Effects of Bubbling N_2 or O_2 Gas in Syntheses of Gold Nanocrystals Using a Polyol Method

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Shapes and sizes of Au nanocrystals prepared by reducing $HAuCl_4$ in ethylene glycol (EG) depended strongly on the presence of O_2 in EG. At 110 °C icosahedrons, one-dimensional (1-D) rods and wires, and spherical particles were major products under bubbling N_2 gas, whereas octahedrons and nanoplates were dominant products under bubbling O_2 gas. At 198 °C decahedrons and icosahedrons were major products under bubbling N_2 gas, whereas the yields of larger octahedrons, nanoplates, and spherical particles increased under bubbling O_2 gas. These results show that bubbling N_2 or O_2 gas at different temperatures can be used as a new experimental parameter for the shape- and size-controlled synthesis of Au nanostructures.

Recently gold nanoparticles have been extensively studied as an active component not only because of unique physical and chemical properties but also because of important applications in catalysts, photoelectronic devices, and biomedicine. It is well known that some chemical and physical properties and application of materials are dependent, to a large extent, on their shapes and textures. Thus, we have studied shape- and size-controlled syntheses of gold nanocrystals using a microwave (MW)–polyol method in the presence of poly(vinylpyrrolidone) (PVP) as a surfactant.[1]

We have recently studied effects of gas dissolved in EG for the synthesis of silver nanostructures from a mixture of $AgNO_3$/NaCl/PVP/EG.[2] Uniform Ag nanowires were obtained in a high yield under bubbling of air owing to shape selective oxidative etching of Ag nanoparticles by Cl^-/O_2.[2] Although effects of O_2 dissolved in EG have been studied for Ag nanostructures, little work has been done for the syntheses of Au nanostructures. In this letter, we studied effects of O_2 in the synthesis of Au nanostructures from $HAuCl_4$/PVP/EG. We found for the first time that different shapes and sizes of Au nanostructures can be prepared by bubbling N_2, O_2, or without gas bubbling in an oil-bath heating at 110 and 198 °C.

Ten milliliters of EG solution was heated to 110 or 198 °C and maintained at this temperature for 20 min by bubbling N_2 or O_2 at a total flow rate of 100 sccm. Then a mixture of $HAuCl_4 \cdot 4H_2O$ and PVP as a polymer surfactant in 10 mL of EG was added and further heated at 110 or 198 °C for 30 min by bubbling N_2 or O_2. The final concentration of $HAuCl_4 \cdot 4H_2O$ was 2.4 mM, whereas that of PVP ($M_w = 40000$ in term of monomeric units) was 1 M. Similar experiments were carried out without gas bubbling to examine effects of O_2 dissolved in EG. Products were characterized by transmission electron microscopic (JEM-2010 TEM; JEOL) observation.

Figures 1a–1f respectively show typical TEM images of Au nanocrystals obtained from $HAuCl_4 \cdot 4H_2O$/PVP/EG under bubbling N_2, O_2, or without gas bubbling at 110 and 198 °C. There

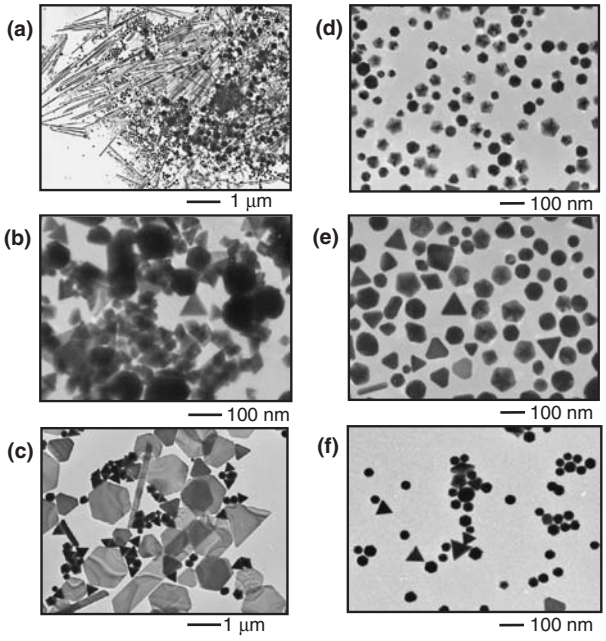

Figure 1. Au nanocrystals prepared from $HAuCl_4 \cdot 4H_2O$/PVP/EG at 110 °C for 30 min by (a) bubbling N_2, (b) bubbling O_2, or (c) without gas bubbling, and at 198 °C for 30 min by (d) bubbling N_2, (e) bubbling O_2, or (f) without gas bubbling.

were many small hexagonal particles (e.g., Figures 1d and 1f). Basis on measurements of TEM images from view angles of ±15° and previous SEM measurements of similar hexagonal particles,[1b] they were assigned to icosahedrons. It should be noted that shapes and sizes of products depend strongly on the presence of O_2 in EG at 110 and 198 °C. At 110 °C major products were mixtures of icosahedrons (24%), 1-D products (24%), and spheres (50%) under bubbling N_2, whereas those were mixtures of octahedrons (34%) and nanoplates (37%) under bubbling O_2. Nanometer sizes of triangular plates (39%) and micrometer sizes of hexagonal plates (36%) were major products without gas bubbling where a small amount of O_2 was dissolved in EG. The yields and average sizes of particles of each condition are summarized in Tables 1 and 2.

Although we could prepare 1-D products from $HAuCl_4 \cdot 4H_2O$/PVP/EG by a MW–polyol method, its maximum yield was only 3% and lengths of products had a wide distribution.[1c] The most significant finding in this work is that 1-D products having narrow size distributions (diameters 42 ± 6 nm, lengths 1.4 ± 0.3 μm) can be produced at a higher yield (24%) under bubbling N_2.

It is known that Au rods and wires can be produced using a seeded growth method developed by Sau and Murphy.[3] How-

Table 1. Yields of products from $HAuCl_4 \cdot 4H_2O$/PVP/EG by bubbling of N_2 or O_2, or without bubbling gas

Gas/ temperature	Yields/%						
	Octa-hedron	Nano-plate	Micro-plate	Deca-hedron	Icosa-hedron	Rods & wires	Others (sphere)
N_2/110 °C	0	2	0	0	24	24	50
O_2/110 °C	34	37	0	1	3	0.5	24
No gas/110 °C	0	39	36	8	4	3	10
N_2/198 °C	0	6	0	44	33	0	17
O_2/198 °C	8	24	0	16	18	4	30
No gas/198 °C	0	6	0	3	86	0	5

Table 2. Average sizes of products from $HAuCl_4 \cdot 4H_2O$/PVP/EG by bubbling of N_2 or O_2, or without bubbling gas

Gas/ temperature	Sizes						
	Octa-hedron /nm	Nano-plate /nm	Micro-plate /μm	Deca-hedron /nm	Icosa-hedron /nm	Rods & wires /μm	Others (sphere) /nm
N_2/110 °C		53 ± 22			48 ± 15	1.4 ± 0.3	105 ± 55
O_2/110 °C	33 ± 8	47 ± 17		56 ± 15	48 ± 9		105 ± 11
No gas/110 °C		310 ± 35	1.1 ± 0.3	275 ± 34	280 ± 25	2.4 ± 1.1	130 ± 34
N_2/198 °C		53 ± 15		57 ± 15	43 ± 17		37 ± 16
O_2/198 °C	78 ± 39	102 ± 14		89 ± 16	79 ± 7	124 ± 17	85 ± 35
No gas/198 °C		79 ± 8		52 ± 21	35 ± 6		69 ± 12

ever, a disadvantage of this method is that the addition of a small amount of Ag^+ to Au^{3+} ions is required. Therefore, a small amount of Ag is involved in the final 1-D products as impurity. The 1-D products obtained here consist of pure Au because the addition of Ag^+ is unnecessary. Thus, the present method gives a new promising method for the preparation of 1-D products of pure Au.

Expanded TEM images and crystal structures of 1-D products are shown in Figure S1,[6] where plate-like structures and pentagonal structures are observed. We found that the relative yields are 82% for plate-like wires and 18% for pentagonal ones.

Shapes and sizes change significantly with increasing the reaction temperature to the boiling point of EG (198 °C) as shown in Figures 1d–1f. The major products obtained under bubbling N_2 were decahedrons (44%) and icosahedrons (33%), whereas those under bubbling O_2 were quasi-spherical particles (30%), nanoplates (24%), and icosahedrons (18%). Without gas bubbling icosahedrons with an average size of 35 ± 6 were prepared in a high yield (86%). It should be noted that particle sizes increased by a factor of about two by changing bubbling gas from N_2 to O_2.

UV and visible absorption spectra of product solutions were measured (Figure S2).[6] Typical plasmon bands of Au nanostructures with peaks at 570 nm region were observed under bubbling N_2 or without gas bubbling at 110 °C, whereas plasmon peak was very weak under bubbling O_2 at 110 °C. When TEM images of products were observed, the total number of products was small under bubbling O_2. A low yield of Au products is a main reason for the weakness of the plasmon band. At 198 °C strong plasmon bands of small Au nanostructures with peaks at 570 or 600 nm were observed. Sufficient amounts of products on TEM grids were observed under bubbling O_2 at 198 °C, which was consistent with absorption spectral data.

We found that the concentration of O_2 in EG gave significant effects on the shapes and sizes of products. One possible effect is the adsorption of O_2 onto the surface of Au nuclei leading to deceleration of the growth rate of Au particles to specific direction. It is known that small sizes of Au particles have a strong catalytic activity for O_2.[4] Such an effect may also participate in the nucleation and crystal growth in the early stage. The other effect is the formation of glycolaldehyde (GA). Skrabalak et al.[5] reported that GA is formed upon EG heating in air to become a dominant reductant for polyol syntheses in the 140–160 °C range.

$$2HOCH_2CH_2OH + O_2 \rightarrow 2HOCH_2CHO + 2H_2O \quad (1)$$

Although the contribution of GA is insignificant at a low temperature of 110 °C, it may be formed at 198 °C in the presence of O_2 and accelerate the reduction rate of Au^{3+}.

In general, shapes of final products depend not only on the stability of crystal structures against etching by $AuCl_4^- + Cl^-$[1b] but also the density of Au^0 atoms around the growing nuclei. A high Au^0 concentration around the nuclei can create an environment with high twinning probability for the formation of such twinned particles as single-twin plates, five-twinned decahedrons and thirty-twin icosahedrons. At a low temperature of 110 °C, the reduction rate of Au^{3+} is slow, so that numbers of nuclei are small. Under such conditions, small numbers of large particles like long 1-D wires and large microplates are grown in the absence and presence of small amount of O_2, respectively. When a saturated amount of O_2 is present, small single crystal octahedrons and single-twin nanoplates are prepared. At 198 °C, the yields of decahedrons and icosahedrons increased. This suggests that the reduction rate of Au^{3+} increased at high temperature, so that the formation of multiple-twin particles becomes favorable. The high yield of icosahedrons in the presence of O_2 implies that a high concentration of Au^0 around the nuclei is established. Whether it is due to the formation of GA or other effects, further detailed experiments are required.

In summary, different Au nanostructures could be prepared by bubbling N_2 or O_2 gas, or without gas bubbling in $HAuCl_4 \cdot 4H_2O$/PVP/EG at 110 and 198 °C. We found that O_2 dissolved in EG takes part in the nucleation and/or crystal growth of Au nanocrystals or the formation of GA. Thus bubbling N_2 or O_2 gas can be used as a new experimental parameter in the synthesis of Au nanostructures in EG.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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