Enhanced Catalytic Activity of Au Core Pd Shell Pt Cluster Trimetallic Nanorods for CO$_2$ Reduction

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.Experimental section

Synthesis of the 49 nm Au@Pd@Pt nanorods

A two-step seed-mediated method was employed to synthesize Au nanorods (NRs) according to the literature with slight modifications.[1] Typically, the seed solution was prepared by adding 0.6 ml of fresh 0.01M NaBH$_4$ quickly into the mixture of 5 mL of 0.2 M cetyltrimethyl ammonium bromide (CTAB) and 5 mL of 0.5 mM H$_2$AuCl$_4$. The solution color changed to light brown once the NaBH$_4$ solution was injected. The solution was stirred for 2 min and aged for at least 2 hours before use. To prepare the growth solution, 4.5 g of CTAB and 125 ml hot water (about 60-70 °C) and 0.55 g of 5-bromosalicylic acid were mixed in a flask. The solution was cooled down to 30°C for 15 min and 8 ml of 4 mM AgNO$_3$ was added. After 15 min, 125 ml of 1 mM H$_2$AuCl$_4$ was added into the flask. The solution was stirred slowly for 15 min, and then 0.064 M ascorbic acid was added with vigorous stirring until it became colorless. Lastly, 1 ml of the Au seed solution was added into the flask, stirred for 30 s and then kept unstirred at 30°C for 12 h to make Au NRs grow.

The synthesis of Pd shell and Pt cluster on 49 nm Au core was used a two-step method. Briefly, 30 ml of Au NRs sol was mixed with 2 ml of 1 mM H$_2$PdCl$_4$ solution, and then1 ml of 10 mM ascorbic acid was added and kept stirring at 30 °C for 30 min to grow Pd shell. Then 0.1, 0.3, 0.5,

0.9, 1.9, 4.4 ml of 10mM ascorbic acid solution and 0.2, 0.6, 0.9, 1.8, 3.7, 8.8 ml of 1 mM H_2PtCl_6 solution were added into the as-prepared solution with stirring for 30 min to coat the Pd shell with different Pt coverage. And 25 % more of the H_2PtCl_6 was added into the solution in order to insure the amount needed of the H_2PtCl_6 to get the corresponding Pt coverage The volume of 1 mM H_2PtCl_6 (V) was precisely calculated according to the following equation:

$$V = \frac{\pi\left\{(R + \theta_{Pt}d)^2 \times (L + 2\theta_{Pt}d) - R^2 \times L\right\}}{V_{mol}}$$

R-the radius of Au@Pd;

L-the length of Au@Pd;

ϑ_{Pt}- the number of Pt monolayer;

d-the thickness of Pt monolayer;

V_{mol}-molar volume of Pt elements

Synthesis of Pd@Pt nanocubes

Pd nanocubes were prepared according to the literature.[2] Firstly, 1 mL of 10 mM H_2PdCl_4 was mixed with 8 mL of 20 mM cetyltrimethyl ammonium chloride (CTAC) solution, and then 1 mL of 100 mM ascorbic acid was added into the mixture rapidly with vigorous stirring at room temperature. To prepare Pd@Pt nanocubes with 0.5 monolayers equivalent Pt, 0.4 mL of 10 mM ascorbic acid and 0.2 mL of 1 mM H_2PtCl_6 was added into the solution while stirring. The solution was then heated to 80 °C and stirred for 30 min.

Nanocatalyst characterization

Nanocatalyst morphologies were characterized by TEM (Fig.S1). Note that it was difficult to visually 'see' the 2 layers of Pd or Pt at the surface since they were too thin. However, the Au@2Pd with various Pt coverage layers were successfully prepared according to the elemental analysis by ICP-AES. The loading amounts for different samples were shown in Table S1. The

mass ratio of Pt was increased with the increase of the Pt coverage thickness, and the composition of Au@Pd@Pt NPs on FTO was in accordance with the mass ratio of precursor.
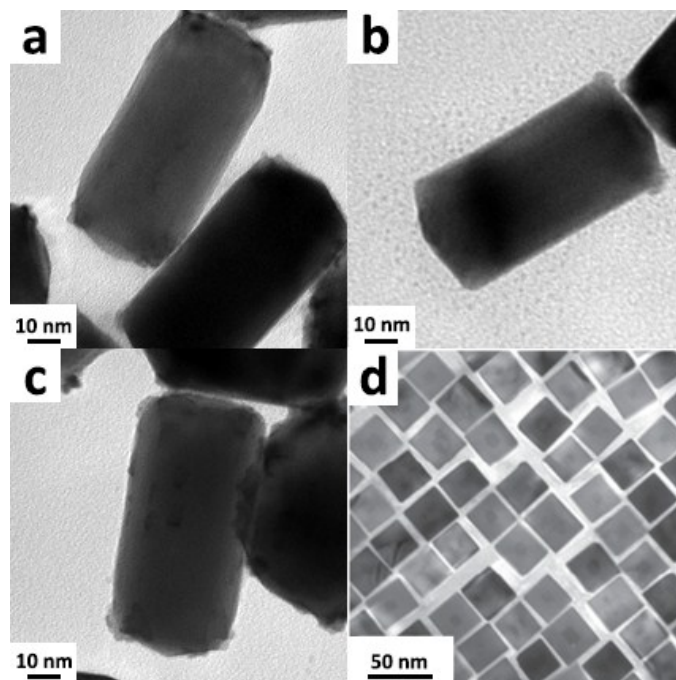
Figure S1 TEM images for Au@2Pd NRs (a) Au@2Pd@0.5Pt NRs (b), Au@2Pd@2Pt NRs (c) and Pd@Pt naocubes (d).

Table S1. The loading of Au@Pd@Pt with different Pt coverage on FTO

Sample	Mass of Au / mg	Mass of Pd / mg	Mass of Pt / mg	Total mass of NPs /mg
Au@2Pd@0.5Pt	0.28102	0.01421	0.0058	0.3011
Au@2Pd@1Pt	0.28772	0.01552	0.0143	0.3176
Au@2Pd@2Pt	0.29237	0.01607	0.0284	0.3368
Au@2Pd@5Pt	0.28045	0.01250	0.0488	0.3418

Electrochemical characterization of the presence of metal ions in Au@Pd@Pt NRs

To illustrate whether metal ions coated accurately at the NRs surface, cyclic voltammograms (CVs) of different metal NRs and nanocubes were measured, as shown in Figure S2. The unique hydrogen adsorption peak in Au was at about 0.8 V. With the increase of the thickness of other metals, the peak became weaker gradually. (Figure S2a) Figure S2b and S2c demonstrated the presence of Pd and Pt on the Au NRs. The peak at about +0.6 V represented the typical hydrogen

adsorption behavior at Pd surface. Since Au atoms was covered by Pd atoms, no peak was detected at +0.8 V for Au@2Pd nanoparticles.[3] In the lower potential region of Figure S2c, the symmetric sharp peaks resulting from the Pt clusters[4] also experienced slight variations with varied coverage of Pt clusters. For Pd@Pt nanocubes without Au core, no obvious peak was detected at about +0.8 V. The existence of Pd and Pt atoms were confirmed by their characteristic peaks at about +0.5 V and the sharp symmetric peaks, respectively.

To compare the catalytic performance of different nanomaterials, the measured currents were all normalized by the electrochemical active surface area (ECSA) of the corresponding nanocatalysts obtained in 0.5 M H_2SO_4. The ECSA of Au@Pd NRs, Au@Pd@Pt NRs and Pd@Pt nanocubes were calculated according to the integrated quantity of charge (Q) of hydrogen absorption peaks at around -0.3 V while ECSA for Au NRs was calculated based on the Q of oxygen absorption peaks in CV curves. Specifically, the ECSA was calculated by this equation:

$$ECSA = \frac{Q}{\Delta Q}$$

ΔQ: Standard quantity of charge of 1 mole ions in solution

ΔQ for hydrogen: 220×10^{-6} C/cm²

ΔQ for oxygen: 420×10^{-6} C/cm²
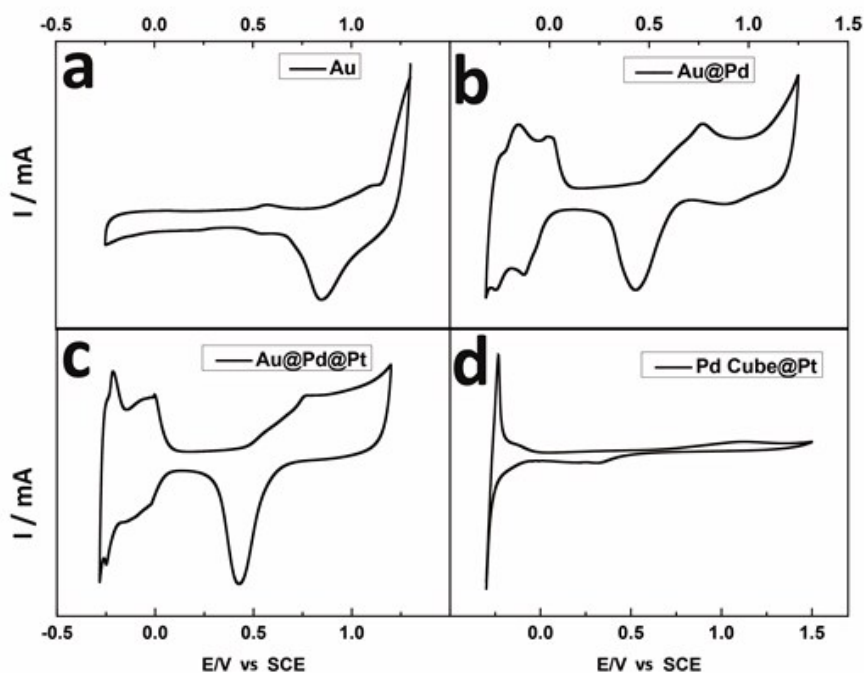
Figure S2 CVs of 49 nm Au NRs (a), 49 nm Au@Pd NRs (b), 49 nm Au@Pd@Pt NRs(c) and Pd@Pt Cubes (d) in 0.5 M H_2SO_4. Scan rates: 50 mV/s.

Control experiments on Au@Pd and Au@Pt nanocrystals

Control experiments were performed both on naked Au@Pd nanocrystals and Au@Pt nanoparticles. As shown in Figure S3, compared to Au@Pd and Au@Pt, the trimetallic catalyst showed better catalytic activity at the dark field, indicating the existence of synergistic effect of these three metals.
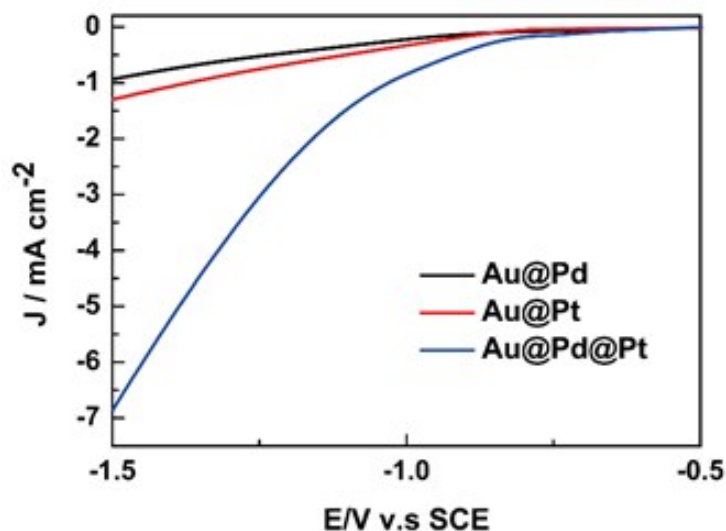

Figure S3 LSV curves of Au@Pd, Au@Pt and Au@Pd@Pt in 0.1 M KHCO$_3$ (pH = 6.8) without illumination. Scan rate: 50 mV/s

Photoelectrochemical measurements of Au@Pd@Pt NRs for CO$_2$ reduction

By tuning the thickness of Pt coverage, we systemically investigated the photocatalytic performance of Au@Pd@Pt NRs and NPs for electroreduction of CO$_2$. Figure S4 shows LSV curves of the 49 nm Au@Pd@Pt NRs with ϑ_{Pt} value ranging from 0.1 to 5. The current density was immediately increased when the working electrode was exposed to light illumination with an intensity of 100 mW cm^{-2}. In addition, Au@Pd nanocrystals coated by 0.5 monolayers of Pt clusters (ϑ_{Pt}=0.5) exhibited the highest catalytic activity as well as the optimum enhancement effect, and the photocatalytic activity decreased with the increase of Pt coverage thickness as the SPR resulting from Au core was gradually blocked by Pt coverage.

The increase of photocatalytic activity with illumination time was supposed to be caused both

by temperature augmentation and the photoelectronic effect from the Au core, inferring the SPR effect contributed to the photoelectrocatalytic reduction of CO_2.
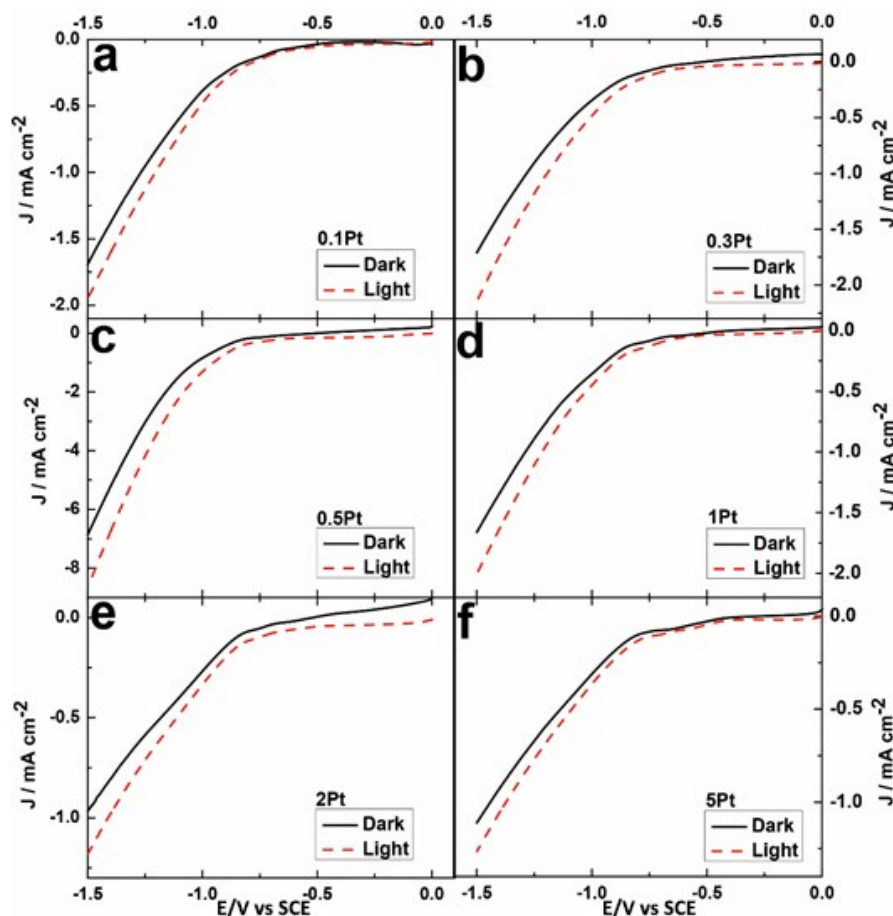

Figure S4 Light influence on LSV curves of Au@Pd@Pt NRs with different ϑ_{Pt} in 0.1 M KHCO$_3$ (pH = 6.8).Scan rate: 50 mV/s.

Product analysis by NMR

To collect the electrocatalytic reduction products of CO$_2$RR, the chronoamperometry was firstly conducted under a constant potential at -0.6 V for 2 h and the content of the electrolyte solution was then tested using NMR.$_1$H NMR data were acquired at 298 K on a Bruker 600 MHz Advance III HD spectrometer equipped with a 5-mm TCI cryoprobe. 1D $_1$H NMR spectra were recorded with a sweep of 16 ppm centered on the water, 1.7 s acquisition time, 2 s relaxation delay, gradient excitation sculpting water suppression, for the total of 16 scans. As presented in Figure 6, the trimetallic Au@Pd@Pt NRs were prone to convert CO$_2$ into liquid products including methanol and ethanol, which was in accordance with our Raman results (C-H stretching at 2800-2970 cm^{-1}). Moreover, larger amount of the liquid products was detected on Au@2Pd@0.5Pt compared to that obtained on Au@2Pd NRs at the same condition.

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