

Mechanism for controlling the shape of Cu nanocrystals prepared by the polyol process

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This study investigated a mechanism for controlling the shape of Cu nanocrystals fabricated using the polyol process, which considers the thermodynamic transition from a faceted surface to a rough surface and the growth mechanisms of nanocrystals with faceted or rough surfaces. The faceted surfaces were stable at relatively low temperatures because of the low entropy of perfectly faceted surfaces. Nanocrystals fabricated using a coordinative surfactant stabilized the faceted surface at a higher temperature than those fabricated using a noncoordinative surfactant. The growth rate of the surface under a given driving force was dependent on the surface structure, i.e., faceted or rough, and the growth of a faceted surface was a thermally activated process. Surface twins decreased the activation energy for growth of the faceted surface and resulted in rod- or wire-shaped nanocrystals.

I. INTRODUCTION

Nanocrystals with uniform sizes and shapes have a wide range of potential applications, such as in biosensing systems, plasmonics, photonics, and recording media. Simultaneously, nanocrystals can serve as templates for nanostructures or as building blocks for more complicated nanostructures.¹⁻³ It has been reported that the physical and chemical properties of nanocrystals are dependent on the materials, and at the same time, particle size and shape.¹⁻³ For example, the plasmonic resonance and catalytic properties of metal nanocrystals are dependent on the crystallographic characterization of surfaces, and the magnetic properties of Fe or Co nanocrystals are dependent on their size and aspect ratio.^{1-3,21} Therefore, monodispersed nanoparticles with a controlled shape and size are required for the application of nanocrystals.

In recent years, there has been intense research on the fabrication of nanocrystals using various processes.¹⁻⁶ Rapid thermal decomposition can produce nanocrystals with a uniform size distribution and an average size below 10 nm by separating the nucleation and growth mechanisms.^{1,3} However, the control of nanocrystal shape during rapid thermal decomposition is relatively difficult. Slow processes, such as reduction with metal salts or slow thermal decomposition, can be used to control the shape of nanocrystals.² The polyol process is one

such slow process in which the metal salts are reduced by polyols. The polyol process has been used to produce metal nanocrystals of Fe, Co, Ni, Cu, Ag, Au, Pt, and their alloys. Moreover, nanocrystals of various shapes can be fabricated using the polyol process, including cubes, spheres, rods, and wires.^{2,4-17} The process parameters such as temperature, reaction time, and type of surfactant can influence the shape of nanocrystals.^{2,4-17} However, the mechanism for controlling the shape of nanocrystals is not fully understood.

The equilibrium concentration of vacancies must exist in pure metal to maintain entropy. The vacancies in pure metal result in a disordering of structure and an increase in the configurational entropy. This principle can be extended to the surface of metals. For a perfectly faceted surface, atoms are located at each lattice point. The entropy of a perfectly faceted surface is extremely low and the faceted surface is unstable thermodynamically at temperature above 0 K. Therefore, a thermodynamic equilibrium concentration of vacancies should exist on the faceted surface to increase entropy.

The shape of nanocrystals is related to their surface facets.¹⁴ In particular, nanowire and nanorod metal nanocrystals are affected by twins within the metal nanocrystals.¹⁵⁻¹⁷ The shape and growth of metals are dependent on their surface structure, i.e., a faceted or round surface.¹⁸ The relationships among surface structure, growth mechanism, and the effect of twins has been researched in metallurgy and crystal growth for several decades.¹⁸ For example, the equilibrium number of vacancies on the surface of fcc-structured crystals, which

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have a coordination number of 6 at the (111) surface, can be obtained as follows¹⁸

$$\frac{n_v}{N_a - n_v} = \exp - \left\{ \frac{3\epsilon}{k_B T} \left[1 - 4 \left(\frac{n_v}{N_a} \right) \right] \right\}, \quad (1)$$

where n_v is number of vacancies in the perfectly faceted surface with total of N_a atoms, ϵ is the bonding energy, and k_B is the Boltzman constant.

In this study, we attempted to interpret the shape-control mechanism using this relationship, focusing on the thermodynamic conditions of the surface structure, i.e., faceted and rough surfaces, and the effect of surface structure and twins on the growth of Cu nanocrystals prepared using the polyol process.

II. EXPERIMENTAL PROCEDURE

Colloidal Cu nanocrystals were fabricated using the polyol process with the surfactants oleylamine, trioctylphosphine oxide (TOPO), and oleic acid. As a Cu source, copper (II) acetylacetonates, which are a common source for Cu preparation, were used. 1,2-Hexadecanediol is used for reducing polyol and octyl ether is used as solvent. We mixed 0.25 mmol copper(II) acetylacetonate [$\text{Cu}(\text{acac})_2$], 0.75 mmol 1,2-hexadecanediol, and various amounts of surfactant in 10 ml of octyl ether in a three-neck flask and heated it to a temperature range of 150 °C–290 °C at a rate of 10 °C/min under Ar gas. After holding at given temperature for 0–120 min, the mixture was air-cooled on the mantle to room temperature. During heating, the $\text{Cu}(\text{acac})_2$ was reduced to Cu at 150 °C. Twenty milliliters of ethanol was added to the solution to precipitate the Cu nanocrystals at room temperature. The Cu nanocrystals were separated from the solution by centrifugation and were then dispersed in 2 ml of n-hexane. Cu nanocrystal specimens were prepared for transmission electron microscopy (TEM) by dropping the suspension onto a carbon film-supported grid, and the morphologies of the Cu nanocrystals were analyzed under field-emission gun TEM (Tecnai 20F; Philips, Amsterdam, The Netherlands).

III. RESULTS AND DISCUSSION

A. Mechanism for surface roughening of Cu nanocrystals

During the polyol process, the Cu nanocrystals are formed within solution by the reduction of Cu ions decomposed from $\text{Cu}(\text{acac})_2$ with protons supplied from 1,2-hexadecanediol, which undergoes dehydration and duplicative oxidation by heating. The characteristics of Cu nanocrystals fabricated using the polyol process at 150 °C with oleylamine are shown in Fig. 1. The Cu

nanocrystals have several different shapes with well-developed faceted surfaces, as shown in Figs. 1(a) and 1(c). The diffraction pattern and energy dispersive x-ray analysis in Fig. 1(b) indicate that the fabricated nanocrystals are metallic Cu. Twins are one of the most important features of Cu nanocrystals in which twins induce a pentagon-shape or a linear fringe within cubic or spherical nanocrystals, as shown in Figs. 1(a) and 1(d).

The shape of a nanocrystal is strongly related to the facets formed on the surface as shown in Figs. 1(e) and 1(f).¹⁴ Therefore, control of the surface facets of nanocrystals is the key to determining their shape.¹⁴ The stability of faceted or rough surfaces during the fabrication process is based on thermodynamics.¹⁸ Therefore, the surface structure of Cu nanocrystals, i.e., faceted or rough, should depend on the reaction temperature and chemical environment, such as the presence of surfactants. The temperature dependence of the faceted surfaces of Cu nanocrystals is supported by the TEM observations in Fig. 2. For Cu nanocrystals prepared with oleylamine, which is a noncoordinative surfactant, the nanocrystals have a faceted surface at a reaction temperature of 150 °C. However, the shape of the Cu nanocrystals becomes round and the surface facets disappear at a reaction temperature of 180 °C. The Cu nanocrystals prepared with TOPO, which is a coordinative surfactant,¹⁹ have faceted surfaces at a reaction temperature of 165 °C and their edges become rounder with increasing reaction temperature. The surface facets finally disappear at a reaction temperature of 290 °C, giving round Cu nanocrystals. In both cases, the faceted surfaces of nanocrystals cannot be maintained at high reaction temperatures, although Cu nanocrystals prepared with the coordinative surfactant have a higher transition temperature from a faceted surface to a rough surface. This phenomenon can be interpreted by applying thermodynamic analysis to the surface roughening of crystals related to surface defects.¹⁸

The equilibrium number of vacancies on the surface is shown with respect to the bonding energy between the atoms forming the nanocrystals, i.e., $3\epsilon/k_B$, in Eq. (1) in Fig. 3(a). In this relationship, the equilibrium number of vacancies increases with the temperature and the number of vacancies increases suddenly at a specific temperature. Note that the faceted surface becomes rough as the number of vacancies at the surface increases. Therefore, the specific temperature above which the equilibrium number of surface vacancies suddenly increases can be defined as the roughening temperature.

The roughening of a faceted surface is not only dependent on temperature, but also on the bonding energy between the surface atoms. When the bonding energy ϵ increases, the roughening temperature increases in Eq. (1) and Fig. 3(a). This explains why the faceted surfaces are maintained at a higher temperature when fabricated

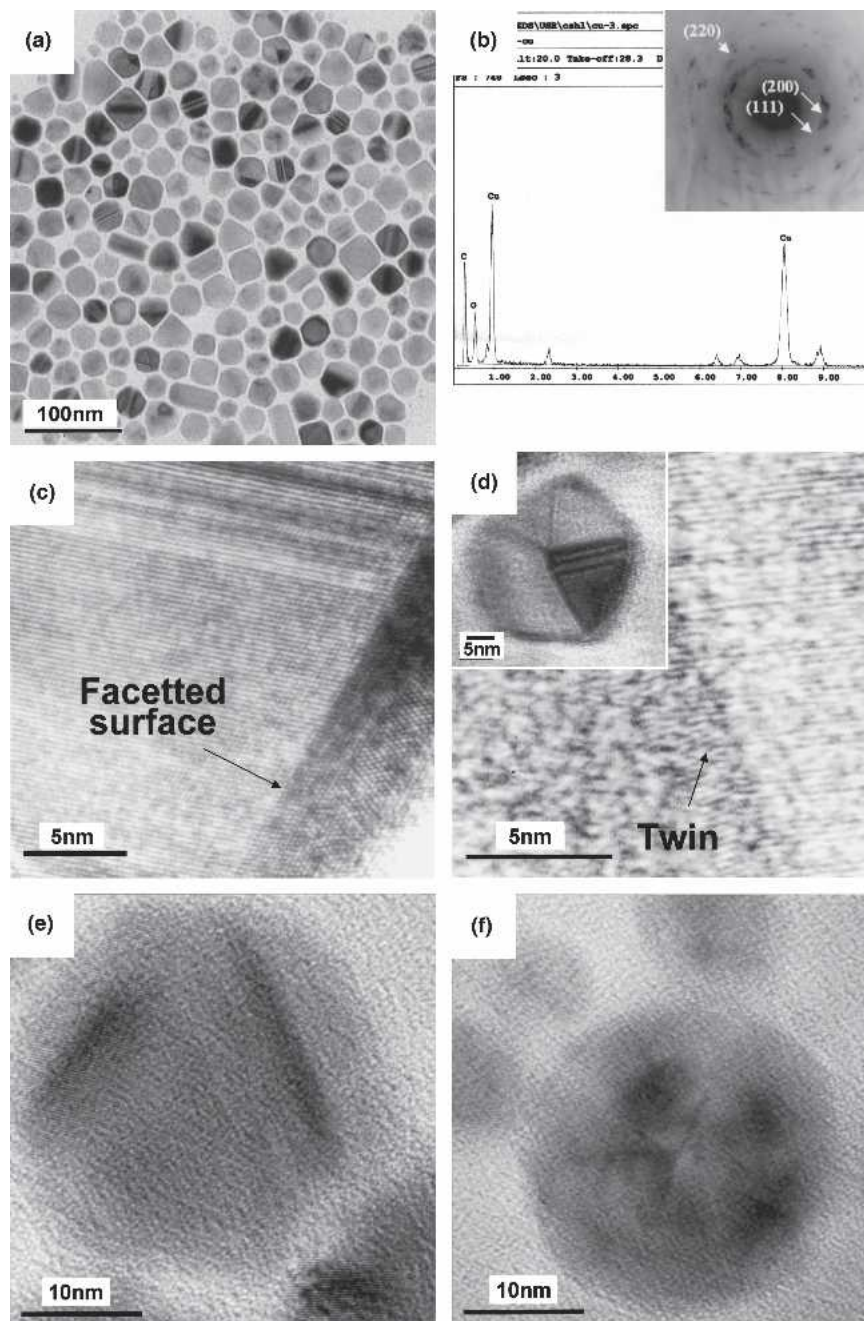


FIG. 1. TEM micrographs of Cu nanocrystals reacted at 150 °C for 0 min with 0.33 mmol oleylamine. (a) Low-magnification micrograph, (b) diffraction pattern and energy dispersive x-ray analysis, (c) high-resolution image of the surface of the Cu nanocrystal, and (d) high-resolution image of twins in a Cu nanocrystal and a pentagon-shaped Cu nanocrystal with a twin. (e) High-magnification micrograph of faceted Cu nanocrystal and (d) round Cu nanocrystal.

with coordinative surfactants. For nanocrystals fabricated with coordinative surfactants, extra energy, ϵ_s , is required to form a vacancy, and this equals the bonding energy between an atom and the surfactant compared with those fabricated with noncoordinative surfactants. The bonding energy in Eq. (1) then becomes $\epsilon + \epsilon_s$, rather than ϵ , as illustrated in Fig. 3(b). Therefore, the coordinative surfactant increases the roughening transition temperature

and induces faceted surfaces to become more stable. This role of coordinative surfactant on surface facet is also observed in Co nanocrystals.²¹

The roughening of the faceted surface is dependent on the size of the nanocrystals, as well as on the temperature and bonding energy of the surface atoms. When a nanocrystal is small, the number of atoms on the surface is limited. Therefore, the roughening temperature

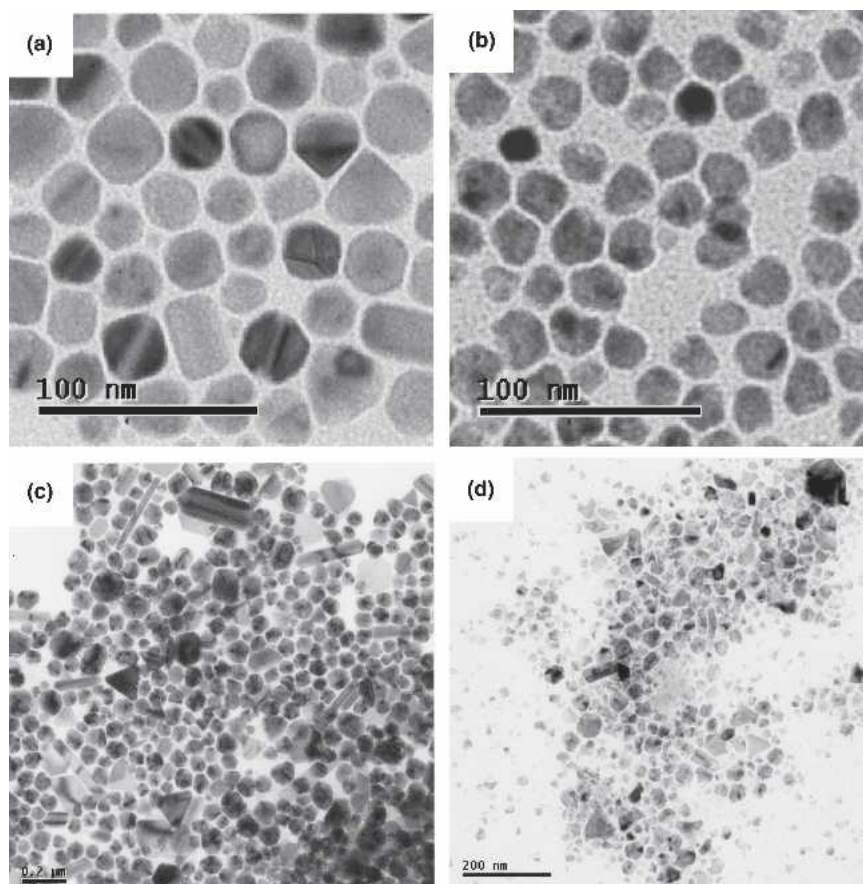


FIG. 2. TEM micrographs of Cu nanocrystals with various surfactants and reaction temperatures. (a) Cu nanocrystals reacted at 150 °C for 0 min with 0.33 mmol oleylamine, (b) nanocrystals reacted at 180 °C for 0 min with 0.33 mmol oleylamine, (c) nanocrystals reacted at 165 °C for 30 min with 0.33 mmol TOPO, and (d) nanocrystals reacted at 290 °C for 30 min with 0.33 mmol TOPO.

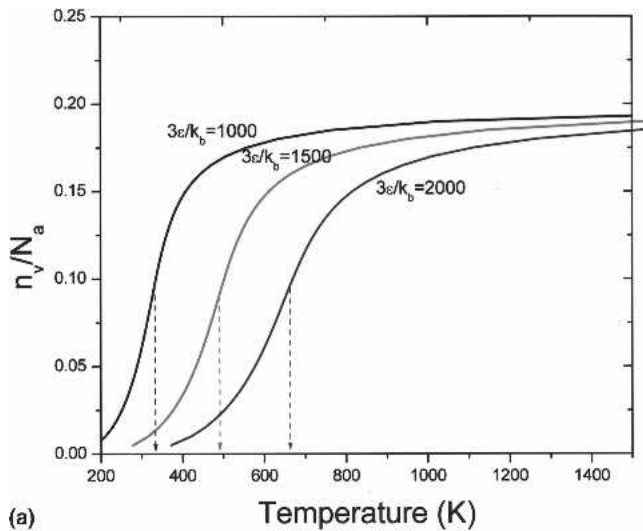
decreases with decreasing size of the nanocrystals. At a fixed temperature, smaller nanocrystals with rough surfaces can coexist with larger nanocrystals with faceted surfaces, as shown in Figs. 2(a) and 2(c), when the nucleation and growth step are not separated by a slow reaction process; as a result, the size distribution of the nanocrystals is relatively broad. This phenomenon can explain why faceted metal nanocrystals larger than 50 nm can be mixed with smaller round metal nanocrystals smaller than 50 nm.

B. Effect of twins and surface structures on the growth of Cu nanocrystals

Crystal growth is based on a kinetic process. The growth rate is dependent on the driving force and activation energy for crystal growth. The surface structure of nanocrystals, i.e., faceted or rough surfaces, determines the activation energy for crystal growth.¹⁸ For rough surfaces, the growth rate of a nanocrystal is proportional to the driving force. However, more complicated growth mechanisms result when the faceted surfaces are maintained during the growth of nanocrystals. For a faceted

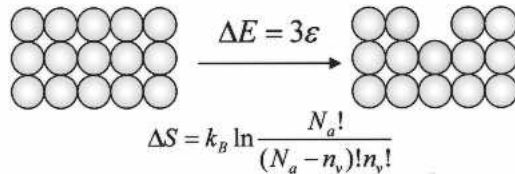
surface, the nanocrystal grows with nucleation and the growth of kinks at ledges via the surface diffusion of absorbed atoms. Therefore, the growth of faceted nanocrystals follows a thermally activated process, as shown in Fig. 4(a).¹⁸ When twins or screw dislocations exist on the faceted surface, they can act as nucleation sites for the growth of ledges and can reduce the activation energy for nucleation. Therefore, the growth rate of the faceted surfaces of nanocrystals containing twins or screw dislocations is faster than that of a perfectly faceted surface, as shown in Figs. 4(a) and 4(b).

The growth mechanisms for faceted or rough surfaces of nanocrystals are supported by the morphologies of the Cu nanocrystals fabricated with a coordinative surfactant, such as TOPO or oleic acid, in which some of them are faceted, as shown in Fig. 5. In Figs. 5(a) and 5(b), the nanocrystals with rough surfaces grow rapidly, whereas the nanocrystals with faceted surfaces do not grow. The reaction rate of the polyol process is slower than that of the rapid injection and thermal decomposition process. Therefore, in isothermal process at reaction temperature, the reaction continues until $t = t_f$ as shown in Fig. 5(c). In this case, when the reaction is continued, i.e., $t = t_f$ in

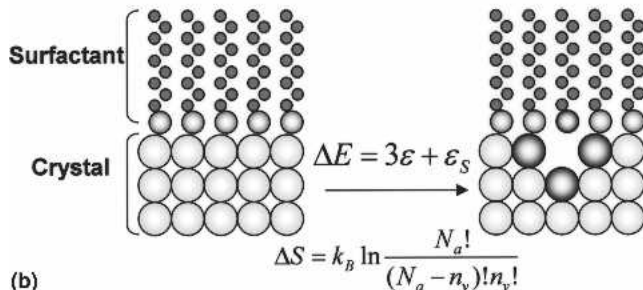


(a)

Non-coordinative surfactant



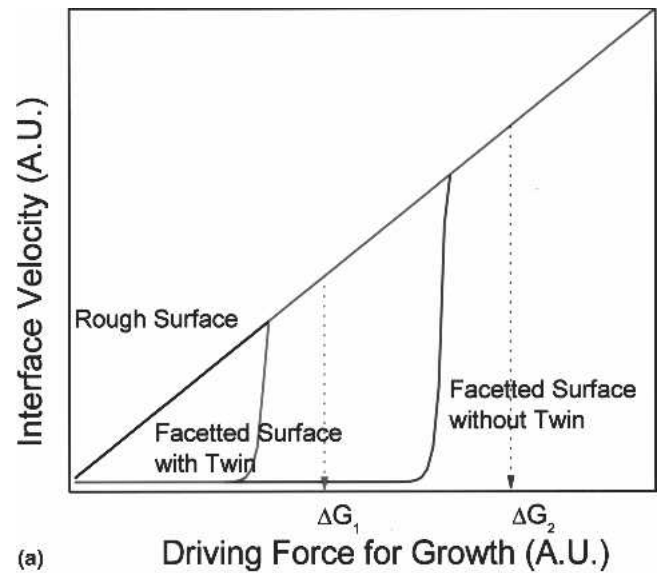
Coordinative surfactant



(b)

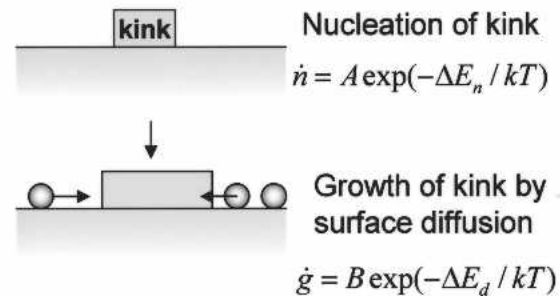
FIG. 3. Schematic illustrations of the equilibrium vacancy concentration at various temperatures. (a) Plots of the equilibrium vacancy concentration versus temperature when $3\epsilon/k_B$ is 1000, 1500, and 2000. (b) Illustration of the formation of a surface vacancy with the addition of a noncoordinative (above) and coordinative (below) surfactants.

Fig. 5(c), the driving force for growth is the sum of driving force by supplying Cu atoms by reaction (ΔG_r) and driving force by Ostwald ripening ($\Delta G_{O,R}$). However, after the reaction is over, i.e., $t = t_2$ in Fig. 5(c), the driving force for growth is only from Ostwald ripening because there are no Cu atoms supplied by reaction. Therefore, when the faceted and round nanocrystals are mixed, as shown in in Fig. 5(a), at the onset of growth, sufficient driving force, ΔG_2 in Fig. 4(a), is supplied by sum of continued reaction and Ostwald ripening for growth of faceted and round nanocrystals. However, as reaction time increases, the reaction is over and the driving force for growth decreases to a growth rate of ΔG_1 and only round nanocrystals can grow.

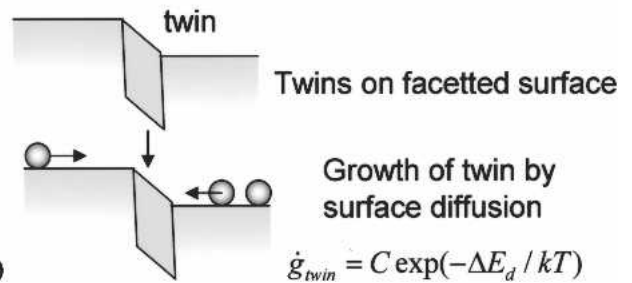


(a)

Growth mechanism of facetted interface



Growth mechanism of twinned interface



(b)

FIG. 4. Schematics of the growth rate according to the driving force for various surface structures. (a) Growth rate versus driving force for a rough surface, perfectly faceted surface, and a faceted surface containing a twin. (b) Illustration of the growth mechanism for a perfectly faceted surface (above) and a faceted surface containing a twin (below); \dot{n} is the nucleation rate, \dot{g} is the growth rate of the surface, E_n is the kink nucleation activation energy, and E_d is the surface diffusion activation energy.

The nanocrystals with faceted surfaces can grow into wire- and rod-shaped nanocrystals. Previous studies found that the formation of nanowires in the polyol process is closely related to twins on the faceted surface.¹⁵⁻¹⁷

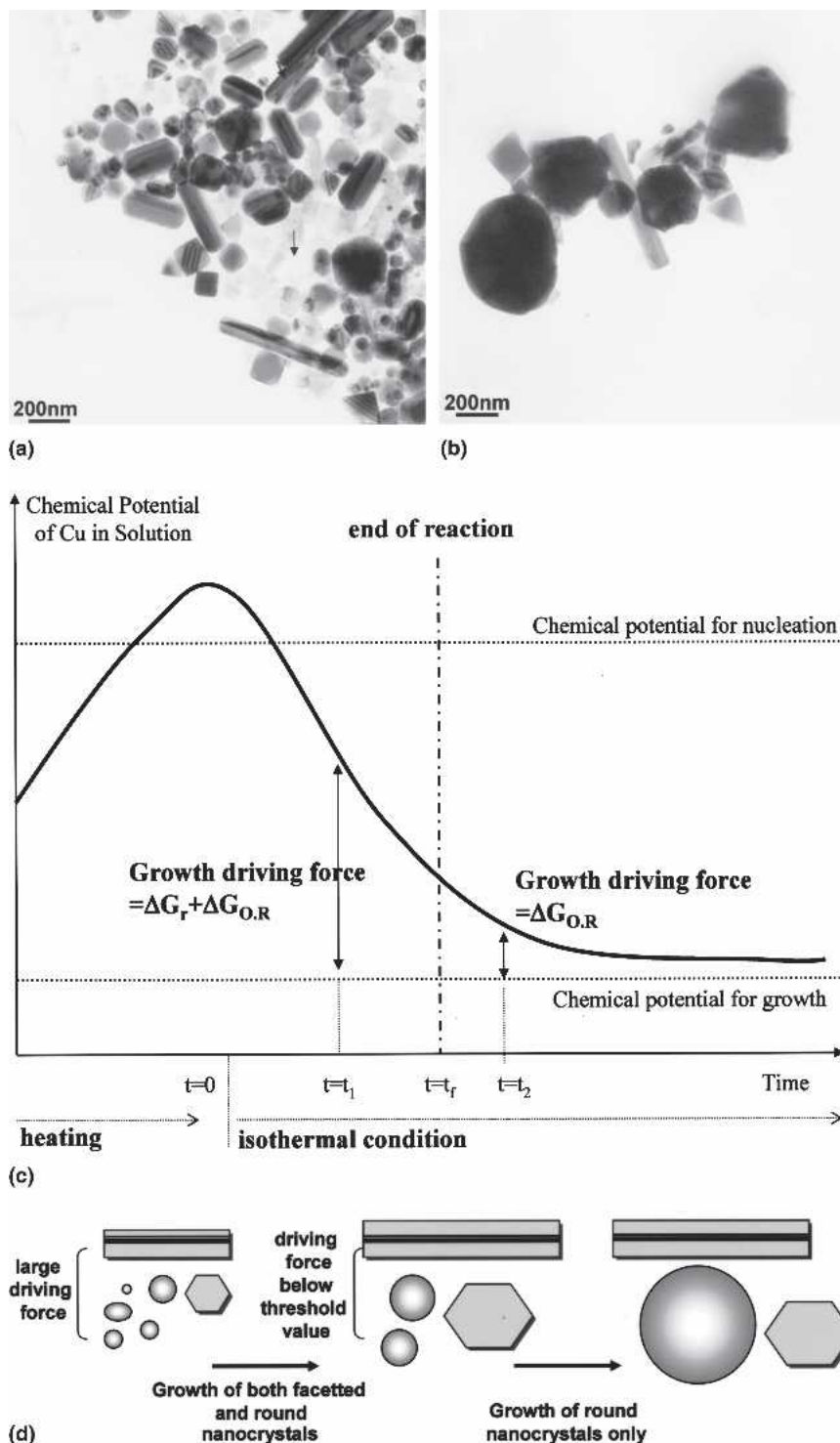


FIG. 5. TEM micrographs of Cu nanocrystals according to the reaction time with a coordinative surfactant. (a) Cu nanocrystals reacted at 240 °C for 30 min with 0.3 mmol oleic acid and (b) Cu nanocrystals reacted at 240 °C for 120 min with 0.3 mmol oleic acid. The arrows in the figures show twins. (c) Schematic illustration of variation of chemical potential and driving force for growth during the polyol process. (d) Illustration of the growth mechanism of Cu nanocrystals with a coordinative surfactant.

Wiley et al.¹⁶ and Sun et al.¹⁷ showed that Ag nanowires are fabricated during the polyol process in the presence of twins. The finding that removal of twins by resolving the nanocrystals contains twins by O and Cl restricts the

formation of nanowires and nanorods in Ag¹⁷ shows that the twin is an origin of anisotropic growth of metal nanocrystals. The formation of anisotropic nanocrystals originated from twin was also clearly observed in our

study, as shown in Figs. 1(d) and 5(a). Nanorods or nanowires of Cu are formed when nanocrystals with faceted surfaces contain twins, as shown in Fig. 5(a). The formation of metal nanowires during the polyol process can be explained by the growth mechanism of faceted surfaces. If all of the surfaces in a nanocrystal are faceted and one of them contains a twin, the faceted surface containing the twin grows much faster than those without a twin under the same driving force, as shown in Figs. 4(a) and 4(b). Therefore, if any twins are removed from all of the faceted surfaces, metal nanowires cannot be fabricated, as Sun et al. observed.¹⁷

In contrast, the existence of twins on a rough surface does not affect the growth rate of nanocrystals, as shown in Fig. 6, in which Cu nanocrystals were fabricated using the noncoordinative surfactant oleylamine at 180 °C. Because the reaction temperature exceeds the roughening temperature, as shown in Fig. 2, the surfaces of the fabricated Cu nanocrystals become rough. Therefore, the Cu nanocrystals grow following the Ostwald ripening

mechanism, which results in monodispersed Cu nanocrystals. The standard deviation of the size of the Cu nanocrystals ranges from 7%–12%, as shown in Fig. 6(d), and is similar to the expected values for nano-Ostwald ripening with diffusion control.²⁰ In this case, the twins on the surface do not affect nanocrystal growth. The nanocrystals remain spherical, although many nanocrystals contain twins, as shown in Fig. 6(c). This is because the growth rate of the rough surface exceeds that of the faceted surface containing twins. Therefore, faceted nanocrystals containing twins are needed to obtain metal nanowires. Simultaneously, the driving force for the growth of nanocrystals must be kept relatively low so that the faceted surface containing a twin grows faster than the faceted surfaces without twins, as shown in Fig. 4(a).

IV. CONCLUSIONS

We have proposed shape-control mechanisms for metal nanocrystals based on the thermodynamic transition

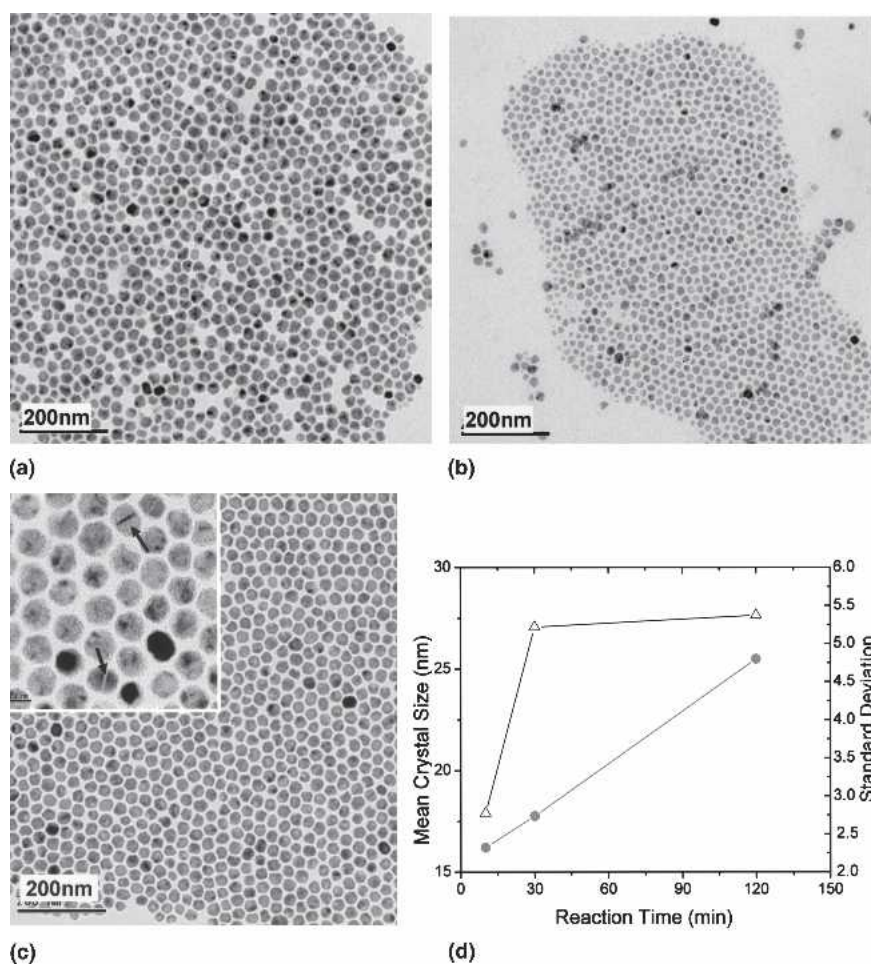


FIG. 6. TEM micrographs of Cu nanocrystals for various reaction times at a reaction temperature of 180 °C with a noncoordinative surfactant and 0.33 mmol oleylamine for (a) 0 min, (b) 30 min, and (c) 120 min. (d) The mean crystal size and standard deviation of Cu nanocrystals with reaction time at a reaction temperature of 180 °C with 0.33 mmol oleylamine. The circle indicates mean crystal size and the triangle indicates standard deviation. The arrows in the figures show twins.

from a faceted surface to a rough surface and the growth mechanisms of faceted and round nanocrystals. The faceted surfaces of nanocrystals induce specifically shaped nanocrystals, such as nanocubes and nanowires. The faceted surfaces are stable at relatively low temperatures because of the low entropy of perfectly faceted surfaces. The faceted surface of nanocrystals fabricated with a coordinative surfactant is stable up to a higher temperature than when fabricated with a noncoordinative surfactant. The growth rate of a nanocrystal under a given driving force is dependent on the surface structure, i.e., faceted or rough. The growth of a faceted nanocrystal is a thermally activated process. Surface twins decrease the activation energy for growth of a faceted surface and this results in rod- or wire-shaped nanocrystals.

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