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An additive-free electrochemical route to rapid synthesis of large-area copper nano-octahedra on gold film substrates

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ABSTRACT

We report the first fabrication of large-area Cu nano-octahedra with well-defined shape, good monodispersity and uniform distribution on a gold film substrate (GFS) by a very simple, rapid and cost-effective low-potential electrodeposition (LPED) technique. Different from general surfactant-assisted electrochemical approaches, LPED is an additive-free strategy that exploits the subtle surface energy differences among various crystallographic planes of metals themselves. The size of the octahedra depends on deposition time and is adjustable over a wide range. The shape evolution is found to be remarkably different from that of octahedral particles formed in solution. A formation mechanism is proposed for the unique evolution of Cu octahedra as resulting from the anisotropic growth under appropriate applied potentials.

1. Introduction

Metal nanocrystals (NCs) are emerging as key materials for catalysis, plasmonics, sensing, and spectroscopy [1–4]. Especially with regard to these applications, the shape, size and distribution of NCs crucially determine properties. The synthesis of metal NCs with specific features is thus important for realizing NC-based devices and for discovering novel properties. The crystal habit of inorganic crystals is determined by the relative order of surface energies [5]. Since the differences between the surface energies of different crystallographic planes are relatively small, a strategy to effectively employ them is always needed and difficult. Crystallographic control by tuning of nucleation and growth of metal NCs is mostly achieved by employing various additives [6,7]. Only few and comparatively elaborate attempts successfully exploited the differences in surface energies without additives, for example by applying square-wave potentials on pre-deposited particles [2,3].

Moreover, while many reports to manipulate the shape of metal NCs successfully in solutions, this often implies elaborate, multistep procedures to ensure the final products' dispersion on substrates. Substrate immobilized metal nanostructures can be directly useful as NC-based nanodevices [8–10]; e.g. in catalysis; separation and recycling of the metal NCs is thus simplified [11]. It remains a challenge to yield specific shapes and high-density distributions of metal NCs over large-areas.

Here, we report a facile route to large-area, high-density and well-dispersed metal NCs. This new strategy exploits the subtle surface energy differences, and does not introduce additives yet is still simple by using low-potential electrodeposition (LPED). Although the synthesis of shape-controlled Cu NCs has been studied in many reports [7–10,12–14], Cu octahedra have not yet been fabricated. Besides being additive-free, the method offers particle size controllability, short reaction time and surprisingly delicate shape selectivity: the successful synthesis of Cu NCs with a octahedral shape is accomplished for the first time.

2. Experimental

2.1. Synthesis of Cu nano-octahedra

Gold film substrates (GFS, 1 cm × 1 cm) were prepared by sputtering Au on Si substrates using a precision coating apparatus (Gatan company, model 682). To eliminate oxygen, deionized water was boiled for five minutes before use. All electrodepositions were carried out potentiostatically at room temperature (R.T.) under high-purity, flowing N_2 gas. The simple two-electrode system consists of a 3 cm × 3 cm polished copper anode 4 cm from the GFS cathode. No reference electrode was used. The GFS were immersed 0.5 cm deep into the electrolyte (always 40 ml). Typically, the concentration of $CuSO_4$ electrolyte (c), applied potential (V) and deposition time (t) were 0.16 mol/l, 15 mV and 60 s. After deposition, the substrates were rinsed several times with deionized water and dried in a vacuum box.

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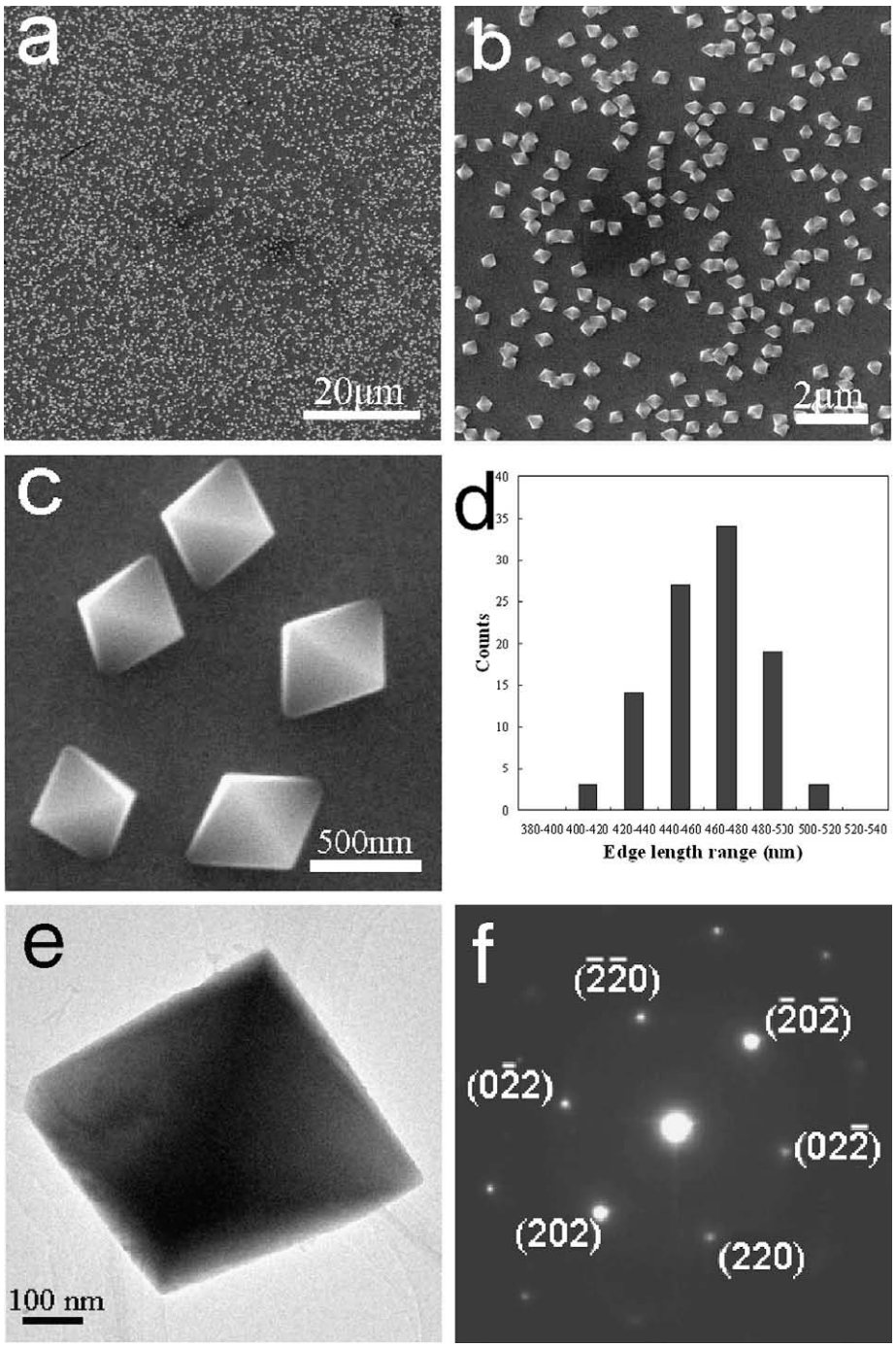

Fig. 1. SEM images at low (a) and high (b, c) magnifications of the as-prepared Cu NCs. (d) Histogram of the edge lengths of Cu octahedra. TEM image (e) and SAED pattern (f) reveal that the nanoparticles are single crystals.

2.2. Characterizations

The shape, size and distribution of NCs were characterized by scanning electron microscopy (SEM) (FEI XL30-ESEM). Composition and structure were analyzed by X-ray diffraction (XRD) (D/Max-RA, Cu Kα = 1.5418 Å), X-ray photoelectron spectra (XPS) (ESCALB MK-II VG), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (FEI Tecnai F20 S-Twin). To prevent oxidation, as-synthesized products were vacuum dried and kept under CO_2 before XPS, SEM and TEM measurements. For TEM samples, fresh Cu NCs were scraped into ethanol quickly. Then several drops of the suspension were placed onto a carbon film covering a molybdenum grid and evaporated in a vacuum box.

3. Results and discussion

Fig. 1a shows a low resolution SEM image of the product from a typical experiment (0.16 mol/l, 15 mV and 60 s). The product is dispersed homogeneously over a large-area of the substrate. SEM images at higher magnifications (Fig. 1b and c) reveal that the particles have octahedral shapes and a high number density ($\sim 1.95 \times 10^8/cm^2$) while still being well-dispersed as mostly from each other isolated, single particles. A sample of 100 octahedral particles was categorized according to size and charted as a histogram in Fig. 1d, resulting in an edge length of (461 ± 20) nm. The surfaces look smooth without obvious defects. Fig. 1e presents a typical TEM image of an octahedron desquamated from the sub-