

Supplementary Information

Facile and efficient synthesis of polystyrene/gold-platinum composite particles and their application for aerobic oxidation of alcohols in water

Yunxing Li*, Yan Gao and Cheng Yang

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

Email: yunxingli@jiangnan.edu.cn; Fax: 86-510- 8591-7763

Experimental section

Materials

Styrene (Sinopharm Chemical Reagent Co.) was purified by distillation under reduced pressure. Azoisobutyronitrile (Sinopharm Chemical Reagent Co.) was purified by recrystallization in absolute ethanol. 1-Phenylethanol was purchased from Sigma-Aldrich. Cinnamyl alcohol, cyclohexanol, 1-octanol, polyvinylpyrrolidone (PVP, K-30), absolute ethanol, 2-propanol, sodium borohydride, trisodium citrate, hydrochloric acid, ethyl acetate, HAuCl₄ and H₂PtCl₆ were obtained from Sinopharm Chemical Reagent Co. and used as received. Ultrapure water (18.2 MΩ.cm) was used throughout the experiments.

Synthesis of Polystyrene (PS) Microspheres

PVP (5.6 g) was dissolved in 2-propanol (160 mL) and then the obtained solution was heated up to 70 °C in a round-bottom flask. Synchronously, the solution was purged with nitrogen to eliminate the inhibiting effect of oxygen. Subsequently, styrene (20 g) and azoisobutyronitrile (0.2 g) were added to the above-mentioned solution under vigorous mechanical stirring. The polymerization was allowed to proceed for 24 h before cooling to ambient temperature. Finally, the PS microspheres were collected and redispersed in water by centrifugation.

Synthesis of Gold-Platinum (Au-Pt) Alloy Nanoparticles

Trisodium citrate (8.2×10^{-2} mmol), HAuCl₄, and H₂PtCl₆ were dissolved in water (148 mL) simultaneously under stirring at room temperature. After 5 min, freshly

prepared NaBH_4 aqueous solution was injected into the above-mentioned solution. The reaction was allowed to proceed for 30 min. Gold-Platinum (Au-Pt) alloy nanoparticles with different composition were obtained by varying the concentration ratio of HAuCl_4 and H_2PtCl_6 , but the total amount of HAuCl_4 and H_2PtCl_6 was set as a constant (0.01 mmol).

Synthesis of PS/Au-Pt Composite Particles

The aqueous dispersion of PS microspheres (2 mL, 10 wt%) was injected into the aforementioned aqueous dispersion of Au-Pt alloy nanoparticles. The mixture was allowed to stir at 300 rpm using a magnetic stirrer for 12 h at room temperature, and then filtered with membrane (pore size, 0.45 μm) to remove the free alloy nanoparticles. Finally, the resultant composite particles were redispersed in water.

Oxidation of Various alcohols Using PS/Au-Pt Composite Particles

The processes for the catalytic oxidation of various alcohols are similar. As a typical example, 1-Phenylethanol (10 mM) and PS/Au-Pt composite particles (Au-Pt, 0.3 mM) were mixed in water and then added to a test tube. The obtained mixture was bubbled with air for 30 min. Then, the test tube was encapsulated and shaken vigorously at a given condition. After the reaction was completed, the catalyst particles were recovered by centrifugation, and the aqueous phase was treated with hydrochloric acid (0.1 M) and then extracted with ethyl acetate (5 mL \times 3). The extract layer was dried over anhydrous Na_2SO_4 , concentrated, and finally analyzed using gas chromatography.

Characterization

High-resolution transmission electron microscopy and energy-dispersive X-ray spectroscopy were performed by a JEM-2100 microscope (JEOL Co., Japan). X-ray diffraction analyses were recorded on a German Bruker-AXS D8 Advance. The contents of gold and platinum on the PS microsphere were quantified by inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent, 700 Series). Gas chromatography analyses were performed on GC9790 apparatus (Fuli, China). UV-vis absorption spectra were recorded at room temperature on a TU-1901 spectrometer (Puxi, China).

TableS1. Composition of Au-Pt alloy nanoparticles and mass loading of Au-Pt alloy nanoparticles of PS/Au-Pt composite particles

Recipe	Au/Pt [mol/mol] ^a	Au _m Pt _n ^b	Mass loading [wt%] ^c
1	4:1	Au _{3.78} Pt ₁	0.67
2	2:1	Au _{1.94} Pt ₁	0.65
3	1:1	Au _{1.25} Pt ₁	0.78
4	1:2	Au _{0.74} Pt ₁	0.80
5	1:4	Au _{0.32} Pt ₁	0.82

^a Feed ratio of HAuCl₄ and H₂PtCl₆. ^b m/n represents the molar ratio of Au and Pt in the alloy nanoparticles determined by ICP. ^c Total content of noble metals of PS/Au-Pt composite particles.

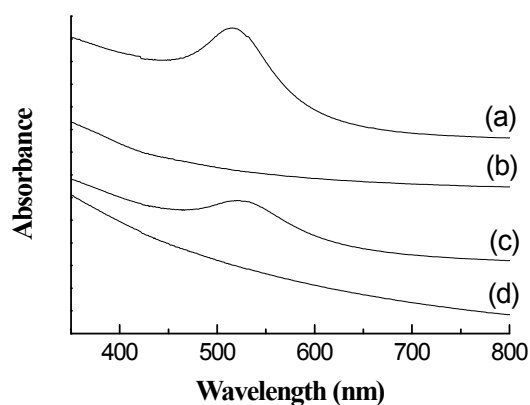


Figure S1. UV-vis absorption spectra of AuNPs (a), PtNPs (b), the physical mixture of AuNPs and PtNPs (c), and Au_{1.25}Pt₁ alloy nanoparticles (d).

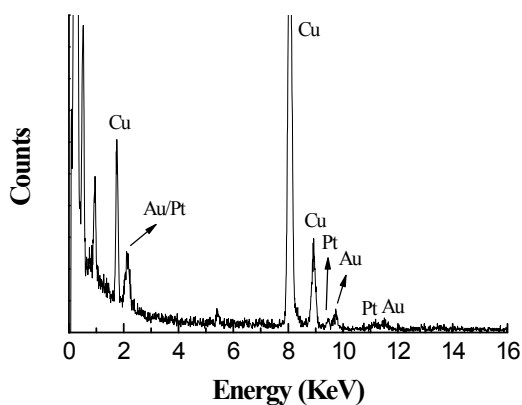


Figure S2. EDX spectrum of PS/Au_{1.25}Pt₁ composite particles.

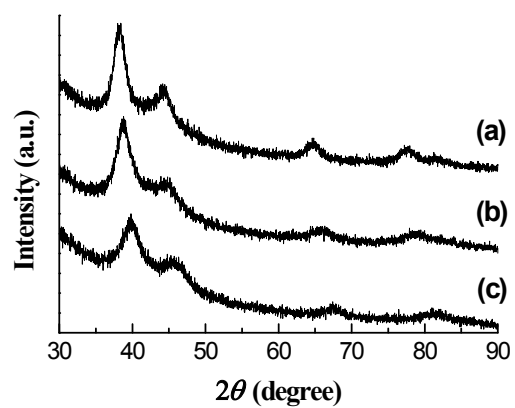
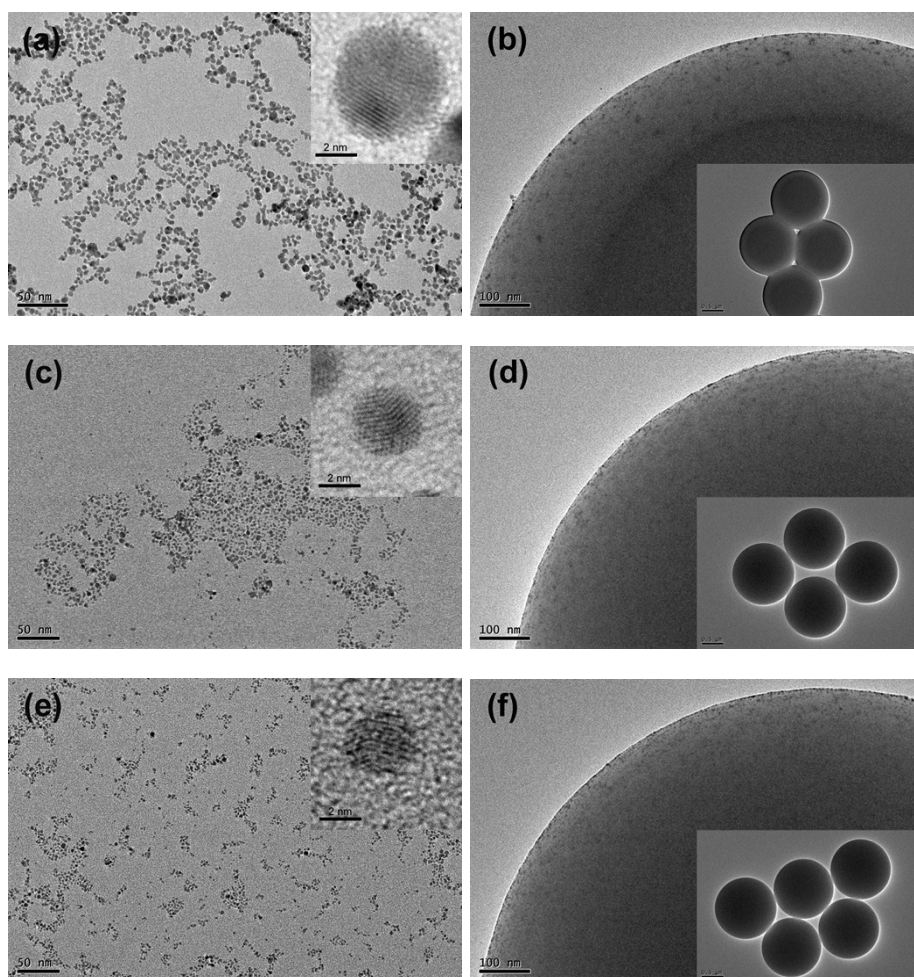


Figure S3. XRD patterns of PS/Au composite particles (a), PS/Au_{1.25}Pt₁ composite particles (b), and PS/Pt composite particles (c).



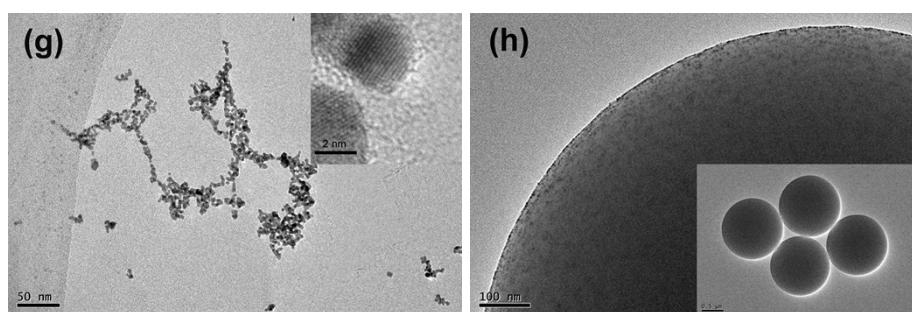


Figure S4. TEM and HR-TEM (insert) images of $\text{Au}_{3.78}\text{Pt}_1$, $\text{Au}_{1.94}\text{Pt}_1$, $\text{Au}_{0.74}\text{Pt}_1$, and $\text{Au}_{0.32}\text{Pt}_1$ alloy nanoparticles and the corresponding TEM images of $\text{PS}/\text{Au}_{3.78}\text{Pt}_1$, $\text{PS}/\text{Au}_{1.94}\text{Pt}_1$, $\text{PS}/\text{Au}_{0.74}\text{Pt}_1$, and $\text{PS}/\text{Au}_{0.32}\text{Pt}_1$ composite particles.

Table S2. Aerobic oxidation of 1-phenylethanol using PS/Au, PS/Pt, and the mixture of PS/Au and PS/Pt composite particles as catalyst^a

Entry	Substrate	Catalyst	Size ^b [nm]	Product	Yield ^c [%]
1	1-phenylethanol	PS/Au	3.5	acetophenone	8%
2	1-phenylethanol	PS/Pt	2.9	acetophenone	54%
3	1-phenylethanol	PS/Au+PS/Pt	3.5/2.9	acetophenone	8%

^a Reaction condition: substrate [10 mM], Au, Pt, or Au+Pt catalyst [0.3 mM], H_2O , air, 24 h, 40 °C. ^b Size of supported AuNPs or PtNPs. ^c Estimated from GC analysis.