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Supporting Information

Localized Surface Plasmon Enhanced Electrocatalytic Methanol Oxidation of AgPt

Bimetallic Nanoparticles with Ultra-thin Shell[†]

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Experimental

Chemicals

Platinum bis(acetylacetonate) (Pt(acac)₂) and cetyl trimethyl ammonium chloride (CTAC) were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 99%) was purchased from Acros. Acetonitrile (ACN, CH₃CN, HPLC grade), glucose (C₆H₁₂O₆), cobalt acetylacetonate (Co(acac)₃), oleylamine (OAM), oleic acid (OA), sodium borohydride (NaBH₄, 99%), silver nitrate (99.99%), polyvinylpyrrolidone (PVP K-30, (C₆H₉NO)_x, Mw \approx 58,000) L-ascorbic acid (AA, C₆H₈O₆, 99%), sodium citrate (NaCA), sodium borohydride (NaBH₄) and thioglycollic acid (TGA) were purchased from Aladdin. All chemicals were used as received without further purification.

Ag Nanoparticle Synthesis

Seed Preparation. In a typical preparation, 1 mL of NaCA (5 mM in H_2O) and 1 mL of HAuCl₄ (5 mM) were added in 18 mL of H_2O contained a 25 mL bottle. After that, 0.6 mL of NaBH₄ (0.1 M) was injected into the bottle under vigorous stirring, giving rise to a yellowish solution of Au nanoparticles. Then, Au seeds were obtained after aging for 4 h, allowing complete decomposition of NaBH₄ before serving as the seeds in the subsequent seeded growth procedure. **Growth Process.** Ag nanoparticle precursor was synthesized according to the previous report with a slight modification.1 In a typical synthesis, 75 mL of PVP (5 wt % in H₂O), 75 mL of ACN and 11.25 mL of AgNO₃ (0.1 M) were added in 75 mL of H₂O. Then, 15 mL of AA (0.1 M) was added, followed by a quick injection of 50 μ L of the Au seed solution. The stirring speed was set as 300 rpm in the whole synthesis process of Ag nanoparticles. The reaction was terminated and centrifuged with H₂O for three times to remove excessive PVP which was adsorbed on the precursor. And then, keep the samples in 60 mL H₂O for further surface ligand exchange process.

Surface Ligand Exchange Process. To remove the surfactant capping on the Ag NPs, TGA molecule was utilized to substitute the PVP in the surface ligand exchange process. In a typical synthesis, 0.5 mL TGA was added to Ag nanoparticles suspension (60 mL) dropwise. After stirring for 15 min, the suspension was centrifuged at 6500 rpm for 5 min and redispersed in 40 mL H₂O. Subsequently, another 0.5 mL TGA was added into the solution drop by drop. The mixture was stirred at 300 rpm at room temperature overnight. Herein, the concentration of Ag nanoparticle slurry was calculated with 3 mg/mL considering the rational mass losing.

Synthesis of AgPt bimetallic hollow nanoparticles

In a typical synthesis, Pt(acac)₂ (10.0 mg), Co(acac)₃ (9.0 mg), CTAC (32.0 mg), glucose (60.0 mg) and 2.5 mL OAM were added into a vial (volume: 25 mL). After the vial had been capped, the mixture was ultrasonicated for 90 min until turning into a homogeneous green mixture. At the same time, 5 mL TGA modified Ag nanoparticles slurry was configured once and ultrasonically dispersed in 2.5 mL OA and transferred to above green mixture stirring for 5min at 300 rpm. The resulting mixture was heated from room temperature to 160 °C in 30 min and maintained at 160 °C for 8 h in an oil bath. The resulting colloidal products were collected by centrifugation and washed three times with an ethanol/cyclohexane mixture.

Etching Process. In a typical etching process, the 40 mL etching mixture contained 2wt% hydrogen peroxide and 2wt% hydrochloric acid was prepared before casting 10 mg catalyst into it. All these experiments were performed in a constant temperature water bath while keeping the temperature 35 °C and stirring rate 300 rpm. The catalyst was loaded on carbon black (Cabot, Vulcan XC-72). We can acquire the unique AgPt-BHNPs when etching for 15 min. After centrifugation, the catalyst was immersed into a 5wt% ammonia solution to remove unnecessary AgCl phase effectively and collected by centrifugation and washing three times with ultra-pure water before further electrochemical characterization.

Characterizations

UV-vis extinction spectra were measured on a UV-vis-NIR spectrophotometer (Hitachi U-4100) with a DH-2000-Bal light source. An X-ray diffractometer (Bruker D8 Advance) with a Cu K α X-ray source (λ =1.5405 Å) recorded the X-ray diffraction (XRD) patterns. Transmission electron microscopy (TEM) analysis was performed with a JEOL JEM-2100 operating at 200 kV. High-resolution transmission electron microscopy (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping analysis were conducted on a JEM-F200 transmission electron microscope at an acceleration voltage of 300 kV. Energy dispersive X-ray spectroscopy (EDS) was performed on a scanning electron microscope (Hitachi, S-4700). The X-ray photoelectron spectroscopy (XPS) spectra of AgPt-BHNPs were performed on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K α X-ray source of 1486.8 eV at a chamber pressure below 1 × 10⁻⁸ Torr and beam power of 200 W. All of the binding energies were corrected with reference to the C 1s peak of the surface adventitious carbon at 284.6 eV. The Pt mass loadings in all the catalysts were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES 5300).

Electrochemical Characterization

All electrochemical experiments were performed in a three-electrode system on a CHI 660 E electrochemical analyzer (CH Instruments, Shanghai, Chenhua Co.). The AgPt-BHNPs modified custom-made L-typed glassy carbon electrode (GCE, 5 mm in diameter) served as a working electrode. A Pt wire (1cm × 1cm) and an Ag/AgCl (0.1989 V vs. NHE, saturated KCl, at 30 °C) electrode were used as the counter electrode and the reference electrode, respectively. All the irradiation intensity was verified by a full spectrum optical power meter (CEL-NP2000-2, Beijing China Education Au-light Co., Ltd). The light source was a xenon lamp (PLS-SXE300/300UV, Trusttech Co., Ltd. Beijing) equipped with a 420 nm cutoff filter.

All the samples were loaded on carbon black (Cabot, Vulcan XC-72) with a Pt mass loading of about 20% to achieve better dispersion. The homogeneous catalyst, in a typical loading process, 500 μ L ink was prepared by ultrasonic dispersing 1.26 mg catalysts into a solution contained 435 μ L isopropanol, 15 μ L Nafion (5%, sigmaaldrich) and 50 μ L H₂O for 1 hour in an ice bath. All electrochemical tests were conducted at 30 °C with a circulating water bath temperature control device refraining from a large perturbation in temperature. The electrochemical measurements for MOR were carried out in an N₂-saturated solution containing 0.5 M NaOH and 1 M methanol at a scan rate of 50 mV s⁻¹.

CV curves were recorded at 30 °C in an N₂-saturated 0.5M NaOH solution at a scanning rate of 50 mV s⁻¹ in the potential range of 0.05 - 1.1 V (vs. RHE). The electrochemical active surface area (ECSA) can be calculated by integrating the charge passing the electrode during the hydrogen adsorption/desorption process after the correction for the double layer formation.^{2,3} The ECSAs were calculated with the following equation:

$$ECSA = \frac{Q_{\rm H}}{0.21 \times [Pt]}$$

where Q_H (mC) was the charge due to the hydrogen desorption in the hydrogen region (0.05 - 0.45 V vs. RHE) of the CV_S, The charge required to oxidize a hydrogen monolayer was 0.21 mC cm⁻², corresponding to a surface density of 1.3×10^{15} Pt atoms per cm^{2,4,5} and [Pt] was the loading of Pt on the working electrode.

CO stripping experiments were performed to conduct the CO adsorption/desorption property of AgPt-BHNPs. While keeping the potential at 0.1V (vs. RHE) for 20 min in a CO-saturated 0.5M NaOH solution, CO adsorbed on the pre-activated catalyst in a dark or 600 mW cm⁻² lumen light intensity circumstance. The CO stripping curves were recorded after purging N_2 for 30 min by sweeping the potential anodically. CO adsorption/desorption property can be measured by integral from the charge of CO oxidation peak after deducting the background charge in the same potential range. Here, the surface charge densities of 0.42 mC cm⁻² for all catalysts were used in the calculations.^{6,7}

All the electrocatalytic performance of commercial Pt/C (20 wt%) catalyst was performed under the same experimental condition while controlling the equivalent amount of Pt loading on the GCE.

Photothermal Experiment

To acquire the photothermal performance of AgPt-BHNPs, photothermal experiments were performed in the ambience and a 30mL electrolyte (0.5M NaOH and 1M methanol) contained in a watch glass with an internal diameter (94 mm). A pure AgPt-BHNPs sample (total mass, 8 mg, without loading on the carbon black support) was loaded on a glass slide (25.4 mm \times 76.2 mm \times 0.9 mm, SAIL BRAND, CAT NO. 7101) with an area (23.5 mm \times 16.5 mm). The sample AgPt-BHNPs and the glass slide were irradiated vertically, in air or the MOR electrolyte media, with a xenon lamp (PLS-SXE300/300UV, Trusttech Co., Ltd. Beijing) equipped with a 420 nm

cutoff filter. The irradiation power density was set as 200 mW cm⁻². A FLUKE Ti 10 infrared camera was used to take infrared photographs. Data collection was conducted with a time interval sampling method from recorded videos both in air and the electrolyte environment. Herein, the ambient temperature was stabilized at 18.2 ± 0.5 °C.

FDTD Calculations

Herein, to verify the extinction spectra and spatial electric field distribution of AgPt-BHNPs when a beam of sunlight radiating on the target structure, the finite-difference-time-domain (FDTD) simulation (8.6.0 version, Lumerical Solutions, Inc.) was performed as an effective approach with perfectly matched layers (PML) in 3D as boundary conditions. A unit cell of 400 nm \times 400 nm \times 400 nm in 3Ds was set for all nanostructure. Total-field scattered-field (TFSF) linearly polarized light waves in the range of 300 – 900 nm were injected to the unit cell along the +z direction. The amplitude of the electric field vector of incident TFSF linearly polarized light vector was set to be 1 V m⁻¹. While a frequency-domain field profile monitor in the x–y plane was utilized to collect field profile data. The complex refractive indexes of Ag and Pt were adopted from tabulated values measured by Johnson and Christy⁸. Geometric parameters of simulation structures were obtained from the average actual dimension of AgPt-BHNPs. For AgPt-BHNPs dispersed in aqueous solutions, the refractive index of the medium was set to be 1.33.

Table S1 Elemental ICP-MASS analysis of AgPt-BHNPs samples

sample	Ag content / wt%	Pt content / wt%	Pt/Agmass	Pt/Agatom
AgPt-BHNPs	17.87	82.13	4.59	2.54

Table S2 EDAX Analysis of AgPt-BHNPs samples

sample	Ag content / wt%	Pt content / wt%	Pt/Agmass	Pt/Agatom
AgPt-BHNPs	16.82	83.18	4.95	2.73

Table S3 The enhanced current density and the relative enhanced current density ratio of AgPt-BHNPs MOR photo-response with different beam power density calculated from the amperometric i-t curves in Fig. 3d

Beam power density / mW cm ⁻²	ΔJ increased current density / $\mu A \ cm^{\text{-}2}$	ΔJ/J relative increased current density ratio / count
600	278.47	29.06%
400	208.47	23.18%
200	137.25	13.88%



Fig. S1 size distribution of Ag NPs calculated from the SEM image in Fig. 1a



Fig. S2. EDAX spectrum of AgPt-BHNPs was performed on JEOL JEM-F200.



Fig. S3 (a) XRD patterns of AgPt BHNPs and pure Ag nanoparticles; (b) the full spectrum of AgPt BHNPs; high-resolution XPS spectra of (c) Pt and (d) Ag from AgPt BHNPs, respectively. Noting that the peak intensities and positions for the pure Ag (blue) and Pt (green) references are presented as different colorful bars at the bottom in (a).



Fig. S4 CV curves recorded in an electrolyte contained with (a) 0.5 M NaOH with a sweep rate of 50 mV s⁻¹ and (b) specific activity (left) and CO poisoning tolerance property (right) of the catalysts calculated from Fig. 2(a).



Fig. S5 MOR performance of commercial Pt/C (a) Electrocatalytic performance of commercial Pt/C catalysts. CV curves recorded in an electrolyte contained with a mixed electrolyte (0.5 M NaOH and 1M methanol) with a sweep rate of 50 mV s⁻¹; (b), amperometric current–time curves performed at -0.28 V (vs. Ag/AgCl) in a 0.5 M NaOH and 1M methanol solution purged with N₂, respectively. Noting that 600/400/200 in the above picture means that the irradiation intensity 600/400/200 mW cm⁻².



Fig. S6 Photothermal performance of AgPt-BHNPs and glass slide was performed in air. Optical photos of (a) AgPt-BHNPs and (b) glass slide, respectively. Infrared images of (c) AgPt-BHNPs and (d) glass slide at the initial time (0 s). Infrared images of (e) AgPt-BHNPs and (f) glass slide at the stable time (127 s and 311 s, respectively).



Fig. S7 Time-dependent surface temperature change curves of AgPt-BHNPs and glass slide in (a) air and (b) the electrolyte media.



Fig. S8 The MOR performance showed a positive correlation with different electrolyte temperature in an electrolyte contained with 0.5 M NaOH and 1M methanol. (a), CV recorded with a sweep rate of 50 mV s⁻¹ in a 0.5 M NaOH and 1 M methanol solution purged with N₂, and (b), forward peak current density, (c), backward peak current density and (d), CO poisoning tolerance property of the catalysts in a 0.5 M NaOH and 1M methanol solution with different temperatures purged with N₂, respectively. Noting that all the catalytic performance was normalized to ECSA of AgPt-BHNPs.



Fig. S9 UV-visible spectroscopy of AgPt-BHNPs



Fig. S10. The schematic of AgPt-BHNPs for FDTD simulation. Noting, total-field scattered-field source is abbreviated as TFSF source.

As shown in Fig. 3c, the charge integral area of CO absorbed on Pt under irradiation significant reduced when compared with that in dark condition, clearly verifying that the LSPR-induced surface charge heterogeneity of AgPt-BHNPs effectively decreased the CO coverage ratio of Pt active sites, and thus leading to the enhanced CO poisoning tolerance property of AgPt-BHNPs. Therefore, the introduced light in this system can suppress the absorption of intermediates (mainly CO) on our catalyst in the MOR process.

Moreover, CO stripping tests of commercial Pt/C (Fig. S11) demonstrated that the converge of CO absorbed on the Pt atoms under irradiation (600 mW cm⁻²) reduced slightly when compared to that of in dark circumstance, revealing the light irradiation had little effect on the CO absorption on commercial Pt/C. Obviously, the difference of charge integral area of absorbed CO obtained from commercial Pt/C (Fig. S11) was distinctly smaller than that acquired from AgPt-BHNPs system (Fig. 3c). It was clearly verified that the LSPR-induced surface charge heterogeneity of AgPt-BHNPs effectively reduced the CO coverage ratio of Pt active site and enhanced the CO poisoning tolerance property of AgPt-BHNPs.



Fig. S11 CO stripping of commercial Pt/C catalysts. CO stripping voltammetry and CVs were obtained in 0.5M NaOH with a scan rate of 50 mV s⁻¹ in the dark and illuminous beam power density 600 mW cm⁻² illuminous circumstance, respectively.



Fig. S12 TEM image of AgPt-BHNPs after MOR electrocatalytic reaction.

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