



Short communication

# PdPt@Au core@shell nanoparticles: Alloyed-core manipulation of CO electrocatalytic oxidation properties



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## ABSTRACT

A series of PdPt@Au core@shell nanoparticles (NPs) of similar size are synthesized with composition controlled cores and thickness controlled shells. Their CO electrocatalytic oxidation properties change with the composition of the cores, showing a volcano curve. A correlation between the properties of CO electrocatalytic oxidation and the location of adsorbed CO ATR-IR peak is discovered. Attenuated Total Reflection-Infrared Spectroscopy (ATR-IR) shows that samples which have the strongest monodentate CO are most active in CO electrocatalytic oxidation.

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## 1. Introduction

Polymetallic nanoparticles (NPs) are not only a simple combination of two distinct metals but also expected to display new properties and capabilities due to a synergy between different metals [1,2,3]. More importantly, core@shell nanoparticles usually show composition-dependent surface structure and atomic segregation behavior [4–6]. Due to their novel catalytic [7,8], electronic [9–13] and magnetic properties [14–16], core@shell nanoparticles attracted more attention in these years. However, preparation of core@shell nanoparticles with ideal monodispersity still is a challenge, and ideal crystal face that is much different from the industrial catalyst is usually used by researchers [17]. In this work, we made model catalysts that are closer to real catalysts to explore the effect of the core and shell. A series of PdPt@Au core@shell nanoparticles of similar size were synthesized with composition controlled cores and thickness controlled shells. They show a volcano curve in electrocatalytic oxidation of CO. And from the Attenuated Total Reflection-Infrared Spectroscopy (ATR-IR) spectra of CO adsorption, we can see the strongest monodentate CO is most beneficial to the CO electrocatalytic oxidation. Furthermore, a correlation between the activity of CO electrocatalytic oxidation and the location of adsorbed CO ATR-IR peak is discovered.

## 2. Experimental

### 2.1. Synthesis of the samples

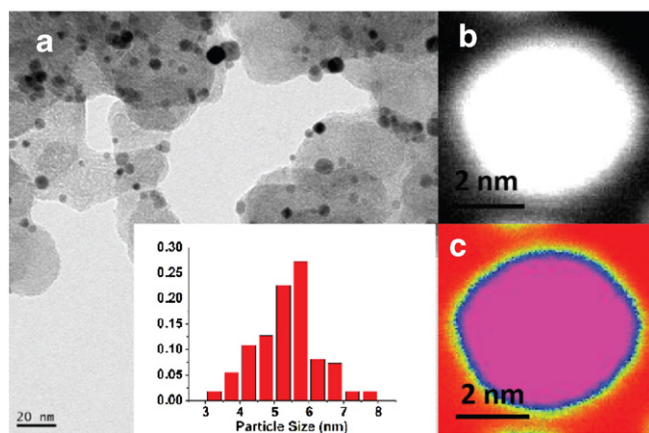
The PdPt@Au NPs were synthesized through a seeded-growth method consisting of two steps. (See the Supporting materials for details.) Firstly, the core seeds that stabilized by PVP were synthesized in the solvent of ethylene glycol. Then, they were transferred into H<sub>2</sub>O to grow the Au shell. Before further study, the samples were washed with ethanol and ultrapure water by repeating the centrifugation and re-dispersion procedure several times to remove the excess PVP, chloride ions and other impurities. Then, these washed core@shell NPs were supported on carbon black Vulcan XC-72 (20 wt%). (See the Supporting materials for details.) The deposited NPs were washed extensively with ethanol and ultrapure water to remove any residual chloride ions and PVP before electrochemical measurements.

### 2.2. Characterization

Powder X-ray diffraction (XRD) data was collected on a Shimadzu XRD-6000 X-ray diffractometer using a Cu K $\alpha$  radiation source operating at 40 kV and 30 mA. Transmission electron microscopy (TEM) observations were collected on a JEOL JEM-2100 TEM. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were collected on a JEOL JEM-2100F TEM. Attenuated Total Reflection-Infrared Spectroscopy (ATR-IR) spectra were acquired using a Bruker Vertex 70 with a liquid-nitrogen-cooled MCT detector.

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**Fig. 1.** (a) TEM image of carbon-supported PdPt@Au (Pd:Pt = 1:1) NPs. The average size of the sample is 5.36 nm. (b) HAADF-STEM image of the sample. (c) Pseudo-colored HAADF-STEM images of the sample. The purple section is the alloy core and the blue section is the Au shell.

### 2.3. CO electrocatalytic oxidation tests

The catalytic activity of the carbon supported core@shell NPs in the electrooxidation of CO was examined by voltammetric measurements. Electrochemical studies were carried out in a standard three-electrode cell connected to a CHI-440 electrochemical workstation, with a Pt foil counter electrode and a standard calomel electrode (SCE) at room temperature in 0.1 M HClO<sub>4</sub> solution. To prepare the working electrode, 5 mg carbon-supported core@shell NPs was dispersed ultrasonically in 1 mL 5 wt% Nafion solution to form an ink, and 10  $\mu$ L of the ink was pipetted onto a glassy carbon (GC) substrate ( $\Phi = 5$  mm), which had been buff-polished with an alumina suspension ( $\Phi = 0.05$   $\mu$ m) prior to use. The catalyst-coated electrode was dried under an infrared lamp.

Before executing the CO oxidation by positive-going linear sweep voltammetry, the electrolyte was firstly deaerated by bubbling Ar for 30 min. Then three cycles of voltammetry were run, with potential limits of  $-0.28$  to  $0.90$  V, to ensure the cleanliness of the sample. In order to adsorb CO at a saturated coverage on the electrode, CO was bubbled through the electrolyte for 30 min while the electrode was under potentiostatic control at  $0.20$  V. After the CO adsorption process, dissolved CO was removed from the electrolyte by bubbling Ar for 1 h. This process simultaneously ensures a full coverage of CO on the electrode and complete removal of CO from the electrolyte [18]. Then, the CO was electro-oxidized by scanning the potential at  $20$  mV/s from  $-0.28$  V to  $0.90$  V, followed by several cycles of voltammetry.

## 3. Results and discussion

### 3.1. TEM and HAADF-STEM characterization

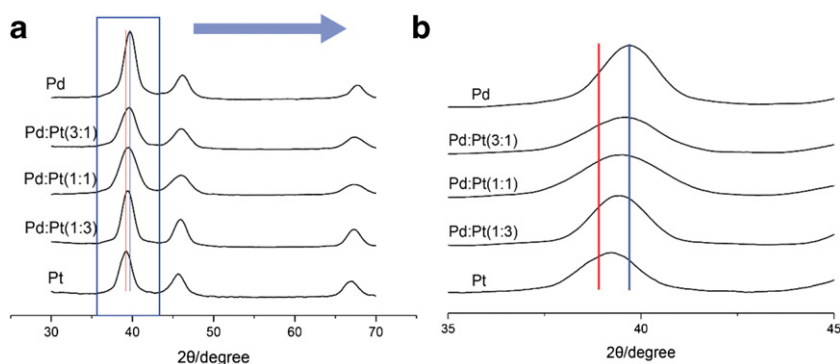
The TEM image in Fig. 1a indicates that the PdPt@Au (Pd:Pt = 1:1) NPs are dispersed uniformly on the carbon support. Most of the NPs are in spherical shape. The size distribution analysis in Fig. 1a shows that the particles have an average size of 5.36 nm. A typical HAADF-STEM in Fig. 1b shows the alloy core appears to be bright relative to the Au shell, but the Au shell is too thin to get clear contrast. There is limited information due to the monochrome image. So we get the pseudo-colored HAADF-STEM image showing in Fig. 1c according to the monochrome one [19]. From the pseudo-colored HAADF-STEM image, we can easily distinguish the alloy core in purple from the Au shell in blue. In addition, we can find that the core is packed by the Au shell perfectly and the Au shell is only about several atomic layers. The rest four samples are almost the same to PdPt (Pd:Pt = 1:1) NPs in pseudo-colored HAADF-STEM image. The average sizes of the five samples are arranging from 4.02 nm to 5.97 nm. TEM, HAADF-STEM and pseudo-colored HAADF-STEM images of Pd@Au, PdPt@Au (Pd:Pt = 3:1), PdPt@Au (Pd:Pt = 1:3) and Pt@Au NPs are in the Supporting materials (Figs. S1–S4).

### 3.2. XRD characterization

The XRD patterns of the alloy seeds without the Au shell are showed in Fig. 2. The data (Fig. 2a) indicate that all of the compositions resulted in a single phase: a solid solution of Pd and Pt atoms. And the (111) peaks of Pt, PdPt (Pd:Pt = 1:3), PdPt (Pd:Pt = 1:1), PdPt (Pd:Pt = 3:1) and Pd NPs locate separately at  $39.22^\circ$ ,  $39.37^\circ$ ,  $39.47^\circ$ ,  $39.59^\circ$ ,  $39.70^\circ$ . They arrange from  $39.22^\circ$  to  $39.70^\circ$ , showing a regular pattern in Fig. 2b. Lattice expansion is also found in these XRD patterns for the peak skewing to low angle contrasting to standard XRD cards, as a result of small size [20].

### 3.3. CO electrocatalytic oxidation and AIR-IR tests of CO adsorption

The catalytic activity of the carbon supported core@shell NPs and alloy NPs in the electrocatalytic oxidation of CO was examined by voltammetric measurements. The influence of the core composition on the positive-going linear sweep voltammetry turn-on potentials is showed in Fig. S7. (CO-stripping voltammetry curves are showed in Fig. S5, see the Supporting materials for details.) The PdPt@Au/C sample with a core of Pd:Pt = 1:1 has the lowest CO stripping turn-on potential. That means that the CO electrocatalytic activity of PdPt@Au (Pd:Pt = 1:1) sample is superior to that of PdPt@Au samples with other PdPt-ratio cores. And we also can conclude that Pt@Au/C sample is more active than Pd@Au/C sample and PdPt@Au/C samples with Pd-rich cores,



**Fig. 2.** (a) XRD patterns of the alloy seeds without the Au shell, containing Pd NPs, PdPt (Pd:Pt = 3:1) NPs, PdPt (Pd:Pt = 1:1) NPs, PdPt (Pd:Pt = 1:3) NPs and Pt NPs. (b) Parts of the XRD patterns from  $25^\circ$  to  $45^\circ$ .

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