Supplementary Information

Amphiphilic Block Copolymer-Stabilized Gold Nanoparticles for Aerobic Oxidation of Alcohols in Aqueous Solution

Xueguang Wang, Hajime Kawanami,* Nazrul M. Islam, Maya Chattergee, Toshirou Yokoyama and Yutaka Ikushima

Experimental

1. Synthesis of Au nanoparticles

Al_2O_3 was purchased from Japan Aerosil. Other chemicals were purchased from Sigma-Aldrich Co., Acros Organics or Wako Pure Chemical Industries, Ltd. and were used without further purification.

Au nanoparticles were synthesized by the reduction of $HAuCl_4$ (99.9%) in a P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800) aqueous solution using $NaBH_4$ as a reducing agent. In a typical synthesis, 190 ml of P123 aqueous solution was stirred at 35 ^{o}C for 30 min. Then 4 ml of 0.05 M $HAuCl_4$ aqueous solution was introduced to the solution and immediately, 6 ml of 0.1% $NaBH_4$ aqueous solution was added very slowly under vigrous stirring within 15 min and further stirred at 35 ^{o}C for 5 min. The final gold concentration was 1.0×10^{-3} M and the molar ratio of Au to P123 was varied in the range from 0 to 7. Upon the addition of $NaBH_4$ aqueous solution to the system, the light yellowish solution was immediately changed to wine red color by visual observation. The UV-Vis absorption band from the surface plasmon of the Au nanoparticles were obtained at 520 nm by a Jasco V-570 UV/Vis spectrophotometer.

To compare the oxidation reactivity, 2.5wt%Au/Al_2O_3, 2.5wt%Pd/Al_2O_3 and 2.5wt%Au/2.5wt%Pd/Al_2O_3 catalysts were prepared by impregnation of Al_2O_3 using aqueous solutions of $PdCl_2$ and/or $HAuCl_4 \cdot 3H_2O$ and calcined at 400 ^{o}C for 3 h according to the literature.[1]

To evaluate the size of Au nanoparticles in Fig 2a to c, we counted 225 particles for all samples from TEM images at each conditions. In Figure 2 of this paper, we used the relative percentage to express the particle size distribution.

2. TEM and XRD mesurements

The sample grids for TEM measurements were prepared by dropping aqueous Au nanoparticle dispersion onto the copper grids. The morphology and size distribution of the Au nanoparticles were determined by a transmission electron microscope (TECNAI-20ST) at an operating voltage of 200 kV. XRD patterns was carried out on a Rigaku RINT2200 diffractometer with CuKα radiation. The XRD patterns of Au nanoparticles were shown in Fig S1.

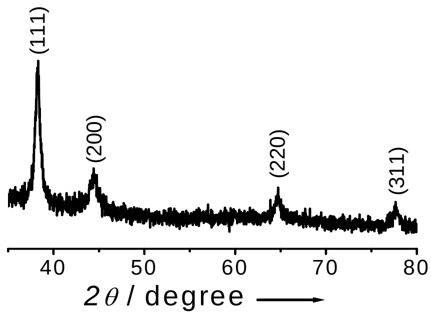

Fig. S1 XRD patterns of Au nanoparticles formed in the system (Au/Pluronic molar ratio = 1 : 7).

2. Oxidation reaction using Au nanoparticle

The oxidatin of alcohols was carried out with O_2 in a two-necked flask of 50 mL with a reflux condenser which was placed in a thermostatic bath with a magnetic stirrer. In a typical experiment, 15 mL of Na_2CO_3 aqeuous solution (0.25 M) and 15 mL of Au nanoparticle colloid were mixed and heated at the set temperature and bubbled O_2 for 30 min. Then 0.75 mmol of alcohol was added into the reaction mixture and started the oxidation reaction under vigorous stirring by bubbling O_2. The reaction mixture (1 mL) was sampled at appropriate reaction intervals. The reaction mixture was quenched with 1 mL of 2 M HCl and extracted with diethyl ether. The extracted layer was analyzed by gas chromatography with FID (Varian CP-3800, MS-5 30 m capillary column) with tridecane as an internal standard and compare to authentic samples, and confirmed products by GC-MS/MS (Varian 1200L, MS-5 30 m capillary column) and NMR (Varian Unity 500).

Reference

1 D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362.