

## Supported Bimetallic PdAu nanoparticles with superior electrocatalytic activity towards methanol oxidation

Zhen Yin,<sup>a</sup> Miaofang Chi,<sup>b</sup> Qingjun Zhu,<sup>c</sup> Ding Ma,<sup>\*d</sup> Junming Sun,<sup>e</sup> Xinhe Bao<sup>f</sup>

<sup>a</sup> School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, P. R. China

<sup>b</sup> Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>c</sup> National Institute of Clean-and-Low-Carbon Energy, Beijing, 102209, P.R.China

<sup>d</sup> Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China. E-mail: dma@pku.edu.cn;

<sup>e</sup> School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, USA

<sup>f</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, P. R. China.

**Chemicals.** Oleic acid (OA, Alfa Aesar, 90%), oleylamine (OAm, Acros, 97%), and gold acetate of  $\text{Au}(\text{CH}_3\text{COO})_3$  (Alfa Aesar, 99.9%) were used as obtained. Palladium acetate of  $\text{Pd}(\text{CH}_3\text{COO})_2$  (AR) and ethylene glycol (EG, AR) were provided from Sino-Platinum Metals Corporation and Sinopharm Chemical Reagent Corporation, respectively, and were used without further purification. Aqueous solutions were prepared with the deionized water purified through a Millipore system (18.2  $\text{M}\Omega\cdot\text{cm}$ ).

**Synthesis of Bimetallic PdAu Nanoparticles.** In a typical synthesis of PdAu nanoparticles studied in this report, 1.5 mmol OA and 1.5 mmol OAm were firstly mixed with 25 mL EG in a three-necked round-bottom flask to form turbid solution under mechanical stirring, two metal precursor solutions of 0.25 mmol  $\text{Pd}(\text{CH}_3\text{COO})_2$  in acetone and 0.25 mmol  $\text{Au}(\text{CH}_3\text{COO})_3$  in water were then added to the solution. The mixture was

stirred vigorously and heated to 120 °C. Subsequently, the solution was hold at 120 °C for two hours with argon flow passing through the reaction system to take away water, acetone and other organic by-products. The as-prepared colloidal nanoparticle mixture was separated by extraction with 50 mL hexane after the solution was cooled down to room temperature. The colloidal solution in hexane was further concentrated in a rotary evaporator, then repeatedly washed by a mixture of hexane/ethanol (1:30) and separated by centrifugation (10000 rpm for 20 min) until the supernatant solution was clear. The obtained PdAu nanoparticle precipitates were black and could be easily re-dispersed in a non-polar organic solvent, such as hexane or toluene.

Bimetallic PdAu nanoparticles with three different compositions were prepared by the same procedures in which different molar ratio of Pd and Au metal precursors were added in the solution. Inductively coupled plasma spectroscopy (ICP) was used to determine the actual Pd and Au contents in Pd/Au nanoparticles. The measured compositions of PdAu nanoparticles, as listed in Table1, were denoted as Pd<sub>30</sub>Au<sub>70</sub>, Pd<sub>45</sub>Au<sub>55</sub> and Pd<sub>64</sub>Au<sub>36</sub>, where the numerical subscripts denote the atomic percentage in the corresponding nanoparticles, with the molar ratio of Pd to Au precursors 1:1, 2:1 and 5:1, respectively. For comparison, pure Pd and Au nanoparticles were synthesized under the same reaction conditions but without the addition of the other component during the synthesis.

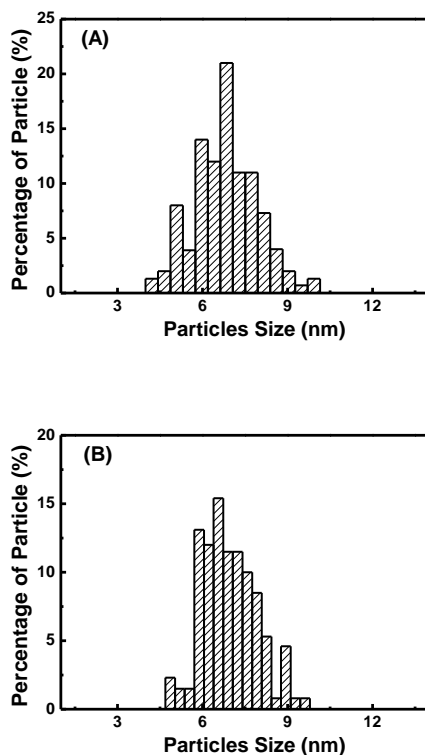
**Preparation of Catalysts with PdAu Nanoparticles Supported on Carbon.** Typically, the Vulcan XC-72 carbon black (Cabot) powder (200 mg) was added slowly to the colloidal suspension of PdAu in hexane (100 mL). The slurry was stirred in air at room temperature. The solid phase was separated by centrifugation after one day, and dried in an oven under

vacuum at 55 °C for another three hours to obtain the supported catalyst. Capping ligands on the nanoparticle surface was removed through ethanol washing as a post-treatment. The metal loadings of carbon-supported PdAu catalysts (PdAu/C) were in the range of 10 - 20 wt %, depending on the concentrations of different PdAu nanoparticles in the colloidal suspension. Pure Pd nanoparticles were loaded on carbon and the sample was designated as Pd/C. In contrast, a commercial catalyst of Pt/C with 28.4 wt % Pt loading was kindly provided from TKK, and the sample was denoted as Pt/C (TKK).

**Characterization.** The UV-vis spectra were acquired with nanoparticles in hexane solution on a JASCO V-550 spectrophotometer in the range from 300 to 900 nm. Electron microscope specimens were prepared by dispersing the suspension of nanoparticles in hexane and drop-casting it onto TEM copper-grids. The transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 Spirit microscope equipped with a Gatan CCD camera and with an energy dispersive X-ray (EDX) system from EDAX Inc at an accelerating voltage of 120 kV. The particle size distribution was obtained by analyzing at least 200 particles on the TEM images using the Image software from Gatan. The high resolution TEM (HR-TEM) images were recorded on a FEI Tecnai G2 microscope at an accelerating voltage of 300 kV with a point resolution of 0.20 nm. High resolution Scanning TEM (STEM) imaging and EDX line scanning were performed on a Cs-corrected JEOL 2200FS equipped with a Bruker SDD X-ray detector. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with a Cu K $\alpha$  X-ray source ( $\lambda=1.5405$  Å) operated at 40 kV with a scan rate of 0.083° 2 $\theta$ /s. The compositions of the nanoparticles were analyzed by an inductively coupled plasma-atomic emission spectrometer

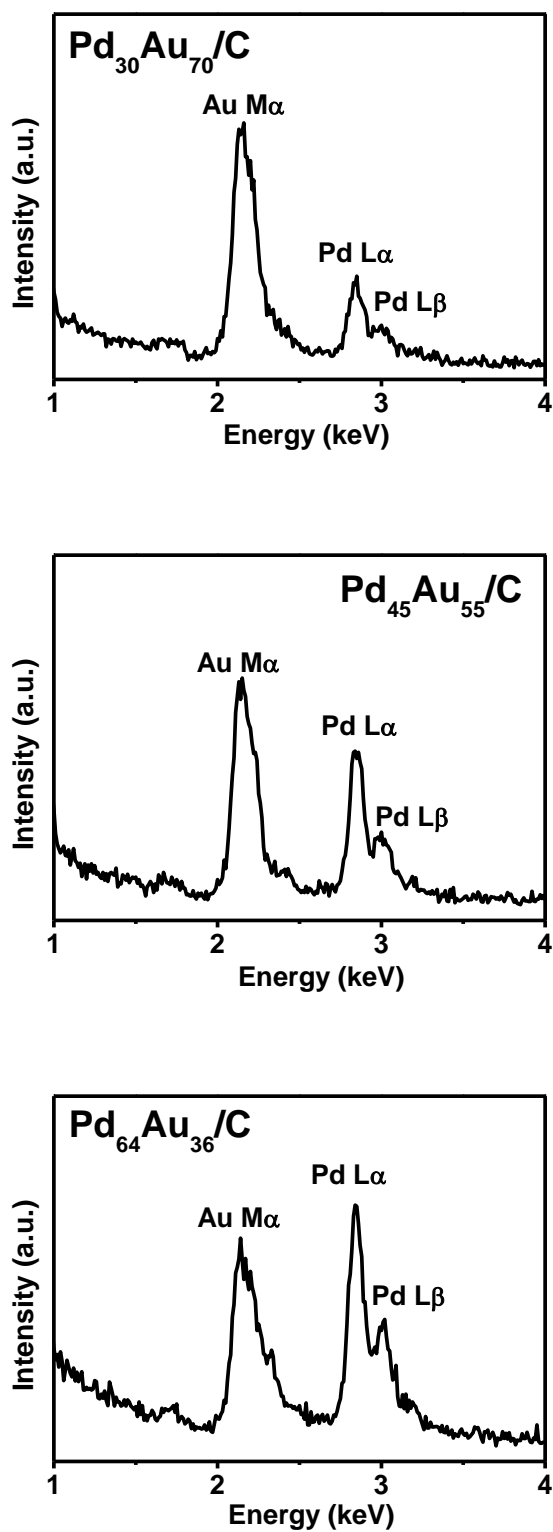
(LEEMAN, PLASMA-SPEC-II). XPS spectra were measured on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K $\alpha$  radiation.

**Electrochemical Measurement.** The electrocatalysis measurements were performed with a thermostated three-electrode glass cell at room temperature. The working electrode was a thin layer of Nafion-impregnated catalyst cast on a glassy carbon electrode (GCE) (4 mm in diameter) prepared as follows: the catalyst slurry was first prepared by mixing 1 mL of isopropanol, 5 mg of catalyst and 50  $\mu$ L of Nafion (5 wt %, DuPont ) under ultrasonic for 30 min to get the catalyst ink. Then 10  $\mu$ L of this ink was transferred onto a freshly polished GCE embedded in a Teflon mold by a syringe, followed by evaporation of solvent in air. A Pt wire was used as the counter electrode, and a Hg/HgO/1 M KOH electrode (0.098 V vs. SHE) served as the reference electrode. Before Cyclic voltammograms (CV) measurements were recorded, the electrolyte was purged with nitrogen for 30 min, and numerous CV cycles (sweeping rate: 50 m V $\cdot$ s $^{-1}$ ) were performed between  $-0.8$  and  $0.35$  V to stabilize the electrode surface. Cyclic voltammograms were carried out at room temperature in 1.0 M methanol + 1.0 M KOH solution, which was degassed with N<sub>2</sub> prior to the experiments. N<sub>2</sub> bubbling was maintained during the measurements. All potentials were referred to the Hg/HgO/1 M KOH electrode in this report. Oleic acid (OA, Alfa Aesar, 90% ,tech), oleylamine (OAm, Acros, 97%), ethylene glycol (Sinopharm), palladium acetate (Sino-Platinum) and copper acetate (Tianjin Kermel) were used as received. Aqueous solutions were prepared with the water purified through a Millipore system (18.2 M $\Omega$ ·cm). A commercially available catalyst of 28.4 wt% Pt/C was obtained from TKK.

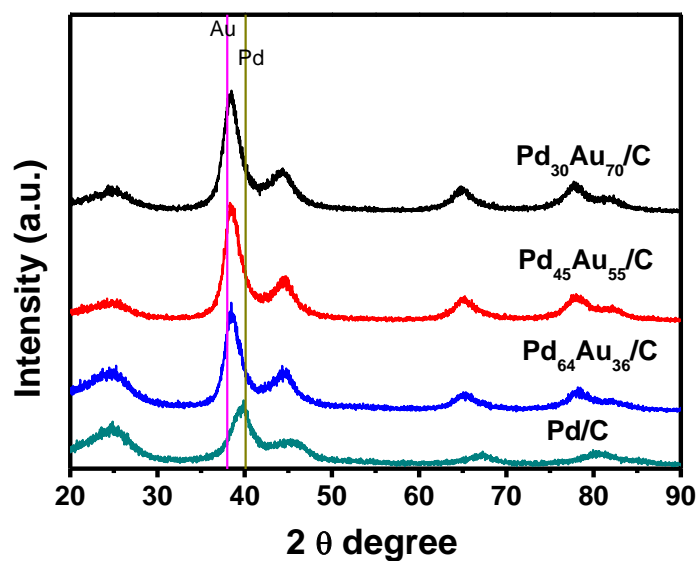


**Figure S1.** Size distributions of the PdAu nanoparticles with different composition: (A)

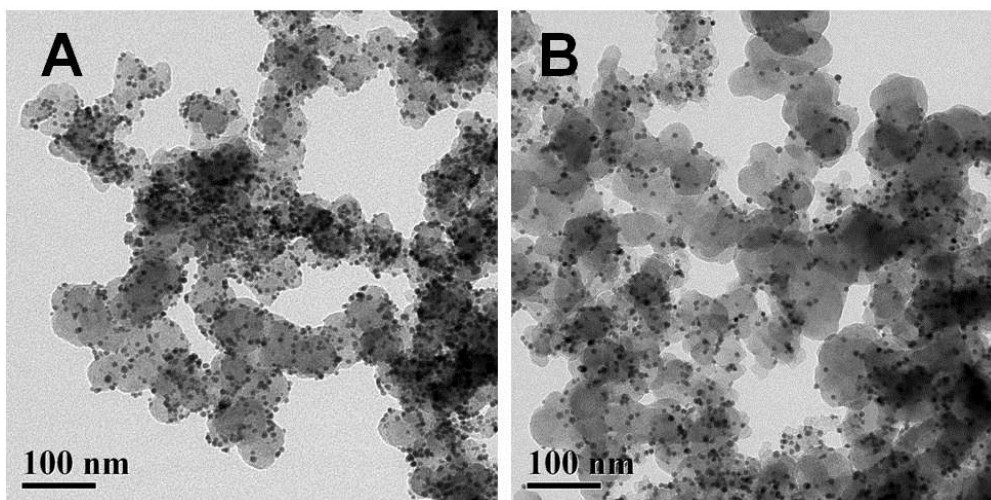
Pd<sub>45</sub>Au<sub>55</sub>, the average size was 6.6 nm; (B) Pd<sub>64</sub>Au<sub>36</sub>, the average size was 6.8 nm.



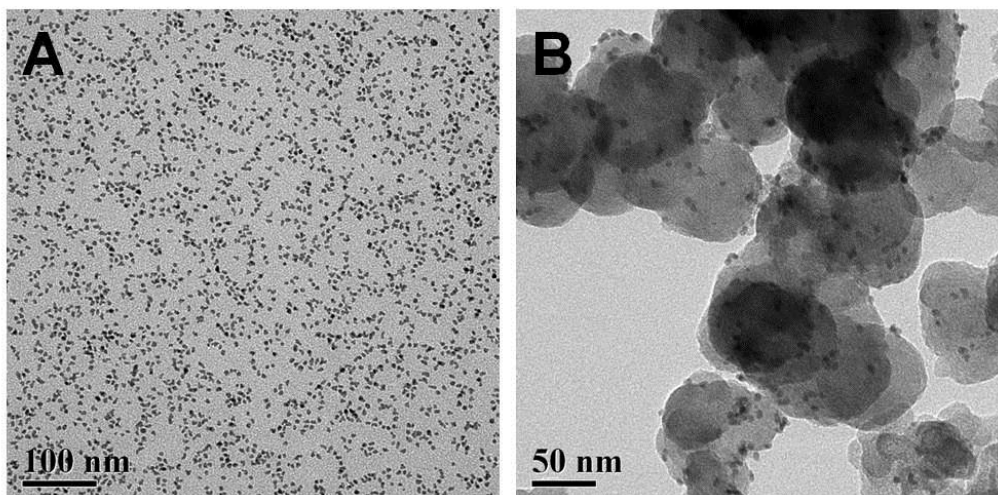
**Figure S2.** EDX spectra obtained from TEM for the bimetallic PdAu/C catalysts.



**Figure S3.** XRD patterns of the bimetallic PdAu and Pd nanoparticles supported on carbon.

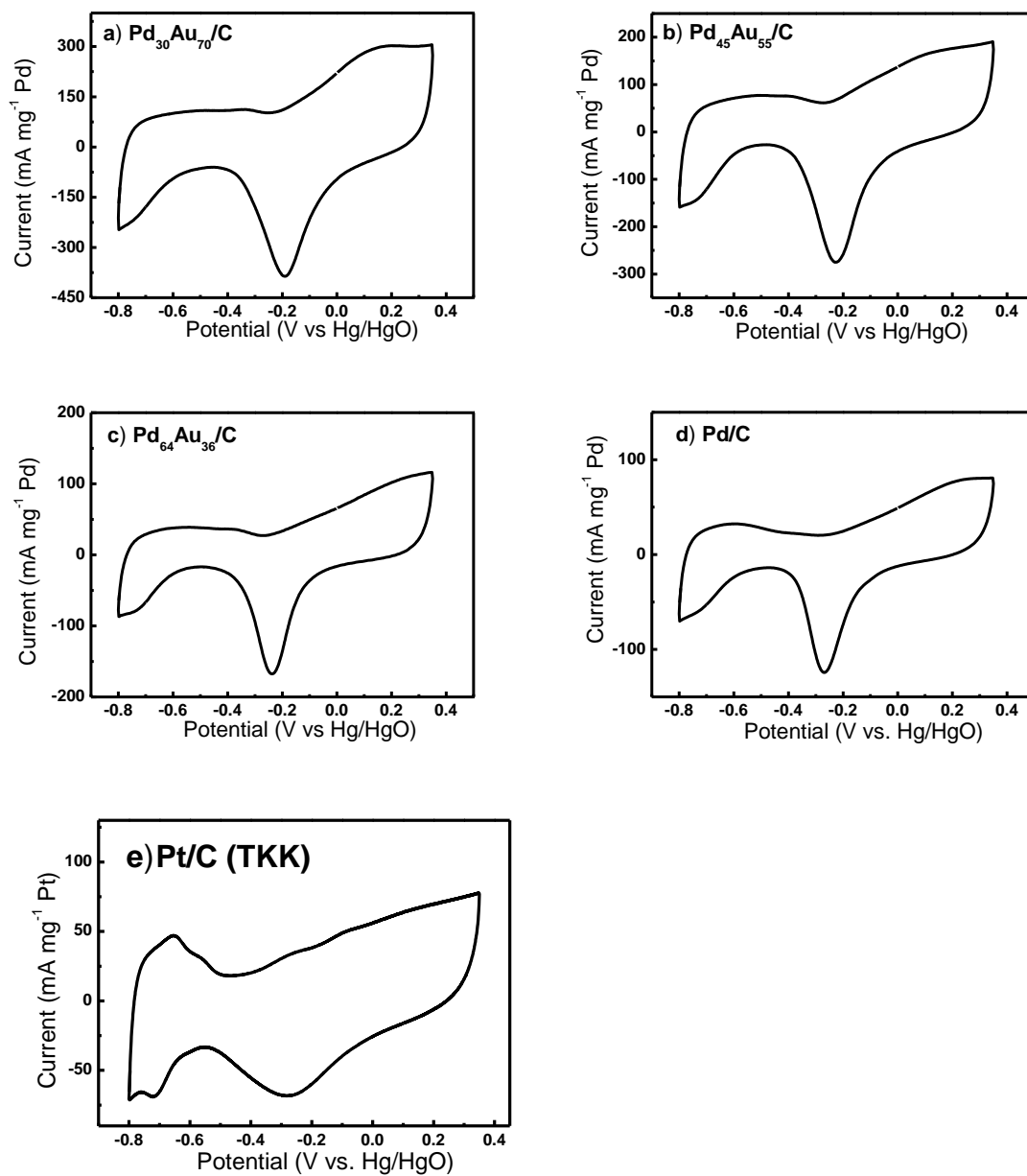


**Figure S4.** TEM images of the bimetallic Pd<sub>45</sub>Au<sub>55</sub>, Pd<sub>64</sub>Au<sub>36</sub> nanoparticles supported on carbon.

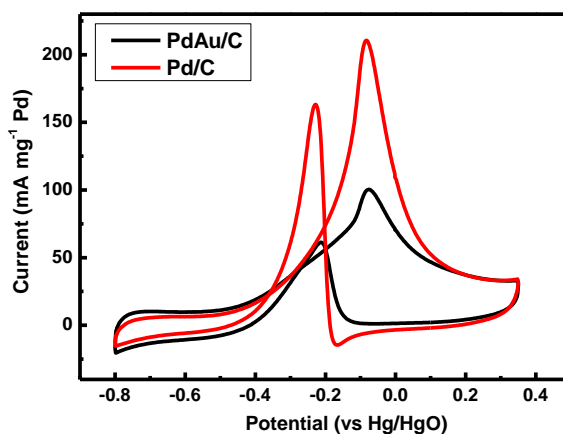


**Figure S5.** TEM images of the mono-metallic Pd nanoparticles prepared by the same emulsion-assisted method (A), average size was ca. 4.2 nm; supported on carbon (B).





**Figure S6.** Cyclic voltammograms of room-temperature with the PdAu/C, Pd/C and commercial Pt/C (TKK) catalysts in 1 M KOH at 100 mV/s.



**Figure S7.** Cyclic voltammograms of room-temperature with the PdAu/C via  $\text{NaBH}_4$  reduction and Pd/C catalysts in 1 M KOH + 1 M  $\text{CH}_3\text{OH}$  at 50 mV/s. The synthesis process of PdAu alloy nanocatalysts via chemical reduction was following: carbon was dispersed by sonication for 30 min in the sodium citrate solution. A mixture of  $\text{Na}_2\text{PdCl}_4$  and  $\text{HAuCl}_4$  solution was added into the above solution under magnetic stirring. The atomic ratio of Pd to Au was kept at 1:1. And then, excess  $\text{NaBH}_4$  was slowly added and the solution was stirred for another 4 h. The resulting precipitate was washed with a copious amount of water and dried at 80 °C overnight in order to make carbon-supported PdAu alloy nanocatalyst.