

# Photochemical Synthesis of Au@Pd Core-Shell Nanoparticles for Methanol Oxidation Reaction: the Promotional Effect of the Au Core

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**Abstract.** A novel method for synthesizing Au@Pd core-shell nanoparticles was proposed based on photochemistry. By irradiating the mixture of Au (III) and Pd (II) ions using ultraviolet light, the Au@Pd core-shell nanoparticles were prepared. The size of the nanoparticles and the thickness of the Pd shell could be efficiently adjusted by changing the molar ratio of Au (III) to Pd (II) ion. In this way, nanoparticles with diameter in the range of 5.6~4.6 nm were obtained. The core-shell structure of the synthesized nanoparticles was showed by the characterization using UV-Vis, TEM/HR-TEM and XPS. The paper investigated the electrocatalysis performance of Au@Pd nanoparticles in the methanol catalytic oxidation reaction, as well as the electron donating effect of Au core to Pd shell and the promotion of this effect on the catalytic activity of Pd shell. The experimental results provided reference for the development of non-platinum catalysts of low-temperature fuel cell anode.

## 1 Introduction

Low-temperature fuel cells, including proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), etc, are a kind of green energy technology which transfers the chemical energy of the fuel directly to electric energy without combustion. At present, the cells are of great significance in solving the energy shortage and environmental pollution worldwide and regarded as one of the most important energies in 21th century. In the cells, the electrode catalyst, particularly anode catalyst generally uses platinum (Pt) -based catalysts. In recent years, owing to the promising application prospect in electronics and optics, and the catalytic effect, the bimetallic nanoparticles have been considered to be widely used in electronics and optics, and the catalysts, and have drawn a lot of attentions.<sup>[1,2]</sup> Among which Au@Pd nanoparticles, which are used as catalysts in low-temperature fuel cells, have been a research focus. Jim Yang Lee et al<sup>[3]</sup> conducted HCOOH oxidation reaction by applying Au@Pd core-shell nanoparticles and found that the nanoparticles showed a high catalytic activity in perchloric acid medium; the small size of Au core possibly promoted the catalytic activity.

Regarding the preparation of Au@Pd core-shell composite nanoparticles, many methods have been studied intensively, including chemical reduction method<sup>[4]</sup>, sonochemical method<sup>[5]</sup> and microwave method<sup>[6]</sup>. However, the synthesis method which can precisely control the size of the composite nanoparticles and the thickness of the shell, with simplified, economic,

and green process, has seldom been reported. The paper presented a novel method for synthesizing Au@Pd core-shell nanoparticles based on photochemistry. The mixture of Au (III) and Pd (II) ions was irradiated by ultraviolet light of 300 nm in the PEG (polyethylene-glycol)-acetone solution system (co-reduction). It was showed from characterization using UV-Vis, TEM, HR-TEM and XPS that the core-shell nanoparticles with uniform size and monodispersity were obtained. Based on the electrochemical workstation, the paper investigated the electrocatalysis performance of Au@Pd nanoparticles for the methanol catalytic oxidation reaction (MOR), as well as the electron donating effect of Au core on the dissimilar metal (Pd) shell and the promotion of this effect on the catalytic activity of Pd shell.

## 2 Experimental methods

### 2.1 Preparation of products

Certain amounts of PEG-400, acetone and different molar ratios of HAuCl<sub>4</sub> and PdCl<sub>2</sub> (the molar ratios of Au to Pd elements are 4:1, 1:1 and 1:4, respectively, and the total molar amount of noble metal is 1.22×10<sup>-5</sup> mol). Then water was used to get the constant volume. After being mixed sufficiently, the solution was transferred into a quartz container and then exposed 4 cm away under ultraviolet light. UV-Vis spectra were recorded as time passed by until the spectral curve was the same as the previous one, which indicated that the reduction finished.

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The single Au and Pd nanoparticles were prepared similarly. All the reagents were analytical pure and the water was ultrapure.

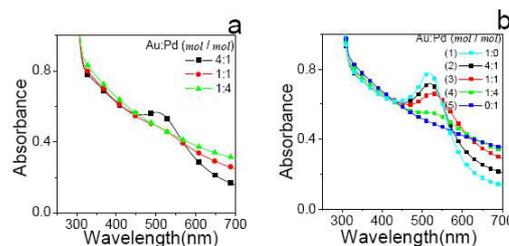
## 2.2 Characterization

Images of the prepared nanoparticles were taken by transmission electron microscopy (TEM). The sample was prepared by dropping several drips of colloidal solution on carbon support film copper grid and dried at room temperature. Then the images were taken on H-800 TEM which operated at a voltage of 200 kV. By adopting lacey support film grid, HR-TEM detection was conducted, and the images were taken on Tecnai G<sup>2</sup> F20 field emission TEM operated at a voltage of 200 kV. Meanwhile, XPS was performed on the sample as well. The obtained nanoparticles were loaded on XC-72 carbon black for electro-chemical measurements based on the method reported in literature<sup>[7]</sup>. The electro-chemical measurement was conducted at 30 °C, and three-electrode system was adopted with Pt as the counter electrode and SCE (Saturated calomel electrode) as reference electrode. The dissolved oxygen in the electrolyte was 0.5 mol·L<sup>-1</sup> KOH + 2.0 mol·L<sup>-1</sup> CH<sub>3</sub>OH. Before the measurement, high pure N<sub>2</sub> was bubbled into the electrolyte to remove the dissolved oxygen and then CV curves were recorded in the N<sub>2</sub> atmosphere. The measuring conditions are as follows: potential is in the range -0.6~0.8 V, potential scan rate is 50 mV·s<sup>-1</sup>, and I-t curves are tested at electric potential of -0.3 V.

## 3 Results and discussion

### 3.1 Characterization of Au@Pd nanoparticles

In the selected solution system, the surface plasmon resonance (SPR) absorption spectra of obtained Au@Pd colloidal solution were shown in Figure 1a, and the absorption spectra of Au and Pd colloidal solutions and their mixture are displayed in Figure 1b. It is clearly demonstrated that the transition feature from Au to Pd of the synthesized Au@Pd bimetallic colloidal particles; while the latter one shows distinct superposition property. This indicated that in the co-reduction of Au (III) and Pd (II) ions based on photochemistry, owing to AuCl<sub>4</sub><sup>-</sup> presents higher reduction potential (AuCl<sub>4</sub><sup>-</sup>/Au E<sup>0</sup>=+1.0 V; PdCl<sub>4</sub><sup>2-</sup>/Pd, E<sup>0</sup>=+0.6 V), Au was photoreduced as the seed in priority and autocatalyzed to nanoparticles; afterward, the Pd (II) ions in the solution were catalyzed on the surface of Au nanoparticles, therefore forming the Au@Pd core-shell composite nano-structure. Considering the Au@Pd nanoparticles, as the molar ratio of Au to Pd reduces, the Au seeds are coated by Pd atoms gradually. When Au:Pd=1:1, the characteristic absorption band of Au does not completely disappear in the SPR absorption spectra of composite particles. It indicates that the Pd shell is still thin or the Pd does not completely coat on Au seed. This was basically consistent with the results in literature<sup>[4]</sup>.



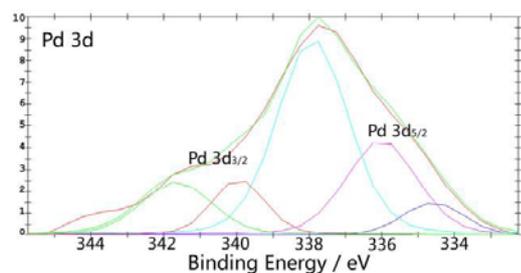
**Figure 1.** UV-Vis spectra of Au@Pd (a) and Au, Pd and their mixture (b) colloidal solution.

The structure of Au@Pd composite nanoparticles was analyzed using X-ray photoelectron spectroscopy (XPS). The results are listed in Table 1. It is observed that the molar ratio of Au to Pd in the surface structure of the nanoparticles is much less than that in the solution in the preparation. This states that there is higher Pd atomic fraction in the surface structure of Au@Pd nanoparticles and further proves the core-shell nano structure of the as-prepared Au@Pd. The results are in line with literature<sup>[6]</sup> and the above characterization using UV-Vis absorption spectra.

**Table 1.** XPS analysis of Au@Pd nanoparticles and Pd 3d<sub>5/2</sub> binding energy.

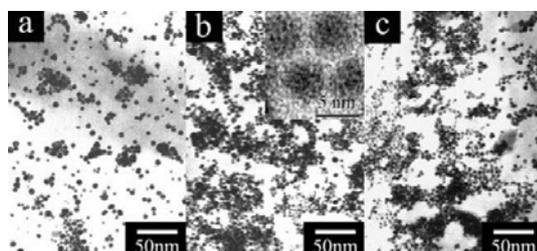
Au:Pd (molar ratio)		4:1	1:1	1:4
Atom ratio	Au%	67.4	32.1	6.6
	Pd%	32.6	67.9	93.4
Pd 3d <sub>5/2</sub> Binding Energy (eV, E <sub>0</sub> = 335.10 eV <sup>[8]</sup> )		333.84	334.59	334.64
Δ E ( Binding Energy, eV; )		-1.26	-0.51	-0.46

In the linear fitting of spectral lines of the XPS energy spectra of the samples, it is observed that there are two spectral peaks in Pd 3d electronic spectrogram (Figure 2). Compared with the energy spectra<sup>[8]</sup> of standard palladium, the peak near 334 eV is simple substance Pd (Pd 3d<sub>5/2</sub>, 335.1 eV); while the one around 336 eV is oxidized Pd (PdO 3d<sub>5/2</sub>, 336.3 eV). This illustrates that the Pd atoms on the surface of Au@Pd composite particles are prone to be oxidized. Furthermore, the binding energy of Pd in Au@Pd particles decreases with the decrease of molar ratio of Au to Pd (Table 1), indicating that the Au core supplies electrons for the Pd on the external surface, and the electron donating intensity is associated with the ratio of core to shell.



**Figure 2.** XPS spectra of Pd 3d of Au@Pd particles (Au:Pd = 1:1).

In the aforementioned molar ratio of Au to Pd condition, the images of synthesized Au@Pd particles taken by the transmission electron microscopy (TEM) are illustrated in Figure 3. The Au@Pd particles with uniform size and good dispersion are observed from the figures, and the average diameters are 5.6, 5.0 and 4.6 nm, respectively. The inset in Figure 3b is the HR-TEM image. Lattice fringes are clearly observed from the spherical Au@Pd particles of 5 nm, which represents that the composite particles are nano-crystalline. However, owing to the similar metallic lattice constants of Au and Pd, these two atoms are prone to mutually permeate to form solid solution. As a result, the clear metallic phase interfaces are hardly observed even from HR-TEM.

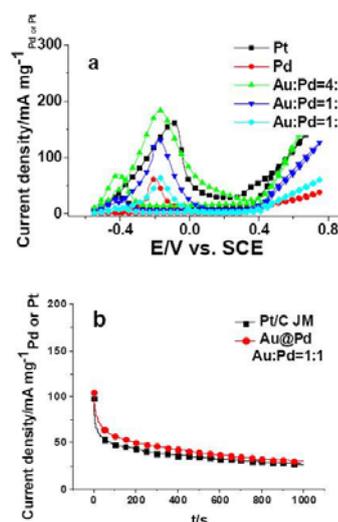


**Figure 3.** TEM images of Au@Pd nanoparticles: Au:Pd=4:1 (a), 1:1 (b) and 1:4 (c).

### 3.2 MOR activity of Au@Pd core-shell nanoparticles

Figures 4a and 4b demonstrate the cyclic voltammograms (CV) curves and time-current (I-t) curves for MOR of prepared Au@Pd/C with different molar ratios of Au to Pd, single Pd/C and Pt/C catalysts in alkaline solution, respectively. Thereinto, the Pt/C was purchased from Johnson Matthey Company. The CV curves in Figure 4a illustrate that in the positive scan of all the electrodes formed by the catalyst samples, methanol is catalyzed and oxidized on the surface of electrode at  $\sim -0.15$  V, therefore generating oxidation peak currents. This indicates that all the samples present catalytic activity for MOR. Based on the calculation according to the data in Figure 4a, it is seen that the activity of pure palladium

sample is apparently lower than that of platinum sample; the peak current of Pd/C merely accounts for 40% of that of Pt/C ( $64.4 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$  and  $161.2 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pt}}$ , respectively). While regarding Au@Pd sample, as the molar ratio of Au to Pd increases from 4:1 to 1:4, the catalytic activity of Pd increases significantly and the peak currents are 68.5, 133.0 and  $181.4 \text{ mA}\cdot\text{mg}^{-1}_{\text{Pd}}$ , respectively. Of which, when Au:Pd=4:1, the activity of Pd is 12.5% higher than that of Pt. This explains that Au core promotes the electrocatalytic activity of Pd shell. Furthermore, it is observed from the comparison of XPS characterization data that the promotion trend of Au core for the electrocatalytic activity of Pd shell is the same with that of Au core supplying electrons for the Pd shell. Based on the analysis and owing to Au is the last element on the 5d complete orbit, it is speculated that Au is affected by the relativistic effect most greatly<sup>[9]</sup>. Moreover, the electron contraction for 6s increases the electron cloud density and decreases the barriers of the hybridization between Au and Pd atoms. This is beneficial for the generation of large conjugated system by the interaction of Au and Pd atoms. Meanwhile, owing to the electronegativity ( $X=2.4$ ) of Au is larger than that of Pd ( $X=2.2$ ), part of 5d electrons of Au flows into the 4d orbit of Pd and causes part of negative charge on Pd. In this way, the shielding effect on the inner shell electrons increases, therefore reducing the electron binding energy on the inner orbit. As observed, there is a displacement of binding energy to low-end on the XPS spectra. The supplement of electrons of Au core to Pd shell efficiently improves the d-electron orbit cavity of Pd shell, which is the key reason of the outstanding catalytic activity exhibited by Au@Pd core-shell nanoparticles<sup>3</sup>. Additionally, the core-shell structure increases the specific surface area of Pd shell, which is possibly another reason for the improvement of Pd catalytic activity. The I-t curves of Pt/C and Au@Pd/C (Au:Pd=4:1) are illustrated in Figure 4b. It is observed that the Au@Pd core-shell nanoparticles exhibit a stable electrocatalysis.



**Figure 4.** CV (a) and I-t (b) of Au@Pd/C in  $0.5 \text{ mol}\cdot\text{L}^{-1}$  KOH +  $2.0 \text{ mol}\cdot\text{L}^{-1}$  CH<sub>3</sub>OH solution.

## 4 Conclusions

In the PEG-acetone system, the paper synthesized the Au@Pd core-shell nanoparticles with uniform size and monodispersion by reducing the mixture of Au (III) and Pd (II) based on photochemistry. The characterization using UV-Vis absorption spectra, TEM/HR-TEM and XPS showed that the core-shell structure nanoparticles were obtained and the Au core supplied electrons for Pd shell. The electrochemical analysis indicated that the activity of Pd for MOR increases with the increase of molar ratio of Au to Pd. Furthermore, the electron donating of Au core for Pd shell was investigated, as well as its promotion for the catalytic activity of Pd shell.

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## References

1. D. Stolten, B. Emons. *Platinum Metals Rev.*, **66**, 57 (2013)
2. Y. N. Dong, S. S. Li, L. Cong. *Yunnan Chemical Technology*, **21**, 39 (2012)
3. W. L. Zhou, J. Y. Lee. *Electrochem. Commun.*, **1725**, 9 (2007)
4. J. f. Li, J. W. Hu, B. Ren. *Acta. Phys-Chim. Sin.*, **825**, 21 (2005)
5. C. Kan, W. Cai, C. Li, L. Zhang. *J. Phys. D*, **1609**, 36 (2003)
6. R. Harpeness, A. Gedanken. *Langmuir*, **3431**, 20 (2004)
7. J. H. Zeng, J. Yang, J. Y. Lee. *J. Phys. Chem. B*, **24606**, 110 (2006)
8. F. M. John. *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Physical Electronics DiVision, 1992)
9. Y. N. Dong, S. A. Dong, C. Tang. *Rare Met Mater and Eng*, **789**, 42 (2013)