

Supporting Information

Solid Phase Metallurgy Strategy to Sub-5nm, Au-Pd and Ni-Pd Bimetallic Nanoparticles with Controlled Redox Properties

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Experimental

Material Synthesis

AuNPs: AuNP is synthesized by reported method (*J. Am. Chem. Soc.* 2006, 128, 6550) with minor revision. In a typical synthesis, 100 mg AuPPh₃Cl was mixed with 400 ul dodecanethiol in 20 ml toluene to form a clear solution, to which 176 mg borane *tert*-butylamine complex (BTBC) was then added in one portion. The mixture was heated with stirring at 55 °C for 5.5h before it was cooled to room temperature. AuNPs was precipitated by addition of 20 ml ethanol. The precipitant was separated by centrifuge, washed by ethanol. It was dried in vacuum box over night before dissolve in organic solvent (CHCl₃, toluene, benzene, et al).

PdNPs: PdNP is synthesized by reported method (*Small*, 2011, 7, 469) with minor revision. In a typical synthesis, 224 mg of Palladium acetate (0.5 mmol) was mixed with 10mmol of oleic amine under 50 °C with stirring to form a clear solution. Then 10 mmol of oleic acid was added, the mixture was kept at 50 °C for 1h. Then 386 mg of tetrabutylamine bromide (TBAB) dissolved in 2 ml CHCl₃ was added in one portion. The mixture was kept heat for another 1h before it was cooled to room temperature. PdNPs was precipitated by addition of 15 ml of ethanol. The precipitant was separated by centrifuge, washed with ethanol. Finally, the precipitate was dried in vacuum box over night before dissolving in organic solvent.

NiNPs: NiNP is synthesized by reported method (*J. Am. Chem. Soc.*, 2010, 132, 1468) with minor revision. In a typical synthesis, Under a nitrogen flow, 257 mg of Ni(acac)₂ (1 mmol) was mixed with 15 mL oleylamine (OAm) and 0.32 mL (1 mmol) oleic acid (OA). The formed solution was heated to 110 °C in 20 min, resulting in a nice green solution (Ni-oleate complex formation). The solution was kept at 110 °C for an hour to remove humidity and

oxygen. Next, the solution was cooled down to 90 °C where 175 mg of BTBC solvated in 2 mL of OAm quickly injected into the solution. A visible color change from green to a dark-brown was observed. The resultant solution was kept at 90 °C for 60 min. The solution was cooled down to room temperature. 30 mL of ethanol was added and the product was separated by centrifugation. The product was then dispersed in organic solvent (hexane or toluene).

EP-FDU-12. Mesoporous silica, EP-FDU-12, is synthesized following the reported procedure (*J. Am. Chem. Soc.*, 2010, 132, 9596). In a typical synthesis, 0.50 g of triblock copolymers EO106PO70EO106 (Pluronic F127), 0.60 g of 1,3,5-trimethylbenzene (TMB) and 1.25 g of KCl were dissolved in 50 ml of 1 M HCl at 14 ± 0.1 °C. After 1h stirring, 2.08 g of tetraethyl orthosilicate (TEOS) was added to this solution. The synthesis composition (in molar ratio) F127/KCl/TEOS/TMB/HCl/H₂O was 0.00256/1.083/0.645/0.323/3.87/100. After stirring for 24 h at 14 °C, the mixture was transferred into an autoclave and heated at 140 °C for 24 h. Then the products was obtained by filtration and dried at room temperature in air. The removal of organic templates was conducted as follows: 0.3 g of as-made EP-FDU-12 sample was mixed with 2 mL 30% H₂O₂ and 5mL 15M HNO₃ in a flask. The system was stirred at 80 °C for 2~5h. The obtained solution was filtered by washing with deionized water for several times and dried at room temperature in air. The structural features of the as-made mesoporous materials are listed as follows:¹ Pore diameter: 33.4 nm; Window size: 10.4 nm; Cell parameter: 45.8 nm; Pore volume: 0.88 cm³/g; BET surface area: 495 m²/g.

SiO₂ Sub-Microsphere: 4ml of ammonia was added into a mixed solution of ethanol (80ml) and distilled water (5ml). After 15min stirring, 4ml of TEOS was added to the above solution under magnetic stirring at 25 °C. After continuous stirring for 3 h, the white solid products were obtained by filtration, repeatedly washed with water and ethanol, then dried in a vacuum oven at 60 °C for 4 h. (*J. Colloid Interface Sci.* 1968, 26, 62).

Colloid Deposition: metal NPs was loaded into mSiO₂ by a colloid deposition method as previously reported (*J. Am. Chem. Soc.* 2006, 128, 14278). Typically, for the AuNP and PdNP co-loaded sample (5% wt/wt) with equal molar ratio (Au:Pd=1, denoted as Au_{1.0}Pd/mSiO₂), the concentrations of AuNPs and PdNPs' stock solution were determined first. Then calculated volumes of stock solution, with Au and Pd equal molar and known

mass, were moved to a vessel with stirring, then desired mass of mSiO₂ (20-fold mass of total metal NPs here) was added to the vessel afterwards. The absorption was carried out for hours at room temperature. The slurry was collected by centrifugation, and then transfers to vacuum box to remove solvent.

Quantification of Au, Pd and Ni.

AuNP stock solution concentration is determined by the visible absorption of AuNPs localized surface plasmon resonance signal (*J. Am. Chem. Soc.* 2010, 132, 9596).

PdNP stock solution concentration is measured by visible absorption peak of Pd²⁺-I⁻¹ complex at 407nm. Palladium standard solution is set by palladium acetate treated by nitric acid with microwave assisted digest. Work curve is determined by certain amount standard solution mixed with 2ml of sulphuric acid (1:3 diluted), 2.5ml of KI solution (3 mol/L), 2ml of ascorbic acid (0.6%), and then diluted to 25ml with water. The solution is transparent with a maximum absorption peak at 407nm, which is linear to Pd concentration.

NiNP stock solution concentration was measured by dimethyl glyoxime—spectrophotometry at 470nm. Nickel standard solution is set by nickel nitrate treated by nitric acid with microwave assisted digest. Work curve is determined by certain amount standard solution mixed with NaOH aqueous solution (5wt %), ammonium persulfate solution (3wt %) and dimethyl glyoxime-NaOH aqueous solution (1wt %). The solution is transparent with a maximum absorption peak at 470 nm, which is linear to Ni concentration.

Catalytic combustion of n-hexane. Catalyst activity for n-hexane combustion was determined using a fixed bed laboratory micro reactor. In order to avoid intra-reactor gradients, the catalyst powder (30 mg) was diluted in 0.3 g of quartz sand. Mass flow controllers were used to prepare the reactant feed composed by 1000 ppm of n-hexane in air. A total flow rate of 200 ml/min was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 10,000 h⁻¹ for all studies. Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame ionisation detectors. Catalytic activity was measured over the range 300~150 °C (from high temperature to low) and temperatures were measured by a thermocouple placed within the catalyst bed. Once the reaction temperature was attained, the catalyst was allowed to stabilize for 20 min before data were collected. Three consistent measurements were taken at each reaction temperature and

then the reaction temperature increased. Conversion data were calculated by the difference between inlet and outlet concentrations. The products are CO₂ and H₂O, and the selectivity towards CO₂ was 99.9%. Experimental errors on conversion were 100%±2% and all carbon balances were in the range 100%±5%.

Characterization

Wide-angle X-ray diffraction (WAXRD) patterns were recorded on a Rigaku Ultimate IV with Cu K α radiation. Solid UV/Vis adsorption spectra were measured with a Shimadzu UV-2450 spectrophotometer in the diffuse reflectance mode. XPS measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. All binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-1230 operated at 80 kV. HAADF-STEM images and elemental mapping were recorded on the TECNAIG²F20 operated at 200 KV. The sample was embedded in epoxy resin, and then microtomed into sub-100-nm ultra thin film at room temperature. These thin film samples floated on water or other solvents were collected by copper mesh with polymer microgrid for HAADF-STEM image and elemental mapping. TPO experiment is carried out on a homemade device we used before (*J. Am. Chem. Soc.* 2009, 131, 15568). In a typical test, O₂ consumption profiles were recorded on a homemade apparatus. 50 mg fresh catalysts were placed in a quartz tube and treated at 200 °C with Ar flow (15 ml/min) for 60 min before the measurement. The TPO was started by switching the gas to O₂/He (40 ml/min) with a ramping rate of 10 °C/min. Oxygen consumption was monitored by GC-TCD.

Figure S1. TEM images and particle size distribution of a) AuNPs; b) PdNPs and c) NiNPs.

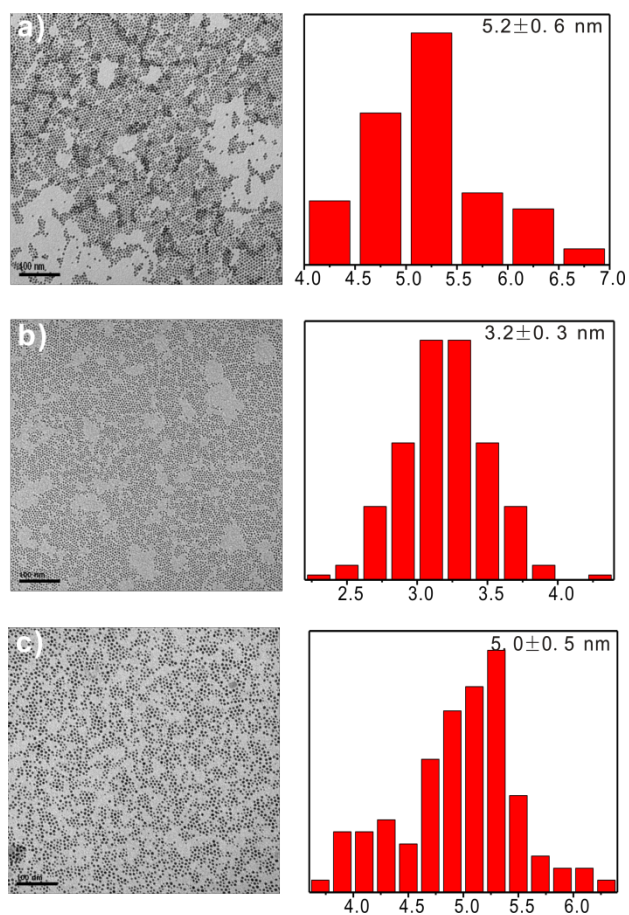


Figure S2. XRD patterns of Au_{1.0}Pd/EP-FDU-12 with different loading amount after annealing at 550 °C for 4 h.

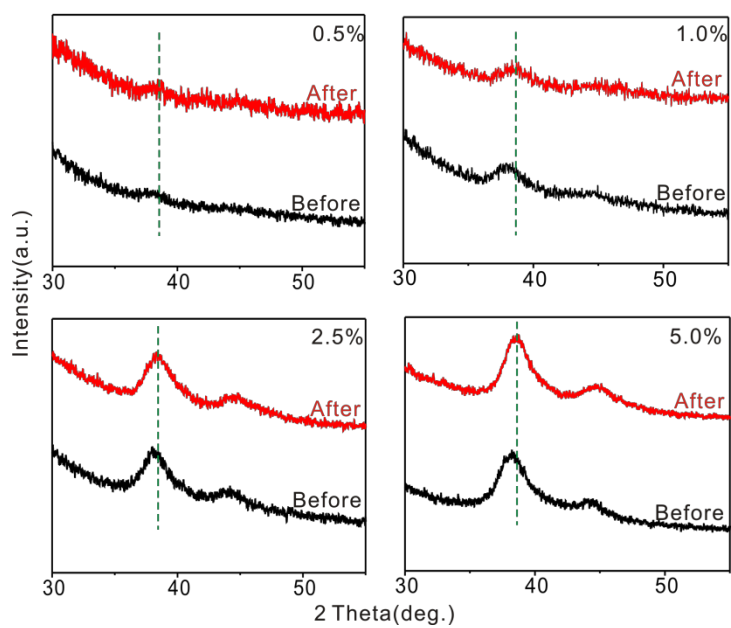


Figure S3. Solid UV-Vis of Au_{1.0}Pd/EP-FDU-12 with different loading amount after annealing at 550 °C for 4 h.

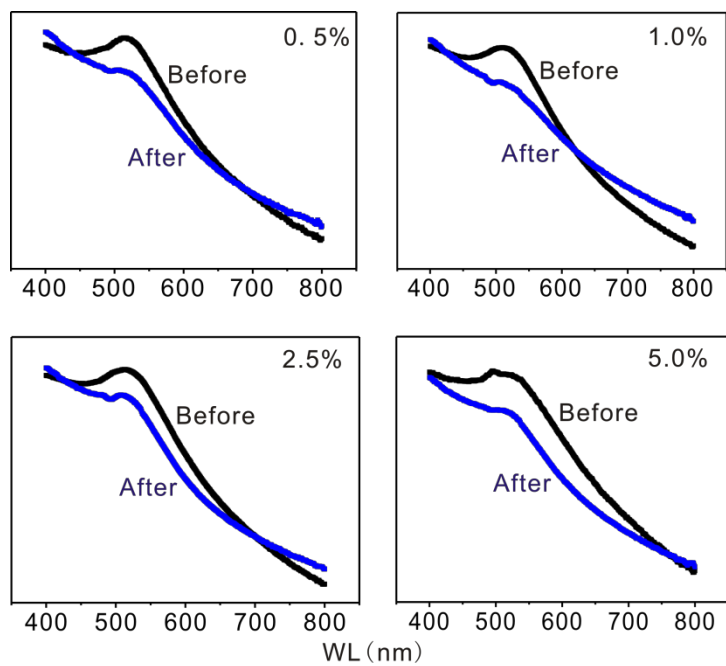


Figure S4. a) XRD and b) corresponding Solid UV-Vis of 5% Au_xPd/EP-FDU-12 with different molar ratio after annealing at 550 °C for 4 h.

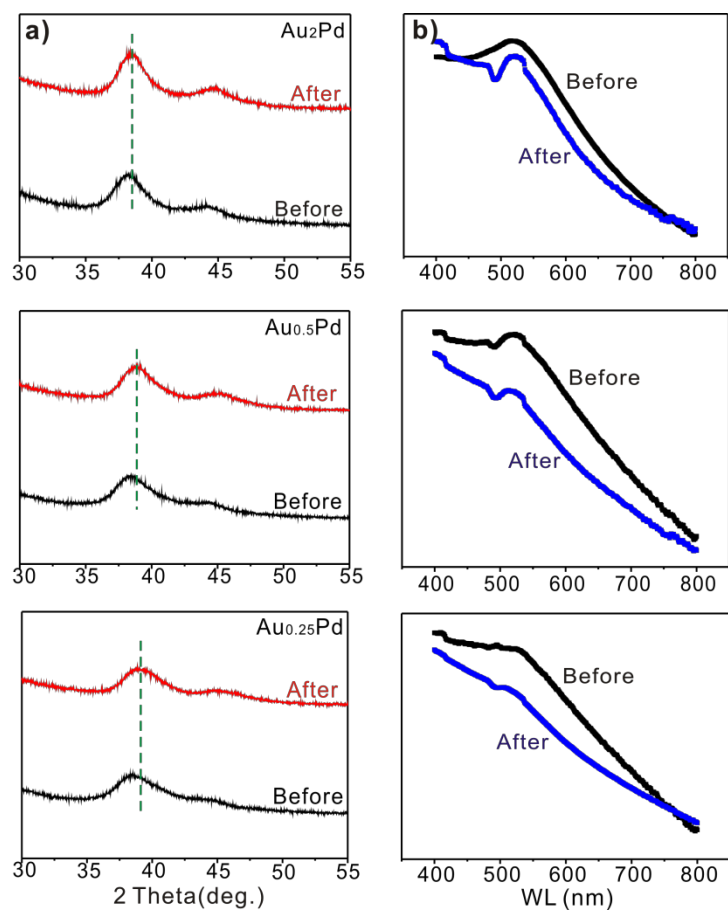
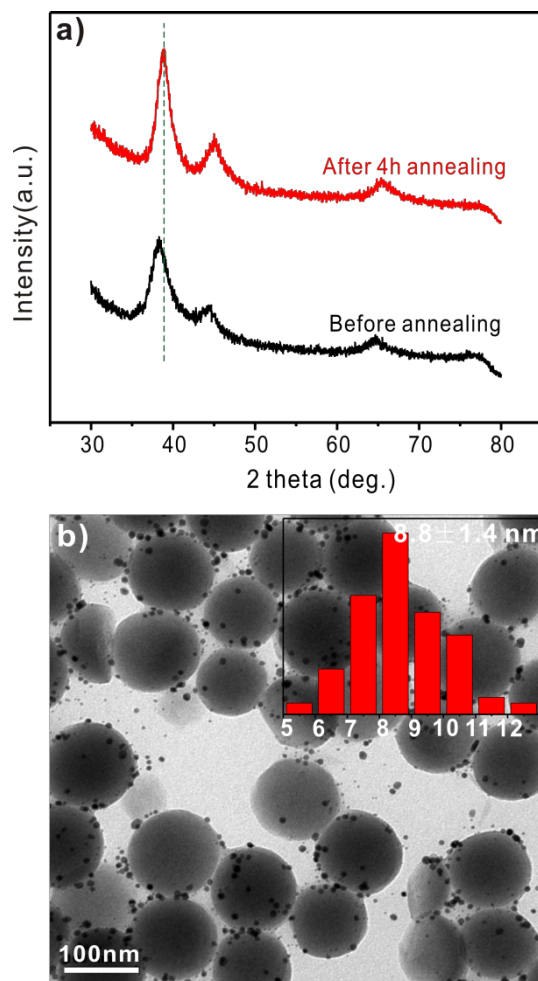


Figure S5. a) XRD patterns; b) TEM image and size distribution (insert graph) of 5% Au_{1.0}Pd/MS which was calcined at 550 °C for 4 h in the H₂/Ar atmosphere.



1. S. Xu, Y. Hong, C. Chen, S. Li, L. Xiao and J. Fan, *J. Mater. Chem. A.*, 2013, **1**, 6191-6198.