Enhancing the Electrocatalytic Property of Hollow Structured Platinum Nanoparticles for Methanol Oxidation Through A Hybrid Construction

Yan Feng, Hui Liu, Pengfei Wang, Feng Ye, Qiangqiang Tan & Jun Yang

State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China 100190.

The integration of different components into a hybrid nanosystem for the utilization of the synergistic effects is an effective way to design the electrocatalysts. Herein, we demonstrate a hybrid strategy to enhance the electrocatalytic property of hollow structured Pt nanoparticles for methanol oxidation reaction. This strategy begins with the preparation of bimetallic Ag-Pt nanoparticles with a core-shell construction. Element sulfur is then added to transform the core-shell Ag-Pt nanostructures into hybrid nanodimers consisting of Ag2S nanocrystals and remaining Pt domains with intact hollow interiors (Ag2S-hPt). Finally, Au is deposited at the surface of the Ag2S domain in each hetero-dimer, resulting in the formation of ternary Ag2S-Au-hPt nanocomposites with solid-state interfaces. The ternary nanocomposites exhibit enhanced electrocatalytic property toward methanol oxidation due to the strong electronic coupling between Pt and other domains in the hybrid particles. The concept might be used toward the design and synthesis of other hetero-nanostructures with technological importance.

Platinum (Pt) nanoparticles are catalytically active for the anodic reaction (methanol oxidation reaction, MOR) of the direct methanol fuel cell (DMFC)1–3. Hollowing platinum (Pt) nanoparticles with galvanic replacement or sacrificial templates offers a promising approach to meet the high performance goals in electrocatalysis4–9. For instance, Fan and co-workers developed a photocatalytic approach using densely packed optically active porpyrins to template the synthesis of well-defined hollow Pt nanostructures which were excellent catalyst for the methanol oxidation reaction (MOR)7. The hollow interior increases the utilization of precious Pt metal by diminishing the number of its buried nonfunctional atoms, and the increase in activity could be attributed mainly to the larger surface area of the hollow structure, where the porous or open shell allows the internal surface of the catalyst to be accessible to the reactants. However, at room and moderate temperatures, Pt nanomaterials are susceptible to the poisoning induced by carbon monoxide (CO), an intermediate product of methanol oxidation10–13, which could not be overcome by simply hollowing the interior of the electrocatalysts.

After a careful review of the recent literature, we found that the integration of materials with vastly different physical and chemical properties into a hybrid nanosystem for the utilization of the synergistic effects between different components is an effective way to design the electrocatalysts for improved activity and resistance to deactivation14–17. Analogous to the bi-functional theory based classical approaches of increasing the Pt catalytic performance for MOR through alloying with oxophilic metals (e.g. Ru)18–21, the design of hybrid electrocatalysts should be rational and based on a sufficiently good understanding of the reaction mechanism. For example, the importance of the Pt–CO bond in MOR has been well documented22,23. The chemisorption of CO on Pt involves the donation of lone pair electrons from the filled carbon σ orbital of CO to the empty 5d-orbital of Pt, which is compensated by the back donation of electrons from the Pt d to the π* orbitals of CO. A high local density of electrons around Pt is associated with weak chemisorption. With this understanding, Ag2S-Pt composite nanocatalysts have been developed to ameliorate CO deactivation24. The electron transfer from Ag2S to Pt in Ag2S-Pt nanocomposites due to the alignment of energy levels increases the electron density around the Pt sites, causing the weakening of CO chemisorption and hence the increase in MOR activity.

In this work, we will demonstrate a hybrid strategy to enhance the electrocatalytic property of hollow structured Pt nanoparticles toward MOR. In this strategy, bimetallic Ag-Pt nanoparticles with a core-shell construction are
first prepared using seed-mediated growth method, which are dispersed in an organic medium and used as starting templates. Element sulfur is then used to transform the core-shell Ag-Pt nanostructures into hybrid nanodimers composed of Ag$_2$S and Pt nanoparticles with hollow interiors (Ag$_2$S-hPt). Finally, Au is deposited at one site on the surface of each Ag$_2$S-hPt hetero-dimer, resulting in the formation of Ag$_2$S-Au-hPt ternary nanocomposites with solid-state interfaces, which are important for the coupling occurrence among different domains in the nanocomposites. We will also demonstrate that the final ternary Ag$_2$S-Au-hPt nanocomposites are more effective for MOR in comparison with their core-shell Ag-Pt and dimeric Ag$_2$S-hPt ancestors due to the electronic coupling effect among the different domains in nanocomposites. This study offers a vivid example to exhibit the enhancement of the material properties by means of a structural tailoring. The concept might be used toward the design and synthesis of other hetero-nanostructures for catalytic applications other than methanol oxidation.

**Results and discussion**

Fig. 1 is a schematic illustration for the synthesis of ternary Ag$_2$S-Au-hPt nanocomposites. Fig. S1a and c in Supplementary Information (SI) show the transmission electron microscopy (TEM) image and histogram of the Ag seeds, respectively, which were used for the subsequent preparation of core-shell Ag@Pt nanoparticles. As displayed, these Ag seeds are multiply twinned decahedral nanoparticles and have an average size of 9.3 nm with a standard deviation of 1.0 nm$^{20}$. The high-resolution TEM (HRTEM) image (SI Fig. S1b) illustrated the lattice planes in these nanoparticles, showing an inter-planar spacing of $\sim 0.24$ nm, which corresponded to the [111] planes of face-centered cubic (fcc) Ag (JCPDS Card File 893722).

In the strategy developed in this work, the preparation of core-shell Ag@Pt nanoparticles is an important step preceding the synthesis of Ag$_2$S-hPt hetero-dimers and Ag$_2$S-Au-hPt ternary nanocomposites. The core-shell Ag@Pt nanoparticles were synthesized using a seed-mediated growth method at elevated temperature. Fig. 2a and 2c show the TEM and HRTEM images of core-shell Ag@Pt nanoparticles prepared by successive reduction of AgNO$_3$ and K$_2$PtCl$_4$ in oleylamine, where the core-shell structure has been confirmed by energy-dispersive X-ray (EDX) analysis of an arbitrarily chosen single particle in the high-angle annular dark-field scanning TEM mode$^{6}$. The core-shell Ag@Pt nanoparticles were uniform in size and had an overall average size of 12.6 nm. The X-ray diffraction (XRD) pattern shows two distinct metal phases, which could be indexed to the cubic Ag and Pt, respectively (SI Fig. S2a).

Subsequently, a previous protocol with slight modification was employed to synthesize the bimetallic Ag-hPt heterodimers$^{26}$. The twinned structure of the Ag seeds provides an expeditious means to modify the internal structure of core-shell Ag@Pt nanoparticles. Multiply-twinned Ag nanoparticles are inherently unstable; known to be slowly etched by dissolved O$_2$ and Cl$^{-}$ dissociated from the Pt precursor (K$_2$PtCl$_4$), and influence strongly on the continuity and compactness of the overlaid Pt shell$^{27}$. The Ag$^+$ released from the O$_2$/Cl$^{-}$ etching of twinned Ag seeds diffuses out through the discontinuous Pt shell due to the prevailing Ag$^+$ concentration gradient between the core of the Ag@Pt nanoparticles and the surrounding solution. This diffusion has been developed into a universal protocol for the production of noble metal nanoparticles with a hollow or cage-bell structure$^{6}$. A variation of this protocol was used in this work to completely remove the Ag core from core-shell Ag@Pt nanoparticles, resulting in formation of hetero-dimers composed of Ag$_2$S and remaining Pt nanoparticles with intact hollow interiors.

After mixing the core-shell Ag@Pt nanoparticles with element sulfur in toluene for 5 hours at 80°C, Ag diffused out from the interior of the core-shell Ag@Pt nanoparticles and was converted into Ag$_2$S on the surface of Pt shells, forming Ag$_2$S-hPt heterodimers (Ag$_2$S and Pt nanoparticles with a hollow interior). The TEM image (Fig. 2b) and HRTEM image (Fig. 2d) after treatment with element sulfur show that only hybrid particles with strong imaging contrast at different domains are observed in the resulting products, which are very different from the starting core-shell nanoparticles (Fig. 2a and 2c). Since metals usually have strong imaging contrast owing to their high electron density$^{20}$, the hybrid dimers formed by Ag$_2$S and hollow Pt could be easily identified – the increase in the image contrast between the core and shell regions is an indication of metal depletion caused by the removal of the Ag cores, while the semiconducting Ag$_2$S appears as lighter domain having a solid-state interface with the metal section. The conversion of Ag into Ag$_2$S was supported by EDX analysis of the dimeric product. In comparison with that of core-shell Ag@Pt nanoparticles (Fig. 2e), as shown in Fig. 2f, besides Ag and the Pt metals, sulfur is also detected in the core-shell nanoparticles after the sulfur treatment. For the core-shell Ag@Pt nanoparticles, the broad absorption in the visible light region due to the surface plasmon resonance of Ag nanoparticles with structural defects also disappears after the sulfur treatment, as shown in SI Fig. S3, substantiating the conversion of Ag diffused from the core region of core-shell Ag@Pt nanoparticles into Ag$_2$S in the hetero-dimers. A typical powder XRD pattern of the Ag$_2$S-hPt hetero-dimers was shown in SI Fig. S2b and indicates the simultaneous presence of monoclinic Ag$_2$S and face-centered cubic (fcc) Pt phases. TEM and HRTEM images in Fig. 2 show that the size and morphology of the remaining Pt domains in the hetero-dimers are virtually unchanged after treatment with element sulfur, suggesting that the diffusion of the Ag from the core of the core-shell nanodimers did not cause the collapse of the particle geometry.

Ternary Ag$_2$S-Au-hPt nanocomposites are found as the dominant product after aging the mixture of Ag$_2$S-hPt hetero-dimers and HAuCl$_4$ in toluene for 2 h, as indicated by the TEM and HRTEM images in Fig. 3. No additional reducing agent is needed. Dodecylamine (DDA) could reduce the Au$^{3+}$ ions sufficiently in the presence of Ag$_2$S-hPt hetero-dimers. Isolated Au nanoparticles are not observed, indicating that Au nucleates preferentially on the existing Ag$_2$S-hPt heterodimers under the experimental conditions. In most cases, Au is deposited only at a single site on the Ag$_2$S domain in each Ag$_2$S-hPt hetero-dimers. The average diameter of the deposited gold patches is ca. 8.3 nm, which could be discernible by the strong brightness contrast in TEM and HRTEM images. As indicated by SI Fig. S4, the EDX analysis confirmed the presence of Ag, Au, Pt, and S after aging the mixture of Ag$_2$S-hPt hetero-dimers and Au$^{3+}$ ions in toluene for 2 h at room temperature. The XRD pattern shown in SI Fig. S2c demonstrates a mixed phase of Au, Pt, and Ag$_2$S in the ternary Ag$_2$S-Au-hPt nanocomposites. In addition, the appearance of a surface plasmon resonance at ca. 520 nm clearly indicates the formation of Au nanoparticles, as displayed in SI Fig. S3 (blue line). The broad feature of the surface plasmon resonance may indicate the presence of structural defects in the Au domains. The more direct evidences for the formation of ternary Ag$_2$S-Au-hPt nanocomposites were provided by the line scanning analysis and elemental mapping of an arbitrary single composite nanoparticle (Fig. 3c) in the high-angle annular dark-field STEM
mode. As shown in Fig. 3d for the line-scanning analysis, the Au and Pt signals are present at left- and right-hand side, respectively, whereas the Ag and S signals are only concentrated at the core region. The line-scanning analysis is well in accord with the nanoscale mapping results (Fig. 3e to 3i), which also manifest that the Au and Pt components are respectively distributed on the two sides of the ternary nanocomposites. Further, HRTEM image revealed that the crystal planes of Au were not parallel to those of AgS in each heterodimer nanoparticle (Fig. 3b), indicating that the growth of Au on the surface of AgS domain takes place in different orientations.

The core-shell Ag@Pt nanoparticles, AgS-hPt hetero-dimers, and ternary AgS-Au-hPt nanocomposites were loaded on Vulcan carbon and tested for their electrocatalytic property for the methanol oxidation reaction (MOR) at room temperature. As shown by the representative TEM images in SI Fig. S5, the core-shell particles, hetero-dimers, and nanocomposites could be dispersed very well on the carbon support by conventional means and their structures are intact.

The electrochemically active surface areas (ECSAs) of core-shell Ag@Pt nanoparticles, AgS-hPt hetero-dimers, and ternary AgS-Au-hPt nanocomposites are determined using cyclic voltammetry (Fig. 4a). The specific ECSAs, based on the unit weight of Pt and calculated by integrating the charge associated with the hydrogen adsorption/desorption potential region after double-layer correction, are 41.6 m² g⁻¹ for core-shell Ag@Pt, 35.3 m² g⁻¹ for AgS-hPt hetero-dimers, and 37.1 m² g⁻¹ for AgS-Au-hPt nanocomposites, respectively. The hollowing of core-shell Ag@Pt nanoparticles by element sulfur may lead to the increase of ECSAs by releasing the inner surface of Pt shell, whereas the growth of AgS domains on the outer surface of Pt shell would result in the decrease of ECSAs due to the solid-state interfaces between hollow Pt and AgS in the hetero-dimers, which may induce some blockage of the surface area of the Pt shells. These two effects might have offset each other, such that the ECSAs of AgS-hPt hetero-dimers are lower than that of core-shell Ag@Pt nanoparticles. Specifically, the ECSAs of Pt in ternary AgS-Au-hPt nanocomposites are similar to that in AgS-hPt hetero-dimers since the Au is only deposited at the surface of AgS domains in the hetero-dimers and has negligible influence on the ECSAs of the Pt domains.

An important feature in hybrid materials is the electronic coupling between the metal and semiconductor domains [24,29–31]. The Pt 4f...
X-ray photoelectron spectroscopy (XPS) spectra of the core-shell Ag@Pt nanoparticles, Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites were analyzed. As displayed in Fig. 4b, in comparison with the Pt 4f$^{7/2}$ and 4f$^{5/2}$ binding energies of core-shell Ag@Pt nanoparticles, an appreciable shift to lower values was observed in the Ag$_2$S-hPt hetero-dimers and ternary Ag$_2$S-Au-hPt nanocomposites, suggesting that electrons were transferred to Pt from other domains of the hetero-dimers or nanocomposites. The comparison of the Pt 4f XPS spectra between Ag$_2$S-hPt hetero-dimers and ternary Ag$_2$S-Au-hPt nanocomposites further reveals that the presence of the Au domain could promote this electron-donating effect. The decrease in the Pt 4f binding energies was ca. 0.7 eV in ternary Ag$_2$S-Au-hPt nanocomposites, and ca. 0.3 eV in Ag$_2$S-hPt hetero-dimers. This electron-donating effect to hPt domains could be explained by intra-particle charge transfer (Fig. 4c for the energy level diagram). The comparison between the electronic affinity of bulk Ag$_2$S (3.63 eV) and the work function of Pt (5.65 eV) predicted that the alignment of energy levels in Ag$_2$S and Pt would be favorable for electron transfer from Ag$_2$S to Pt to fill the hole generated by the electron transfer to hPt domains, further promoting the electron transfer from Ag$_2$S to hPt in order for the Fermi levels to match at the interface. The electron-donating effect from Au to Ag$_2$S has also been supported by the XPS analysis of Au 4f region (SI Fig. S6), whereby an appreciable shift in the 4f binding energies of Au in the ternary nanocomposites to higher values was found as compared to the Au 4f binding energies of monometallic Au particles. Analogous to the electron donation from Sn to Pt in the Pt-Sn system, the charge transfer from Ag$_2$S to Pt in the Ag$_2$S-hPt hetero-dimers or ternary Ag$_2$S-Au-hPt nanocomposites leads to a substantial increase in the electron density around the Pt domains, resulting in the weaker chemisorption of CO, an intermediate product of methanol oxidation on the surface of hPt, and hence promoting the MOR.

Fig. 4d shows the CO stripping voltammograms of core-shell Ag@Pt nanoparticles, Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites after the working electrode has been held at $-0.15$ V for 30 min in CO saturated 0.1 M HClO$_4$. The CO stripping peaks of the Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites shifted to a more negative potential as compared to the core-shell Ag@Pt nanoparticles, indicating a more facile CO removal, and hence, an improved CO tolerance in
practice. In addition, the CO stripping peak of ternary Ag$_2$S-Au-hPt nanocomposites was located at a more negative potential than that of Ag$_2$S-hPt hetero-dimers, suggesting a more facile CO removal from the hPt surfaces in the Ag$_2$S-Au-hPt composite system. The ease of CO removal over Ag$_2$S-hPt and Ag$_2$S-Au-hPt relative to the core-shell Ag@Pt nanoparticles reflects the effectiveness of electron coupling among the different domains in hybrid particles.

Voltammograms of methanol oxidation were obtained in the potential window of 0.2–1 V at a swept rate of 20 mV s$^{-1}$ (Fig. 4e).

The current densities in the voltammograms were normalized by the ECSA of Pt. As expected, the comparison in current densities indicates that the Ag$_2$S-hPt hetero-dimers and ternary Ag$_2$S-Au-hPt nanocomposites show greater specific activities than those of the core-shell Ag@Pt nanoparticles. In particular, the ternary Ag$_2$S-Au-hPt nanocomposites display the highest catalytic activities for methanol oxidation. The enhanced catalytic activity of Ag$_2$S-hPt heterodimers and ternary Ag$_2$S-Au-hPt nanocomposites could be attributed to the electronic coupling between Pt and the other domains in the hybrid particles. The long-term performance of core-shell Ag@Pt nanoparticles, Ag$_2$S-hPt heterodimers, and ternary Ag$_2$S-Au-hPt nanocomposites in methanol oxidation was illustrated by the chronoamperograms in Fig. 4f. The slower rate of decay for the Ag$_2$S-hPt heterodimers, and ternary Ag$_2$S-Au-hPt nanocomposites indicates their superior CO tolerance to the core-shell Ag@Pt nanoparticles.

In summary, a hybrid strategy has been demonstrated to enhance the electrocatalytic property of hollow structured Pt nanoparticles for methanol oxidation reaction. This strategy began with the preparation of bimetallic Ag-Pt nanoparticles with a core-shell construction using the seed-mediated growth method. Element sulfur was then added to transform the core-shell Ag-Pt nanostructures into Ag$_2$S-hPt hybrid nanostructures. Subsequently, Au was deposited at the surface of the Ag$_2$S domain in each Ag$_2$S-hPt hetero-dimer, resulting in the formation of ternary Ag$_2$S-Au-hPt nanocomposites.
In comparison with their core-shell parents, the Ag$_2$S-hPt hetero-nanodimers and ternary Ag$_2$S-Au-hPt nanocomposites were more active in catalyzing methanol oxidation reaction. The electronic coupling between hPt and other domains in hetero-dimers and ternary nano-composites was the major contributor to the enhancement of MOR activity. Although it is difficult to apply these hybrid nanomaterials as practical electrocatalysts due to the low ECSA of Pt in the hybrid structure and the lack of strategies to maintain their complex structures after long-term use, this study offers a vivid example to demonstrate the tuning of the material properties by means of a hybrid approach, and the concept might be used toward the design and synthesis of other hetero-nanotechnologies with structural importance.

**Methods**

**General materials.** Potassium tetrachloroplatinate(II) (K$_2$PtCl$_4$, 98%), silver nitrate (AgNO$_3$, 99%), gold(III) chloride trihydrate (HAuCl$_3$·3H$_2$O, ACS reagent, >98.0% Au basis), sulfur powder (S, chemical grade), and dodecylamine (DDA, 98%) from Aldrich, oleylamine (95.4%, primary amine) from J&K Scientific, aqueous HClO$_4$ solution (70%, ACS reagent) and Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) from Aladdin Reagents, ethanol (99%), methanol (99%) and toluene (99.5%) from Beijing Chemical Works, and Vulcan XC-72 carbon powder from Cabot Corporation were used as received. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by copious washing with de-ionized water before drying in an oven.

**Synthesis of core-shell Ag$_2$S-Pt nanoparticles.** The seed-mediated growth method was used for the synthesis of core-shell nanoparticles with a Ag core and a monometallic Pt shell. Typically, 51 mg of AgNO$_3$ was added to 30 mL of oleylamine in a three-necked flask equipped with a condenser and a stir bar. The solution was heated to 150 °C and kept at this temperature under flowing N$_2$ for 1 h for the reduction of Ag ions by oleylamine. Then 62 mg of K$_2$PtCl$_4$ was added swiftly, followed by heating the mixture to 160 °C, and keeping there for 3 h under flowing N$_2$ for the reduction of the Pt shell metal precursor. After the reactions, the core-shell Ag$_2$Pt nanoparticles were recovered by precipitation with methanol, centrifugation, and washing with methanol, and re-dispersed in 30 mL of toluene.

**Synthesis of Ag$_2$S-hPt heterogeneous nanodimers.** For the synthesis of heterogeneous nanodimers consisting of Ag$_2$S and Pt nanoparticles with hollow interiors, 32 mg of element sulfur was added to 20 mL of core-shell Ag$_2$Pt nanoparticle solution in toluene. The molar ratio of S/Ag in the mixture was calculated to be ca. 5/1. The mixture was heated to 80 °C for 5 h to extract Ag component from the core–shell nanoparticles and to convert the Ag into Ag$_2$S on the surface of the leaving hollow structured Pt nanoparticles. The Ag$_2$S-hPt hetero-dimers prepared as such were recovered by precipitation with methanol, centrifugation, and washing with methanol, and re-dispersed in 20 mL of toluene.

**Phase transfer of Au ions from aqueous phase to toluene.** The transfer of HAuCl$_4$ (aqueous solution, 1 mM) from aqueous phase to toluene followed an ethanol–analyzer attached to the TEM operating in the scanning transmission electron microscopy (STEM) mode was used to analyze the chemical compositions of the synthesized nanoparticles. UV-visible spectra of the colloidal solution of core-shell Ag$_2$Pt nanoparticles, Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites were collected on a Hitachi U-3900 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was conducted on a VG ESCALAB MKII spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 1800 X-ray diffractometer, using Cu Kα radiation (λ = 1.54056 Å). Samples for XPS and XRD analyses were concentrated from the toluene solution of nanoparticles to 0.5 mL using flowing N$_2$. 10 mL of methanol was then added to precipitate the nanoparticles, which were recovered by centrifugation, washed with methanol several times, and then dried at room temperature in vacuum.

**Electrochemical measurements.** Electrochemical measurements were carried out in a standard three-electrode cell connected to a Bio-logic VMP3 (with EC-lab software version 9.56) potentiostat. A leak-free Ag/AgCl (saturated with KCl) electrode was used as the reference electrode. The counter electrode was a platinum mesh (1 × 1 cm$^2$) attached to a platinum wire. For the loading of the catalyst on Vulcan XC-72 carbon support, a calculated amount of carbon powder was added to the toluene solution of core-shell Ag$_2$Pt nanoparticles, Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites. After stirring the mixture for 24 h, the Ag$_2$Pt/C, Ag$_2$S-hPt/C, or Ag$_2$S-Au-hPt/C catalysts (20 wt% Pt on carbon support) were collected by centrifugation, washed thrice with methanol, and then dried at room temperature in vacuum.

**General characterization methods.** The transfer of HAuCl$_4$. 1 and used for the determination of electro-catalytic activity surface area (ECSA) of Pt. For the loading of the catalyst on Vulcan XC-72 carbon support, a calculated amount of carbon powder was added to the toluene solution of core-shell Ag$_2$Pt nanoparticles, Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites. The as-prepared Ag$_2$S-hPt nanoparticles were washed twice with methanol to remove non-specifically bonded DDA, followed by re-dispersion in 20 mL of toluene. The transfer of HAuCl$_4$. 1 and used for the determination of electro-catalytic activity surface area (ECSA) of Pt. For the loading of the catalyst on Vulcan XC-72 carbon support, a calculated amount of carbon powder was added to the toluene solution of core-shell Ag$_2$Pt nanoparticles, Ag$_2$S-hPt hetero-dimers, and ternary Ag$_2$S-Au-hPt nanocomposites. The as-prepared Ag$_2$S-hPt nanoparticles were washed twice with methanol to remove non-specifically bonded DDA, followed by re-dispersion in 20 mL of toluene.
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Author contributions
Y.F., H.L., P.W. and F.Y. performed the materials synthesis, characterization and electrochemical measurements. Q.T. and J.Y. supervised the project. J.Y. wrote the main manuscript text, and all authors participated in the review of the manuscript.

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