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RESEARCH PAPER

Shape evolution of gold nanoparticles

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Abstract The tetraoctylammonium bromide-stabilized gold nanoparticles have been successfully fabricated. The shape evolution of these nanoparticles under different annealing temperatures has been investigated using high-resolution transmission electron microscopy. After an annealing at 100 °C for 30 min, the average diameters of the gold nanoparticles change a little. However, the shapes of gold nanoparticles change drastically, and facets appear in most nanoparticles. After an annealing at 200 °C for 30 min, not only the size but also the shape changes a lot. After an annealing at 300 °C for 30 min, two or more gold nanoparticles coalesce into bigger ones. In addition, because of the presence of Cu grid during the annealing, some gold particles become the nucleation sites of Cu_2O nanocubes, which possess a microstructure of gold-particle core/Cu_2O shell. These Au/Cu_2O heterostructure nanocubes can only be formed at a relatively high temperature ($\geq$300 °C). The results can provide some insights on controlling the shapes of gold nanoparticles.

Keywords Gold nanoparticles · Shape · High-resolution transmission electron microscopy · HRTEM · Nanostructure

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Introduction

Many of the unique properties of metallic nanoparticles are determined not only by their finite size but also by their shape, defined by the crystallographic orientation of the surface facets (Wang 2000). These surfaces may differ in a number of ways including surface atom densities, electronic structure, bonding, chemical reactivities, and thermodynamic properties. In the case of gold, it is known that the melting temperature of nanoparticles strongly depends on the crystal size (Buffat and Borel 1976) and that the shape may alter considerably during annealing. However, much of the research has mainly focused on the size effect (El-Sayed 2001). To understand the energy and stress of different crystal surfaces (facets) and how the surface ligand binds to different surfaces, systematic studies of annealing temperature effects on the size and shape of gold nanoparticles are needed.

In this article, we report the synthesis of the tetraoctylammonium bromide (TOAB)-stabilized gold nanoparticles and how their shapes evolve with annealing temperature. High-resolution transmission electron microscopy (HRTEM) observation shows that most of the as-synthesized gold nanoparticles are spherical, although a small fraction (<10%) shows faceting. After an annealing at 100 °C for 30 min, the average sizes of the particles change a little, from 5.2 to 6 nm. However, their shapes change drastically, and facets appear in most particles. After an annealing at 200 °C for 30 min, not only the size (the average size is around 15 nm) but also the shape (facetted shape) changes a lot. After an annealing at 300 °C for 30 min, two or more gold nanoparticles coalesce into bigger ones with an elongated shape. In addition, due to the presence of Cu grid, some particles become the nucleation sites of Cu_2O nanocubes at 300 °C, which possess a microstructure of gold nanoparticle core/Cu_2O shell. The effect of longer annealing time (at 200 °C) on the size and shape of gold nanoparticles is also discussed.

Experimental

Gold nanoparticles were synthesized via a modification of a literature protocol (Brust et al. 1994; Gittins and Caruso 2001). Briefly, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.03 M, 6 mL) was added to a solution of TOAB in toluene (0.15 M, 6 mL). The yellow aqueous phase became colorless, and the toluene phase turned orange as a result of phase transfer and complexing of $[AuCl_4]^-$ with tetraoctylammonium cations. After stirring for 10 min at room temperature, a freshly prepared aqueous solution of sodium borohydride, $NaBH_4$ (0.26 M, 6 mL) was added dropwise into the reaction mixture over a period of 30 min, after which the mixture was vigorously stirred for additional 30 min. Subsequently, the organic phase was separated and was washed with 1% H_2SO_4 once and then with distilled-deionised water five times. Finally the organic phase was dried using $MgSO_4$ and filtered through a filter paper. The as-synthesized gold nanoparticles were characterized using conventional transmission electron microscopy (TEM) and HRTEM. The specimen for TEM observation was prepared by evaporating a drop (5 μL) of the nanoparticle dispersion onto a carbon-film-coated copper grid.

To investigate the annealing temperature effect on the size and shape of gold nanoparticles, the copper grids covered with TOAB-stabilized gold nanoparticles were placed in an oven and the temperatures were raised to and kept constant at 100, 200, and 300 °C for 30 min, respectively. After the annealing, the products were examined extensively using HRTEM. The bright-field (BF) imaging, selected-area electron diffraction (SAED) and HRTEM were carried out using a field emission gun (FEG) transmission electron microscope operating at 200 kV.

Results and discussion

In our work, the gold nanoparticles were synthesized via a surfactant-aided chemical process. It has been previously reported that micrometer-sized gold crystals with different shapes can also be synthesized by a slow reduction method (Liu et al. 2006). During the synthesis of gold nanoparticles, TOAB serves as the phase transfer catalyst. TOAB is a positively charged tetrahedron compound with a long hydrophobic tail, and the growth unit of gold is negatively charged, so the ion pairs between TOA^+ and $[AuCl_4]^-$ can form due to electrostatic interaction. In this way, the $[AuCl_4]^-$ can be transferred from the aqueous to the toluene solution. When the synthesis process ends, the TOAB can serve as a stabilizing agent to prevent the neighboring gold nanoparticles from coagulation. Figure 1a shows a typical BF image of the as-synthesized gold nanoparticles. It can be seen that most particles (>90%) are spherical with an average diameter of about 5.2 nm. The inset is the corresponding SAED pattern, which confirms that the particles are of pure gold. Two typical HRTEM images of gold nanoparticles, one being viewed along the [011] direction and the other being viewed along the [001] direction, are shown in Figs. 1b and c. Both nanoparticles show a spherical morphology.

After an annealing at 100 °C for 30 min, the sample was examined using HRTEM extensively. TEM examination of more than 200 particles shows that there is no drastic change either in the size or the size distribution, but there is a great change in the shapes of the gold nanoparticles. The average size of the gold nanoparticles changes from 5.2 to 6 nm, and facets are observed in most particles. Due to the relatively small size, facets cannot be clearly shown in the low-magnification TEM image. HRTEM imaging has been carried out to investigate the nature of facets. Different projected shapes including a hexagon, a square, and a pentagon have been commonly observed. Figure 2 a, b, and c shows three single-crystalline particles with projected shapes of a hexagon, a square and a pentagon. The corresponding three-dimensional shapes are a cubo-octahedron, a cube, and an isocahedron, respectively. Facets can be clearly seen in these particles, and can be indexed as {111} and (100) faces. Figure 2d shows an elongated particle also with evident facets. Apart from single crystalline particles, there are also many particles with twinning defects.

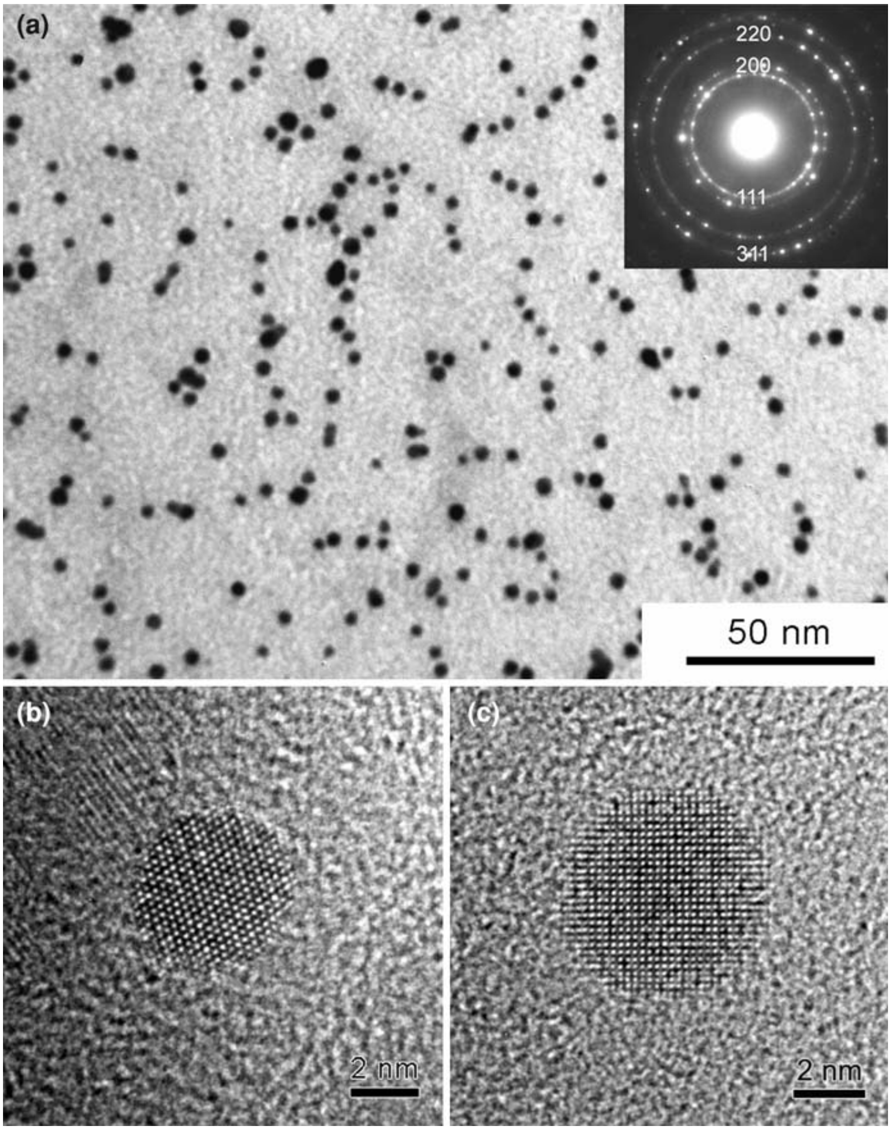

Fig. 1 **a** A typical low-magnification BF image of gold nanoparticles, the inset showing the corresponding SAED pattern; **b** [011] zone-axis HRTEM image of a spherical particle; **c** [001] zone-axis HRTEM image of a nearly spherical particle

Figure 2e shows a particle with a single-twin configuration while Fig. 2f shows a particle with fivefold twinning configuration. Clear facets can also be seen in these particles.

After an annealing at 200 °C for 30 min, the sample was also investigated using TEM. Figure 3a shows a low-magnification BF image of the gold nanoparticles after the annealing. Not only the size but also the morphology changes drastically. The average size of the gold nanoparticles after the annealing at 200 °C for 30 min is around 15 nm. From Fig. 3a, facets can be clearly seen in these particles because the particles are bigger compared to those after the annealing at 100 °C for 30 min. The typical projected shapes include hexagon, triangle, and pentagon. Figures 3b, c, and d show HRTEM images of three particles with projected shapes of a hexagon, a triangle, and a pentagon, respectively. The facets are {111} and {100} faces.

From our TEM observations, the nanoparticles are still pure gold after an annealing at a temperature not higher than 200 °C, which is consistent with the report in the literature (Teranishi et al. 2001). For a spherical single-crystalline particle, its surface must contain high-index crystallography planes, which possibly results in a high surface energy. Facets tend

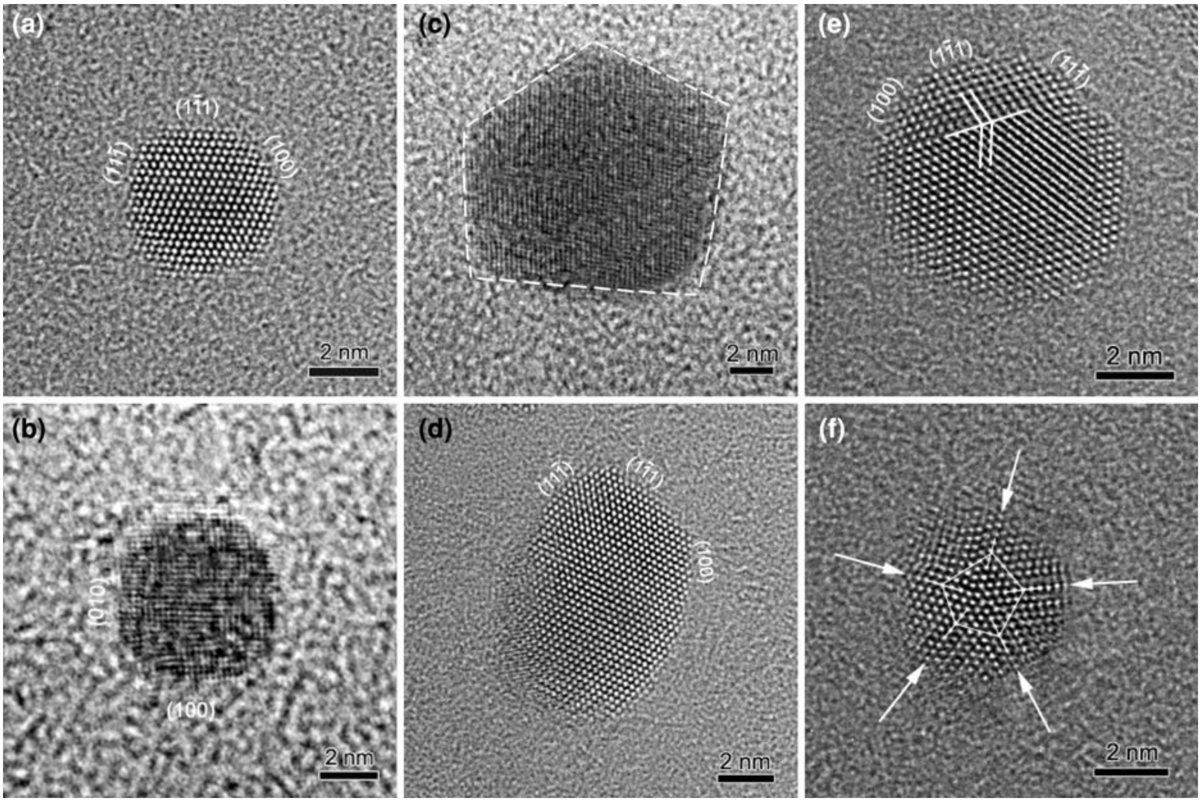

Fig. 2 HRTEM images of gold nanoparticle with facets, **a–c** regular shapes: **a** a hexagon; **b** a square; **c** a pentagon; and **d** an elongated shape; **e** a particle with a single-twin configuration; **f** particle with a fivefold twinning configuration

to form on the particle surface to increase the portion of the low-index planes. This explains why facets are commonly observed in the gold nanoparticles after annealing at 100 and 200 °C for 30 min. When the gold nanoparticles go through the heat treatment, the surfaces undergo a re-organization process and they tend to form lowest energy surfaces if possible. For face-centered cubic (fcc) gold, the {111} planes are the faces with the lowest surface energy and {100} planes are the second lowest energy faces, so it is understandable that these planes form the facets of most gold nanoparticles after the annealing.

Gold nanoparticles have been observed as cubo–octahedral face-centered cubic (fcc) structures (Pauwels et al. 2000), singly or multiply twinned fcc structures (Pinto et al. 1995; Buffat et al. 1991), icosahedral and truncated icosahedral structures (Buffat et al. 1991; Marks 1994; Martin 1996; Ascencio et al. 1998; Ascencio et al. 2000) as well as the Marks decahedral (Buffat et al. 1991; Marks 1994), and truncated decahedral structures (Marks 1994; Martin 1996). Up to now, gold nanoparticles have been observed to have a projected shape of a pentagon with a multiply twinned structure (Buffat et al. 1991). Here we observed a projected shape of a pentagon with a single crystalline structure after the annealing. As we all know, fivefold symmetry breaks the conventional concept of symmetry, which has only been observed in quasicrystals. It is not clear whether the gold particles with a fivefold symmetry are thermodynamically stable or not. Further investigation is still under the way to clarify the nature.

After an annealing at 300 °C for 30 min, the morphologies of the nanoparticles changed drastically. Figure 4a shows a typical low-magnification BF image of the nanostructures after the annealing. From Fig. 4a, we can see that there are two types of nanostructures, one being nanoparticles, and the other being the nanocubes. Careful examination shows that the center and the outside of the nanocubes have different contrasts, and we can attribute the center to

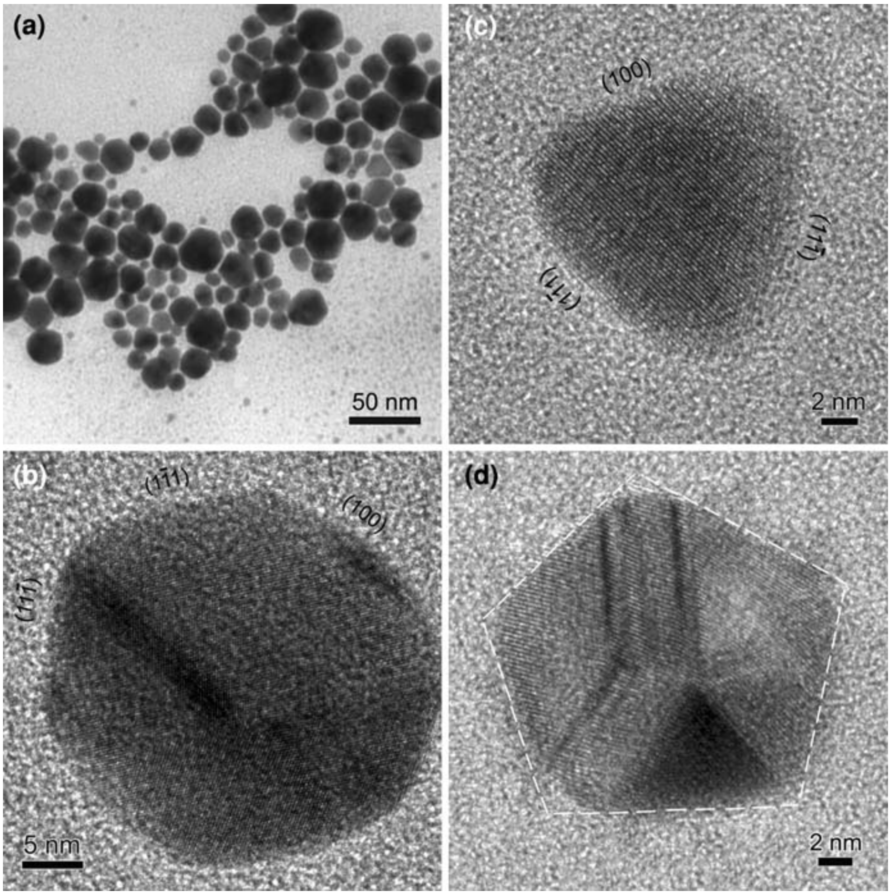

Fig. 3 **a** A typical low-magnification BF image of gold nanoparticles after the annealing at 200 °C for 30 min; several HRTEM images of gold nanoparticles with projected shapes of **b** a hexagon; **c** a triangle; and **d** a pentagon

be gold nanoparticles, and the outside to be Cu_2O (Wang et al. 2008). Chemical analysis also confirmed that the nanocubes are composed of gold, copper and oxygen (Wang et al. 2008). HRTEM observations show that some gold nanoparticles coalesce into bigger ones with twins dominant inside the coalesced particle, while other gold nanoparticles become the nucleation sites and form a microstructure of gold nanoparticle core/Cu_2O shell. One example of the coalesced gold nanoparticles is shown in Fig. 4b. The gold nanoparticle is viewed along the [011] direction. In Fig. 4b, the twinning configuration is labeled, and the twinning boundary is {111}, labeled as TB1, 2 and 3. We can see that the particle is elongated after the coalescence. One example of the nanocube heterostructures is shown in Fig. 4c. The nanocube is viewed along the [001] direction. We can see that the center has a dark contrast while the outside has a grey contrast. In addition, the four edges of the nanocube are a little truncated.

It is interesting to observe the twinning in the coalesced gold nanoparticles. Twinning has also been observed in the coalesced Si nanoparticles (Wang et al. 2004; Wang et al. 2005). It is believed that the twinning boundary is coherent, and can reduce the total energy of the system. Two factors are important for the formation of Au–Cu_2O heterostructure nanocubes: one is the presence of oxygen (Zhou et al. 2006); the other is a relatively high annealing temperature (Wang et al. 2008). Detailed discussion for the formation of these nanocubes can be found in reference Wang et al. 2008.

From TEM observations, it can be clearly seen that the size and shape of the gold nanoparticles change with the different annealing temperatures. When the temperature increases, the TOAB starts to melt. During the heat-treatment process, the molten TOAB is thought to serve as a solvent in the particle growth process, and the gold nanoparticles go through a coalescence process and a surface re-organization

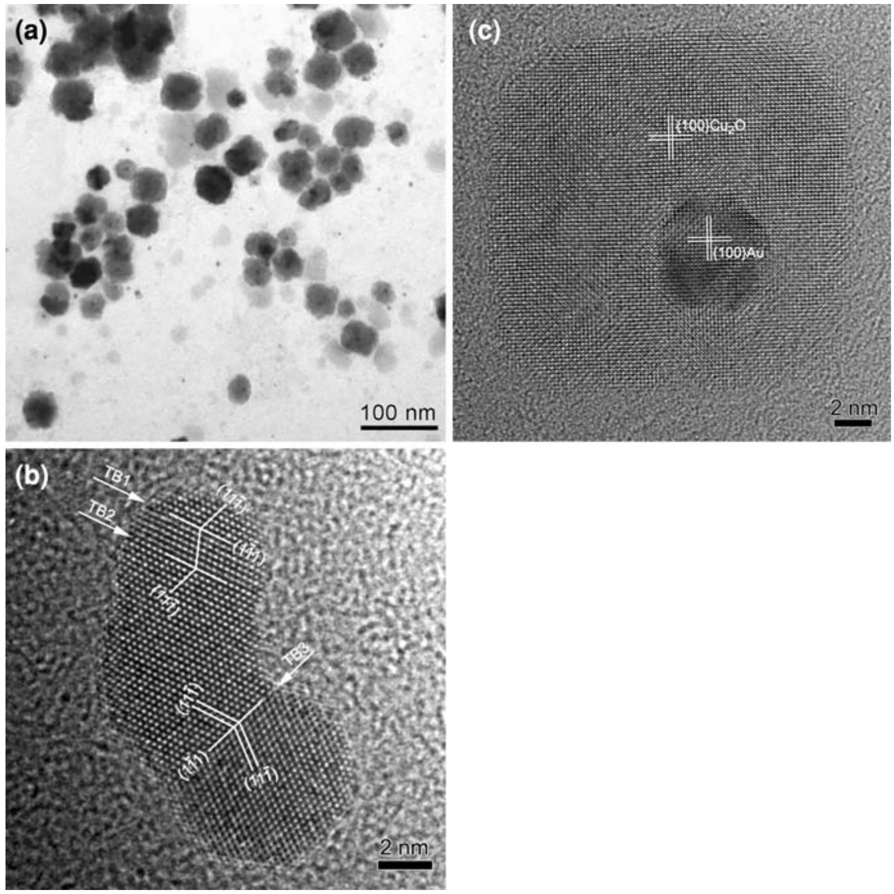

Fig. 4 **a** A typical low-magnification BF image of the nanostructures after the annealing at 300 °C for 30 min; **b** [011] zone-axis HRTEM image of a coalesced gold nanoparticle; **c** [001] zone-axis HRTEM image of an Au–Cu_2O nanocube heterostructure

process. This can explain why the size and shape change drastically at different annealing temperatures. The shapes of gold nanoparticles evolve from the spherical (as-synthesized) to a facetted shape such as a cubo-octahedron, a cube, a triangular prism, and an isocahedron (after the annealing at 100 and 200 °C for 30 min), and then to irregular elongated shapes (after the annealing at 300 °C for 30 min).

We also investigated the effect of longer annealing time on the size and shape of the gold nanoparticles at 200 °C. Figure 5 shows a typical low-magnification TEM image of the gold nanoparticles after the annealing at 200 °C for 60 min. It can be seen from this TEM image that the gold nanoparticles are more elongated than before [compared with Fig. 3a], which indicates that the gold nanoparticles undergo more coalescence during the annealing. In addition, the average size of the gold nanoparticles increases a lot, which is also the result of more coalescence.

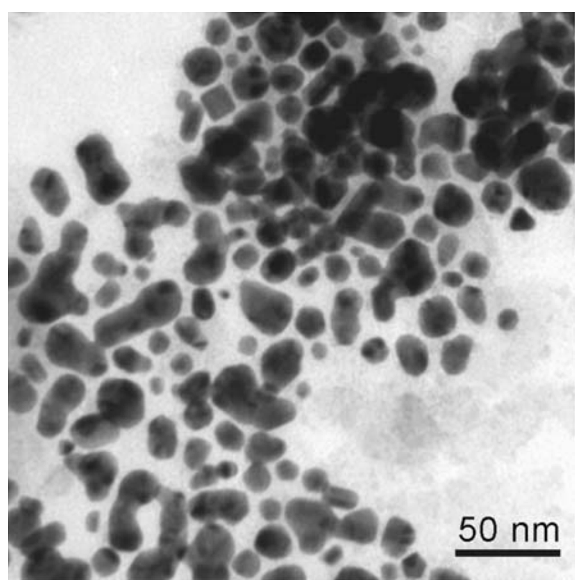

Fig. 5 A typical low-magnification TEM image of the gold nanoparticles after the annealing at 200 °C for 60 min

Conclusions

In summary, the shape evolution of gold nanoparticles with annealing temperature has been investigated using HRTEM. After an annealing at a temperature not higher than 200 °C for 30 min, the nanoparticles are still pure gold, and facets appear in most nanoparticles. The facets are {111} and {001} faces. After an annealing at 300 °C for 30 min, two or more gold nanoparticles coalesce into bigger ones. In addition, because of the presence of Cu grid during the annealing, some gold particles become the nucleation sites of Cu_2O nanocubes, which possess a microstructure of gold-particle core/Cu_2O shell. These Au/Cu_2O heterostructure nanocubes can only be formed at a relatively high temperature (≥300 °C). The shapes of gold nanoparticles evolve from the spherical (as-synthesized) to a facetted shape such as a cubo-octahedron, a cube, a triangular prism and an isocahedron (after the annealing at 100 and 200 °C for 30 min), and then to irregular elongated shapes (after the annealing at 300 °C for 30 min). The results can provide some insights on controlling the shapes of gold nanoparticles.

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