

# Control of nucleation and growth of gold nanoparticles in AOT/Span80/isooctane mixed reverse micelles

Chen-Li Chiang\*, Meng-Bor Hsu, Long-Biao Lai

*Department of Chemical Engineering, Southern Taiwan University of Technology, No. 1 Nan-Tai Street, 710 Yung-Kang City, Tainan Hsien, Taiwan, ROC*

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## Abstract

In this study, we demonstrate that mixed reverse micelles are good candidates to be used as nanoreactors for formation of shape-controlled high-quality colloidal nanocrystals and nanowires under mild conditions. Manipulation of the rate of nucleation and subsequent growth of the Au in the mixed reverse micelles induce drastic changes in the particle shape and structure. Here we demonstrate that control of the nucleation and growth kinetics of the Au in the mixed reverse micelles can be used to vary the shapes of the resulting particles from a nearly spherical morphology to cylinders, trigons and cubics. The characterization of the resultant particles, the effects of synthesis conditions (such as concentration of NaCl, addition of glycerol, and reaction temperature) on particle sizes, particle size distribution, and shape of particle formation have been investigated. This study will help us to understand the chemical control synthesis of crystal growth processes at the atomic level.

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## 1. Introduction

The possibility of preparing nanosized metal particles with homogeneous morphology and size is of great interest because such particles have extremely small size and large specific surface area that can be applied in a wide range of chemical and physical applications. Among the most appealing properties are electronic, optical, magnetic and catalytic ones [1–4]. These applications are strongly dependent on the size and shape (or morphology) of the metal nanoparticles; therefore, the synthesis of controlled shapes and sizes of nanoparticles could be potentially important for these applications [5–7]. However, many studies on nanoparticles have focused on the synthesis of uniform spherical forms and the control of their particle sizes. Recently, the shape control of nanoparticles was recognized as a

very important issue in the nanoparticle synthesis, which became a challenging task [8–13]. Reverse micelles are generally described as nanometer-sized water droplets dispersed in apolar solvent with the aid of a surfactant monolayer, forming a thermodynamically stable and optically transparent solution. Reverse micelles are used as microreactors because they exchange the content of their water pools by collision process [14–16]. Such a micellar core can be considered as a nanoreactor, where nucleation and growth of metal particles upon reduction are restricted to the mesoscale level. The structure of mixed reverse micelles is mainly utilized as a template to limit the crystal nucleation and growth; thus crystals with a specific size and shape can be produced. Many monodispersed metal particles have been obtained in the reverse micellar system, but most of their shapes have been limited to spheres. In earlier works [17,18], we reported the preparation of a wide range of shapes of Au nanoparticles, including cylinders and trigons, in mixed reverse micelles. There are two strategies that we have

\*Corresponding author. Fax: +886-6-2425741

E-mail address: [chiang@mail.stut.edu.tw](mailto:chiang@mail.stut.edu.tw) (C.-L. Chiang).

learned from the earlier work used here to produce anisotropic gold nanoparticles with high crystallinity, narrow size distributions, and a high degree of shape control. The first lesson from the earlier work is that the precursor was injected directly to the mixed reversed micelles containing hydrazine. Second, anisotropic gold nanoparticles were obtained at the lower molar ratio of hydrazine to  $\text{HAuCl}_4$ . According to our previous studies, the control of the final Au nanoparticle size and shape was related to molar ratio of reduction agent to precursor and the sequence of addition of metal salt into the mixed reverse micelles. A decrease in the molar ratio of reduction agent to precursor and direct injection of precursor to mixed reverse micelles containing the reduction agent resulted in the formation of anisotropic gold nanoparticles, such as cylinders and trigons. Here we demonstrate that control of the nucleation and growth kinetics of the Au in the mixed reverse micelles can be used to vary the shapes of the resulting particles from a nearly spherical morphology to cylinders, trigons and cubics. The characterization of the resultant particles, the effects of synthesis conditions (such as concentration of NaCl, addition of glycerol, and reaction temperature) on particle sizes, particle size distribution, and shape of particle formation have been investigated.

## 2. Materials and methods

### 2.1. Materials

The metal salt tetrachloroauric acid ( $\text{HAuCl}_4$ ) was obtained from Acros Organics (Belgium). Sodium borohydride ( $\text{NaBH}_4$ ) was the guaranteed reagent of E. Merck (Darmstadt). Sodium di-2-ethylhexylsulfosuccinate (AOT) purchased from Sigma Chemical Co. (St. Louis, MO) was vacuum dried at  $60^\circ\text{C}$  for 24 h and stored in a vacuum desiccator prior to use. HPLC-grade isooctane supplied by TEDIA (Fairfield) was dehydrated with molecular sieves 4A (8–12 mesh, Janssen) for at least 24 h and kept in a vacuum desiccator before use. Non-ionic cosurfactant sorbitan monooleate (Span80) was also purchased from Sigma. The residual water of the isooctane solution of AOT was recognized to be negligible using a Karl–Fisher moisture titrator (Kyoto Electronics MKC-500). The water used throughout this work was the reagent-grade water produced by Milli-Q SP Ultra-Pure-Water Purification System of Nihon Millipore Ltd., Tokyo.

The mixed reverse micellar solutions containing  $\text{HAuCl}_4$  or sodium borohydride were prepared by injecting the required amounts of the corresponding aqueous solution into an isooctane solution of AOT, and then were used for the preparation of nanosize particles.

### 2.2. Preparation of gold nanosize particles

A stock solution of 0.10 M AOT/isooctane was first made up. Then, the reverse micellar solution was prepared containing equal amounts of aqueous stock solutions of  $\text{HAuCl}_4$  or  $\text{NaBH}_4$  to give the required  $\omega_0$  value, where  $\omega_0$  is defined as the molar ratio of water to surfactant. An appropriate amount of nonionic surfactant (Span80) was dissolved in AOT/isooctane solution to form a mixed reversed micellar solution.

### 2.3. Characterization

The shape and dimension distributions were measured by either a JEOL JEM-1200EX transmission electron microscope (TEM) or a Hitachi Model HF-2000 field emission TEM operated at accelerating voltages of 80 and 200 kV, respectively. Bright-field and dark-field images were taken to reveal the morphology of particles. Structure information was obtained using selected area electron diffraction and HRTEM lattice imaging. Samples were prepared by placing a drop of the dispersed solution onto a Formvar-covered copper grid and evaporated in air at room temperature for 24 h. Before withdrawing the samples, the dispersed solutions were sonicated for 1 min.

## 3. Results and discussion

### 3.1. Effect of addition of NaCl on the formation of anisotropic Au nanoparticles

Experimentally, the precursor  $\text{HAuCl}_4$  was injected directly to the AOT/Span80/Isooctane mixed reversed micelles containing sodium borohydride. In the absence of NaCl added to the mixed reversed micelles, very few elongated and cylindrical Au nanoparticles are observed (Fig. 1A). Most of the particles are many faceted and multiply twinned. Addition of 2.5 M of NaCl in the water pool of mixed reversed micelles induces a marked change in the particle shape with appearance of cylinders, trigons and cubics (Fig. 1B). The length and width of the longest are about 46 and 10 nm, respectively. Increasing the NaCl concentration in the system was found to be favorable for the formation of the Au nanoparticles with more regular shape and narrow particle size distribution. The corresponding electron diffraction (ED) pattern of a single trigon Au nanoparticle (Fig. 2A) reveals that a hexagonal diffraction spot pattern was generated, which demonstrated that the plate-like triangular Au nanoparticles prepared with the addition of NaCl are highly individuated crystals with a preferential growth direction along the Au  $\{111\}$  plane. Fig. 2B shows the ED patterns of selected areas of a single Au cylinder. It shows that the Au cylinder is a

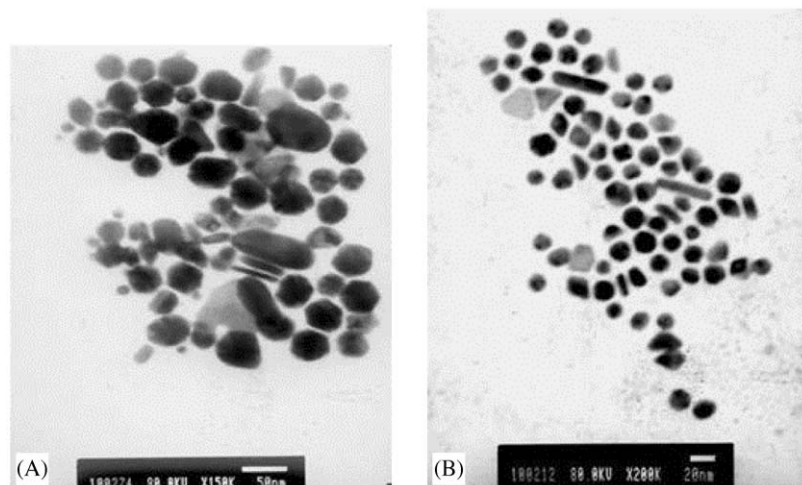


Fig. 1. Effect of addition of NaCl on the formation of anisotropic Au particles in mixed reverse micelles.  $[\text{NaBH}_4]/[\text{HAuCl}_4] = 1.0$ ;  $[\text{AOT}] = 0.10 \text{ M}$ ;  $[\text{Span80}] = 0.20 \text{ M}$ ;  $\omega_0 = 10$ ;  $25^\circ\text{C}$ . (A)  $[\text{NaCl}] = 0$ , (B)  $[\text{NaCl}] = 2.5 \text{ M}$ .

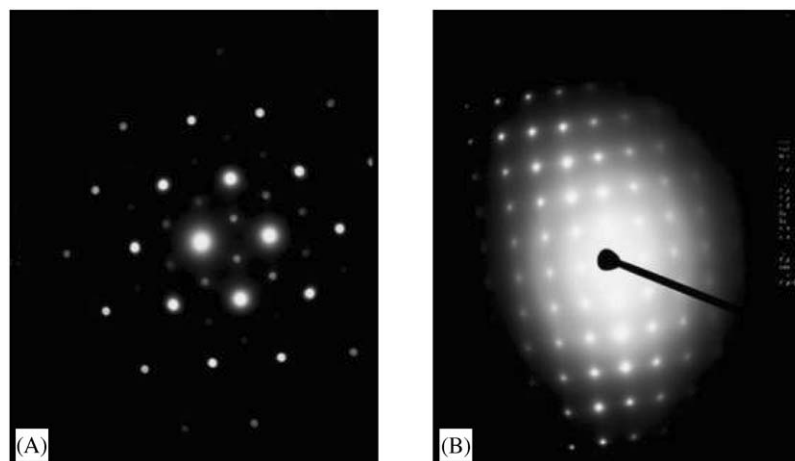


Fig. 2. Corresponding ED pattern of (A) a single trigon Au nanoparticle; (B) a single-cylinder Au nanoparticle.

single crystal. The cylinder axis (growth direction) was  $\{111\}$ . According to the Hofmeister series, a low solubility of organic molecules (salt out) is obtained by the addition of  $\text{Cl}^-$  in aqueous solution. The initial nucleation of this new approach can be accelerated, which results in the formation of many nuclei in a short burst. It tends to produce smaller and more numerous particles as observed in Fig. 1B. In general, the size distribution of a colloidal dispersion of solid particles is determined by the rate of nucleation of the solid cores and the subsequent growth. For a given amount of material, the ratio between the rates of these two processes determines the size and number of particles. In colloids, addition of salts is well known to induce an increase in the interface rigidity. Taking into account such changes in the local microstructure of the template, we could assume that the growth rate of Au

nanoparticles was reduced. Therefore, it was enough time for the Au cluster to aggregate and grow into Au nanoparticles with a more regular shape. The formation of trigons and cylinders having a high crystallinity indicates that the micellar structure governs a fast nucleation and a slow growth with addition of NaCl. The above results suggest that NaCl has a subtle influence on the crystallization of Au nanoparticles from  $\text{Au}^{+3}$  solution. Consequently, control over  $[\text{Cl}^-]$  levels may therefore be an important factor in establishing unique Au morphologies in the mixed reverse micellar system. Composition of particle was analyzed by energy-dispersive X-ray analysis (EDX) with a Noran Model Voyager 1000 system. According to the results of EDX (data not shown), there is no trace of any impurities in Au particles investigated. It clearly indicates that pure Au is contained.

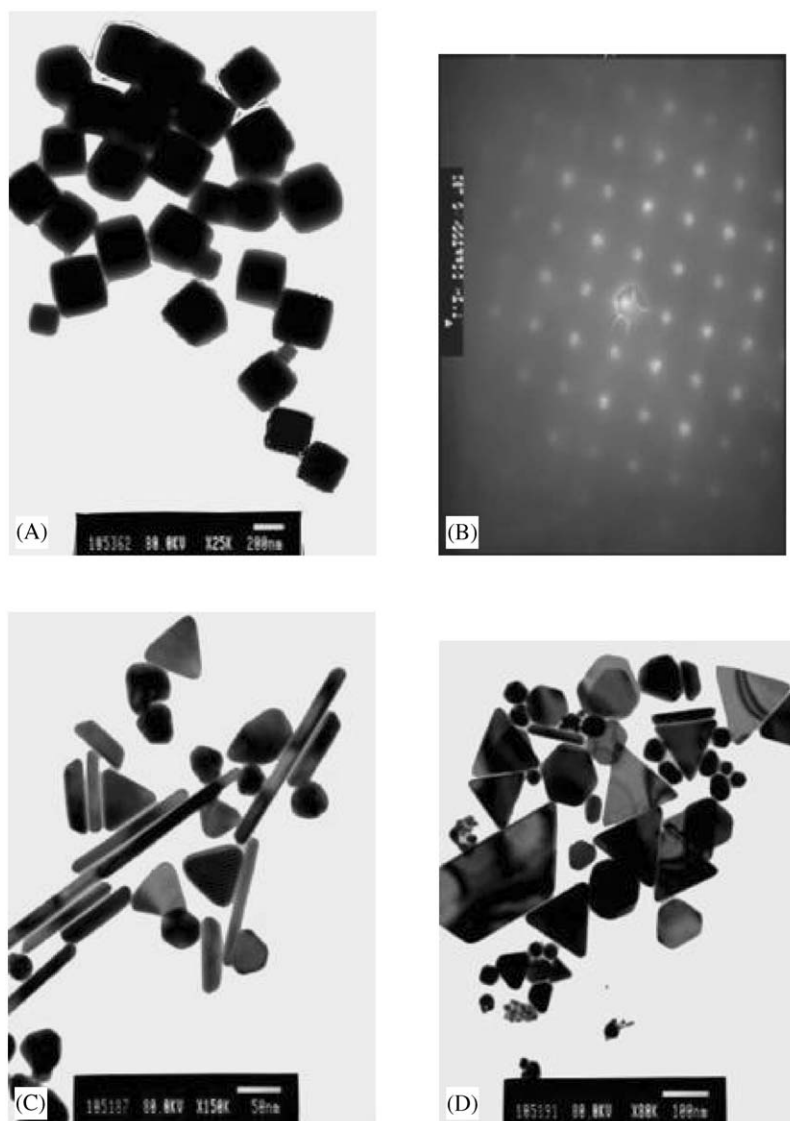


Fig. 3. Effect of the reaction temperature on the formation of anisotropic Au nanoparticles with addition of glycerol.  $[\text{NaBH}_4]/[\text{HAuCl}_4]=0.22$ ;  $[\text{AOT}]=0.10\text{ M}$ ;  $[\text{Span80}]=0.20\text{ M}$ ;  $\omega_0 = 10$ . (A) Glycerol=10%, 25 °C; (B) corresponding ED pattern of a single cubic Au nanoparticles; (C) Glycerol=10%, 4 °C; (D) Glycerol=10%, 50 °C.

### 3.2. Effect of temperature on the formation of anisotropic Au nanoparticles

It was found in Fig. 3A that the crystal morphology of the Au nanoparticles is predominately cubic, about 168 nm in size with addition of 10% glycerol in a water pool of mixed reverse micelles at 25 °C. The corresponding ED pattern in Fig. 3B showed that these cubic Au nanoparticles also obtained highly crystallized single crystals with a preferential growth direction along the Au {111} crystal plane. The reaction temperature was also found to be an important parameter in the control of size and shape for the production of Au nanoparticles. A decrease in the reaction temperature to 4 °C, as shown in Fig. 3C, resulted in the formation of cylinders, polyhedrons and trigons of Au nanoparticles. It can be

interpreted that in this case the gold atoms produced during the chemical reaction are in a more viscous and low-temperature environment. The increase in viscosity of the water pool of reverse micelles with an addition of glycerol and lower reaction temperature can be related to the decrease in growth rate of Au nanoparticles. This prevents the atoms from diffusing inside the matrix and the atoms one by one bound to the cubic, cylinder and trigon nucleus. However, in the case of an increase in the temperature to 50 °C, as shown in Fig. 3D, the larger particle size and the broader size distribution of the Au nanoparticles are obtained. An increase in temperature facilitates the opening of droplets owing to a decrease in interfacial rigidity, enhanced interdroplet interaction, and rapid diffusion of Au from one droplet to another in the transient droplet dimmers. The rate of Au reduction

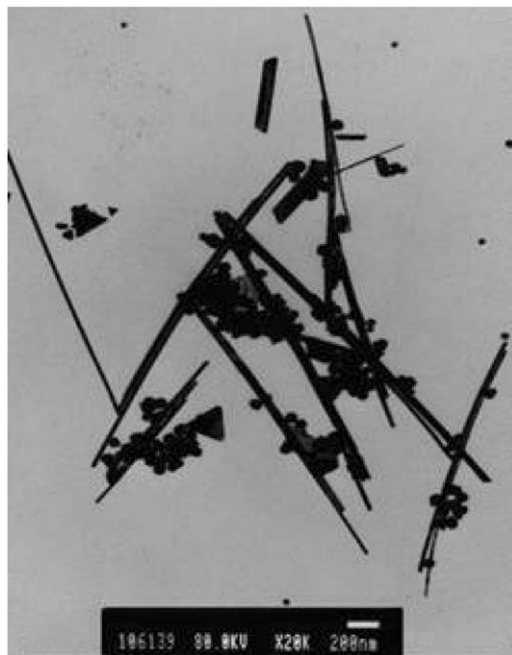


Fig. 4. TEM of Au nanowires prepared as per the condition in Fig. 3C and incubated in 25 °C for 24 h.

reaction is also increased as the temperature rises. When the Au concentration increases above the saturation concentration, the secondary nucleation occurs. All these factors, in combination, are responsible for the nucleation and growth processes continuing in parallel, resulting in a broader range in the size of the particles, as seen in Fig. 3D. The mechanism of controlling colloid morphologies by appropriate synthesis conditions, however, requires more detailed examination and will be part of forthcoming work. The sample of the condition in Fig. 3C was withdrawn and incubated at 25 °C for 24 h. The morphologies of the particles were similar to those shown in Fig. 3C. Typically, the diameters of Au nanowires were in the range of 22–88 nm, and their lengths were up to several  $\mu\text{m}$ , as shown in Fig. 4. These results indicate that the growth of Au nanowires can start from the cylinder shape.

#### 4. Summary

In this study, we demonstrate that mixed reverse micelles are good candidates to be used as nanoreactors

for formation of shape-controlled high-quality colloidal nanocrystals and nanowires under mild conditions. The manipulation of the rate of nucleation and the subsequent growth of the Au in the mixed reverse micelles induces drastic changes in the particle shape and structure. This study will help us to understand the chemical control synthesis of crystal growth processes at the atomic level.

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