

Supplementary Information

Facile Synthesis of Polystyrene/Gold Composite Particles as Highly Active and Reusable Catalyst for Aerobic Oxidation of Benzyl Alcohol in Water

Yunxing Li*, Yan Gao, Cheng Yang, Shengsheng Sha, Jiefu Hao, Yan Wu

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of

Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China. Fax: (86-510)

8591-7763; Tel: (86-510) 8591-7763; Email: yunxingli@jiangnan.edu.cn

Experimental section

Materials

Styrene (Shanghai Chemical Reagent Co.) was purified by distillation under reduced pressure. Azobisisobutyronitrile (Shanghai Chemical Reagent Co.) was purified by recrystallization in absolute ethanol. Benzyl alcohol was purchased from Sigma-Aldrich. Polyvinylpyrrolidone (PVP, K-30), absolute ethanol, 2-propanol, potassium carbonate, potassium hydroxide, sodium borohydride, trisodium citrate, hydrochloric acid, ethyl acetate, and H₂AuCl₄ were obtained from the Shanghai Chemical Reagent Co. and used as received. Ultrapure water (18.2 MΩ·cm) was used throughout the experiments.

Synthesis of Polystyrene microspheres

PS microspheres with an average diameter of about 2.2 μm were synthesized by dispersion polymerization. The PVP (2.8 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 azobisisobutyronitrile (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 dispersed in water by centrifugation.

Synthesis of Gold Nanoparticles

Trisodium citrate (8.2×10^{-2} mmol) and H₂AuCl₄ (6.5×10^{-2} mmol) were dissolved in water (126 mL) under stirring at room temperature. After 5 min, freshly prepared NaBH₄ (0.2 mmol) aqueous solution was injected into the above-mentioned solution. The reaction was allowed to proceed for 30 min. As the concentration of H₂AuCl₄ remains constant, gold nanoparticles with different size

were obtained by varying the concentration of NaBH₄ (e.g., 0.02 and 0.1 mmol).

Synthesis of PS/Au Composite Particles

The appropriate amount of aqueous dispersion of PS microspheres (1 g, 10 wt%) was injected into a certain volume of aqueous dispersion of gold nanoparticles. The mixture was allowed to stir at 300 rpm using a magnetic stirrer for 12 h at room temperature. Herein the weight ratio of gold nanoparticle to PS microsphere (W_{Au}/W_{PS}) was determined by the following equation:

$$W_{Au}/W_{PS} = 4(R+r)^2r\rho_{Au}/(R^3\rho_{PS})$$

where R , r , ρ_{PS} , and ρ_{Au} are the radius and density of individual PS microsphere (subscript PS) and gold nanoparticle (subscript Au), respectively.

Oxidation of Benzyl Alcohol Using PS/Au Composite Particles

Benzyl alcohol (0.1 mmol), K₂CO₃ (0.3 mmol), PS/Au composite particles (Au, 0.003 mmol), and water (10 mL) were added to a test tube in turn. The obtained mixture was bubbled with air or oxygen 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 reused when a new substrate, base, and water were added. The aqueous phase was treated with hydrochloric acid (0.1 M) and then extracted with ethyl acetate (5 mL × 3). The extracted layer was dried over anhydrous Na₂SO₄, 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 pattern of PS/Au composite particles was recorded on a German Bruker-AXS D8 Advance. The gold content on the PS microsphere was quantified by inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent, 700 Series). Gas chromatography analyses were performed on Agilent 7890A apparatus (USA).