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

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Stable Au nanoparticles in P123 aqueous solution using a simple method have been developed and the colloidal Au nanoparticles were successfully applied for the effective oxidation of various alcohols using molecular O_2 as oxidant at 30 °C in aqueous solution.

Gold nanoparticles have been shown to be very highly active catalysts for many important industrial reactions such as low-temperature oxidation of CO,[1] hydrogenation of α,β-unsaturated aldehydes,[2] epoxidation of alkenes,[3] oxidation of alcohols[4] and synthesis of H_2O_2.[5] In general, these Au nanoparticles are stabilized with metal oxides or activated carbon as support. Although they were considered to be active, these solid supported catalysts still have some drawbacks such as an inherent heterogeneity of the reaction, and inaccessibility of the substrate to the catalysts.[6] To combine the advantages of both homogeneous and heterogeneous catalysts, well-dispersed colloidal nanoparticles have received significant attention as an alternative, such as water-dispersed gold–glucose colloidal sols for the oxidation of glucose to gluconic acid,[7a,b] β-D-glucose-stabilized Au nanoparticles for the reduction of 4-nitrophenol in the presence of $NaBH_4$,[7c,d] Au nanoparticles with agarose.[7c,d] Recently, gold nanoclusters in water stabilized with poly(*N*-vinyl-2-pyrrolidone) has been developed for the effective oxidation of benzyl alcohol using oxygen.[8]

The synthesis of gold nanoparticles with amphiphilic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers in aqueous solution has been reported.[9] These block copolymers acted as both reductants and colloidal stabilizers. However, only low concentration of Au nanoparticles ($HAuCl_4$: 2.0×10^{-4} M) with a large particle size distribution could be obtained under long reaction times. In this communication, we report a simple preparation of Au nanoparticles from $HAuCl_4$ in an aqueous solution of P123 ($EO_{20}PO_{70}EO_{20}$) by reduction of $NaBH_4$. The synthesized material was subsequently used for the oxidation of alcohols with molecular oxygen, and the products were easily separated from the aqueous colloidal Au nanoparticles by extraction with diethyl ether.

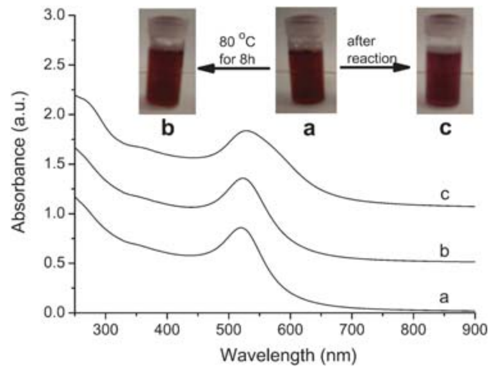

Fig. 1 UV-VIS spectra of colloidal Au nanoparticles in aqueous solution (5×10^{-5} M) at each condition: (a) as-prepared, (b) after treated at 80 °C, and (c) after reaction.

Gold nanoparticles (1.0×10^{-3} M) were prepared at 35 °C with an Au : P123 molar ratio = 1 : 7 (see ESI†). The formation of the colloidal Au nanoparticles were confirmed by the characteristic UV-Vis absorption band of Au nanoparticles at 520 nm as shown in Fig. 1(a), and the remaining of Au nanoparticles are observed after 80 °C treatment and after oxidation reaction of alcohols as shown in Fig. 1(b) and (c), respectively. Fig. 2(a) presents a typical transmission electromicrograph of gold nanoparticles formed in a P123 aqueous solution. The characteristic spherical Au particles are observed with a relatively narrow particle size distribution in the range of 4–12 nm. A histogram of the Au particle size distribution is

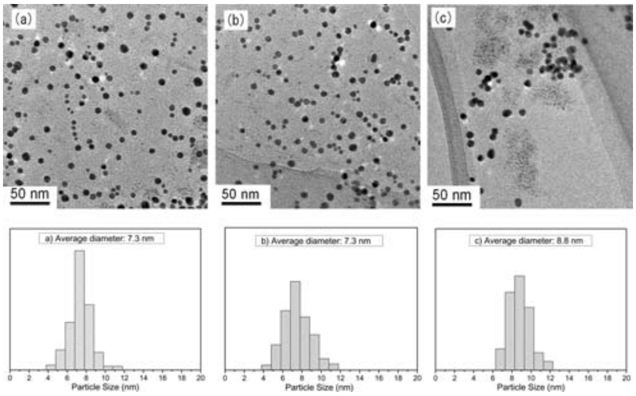

Fig. 2 Typical TEM images and size distributions of Au nanoparticles in the condition of (a) as-prepared, (b) treated at 80 °C for 8 h, and (c) after reaction.

Research Center for Compact Chemical Process, AIST (National Institute of Advanced Science and Technology), 4-2-1 Nigatake, Miyagino-ku, Sendai, Miyagi, 983-8551, Japan.
E-mail: h-kawanami@aist.go.jp; Fax: +81 22-237-5215

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also presented in Fig. 2(a). The mean particle diameter of Au nanoparticles is 7.3 nm and more than 95% of the nanoparticles are in the range from 5 to 9 nm, indicating a relatively high monodispersity of the Au nanoparticles formed in the system.

Powder X-ray diffraction (XRD) was also used to examine the crystal structure of the Au nanoparticles.† XRD pattern of the Au particles clearly shows the diffraction peaks corresponding to (111), (200), (220) and (311) lattice planes, indicating a face-centered-cube (fcc) phase.[10] The average Au particle size from the Scherrer equation[11] was estimated as 7.9 nm, which is comparable with the result obtained from the statistical analysis of the TEM image.

The stability of nanoparticles in solution is an important factor from the application viewpoint. The current colloidal system strongly depends on the use of P123. Immediate precipitation was observed upon addition of $NaBH_4$ in the absence of P123. For the colloids with low molar ratio of P123 to Au ($\leq 2:1$), the precipitates were stable up to 2 months. However, when the molar ratio of P123 to Au was increased up to 3.5 : 1, the colloidal Au nanoparticles were found to be very stable for prolonged period (at least 5 month observation period) and show no sign of color change. Thermal stability of the system (P123 : Au molar ratio = 7 : 1) was also examined at 80 °C for 8 h in a sealed glass bottle. No color change and no precipitation were observed visually, as also confirmed by UV-Vis spectra in Fig. 1(b). The TEM image in Fig. 2(b) also demonstrates that no aggregation took place during the treatment and the average particle size is still 7.3 nm. Interestingly, after highly centrifuging the colloidal Au nanoparticles with a speed of 15 000 rpm, the Au particles can completely re-dispersed in aqueous media by simply shaking. This indicates that the Au nanoparticles stabilized by P123 can be isolated from the colloidal system without irreversible aggregation.[7c] The polymer-assisted colloidal system of metal nanoparticles is believed to be stabilized by steric factors, unlike the thiol-stabilized metal colloidal system in which a strong interaction on the metal particle surface poisons the catalytic properties of the metal nanoparticles.[12]

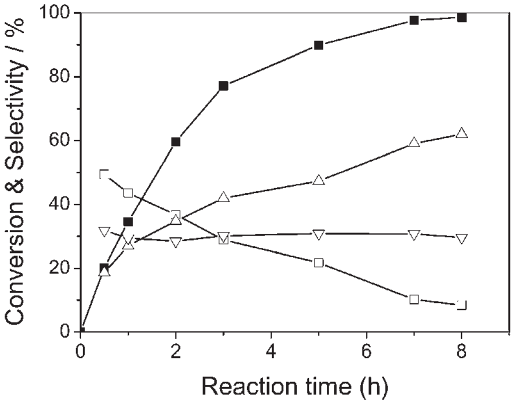

Fig. 3 Conversion of benzyl alcohol and product selectivity with the reaction time at 30 °C: (■) conversion of benzyl alcohol, (□) selectivity to benzaldehyde, (△) selectivity to benzoic acid and (▽) selectivity to benzyl benzoate (see Table 1 for reaction conditions).

The current facile synthesis of Au nanoparticles with P123 in aqueous solution provides the opportunity to explore the catalytic application of Au nanoparticles in aqueous solution. The oxidation of benzyl alcohol was initially investigated with O_2 as oxidant at 30 °C in the presence of Na_2CO_3 over colloidal Au nanoparticles and the results are shown in Fig. 3. The gold nanoparticles were active for the reaction and the conversion of benzyl alcohol was achieved up to 99% within 8 h. Benzaldehyde, benzoic acid and benzyl benzoate were formed during the reaction. The reaction selectivity for benzaldehyde decreases with the reaction time due to the further oxidation of benzaldehyde to benzoic acid. It is notable that benzoic acid and benzyl alcohol reacts to form benzyl benzoate and no other by-products are observed.

Table 1 Oxidation of alcohols catalyzed by colloidal Au nanoparticles (Au-sol) and supported Au or/and Pd catalysts in aqueous solution[a]

						Selectivity (%)		
Entry	Catalyst	Substrate	*T*/°C	*t*/h	Conv. (%)	Aldehyde or ketone	Acid	Ester
1	Au-sol	Benzyl alcohol	30	8	99	8	62	30
2	Au-sol	4-Methoxybenzyl alcohol	30	3	100	82	18	0
3[b]	Au-sol	4-Methoxybenzyl alcohol		8	49	100	0	0
4	Au-sol	4-Isopropylbenzyl alcohol	30	4	100	78	22	0
5	Au-sol	*p*-Chlorobenzyl alcohol	30	12	94	5	76	19
6	Au-sol	1-Heptanol	30	24	27	0	100	0
7	Au-sol	2-Heptene-1-ol	30	8	88	13	55	20
8	Au-sol	Cyclooctanol	20	24	27	100	—	—
9	Au-sol	Cyclooctanol	30	24	58	100	—	—
10	Au-sol	Cyclooctanol	40	9	92	100	—	—
11[c]	2.5wt% Au/Al_2O_3	4-Methoxybenzyl alcohol	30	8	9	100	0	0
12[c]	2.5wt% Pd/Al_2O_3	4-Methoxybenzyl alcohol	30	8	<1	—	—	—
13[c]	2.5wt% Au/2.5wt% Pd/Al_2O_3	4-Methoxybenzyl alcohol	30	8	<1	—	—	—
14[d]	Au-sol	Cyclooctanol	40	9	72	100	—	—

[a] *Reaction conditions*: Au, 0.015 mmol, Au : P123 = 1 : 7 (mol : mol); substrate, 0.75 mmol; Na_2CO_3, 3.75 mmol; solution volume, 30 mL, O_2 bubbling unless specified. [b] In the absence of Na_2CO_3. [c] In the absence of P123. [d] The Au-sol was recycled after the reaction of run 10.

Results of the oxidation of various alcohols catalyzed by the colloidal Au nanoparticles are shown in Table 1, together with those over supported Au or/and Pd catalysts for comparison. The colloidal Au nanoparticles can efficiently catalyze the oxidation of primary aromatic alcohols using O_2 and show good conversion at 30 °C. Benzyl alcohols with electron-donating groups (CH_3O– and $(CH_3)_2CH$–) at *para*-position are completely transformed to the corresponding oxidized products with high selectivities to aldehydes (entries 2 and 4), while electron-withdrawing groups such as Cl markedly decrease the reaction rate (entry 5). Interestingly, the Cl group promotes the oxidation of aldehyde to acid and further forms a certain amount of ester with reactant in the presence of Na_2CO_3. Primary aliphatic alcohols such as 1-heptanol and 2-heptene-1-ol (entries 6 and 7, respectively) show lower reactivity than aromatic alcohols. It should be noted that 1-heptanol only forms heptanoic acid as the product, while 2-heptene-1-ol not only shows higher activity due to stabilization of the C=C double bond but also forms certain amounts of 2-heptenal and ester. The colloidal Au nanoparticles exhibit high conversion for the oxidation of cyclooctanol with 100% selectivity to the corresponding ketone (entries 8–10).

In the colloidal Au nanoparticle system, the presence of Na_2CO_3 has a significant influence on the activity and the product selectivity. As seen in Table 1, entries 2 and 3, for the oxidation of 4-methoxybenzyl alcohol, the conversion of the oxidation of alcohol by Au nanoparticles in the presence of Na_2CO_3 (the molar ratio of substrate to Na_2CO_3 = 1:5) is much higher than that in the absence of Na_2CO_3, but the selectivity to aldehyde decreased. The influence of the reaction temperature was also examined. Entries 8–10 in Table 1 show the results of oxidation of cyclooctanol with O_2 over Au nanoparticles in aqueous solution at different temperatures. The conversion of cyclooctanol increases with reaction temperature.

For comparison, supported Au, Pd and Au–Pd catalysts obtained by impregnation,[13] which were reported to be the most active and the most promising catalysts for the selective oxidation of alcohols, were tested for the oxidation of 4-methoxybenzyl alcohol under the same reaction conditions. The reaction results (Table 1, entries 11–13) show that these Al_2O_3-supported catalysts have negligible catalytic reactivity relative to colloidal Au nanoparticles at 30 °C. Efficient oxidation of alcohols by colloidal Au nanoparticles is attributed to the homogenization of heterogeneous Au nanoparticles. Au nanoparticles in P123 aqueous solution are uniformly dispersed and mixed intimately with reactants resembling a homogeneous catalytic system.

However, the colloidal Au nanoparticles show no visible change in color (Fig. 1(c)) and showed no observable precipitation after the reaction. When the catalyst was recycled, the conversion for the oxidation of cyclohexanol was decreased whereas the selectivity was retained as shown in run 14 in Table 1. The UV-Vis spectrum of the colloidal Au nanoparticles after the oxidation reaction of cyclooctanol in the presence of Na_2CO_3 at 40 °C for 9 h is illustrated in Fig. 1(c). The absorption peak of Au nanoparticles at 520 nm before the oxidation reaction red shifts to 528 nm and the half-maximum width is broader. These imply that the average size of Au nanoparticles might be increased after the reaction. This is confirmed by a TEM image of Au nanoparticles in Fig. 2(c). The histogram of Au particle size distribution (Fig. 2(c)) demonstrates that small Au nanoparticles less than 6 nm disappear and the average diameter of Au particles increases from 7.3 to 8.8 nm after the reaction.

In summary, we have synthesized stable Au nanoparticles in P123 aqueous solution using a simple method and the colloidal Au nanoparticles were successfully applied for the oxidation of various alcohols using O_2 as oxidant at 30 °C in aqueous solution. The current investigation can be reasonably extended to the synthesis of other metal nanoparticles. These results will also contribute to the development of efficient and environmentally friendly metal nanocatalysts for various organic reactions without organic solvent.

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