placed in 1 mM 4-MBT and 1 mM of rhodamine 6G (R6G) solutions for at least 12 h. These samples were then rinsed with ethanol and subsequently dried under N_2 gas. Unlike 4-MBT molecule which has a thiol functional group and has strong affinity

to silver⁷⁷, R6G molecule has weak affinity to the silver. The purpose of using R6G as Raman probe is to study the SERS enhancement effect of species that have weak interactions with silver. Raman spectra were obtained for each sample and the average results are shown below in Figure 3.9 and 3.10.

Figure 3.9. Raman spectra of 4-MBT ligand exchanged FS AgNW, 2 s acquisition time.

The average intensity of the Raman peak at 1077 cm^{-1} for the $29\text{ }\mu\text{m}$ thick FS AgNW film was 7582 ± 1627 counts which was higher than that obtained by the thicker FS AgNW. Despite a decrease in the thickness of FS AgNW, the intensity of Raman peak at 1077 cm^{-1} did not decrease. This suggests that the

samples produced were not very homogenous with some areas having more AgNW junctions and hot spots than others. Hence, in future, a larger mapping area and more Raman acquisition points are needed to obtain more reliable statistics.

Figure 3.10. Raman spectra of R6G molecules absorbed on the FS AgNW, 1 s acquisition time.

When 2 s acquisition time was used, the peak intensities of R6G molecule were too high and exceeded the detection limit of the Raman machine. Hence, the acquisition time was decreased to 1 s to obtain the Raman mapping spectra. From

Figure 13, distinct peaks at can be observed at 610 cm^{-1} , 768 cm^{-1} , 1360 cm^{-1} , 1572 cm^{-1} and 1650 cm^{-1} . The peak at 610 cm^{-1} can be assigned to C-C-C ring in-plane bending, peak at 768 cm^{-1} to the out-of-plane bending motion of H atoms on the xanthene skeleton, and peaks at 1360 cm^{-1} , 1570 cm^{-1} and 1647 cm^{-1} to aromatic C-C stretching.⁷⁸ Unlike 4-MBT, R6G has weak affinity with PVP capped Ag nanowire. Yet, strong SERS intensity was still detected after washing the FS AgNW sample with ethanol indicating the high SERS enhancement effect of the FS AgNW. The strong intensity of R6G Raman peak intensity is due to the Raman laser excitation wavelength (514.5nm) which coincides with the electronic excitation energy of R6G. This causes the vibrational modes involved in the electronic transition (the aromatic C-C stretching) to be enhanced by a factor of up to 10^6 in comparison to non-resonant Raman probe such as 4-MBT.⁷⁹

3.3 Conclusions

We have successfully demonstrated highly SERS active FS AgNW prepared using vacuum filtration technique. The high SERS enhancement is due to the increase in SERS hot spots formed at the junctions of the overlapping Ag nanowires within the free standing networks. The lack of correlation between thickness of the prepared free standing Ag nanowires and the SERS intensity measured might be due to the excessive thickness of FS AgNW. The thinnest FS SERS substrate ($29\text{ }\mu\text{m}$) is sufficient to show high SERS enhancement. To the best of our knowledge, the SERS effect of free standing Ag nanowire has not been

investigated. Our study shows that FS AgNW is highly SERS active and can be used as potential SERS sensing platforms for life science and environmental science application.

Chapter 4 Fabrication of anatase TiO₂ nanowire and investigation of their photocatalytic activities

4.1 Experimental procedures

Materials. Titanium (IV) oxide (Aeroxide P25) was purchased from Acros Organics. Sodium hydroxide was purchased from Sinopharm Chemical Reagent Co Ltd. Hydrochloric acid (37%) was purchased from Schedelco Pte Ltd. Methyl orange was purchased from VWR. All chemicals were used without further purification. Milli-Q water (> 18.0 MΩ.cm) was purified with a Sartorius arium® 611 UV ultrapure water system.

Synthesis of nanowires. The nanowires were synthesized based on a modified literature method.⁷¹ In a clean Teflon liner, 0.5 g of P25 TiO₂ and 20 mL of 10 M NaOH were stirred for 10min. Then, the Teflon liner was sealed in a hydrothermal autoclave, heated at 200 °C for 20 h (ramping rate 10 °C/min) and air cooled to room temperature. The samples were washed with HCl (0.1 M) till approximately pH 6, followed by a subsequent single wash with ultrapure water. After drying at 60 °C in air, the products were calcinated at 700 °C for 2 h with ramping rate of 5 °C/h.

Photocatalytic activity studies. The photocatalytic activities of the prepared samples were evaluated by degradation of methyl orange (MO) in water. In a

typical reaction, approximately 0.2 mg of TiO₂ nanoparticles was suspended with sonication in 2 ml of 7.5 mg/l of MO solution in a quartz cuvette. The mixture was stirred for 30 minutes in the dark to ensure that the adsorption/desorption equilibrium of MO was reached. UV irradiation was provided by a 300 W Xenon lamp (Newport) with UV filter, transmitting wavelengths of < 420 nm and intensity of 1.5 Wcm⁻². After irradiation for a fixed period of time, the relative concentration of MO was determined by the UV-vis absorption peak intensity at 462 nm from the UV-vis spectra.

Characterization. The crystal structure of the synthesized TiO₂ nanowire was characterized by Raman spectroscopy. Raman measurements were performed using a Horiba JY LabRAM HR Raman system with an excitation wavelength of 514.5 nm (Laser power = 0.44 mW). All Raman measurements were performed using a 100 × objective lens (NA = 0.9) and an acquisition time of 2 s was used (unless stated otherwise). Scanning electron micrographs were obtained using JEOL-JEM-1400 electron microscope. Images were obtained with an operating voltage of 5 kV. Transmission electron microscope images were obtained using a JEM-1400 Transmission Electron Microscopy (JEOL) operated at 100 kV. UV – vis spectra were recorded using a Cary 60 UV – vis spectrophotometer.

4.2 Results and discussion

Figure 4.1. SEM image of the commercial TiO₂ P25 nanoparticles.

The high aspect ratio titanate nanowires were synthesized using a modified hydrothermal method reported by literature.⁷¹ In summary, commercial P25 TiO₂ nanoparticles and NaOH were mixed in a Teflon - line autoclave and heated at 200 °C for 20 h (ramping rate 10 °C/min) in an oven to produce the nanowires. From the SEM image in Figure 4.1, the size of the starting material (commercial TiO₂ P25 nanoparticles) was 25-30 nm. After hydrothermal treatment and washing

with acid till pH 6 was obtained, the products were transformed into titanate nanowire as shown in Figure 4.2.

Figure 4.2. SEM image of the uncalcinated titanate nanowire; (A) low magnification, (B) high magnification. TEM image of the uncalcinated titanate nanowire before annealing; (C) low magnification, (D) high magnification.

The nanowires synthesised were typically longer than 5 μm and their diameter ranged from 20 to 60 nm which was consistent with that reported in literature.^{38,80} However, the nanowires had the tendency to form bundles thus appearing thicker than actual in the SEM images. From the TEM images in Figure 4.2, we can confirm that the products were solid nanowires and not hollow nanotubes. From literature, formation of nanotubes will occur at lower heating temperatures in the hydrothermal process (around 90 -160 $^{\circ}\text{C}$) while formation of nanowires will occur higher temperatures (above 180 $^{\circ}\text{C}$).⁷⁰

After acid washing of the synthesized nanowires, we followed a literature method to calcinate the nanowires at 700 $^{\circ}\text{C}$ to convert them to anatase phase thus improving their photoactivity.⁷¹ The end product was characterized using SEM and Raman as shown in Figure 4.3 and Figure 4.4 below.

Figure 4.3. SEM image of the titanate nanowire calcinated at 700 $^{\circ}\text{C}$.

Figure 4.4. Raman spectra of titanate nanowire calcinated at 700 °C and commercial anatase TiO₂ powder, 2 s acquisition time.

Figure 4.3 shows that the titanate nanowire structure remained intact after calcinating at 700 °C. However, from Figure 4.4, the Raman spectrum of the calcinated nanowire is not identical to that of anatase. For anatase TiO₂ nanoparticles, the Raman spectra has a very intense and sharp peak at 144 cm⁻¹ and several weaker peaks at 409, 515 and 633 cm⁻¹ which can be assigned as the E_g, B_{1g}, A_{1g} or B_{1g}, and E_g modes of the anatase phase, respectively.⁸¹ In contrast, the Raman spectra of the calcinated nanowire closely resembled that of Na₂Ti₆O₁₃ reported in literature.⁸² Hence, instead of transforming into anatase nanowire after

calcinating at 700 °C as reported in literature,⁷¹ we have transformed it into Na₂Ti₆O₁₃ nanowires instead. This might be due to the fact that acid washing of the initial uncalcinated sodium titanate nanowires till pH 6 was insufficient to completely replace the sodium ions with hydrogen ions in the sodium titanate nanowires. Therefore, we had calcinated sodium titanate nanowires instead of hydrogen titanate nanowires, leading to the formation of Na₂Ti₆O₁₃ instead of anatase nanowire. This is in agreement with literature which showed that calcination of sodium titanate nanowire could result in the formation of Na₂Ti₆O₁₃ nanowires.^{70,72}

Hence, in order to fabricate anatase nanowire, we washed the initial sodium titanate nanowire with additional 5 rounds of HCl and ultrapure water to ensure complete ions exchange of sodium ions with hydrogen ions had taken place. The end product was dried at 60 °C in air and calcinated at 700 °C.

Figure 4.5. SEM image of the TiO₂ anatase nanowire calcinated at 700 °C.

Figure 4.6. Raman spectra of TiO₂ anatase nanowires after annealing at 700 °C and commercial anatase TiO₂ powder, 2 s acquisition time.

From Figure 4.5, it indicates that the nanowire structure is preserved at 700 °C, although some fragmentation had occurred. As compared to sodium titanate nanowires, the hydrogen titanate nanowire is less stable towards heating due to the weaker bonding strength between H⁺ ions and the Ti₃O₇ layers as compared to Na⁺ ions.^{72,83} From the Raman spectrum in Figure 4.6, we can confirm that after calcination at 700 °C, hydrogen titanate nanowire was converted to anatase nanowires. The photocatalytic activities of the various titanate

nanostructures were evaluated by studying the photocatalytic degradation of methyl orange (MO) under UV light.

Figure 4.6. UV vis spectra of blank methyl orange solution before and after 1 h of UV irradiation without the presence of any titanate sample.

Figure 4.7. Photocatalytic activity of the prepared nanowires samples and commercial p 25 nanoparticles under UV irradiation.

First, a control experiment was carried out by irradiating UV light onto blank methyl orange solution that did not contain any titanate nanowires. Methyl orange is an azo dye with strong light absorption at 462 nm.⁵⁰ From Figure 4.6, in the absence of catalyst, the photodegradation of methyl orange was very slow, with only 0.28 % of methyl orange removed after 1 hour of UV irradiation. Hence, this eliminates the possibility that the discoloration of methyl orange was caused by photolysis of methyl orange under UV light.

In the presence titanate sample, UV irradiation can lead to damage of methyl orange's conjugation system which consists of the azo groups and aryl

groups. This leads to discoloration of methyl orange and a decrease in the 462 nm absorption peak intensity. Hence, photocatalytic activity of the different titanate samples can be studied by comparing the change in concentration of methyl orange caused by the prepared nanowires samples and commercial p25 nanoparticles under UV irradiation.

From Figure 4.7, after 45 min of UV irradiation, 100 % of methyl orange was removed by commercial p25 nanoparticles after 15 min while 100 %, 81 %, 21.4 % and 8.3 % of methyl orange were removed by annealed sodium titanate (Na₂Ti₆O₁₃) nanowires, anatase nanowire, sodium titanate nanowires without annealing and hydrogen titanate (H₂Ti₃O₇) nanowires respectively after 45 min of UV irradiation. Even though the degradation rate is not significant for the non-annealed samples (21.4 % and 8.3 % for the synthesized sodium titanate nanowires and hydrogen titanate (H₂Ti₃O₇) nanowires respectively), they still exerted some catalytic activity. The non-acid washed sodium titanate nanowires had slightly higher photocatalytic rate than acid washed H₂Ti₃O₇ nanowires. This might be due to the presence of intercalated sodium ions which were able to facilitate the charge separation between electrons and holes, leading to higher photocatalytic rates.⁸⁴

Calcinating both titanate nanowires increased the photocatalytic activity as observed from the results of the Na₂Ti₆O₁₃ and anatase nanowire. Calcination can improve the crystallinity and decrease the bulk defects.⁷² These can facilitate the internal charge carrier transfer and decrease charge recombination, resulting in higher photocatalytic rates.⁸⁴ In this study, among all the synthesized nanowires,

anatase nanowire had the highest photocatalytic rate. This may be due to the fact that anatase phase has more oxygen vacancy sites which contributes to the photocatalytic oxidation process.⁸⁵ Although the photocatalytic rates of the nanowires were slower than that of commercial p25 nanoparticle under UV irradiation, the nanowires can be easily separated from the solution than the p25 nanoparticles, allowing the nanowires to be more useful in practical application.⁸⁶

4.3 Conclusions

In summary, TiO₂ anatase nanowires have been successfully synthesized via hydrothermal method. In this study, it shows that acid washing plays an important role in determining the final crystal structure of the synthesized nanowires. Incomplete ion exchanged of sodium ions with hydrogen ions during the acid washing process will lead to the formation of Na₂Ti₆O₁₃ nanowire instead of anatase nanowire after calcination. Calcination of the nanowire will increase their photocatalytic rate and the anatase nanowire has the highest photocatalytic rate among all the synthesized nanowires.

Conclusions

We have successfully fabricated highly SERS active 3D multi-layered wood pile like AgNW using LB technique. The 3D multilayer nanowire substrate has higher SERS enhancement that is brought about by the increased in hot spots created by vertical stacking of the nanowires layers as compared to the 2D monolayer of AgNW. However, the increased in SERS enhancement reached a saturation when more than three layers of AgNW were used. Hence, a relatively thin SERS substrate is sufficient to fabricate a highly sensitive SERS platform. In addition, the SERS intensity obtained from assembled multi-layered silver AgNW substrate was angle independent, indicating that it is SERS active regardless of sample orientation.

Highly SERS active free standing silver nanowires film has been prepared using vacuum filtration technique. The high SERS enhancement effect is due to the increase in SERS hot spots formed at the junctions of the overlapping AgNW within the free standing networks. The lack of correlation between thickness of the prepared free FS AgNW and the SERS intensity measured might have been due to the excessive thickness of the FS AgNW film. The thinnest FS SERS substrate (29 μm) was sufficient to show high SERS enhancement. To the best of our knowledge, the SERS effect of FS AgNW has not been yet investigated. Our study

shows that FS AgNW film is highly SERS active and can be used as potential SERS sensing platforms for life science and environmental science application.

TiO₂ anatase nanowires have been successfully synthesized via hydrothermal method. Acid washing of the synthesized sodium titanate nanowires plays an important role in determining the final crystal structure of the synthesized nanowires. Incomplete ion exchanged of sodium ions with hydrogen ions during the acid washing process will lead to the formation of Na₂Ti₆O₁₃ nanowire instead of anatase nanowire after calcination. Calcination of the nanowire will increase their photocatalytic rate and the anatase nanowire has the highest photocatalytic rate among all the synthesized nanowires.

References

- (1) Raman, C.; Krishnan, K. *Nature* **1928**, *121*, 501.
- (2) Le Ru, E.; Etchegoin, P. *Principles of Surface-Enhanced Raman Spectroscopy: and related plasmonic effects*; Elsevier Science, 2008.
- (3) Kneipp, K. *Physics Today* **2007**, *60*, 40.
- (4) Fleischm.M; Hendra, P. J.; McQuilla.Aj *Chem. Phys. Lett.* **1974**, *26*, 163.
- (5) Jeanmaire, D. L.; Van Duyne, R. P. *J. Electroanal. Chem* **1977**, *84*, 1.
- (6) Albrecht, M. G.; Creighton, J. A. *Journal of the American Chemical Society* **1977**, *99*, 5215.
- (7) Mulvihill, M.; Tao, A.; Benjauthrit, K.; Arnold, J.; Yang, P. *Angewandte Chemie* **2008**, *120*, 6556.
- (8) Kim, A.; Barcelo, S. J.; Williams, R. S.; Li, Z. *Analytical Chemistry* **2012**.
- (9) Zhang, X.; Young, M. A.; Lyandres, O.; Van Duyne, R. P. *Journal of the American Chemical Society* **2005**, *127*, 4484.
- (10) Kaya, M.; Volkan, M. *Analytical Chemistry* **2012**, *84*, 7729.
- (11) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Physical Review Letters* **1997**, *78*, 1667.
- (12) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102.

-
- (13) Rycenga, M.; Camargo, P. H. C.; Li, W.; Moran, C. H.; Xia, Y. *The Journal of Physical Chemistry Letters* **2010**, *1*, 696.
- (14) Li, W.; Camargo, P. H. C.; Lu, X.; Xia, Y. *Nano Letters* **2008**, *9*, 485.
- (15) Lee, J.-H.; Nam, J.-M.; Jeon, K.-S.; Lim, D.-K.; Kim, H.; Kwon, S.; Lee, H.; Suh, Y. D. *ACS Nano* **2012**.
- (16) Wang, H.; Levin, C. S.; Halas, N. J. *Journal of the American Chemical Society* **2005**, *127*, 14992.
- (17) Hu, X.; Cheng, W.; Wang, T.; Wang, Y.; Wang, E.; Dong, S. *The Journal of Physical Chemistry B* **2005**, *109*, 19385.
- (18) Baia, M.; Toderas, F.; Baia, L.; Maniu, D.; Astilean, S. *ChemPhysChem* **2009**, *10*, 1106.
- (19) Addison, C. J.; Brolo, A. G. *Langmuir* **2006**, *22*, 8696.
- (20) Olson, L. G.; Lo, Y.-S.; Beebe, J. M. *Analytical Chemistry* **2001**, *73*, 4268.
- (21) Zhou, Q.; He, Y.; Abell, J.; Zhang, Z.; Zhao, Y. *Chemical Communications* **2011**, *47*, 4466.
- (22) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Letters* **2002**, *2*, 165.
- (23) Sun, Y.; Mayers, B.; Herricks, T.; Xia, Y. *Nano Letters* **2003**, *3*, 955.
- (24) Sun, Y.; Xia, Y. *Advanced Materials* **2002**, *14*, 833.
- (25) Sun, Y.; Yin, Y.; Mayers, B. T.; Herricks, T.; Xia, Y. *Chemistry of Materials* **2002**, *14*, 4736.

-
- (26) Wei, H.; Hao, F.; Huang, Y.; Wang, W.; Nordlander, P.; Xu, H. *Nano Letters* **2008**, 8, 2497.
- (27) Goh, M. S.; Lee, Y. H.; Pedireddy, S.; Phang, I. Y.; Tjiu, W. W.; Tan, J. M. R.; Ling, X. Y. *Langmuir* **2012**, 28, 14441.
- (28) Gunawidjaja, R.; Peleshanko, S.; Ko, H.; Tsukruk, V. V. *Advanced Materials* **2008**, 20, 1544.
- (29) Kang, T.; Yoon, I.; Jeon, K. S.; Choi, W.; Lee, Y.; Seo, K.; Yoo, Y.; Park, Q. H.; Ihee, H.; Suh, Y. D. *The Journal of Physical Chemistry C* **2009**, 113, 7492.
- (30) Du, C.; You, Y.; Chen, T.; Zhu, Y.; Hu, H.; Shi, D.; Chen, H.; Shen, Z. *Plasmonics* **2011**, 6, 761.
- (31) Lee, S. J.; Morrill, A. R.; Moskovits, M. *Journal of the American Chemical Society* **2006**, 128, 2200.
- (32) Jeong, D. H.; Zhang, Y. X.; Moskovits, M. *The Journal of Physical Chemistry B* **2004**, 108, 12724.
- (33) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano Letters* **2003**, 3, 1229.
- (34) Tao, A. R.; Yang, P. *The Journal of Physical Chemistry B* **2005**, 109, 15687.
- (35) Peng, X.; Jin, J.; Ericsson, E. M.; Ichinose, I. *Journal of the American Chemical Society* **2007**, 129, 8625.
- (36) Nogi, M.; Iwamoto, S.; Nakagaito, A. N.; Yano, H. *Advanced Materials* **2009**, 21, 1595.
- (37) Peng, X.; Luo, Y.-H.; Jin, J.; Huang, J.; Ichinose, I.; Kurashima, K.; Papadimitrakopoulos, F. *Chemical Communications* **2006**, 4688.

-
- (38) Zhang, X.; Du, A. J.; Lee, P.; Sun, D. D.; Leckie, J. O. *Journal of Membrane Science* **2008**, *313*, 44.
- (39) Decher, G. *Science* **1997**, *277*, 1232.
- (40) Goulet, P. J. G.; dos Santos, D. S.; Alvarez-Puebla, R. A.; Oliveira, O. N.; Aroca, R. F. *Langmuir* **2005**, *21*, 5576.
- (41) He, D.; Hu, B.; Yao, Q.-F.; Wang, K.; Yu, S.-H. *ACS Nano* **2009**, *3*, 3993.
- (42) Zhang, C.-L.; Lv, K.-P.; Cong, H.-P.; Yu, S.-H. *Small* **2012**, *8*, 648.
- (43) Wang, Y.; Du, G.; Liu, H.; Liu, D.; Qin, S.; Wang, N.; Hu, C.; Tao, X.; Jiao, J.; Wang, J.; Wang, Z. L. *Advanced Functional Materials* **2008**, *18*, 1131.
- (44) De, S.; Higgins, T. M.; Lyons, P. E.; Doherty, E. M.; Nirmalraj, P. N.; Blau, W. J.; Boland, J. J.; Coleman, J. N. *ACS Nano* **2009**, *3*, 1767.
- (45) Endo, M.; Muramatsu, H.; Hayashi, T.; Kim, Y.; Terrones, M.; Dresselhaus, M. *Nature* **2005**, *433*, 476.
- (46) Gu, G.; Schmid, M.; Chiu, P.-W.; Minett, A.; Fraysse, J.; Kim, G.-T.; Roth, S.; Kozlov, M.; Munoz, E.; Baughman, R. H. *Nat Mater* **2003**, *2*, 316.
- (47) Coskun, S.; Aksoy, B.; Unalan, H. E. *Crystal Growth & Design* **2011**.
- (48) Yoneyama, H.; Yamashita, Y.; Tamura, H. *Nature* **1979**, *282*, 817.
- (49) Kabra, K.; Chaudhary, R.; Sawhney, R. L. *Industrial & Engineering Chemistry Research* **2004**, *43*, 7683.

-
- (50) Guo, C.; Xu, J.; He, Y.; Zhang, Y.; Wang, Y. *Applied Surface Science* **2011**, 257, 3798.
- (51) Zhang, C.-L.; Lv, K.-P.; Hu, N.-Y.; Yu, L.; Ren, X.-F.; Liu, S.-L.; Yu, S.-H. *Small* **2012**, 8, 2936.
- (52) Xu, T.; Cai, Y.; O'Shea, K. E. *Environ. Sci. Technol.* **2007**, 41, 5471.
- (53) Khan, U.; Benabderrazik, N.; Bourdelais, A. J.; Baden, D. G.; Rein, K.; Gardinali, P. R.; Arroyo, L.; O'Shea, K. E. *Toxicon* **2010**, 55, 1008.
- (54) Herrmann, J. M. *Catalysis Today* **1999**, 53, 115.
- (55) Blake, D. M. *Bibliography of work on the heterogeneous photocatalytic removal of hazardous compounds from water and air*; National Renewable Energy Laboratory, 1994; Vol. 1617.
- (56) Kim, B.; Podsiadlik, D.; Kalis, E.; Hartlund, J.; Gaines, W. *Journal of Environmental Engineering* **1998**, 124, 1108.
- (57) Matthews, R. W. *Water Research* **1990**, 24, 653.
- (58) Zan, L.; Fa, W.; Peng, T.; Gong, Z.-k. *Journal of Photochemistry and Photobiology B: Biology* **2007**, 86, 165.
- (59) McCullagh, C.; Robertson, J. M.; Bahnemann, D. W.; Robertson, P. K. *Research on Chemical Intermediates* **2007**, 33, 359.
- (60) Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. *Water Research* **2010**, 44, 2997.
- (61) Chen, X.; Mao, S. S. *Chemical Reviews* **2007**, 107, 2891.
- (62) Linsebigler, A. L.; Lu, G.; Yates, J. T. *Chemical Reviews* **1995**, 95, 735.

-
- (63) Armstrong, A. R.; Armstrong, G.; Canales, J.; Bruce, P. G. *Angewandte Chemie International Edition* **2004**, *43*, 2286.
- (64) Zhang, Y. X.; Li, G. H.; Jin, Y. X.; Zhang, Y.; Zhang, J.; Zhang, L. D. *Chem. Phys. Lett.* **2002**, *365*, 300.
- (65) Yuan, Z.-Y.; Su, B.-L. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2004**, *241*, 173.
- (66) Poudel, B.; Wang, W.; Dames, C.; Huang, J.; Kunwar, S.; Wang, D.; Banerjee, D.; Chen, G.; Ren, Z. *Nanotechnology* **2005**, *16*, 1935.
- (67) Wu, D.; Liu, J.; Zhao, X.; Li, A.; Chen, Y.; Ming, N. *Chemistry of Materials* **2005**, *18*, 547.
- (68) Wei, M.; Qi, Z.-m.; Ichihara, M.; Honma, I.; Zhou, H. *Chem. Phys. Lett.* **2006**, *424*, 316.
- (69) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. *Chemical Reviews* **1995**, *95*, 69.
- (70) Doong, R.-a.; Kao, I.-l. *Recent patents on nanotechnology* **2008**, *2*, 84.
- (71) Kiatkittipong, K.; Scott, J.; Amal, R. *ACS Applied Materials & Interfaces* **2011**, *3*, 3988.
- (72) Kiatkittipong, K.; Iwase, A.; Scott, J.; Amal, R. *Chemical Engineering Science* **2013**, *93*, 341.
- (73) Jitputti, J.; Suzuki, Y.; Yoshikawa, S. *Catalysis Communications* **2008**, *9*, 1265.
- (74) Lu, H.; Zhang, H.; Yu, X.; Zeng, S.; Yong, K.-T.; Ho, H.-P. *Plasmonics* **2012**, *7*, 167.

- (75) Rycenga, M.; Kim, M. H.; Camargo, P. H. C.; Cobley, C.; Li, Z.-Y.; Xia, Y. *The Journal of Physical Chemistry A* **2009**, *113*, 3932.
- (76) Halas, N. J.; Lal, S.; Chang, W.-S.; Link, S.; Nordlander, P. *Chemical Reviews* **2011**, *111*, 3913.
- (77) Camargo, P. H.; Rycenga, M.; Au, L.; Xia, Y. *Angewandte Chemie International Edition* **2009**, *48*, 2180.
- (78) Liu, J.-W.; Wang, J.-L.; Huang, W.-R.; Yu, L.; Ren, X.-F.; Wen, W.-C.; Yu, S.-H. *Scientific reports* **2012**, *2*.
- (79) Gao, Y.; Jiang, P.; Song, L.; Liu, L.; Yan, X.; Zhou, Z.; Liu, D.; Wang, J.; Yuan, H.; Zhang, Z. *Journal of Physics D: Applied Physics* **2005**, *38*, 1061.
- (80) Dong, W.; Cogbill, A.; Zhang, T.; Ghosh, S.; Tian, Z. R. *The Journal of Physical Chemistry B* **2006**, *110*, 16819.
- (81) Zhang, W. F.; He, Y. L.; Zhang, M. S.; Yin, Z.; Chen, Q. *Journal of Physics D: Applied Physics* **2000**, *33*, 912.
- (82) Bamberger, C. E.; Begun, G. M. *Journal of the American Ceramic Society* **1987**, *70*, C.
- (83) Mori, M.; Kumagai, Y.; Matsunaga, K.; Tanaka, I. *Physical Review B* **2009**, *79*, 144117.
- (84) Amano, F.; Yasumoto, T.; Shibayama, T.; Uchida, S.; Ohtani, B. *Applied Catalysis B: Environmental* **2009**, *89*, 583.
- (85) Ding, Z.; Lu, G. Q.; Greenfield, P. F. *The Journal of Physical Chemistry B* **2000**, *104*, 4815.
- (86) Yu, Y.; Xu, D. *Applied Catalysis B: Environmental* **2007**, *73*, 166.