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COMMUNICATION

Triangular AgAu@Pt Core-shell Nanoframes with Dendritic Pt Shell and Enhanced Electrocatalytic Performance toward Methanol Oxidation Reaction

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Triangular AgAu@Pt nanoframes with dendritic Pt shell were synthesized by employing Ag nanoprisms as sacrificial templates. Due to the unique frame-like nanostructure and ternary components, the AgAu@Pt nanoframes exhibit impressive electrocatalytic performance toward the methanol oxidation reaction with much higher activity, and better anti-poisoning capability than commercial Pt/C catalyst.

Platinum (Pt) nanocrystals have been considered as the most efficient electrocatalysts for sustainable energy conversion devices, such as direct methanol fuel cell devices (DMFCs), in the foreseeable future.^{1–6} Unfortunately, the scarce reserves, high cost and poor stability of Pt nanoparticles that are vulnerable to CO poisoning severely impede the large-scale commercialization and widespread applications of the fuel cells.^{7, 8} Therefore, it is highly urgent to develop more effective electrocatalysts having relatively lower Pt content with retained high activity and enhanced poisoning resistance. To address these issues, one of the most powerful strategies is constructing core-shell bimetallic or trimetallic nanostructures by depositing ultrafine Pt nanoparticles onto other nano-architectures composed by less expensive metals. In the resultant core-shell nanostructure, the non-Pt core can not only maximize the Pt utilization efficiency, but also endow enhanced electrocatalytic activity and durability because the core metals may have strong interactions with the shell Pt atoms by altering the electronic structure, local coordination environment and lattice strain.^{9–13} In particular, trimetallic ternary systems may afford an even superior catalytic activity and selectivity as compared with the monometallic or bimetallic counterparts through delicate optimization of the constituents.^{14–17}

Moreover, nanostructure engineering enables elaborate development to enhance the electrocatalytic performance. Among various shapes, nanoframes are of particular interest for catalysis due to their unique structural features, including highly open structure, large ratio of surface area to volume, and three-dimensionally (3D) accessible surface.^{18–21} Additionally, the corner and edge atoms in nanoframes are usually coordinatively unsaturated and would serve as the catalytically active sites.²² Therefore, Pt-based trimetallic nanoframes are undoubtedly anticipated as a highly efficient electrocatalyst with excellent activity and superior durability. To date, a myriad of synthetic strategies, including Kirkendall effect²³, galvanic replacement^{24, 25} and selective etching^{26–28}, have been developed to fabricate noble metal nanoframes. Despite these accomplished achievements, tremendous challenges still remain in design and synthesis of trimetallic nanoframes.

Herein, for the first time, we combine the benefits of ternary system and nanoframes, and demonstrate a facile approach to synthesize triangular AgAu@Pt core-shell nanoframes with dendritic Pt shell by employing triangular Ag nanoprisms as sacrificial templates due to their unique anisotropic structure. Impressively, with both geometric and electronic effects, the as-prepared AgAu@Pt core-shell nanoframes exhibit extraordinary electrocatalytic performance for methanol oxidation reaction (MOR) with remarkably lower onset potential, two times higher activity, and better anti-poisoning capability as compared with the commercial Pt/C catalyst.

As schematically illustrated in Figure 1a, the overall fabrication procedure for triangular AgAu@Pt nanoframes mainly includes three steps: 1) the rim-preferential growth of a thin layer of Au on the edges of triangular Ag nanoprisms; 2) etching of the Ag segment by hexadecyltrimethylammonium bromide (CTAB) to form AgAu nanoframes; 3) growth of Pt nanoparticles on the AgAu nanoframes. The triangular Ag nanoprisms were prepared through a facile photo-induced approach,²⁹ and employed as sacrificial templates to guide the formation of AgAu@Pt nanoframes. A typical transmission electron microscopy (TEM) image shown in Figure 1b indicates that the average edge length of the Ag nanoprism templates is approximately 80 nm. Structurally, each Ag nanoprism is consisting

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Figure 1 (a) A schematic illustration demonstrating the essential steps involved in the preparation of triangular AgAu@Pt nanoframes from triangular Ag nanoprisms, and TEM images of (b) triangular Ag nanoprism templates, (c) Ag@Au core-shell nanoprisms after Au coating, (d) AgAu nanoframes obtained after CTAB etching, and (e) AgAu@Pt nanoframes formed after Pt deposition. The scale bars in (b)–(e) are 60 nm.

of two (111) basal facets on the triangular planes and three (110) facets on the lateral edges. Subsequently, the gold coating process was accomplished by simultaneously introducing solutions of HAuCl_4 and hydroxylamine (HyA) as mild reductant into the Ag nanoprism suspension through a mechanical syringe pump. To prevent self-nucleation and to achieve kinetically controlled growth, the infusion rate of HAuCl_4 and HyA was deliberately maintained at a relatively low value (1.0 mL h^{-1}). For face-centered-cubic (fcc) noble metal nanocrystals, the free energies of different facets follow the sequence of $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$.³⁰ Thus the newly-generated Au atoms would preferentially nucleate and epitaxially grow on the Ag nanoprism edges with high-energy (110) facets, leading to the formation of Ag@Au-framed nanoprisms (Figure 1c). Prior to Pt deposition, the resultant Ag@Au-framed nanoprisms solution was heated to 80°C . Under this condition, the exterior Au thin layer would spontaneously diffuse into the adjacent Ag matrix to produce homogeneous AgAu alloyed phase at the periphery of the Ag@Au-framed nanoprisms. For Pt growth, CTAB solution was injected into the above solution to serve as a surface stabilizing agent because of the supermolecular architecture formed by CTAB.^{31, 32} Upon the addition of CTAB solution, the Br^- ions in the CTAB could coordinate with the Ag atoms which consequently dissociate from the nanoprisms and strongly adsorbed on the Au atoms.^{12, 33} As a result, metallic Ag segments in Ag@AgAu-framed nanoprisms were rapidly etched away from the (111) facets, leading to triangular AgAu alloyed nanoframes with large hollow interiors (Figure 1d). Finally, reduction of H_2PtCl_6 by ascorbic acid (AA) created Pt islands on the AgAu nanoframes as dendritic Pt shell (Figure 1e) because nucleation of Pt is preferred on the AgAu surface, while further growth of Pt nanoparticles adopts island growth mode, known as the Volmer-Weber mode,³⁴ due to the higher surface energy of Pt than that of AgAu.

It is noteworthy that the gold coating process and the introduction of CTAB are indispensable for the successful generation of AgAu@Pt nanoframes. The thin layer of gold coating could serve as a robust protection sheath, effectively preventing deformation of the original triangular structure during the entire synthetic processes. Without gold coating, the resultant products were quasi-cubic nanoboxes (Figure S1a and b). CTAB is the key agent for creating framed structures due to its unique etching capability for the free Ag atoms in the Ag@Au-framed nanoprisms. As illustrated in Figure S1c and d, without using CTAB, Pt nanoparticles were sparsely decorated on the surface of intact Ag@Au nanoprisms instead of nanoframes. This

observation also suggests that CTAB is critical to control the nucleation and kinetic growth of Pt to preferentially occur on the AgAu surface.

Figure 2 Detailed morphological characterizations of the as-prepared AgAu@Pt nanoframes. (a)–(b) TEM images, (c) HRTEM, (d) HAADF-STEM and elemental mapping images, and (e) EDX line-scan profiles along different directions.

The TEM images (Figure S2, Figure 2a and b) of as-prepared AgAu@Pt nanoframes present well-defined triangular framed-structures with numerous dendritic branches protruding from the edges. Comparing with the parent AgAu nanoframes (Figure 1d), the average edge length of AgAu@Pt nanoframes almost keeps identical, while the average ridge thickness expands from sub-5 nm to around 7.3 nm. The particle size histogram of the decorated Pt nanoparticles (Inset of Figure 2a) shows a narrow distribution with an average size of 3.2 nm. From the magnified TEM image (Figure 2b) of an individual AgAu@Pt nanoframe, one can clearly see that ultrafine Pt nanoparticles reside uniformly on the surface of the entire triangular nanoframe. Furthermore, the Pt dendritic branches could introduce a large number of nanopores within the outer shell, which might be beneficial for catalytic applications since the pores could remarkably provide more active sites and facilitate mass diffusion and transport. The high-resolution TEM (HRTEM) image of an isolated Pt nanoparticle (Figure 2c) shows the d -spacing for adjacent lattice fringes as 0.226 nm, corresponding to that of the (111) planes of fcc Pt. The high-angle annular dark-field scanning TEM (HAADF-STEM) image (Figure 2d) further confirms the structural features as triangular nanoframes covered by dendritic nanothorns, and the concurrent energy-dispersive X-ray spectroscopy (EDS) mapping reveals that Pt homogeneously distributes on the whole nanoframe, while Ag and Au locate a little more inside the nanoframe, suggesting the core-shell structure of the AgAu@Pt nanoframe. The core-shell feature can be further supported by the cross-sectional compositional line profiles (Figure 2e) along a single edge and edge-to-edge directions, which reveal that the AgAu nanoframes are conformally covered by thin Pt-skins.

The X-ray diffraction (XRD) patterns (Figure S3a) of all samples, the Ag nanoprisms, AgAu alloyed nanoframes and AgAu@Pt nanoframes, present diffraction peaks of typical fcc-phased metals.

Figure 3 Electrochemical properties of triangular AgAu@Pt nanoframes and commercial Pt/C catalyst. (a) CV curves of the two catalysts for MOR performed in 0.2 M KOH + 1.0 M CH₃OH solution, (b) histogram of mass and specific activities, (c) histogram of TOF and I_f/I_b values, and (d) i - t curves recorded at -0.3 V of the two catalysts.

Notably, due to the extremely close lattice constant of Ag (4.09 Å) and Au (4.08 Å), there is no obvious shift of diffraction peaks upon the formation of AgAu alloy phase. However, as compared with pure Pt, a minor negative shift of the Pt (111) diffraction peak can be observed for the AgAu@Pt nanoframes (Figure S3b). This might be ascribed to the tensile effect on the Pt atoms exerted by the AgAu cores since AgAu alloy has larger lattice constant than Pt (3.92 Å).³⁵ The energy dispersive X-ray (EDX) spectrum (Figure S4) verifies the elemental composition of Ag, Au and Pt in the AgAu@Pt nanoframes, and the atomic ratio of Ag: Au: Pt was estimated to be 60.14: 12.7: 27.16 by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray photo electron spectroscopy (XPS) spectra (Figure S5) clearly demonstrate that the Ag, Au and Pt elements are predominantly in metallic states on the nanoframe surface.

As is well known, Pt-based nanostructures have been widely used as efficient electrocatalysts for fuel cell devices. In particular, the present triangular AgAu@Pt nanoframes, having highly open framed-structure with dendritic shell and multi-metallic composition, are expected to have extraordinary electrocatalytic performance. As a proof-of-concept application, the MOR was chosen as a model reaction to investigate the catalytic performance of the AgAu@Pt nanoframes, and the activity was benchmarked against the commercial Pt/C (10 wt%) catalyst. For comparison, the AgAu nanoframes was also tested under the identical test condition, but unfortunately, showed negligible electrocatalytic activity toward the MOR (Figure S6). Figure S7a shows the cyclic voltammograms (CVs) of the triangular AgAu@Pt nanoframes and commercial Pt/C catalyst performed in N₂-saturated 0.5 M H₂SO₄ solution at a sweep rate of 50 mV s⁻¹. The electrochemically active surface areas (ECSAs) of the two catalysts were estimated by calculating the charge in the hydrogen adsorption/desorption region after double-layer correction, and assuming a value of 210 μC/cm² for the adsorption of a hydrogen monolayer. As shown in Figure S7b, the ECSA of the AgAu@Pt nanoframes is identified as 24.6 m² g⁻¹, which is lower than that of the commercial Pt/C catalyst (34.8 m² g⁻¹).

Figure 3a shows the ECSA-normalized CVs of triangular AgAu@Pt nanoframes and commercial Pt/C catalyst recorded in N₂-saturated

Figure 4 Schematic illustration demonstrating the structural and compositional features of the triangular AgAu@Pt nanoframes as an efficient MOR electrocatalyst.

0.2 M KOH and 1 M CH₃OH solution with a sweep rate of 50 mV s⁻¹. Apparently, the AgAu@Pt nanoframes exhibit a much more negative onset oxidation potential (~ -170 mV) with higher activity as compared with the commercial Pt/C. Moreover, as shown in Figure 3b and Figure S8, the specific kinetic activity of AgAu@Pt nanoframes (1.96 mA cm⁻²) is almost 1.96-times higher than that of the commercial Pt/C catalyst (1.00 mA cm⁻²), suggesting higher intrinsic activity of the triangular AgAu@Pt nanoframes. Meanwhile, the Pt mass-normalized current density (483.1 mA mg_{Pt}⁻¹) of the AgAu@Pt nanoframes is almost 1.4-fold as large as that of the commercial Pt/C catalyst (351.0 mA mg_{Pt}⁻¹). Furthermore, the turnover frequency (TOF) number (Figure 3c) of the triangular AgAu@Pt nanoframes is calculated to be 2.18 atom⁻¹ s⁻¹, which is almost 2.06 times higher than that of commercial Pt/C catalyst (1.06 atom⁻¹ s⁻¹). All these results consistently demonstrate that the AgAu@Pt nanoframes exhibit superior electrocatalytic performance toward the MOR as compared with the commercial Pt/C catalyst.

It has been well-documented that the ratio of forward oxidation peak current density (I_f) to the backward peak current density (I_b), I_f/I_b , can represent the catalyst tolerance to the poisoning species. A higher ratio of I_f/I_b is corresponding to a more complete MOR, less accumulation of poisoning species on the catalyst surface, and thus a better CO-tolerance.^{7, 25, 36} According to figure 3a, the I_f/I_b value of the triangular AgAu@Pt nanoframes is estimated as 34.3, which is significantly higher than that of the commercial Pt/C catalyst (7.4), implying the superior anti-poisoning capability of the triangular AgAu@Pt nanoframes. To evaluate the long-term stability of the AgAu@Pt nanoframes, chronoamperometry (CA) measurements were carried out at -0.3 V for 1500 s. The i - t curves (Figure 3d) manifest that the current density for MOR on the AgAu@Pt nanoframes is remarkably higher than that on the commercial Pt/C catalyst during the entire time course. Impressively, the current retention of AgAu@Pt nanoframes is 54.1% of its initial value after

1500 s, which is much larger than that of commercial Pt/C catalyst (23.8%), corroborating the excellent stability of the as-prepared AgAu@Pt nanoframes.

The extraordinary electrocatalytic performance of AgAu@Pt nanoframes toward the MOR might be attributed to their highly open framework structure, dendritic shell surface and synergistic effect between multi-components, as schematically illustrated in Figure 4. Specifically, first, the AgAu@Pt nanoframes possess large exposed exterior and interior surfaces, which provides a large number of accessible active sites for catalytic reactions. Meanwhile, the broad void space inside the triangular nanoframes could facilitate mass transfer and diffusion for the MOR, which would enhance the reaction efficiency.³⁷ Second, since the ultrafine Pt nanoparticles are chemically grown and firmly anchored on the surface of AgAu nanoframe edges, the strong affinity could ensure a high electrical conductivity to promote rapid electron transfer, and a high structural stability to prevent the Pt nanoparticles from dissolution, and aggregation of during the MOR. In addition, the dendritic Pt shell on AgAu nanoframes could offer abundant active sites due to the edges, corners, and stepped atoms existed on the branches.^{26, 38} Third, according to the d-band center theory, since the constant of Pt (3.92 Å) is smaller than those of Au (4.08 Å) and Ag (4.09 Å), the coupling of Pt with AgAu would induce a upshift of the d-band center of Pt, which will lead to a stronger adsorption ability of hydroxyl groups (OH_{ads}) and facilitate to catalyze the methanol oxidation on the surface of Pt.²⁵ Additionally, the presence of buried AgAu core may not only significantly decrease the usage of precious Pt metal, but also allow for activation of water at a lower potential and thus enhance the generation of Pt–OH_{ads} groups, which are beneficial to improve the reaction kinetics and CO tolerance during the MOR. Moreover, the electrochemically more inert Au in the core could facilitate the stabilization of the Pt shell.^{14, 39}

Conclusions

In conclusion, we have presented the synthesis of triangular AgAu@Pt nanoframes with a uniform dendritic Pt nanoshell using triangular Ag nanoprisms as the sacrificial templates. The preferential edge-Au-coating, selective etching by CTAB, and Pt deposition eventually resulted in the formation of AgAu@Pt nanoframes. Notably, the gold coating process and the introduction of CTAB are indispensable for the successful generation of triangular AgAu@Pt nanoframes. The thin layer of Au coating not only prevents the AgAu@Pt nanoframes from deformation, but also greatly contributes to the electrocatalytic performance. CTAB exerts dual functions as an etching agent for removing free Ag and a surfactant for controlling Pt growth. Due to the intriguing hollow framework structure with dendritic surface and compositional synergy, the well-designed AgAu@Pt nanoframes exhibit excellent electrocatalytic performance toward MOR with much lower onset potential, 2-times higher activity, and better anti-poisoning capability as compared with the commercial Pt/C catalyst. We expect that the present work not only presents a promising strategy for the rational design of efficient electrocatalysts with improved electrocatalytic activity for fuel cells, but also can be extended to develop other multimetallic nanostructures with different shape for diverse applications.

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Conflicts of interest

There are no conflicts to declare.

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