Shape-controlled Preparation of Gold Nanocrystals Using a Microwave–polyol Method

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Gold nanocrystals were prepared by a microwave (MW)–polyol method using di-, tetra-, and poly(ethylene glycol)s. When these polyols were heated to 240 °C at a heating rate of 160 °C/min and held at 240 °C for 5 min, icosahedral particles with average diameters of 55–85 nm were prepared from $HAuCl_4$/PVP in di-, tetra- and poly(ethylene glycol)s at high yield (≥91%). Plate-like and decahedral particles were obtained at high yields from $HAuCl_4$/PVP/NaCl.

Recently, nanostructured gold has attracted considerable attention mainly as a result of its remarkable optical properties and numerous applications such as catalysis, surface plasmonics, surface-enhanced Raman scattering, and chemical and biological sensing. Different chemical and physical properties of metallic crystals arise from different crystal shapes and sizes. Therefore, controllable preparation of nanocrystals with different shapes and sizes is important and challenging.

The polyol method is a typical technique used for preparation of metallic nanocrystals in solutions by reducing their ionic salts.[1] In general, a mixture of reaction reagents and a polymer surfactant such as poly(vinylpyrrolidone) (PVP) in ethylene glycol (EG) is heated in an oil bath for several hours. Microwaves (MWs) are useful as a heating source to initiate and prepare metallic nanoparticles rapidly in the polyol system. This method, called MW-polyol, has been applied for rapid preparation of Au nanoparticles within a few minutes.[2] Because substances can be heated rapidly from the inside under MW heating, higher-crystallinity nanoparticles can be obtained than those in conventional oil-bath heating. In our previous studies of the preparation of Au nanoparticles using the MW-polyol method with EG as a solvent and reductant, mixtures of anisotropic polygonal Au nanocrystals were generally produced.[2]

In the present study, shape-controlled preparation of Au nanocrystals is investigated using the MW-polyol method. In this work, diethylene glycol (DEG), tetraethylene glycol (TEG), and poly(ethylene glycol) (PEG) with higher boiling points than that of EG (198 °C) are used as new reducing solvents and reductants.

First, $HAuCl_4 \cdot 4H_2O$ was used as starting material for Au nanoparticles. It was dissolved in 20 mL of EG, DEG, TEG, or PEG at a constant concentration of 2.4 mM. Then, 500 mM of PVP ($M_w = 40000$ monomeric units) was added as polymer surfactant to the solution described above. When effects of oxidative etching by $AuCl_4^- + Cl^-$ anions were studied, 4.8 mM of NaCl was added to the reagent solution. The reaction system was heated from room temperature to 240 °C for DEG, TEG, and PEG at a heating rate of 160 °C/min and was held at 240 °C for 5 min by MW irradiation in a continuous wave mode (μReactor; Shikoku Instrumentation Co. Ltd.).

Product solutions were centrifuged at 13000 rpm for 60 min. For transmission electron microscopic (JEM-2010 TEM; JEOL) observation, samples were prepared by dropping colloidal solutions of the products onto carbon-coated Cu grids. Absorption spectra of the product solutions were measured in the UV-visible region using a spectrometer (UV-3600; Shimadzu Corp.).

Figures 1a, 1c, and 1e, respectively, show typical TEM images of the Au nanoparticles obtained from $HAuCl_4 \cdot 4H_2O$/PVP in DEG, TEG, and PEG. It is noteworthy that shapes and sizes of products depend strongly on the polyol solvent. The yields and average sizes of particles in each polyol are shown in Tables 1 and 2 together with corresponding data obtained in EG in our previous studies.[2c]

Dominant products are hexagonal particles in all polyols. Based on measurements of TEM images from view angles of ±15° and SEM observation (Figure S1 in Supporting Information),[5] hexagonal particles were assigned to icosahedral particles. Although no icosahedrons were prepared from $HAuCl_4 \cdot 4H_2O$/PVP in EG at a low reagent concentration,[2c] they were prepared at high yields (≥91%) in DEG, TEG, and PEG. Their yields were especially high in TEG (100%) and PEG (97%), and their average sizes were, respectively, 62 ± 17 and 55 ± 21 nm. In addition to icosahedral particles, a small amount

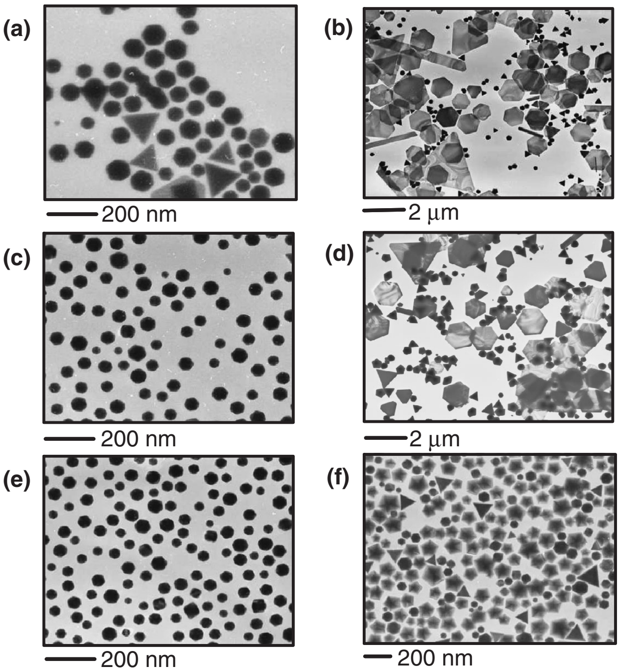

Figure 1. Au nanocrystals prepared in DEG (a and b), TEG (c and d), and PEG (e and f) under MW heating at 240 °C for 5 min: (a), (c), (e) NaCl (0 mM); (b), (d), (f) NaCl (4.8 mM).

Table 1. Yields of products obtained using a MW–polyol method from mixtures of $HAuCl_4 \cdot 4H_2O$/PVP/polyol and $HAuCl_4 \cdot 4H_2O$/PVP/NaCl/polyol[a]

Solvent	NaCl /mM	Yields of products/%					
		Octa-hedron	Nano-plate	Micro-plate	Deca-hedron	Icosa-hedron	Others (sphere)
EG	0	37	21	0	9	0	33
	4.8	2	25	0	12	47	14
DEG	0	0	8	0	0	91	1
	4.8	0	27	39	14	18	2
TEG	0	0	0	0	0	100	0
	4.8	0	32	12	22	5	29
PEG	0	0	0	0	3	97	0
	4.8	0	5	0	71	24	0

[a] Data for EG at 198 °C for 3 min are obtained from ref 2c.

Table 2. Average sizes of products obtained using a MW–polyol method from mixtures of $HAuCl_4 \cdot 4H_2O$/PVP/polyol and $HAuCl_4 \cdot 4H_2O$/PVP/NaCl/polyol[a]

Solvent	NaCl /mM	Average sizes of products					
		Octa-hedron /nm	Nano-plate /nm	Micro-plate /µm	Deca-hedron /nm	Icosa-hedron /nm	Other (sphere) /nm
EG	0	37 ± 8	67 ± 22		60 ± 9		58 ± 28
	4.8	30 ± 6	85 ± 17		78 ± 18	43 ± 5	67 ± 24
DEG	0		130 ± 13			85 ± 11	
	4.8		250 ± 15	0.91 ± 0.14	260 ± 34	210 ± 13	
TEG	0					62 ± 17	
	4.8		450 ± 90	1.2 ± 0.40	470 ± 47	420 ± 45	340 ± 37
PEG	0				74 ± 24	55 ± 21	
	4.8		110 ± 20		145 ± 51	73 ± 14	

[a] Data for EG at 198 °C for 3 min are obtained from ref 2c.

of triangular plates (8%) with an average diameter of 130 ± 13 nm was generated in DEG. Although highly crystalline polygonal nanocrystals were formed in EG under MW heating from room temperature to the boiling point of EG (198 °C) for 3 min, they had a wide shape distribution.[2c] We found that icosahedrons can be prepared from $HAuCl_4 \cdot 4H_2O$/PVP in high yields using DEG, TEG, and PEG at a high temperature of 240 °C.

When NaCl was added to the reagent solutions, shapes and sizes of product particles changed considerably, as shown in Figures 1b, 1d, and 1f. Dominant products in DEG and TEG were mixtures of large micrometer order plates and smaller plates, decahedrons, icosahedrons, and other particles including quasi-spherical particles. The yields of triangular and hexagonal microplates were 39% in DEG and 12% in TEG; their average sizes in DEG (0.91 ± 0.14 µm) were smaller than those in TEG (1.2 ± 0.40 µm). On the other hand, dominant products from $HAuCl_4 \cdot 4H_2O$/PVP/NaCl in PEG were decahedrons (71%) and icosahedrons (24%); no microplates were produced. In DEG, a small amount of one-dimensional products (rods) was also obtained. When Au particles were prepared from $HAuCl_4 \cdot 4H_2O$/PVP/NaCl in EG at 198 °C, major products were icosahedrons (47%) and nanoplates (25%).[2c] We found that yields of icosahedrons decrease to $\leq$24% in DEG, TEG, and PEG. Outstanding features obtained here are that large microplates are produced in DEG (39%) and TEG (12%); also, decahedrons with 145 ± 51 nm average diameter are produced in PEG at a high yield (71%). Although decahedral and icosahedral Au nanocrystals were produced at high yields by using conventional oil-bath heating and a hydrothermal method, it took more than 40 min.[3] An advantage of the present MW-polyol method is that they could be prepared by MW heating for only 5 min.

Figure S2 in Supporting Information[5] portrays UV and visible spectra of Au nanoparticles prepared in four polyols under MW heating. Without addition of NaCl, a symmetrical plasmon band of icosahedrons with a peak at 530–580 nm was observed in DEG, TEG, and PEG. On the other hand, in the presence of NaCl, plasmon bands of Au disappeared in DEG and TEG, whereas a symmetrical plasmon band of decahedra with a peak at 640 nm was observed in PEG. The lack of a plasmon band for DEG and TEG is probably attributable to plate-like products that were too large to show a plasmon resonance band.

When we prepared Au nanoparticles under oil-bath heating using the same polyol solvents, mixtures of octahedrons, plates, decahedrons, and icosahedrons were obtained.[4] Their product distributions were wider than those obtained in this work, which indicates that MW heating is the more rapid and useful technique for shape-selective preparation of Au nanocrystals. One reason is the skin effects of MW that penetrate inside the particles and heat conductive electrons of Au particles. In general, shapes of final products depend not only on the stability of crystal structures against etching by $AuCl_4^- + Cl^-$ but also the density of Au^0 atoms around the growing nuclei. A high related ion 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 multiple-twin icosahedrons. We found that a high ion concentration is achieved using DEG, TEG, and PEG and an additive such as NaCl. Therefore, these twinned crystals are producible under MW heating. This process can be applied widely to the rapid formation of decahedrons and icosahedrons at high yields. Although differences in the concentration, reduction ability and viscosity of each polyol, and the presence or absence of Cl^- anions affect the final shapes of Au nanocrystals, more detailed studies must be undertaken to clarify the growth mechanism of Au nanocrystals under MW heating.

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