Chem. Mater. **2006,** *18,* 6097−6099

Synthesis of Pyramidal Copper Nanoparticles on Gold Substrate

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Received October 3, 2006
Revised Manuscript Received November 21, 2006

Shape-controlled nanostructures of metal nanoparticles (NPs) can offer remarkable electronic, magnetic, and optical properties, giving great opportunities for the development of feature nanotechnology including photography, catalysis, biological labeling, photonics, and surface-enhanced Raman scattering (SERS).[1−4] Various shapes of metal NPs, from prism[5−8] and cubic[9−12] to tetrapods,[13,14] particularly those of silver, gold, and platium, have been prepared by using a variety of methodologies. Particle shape control in wet chemical synthesis can be achieved, but it often requires elaborate, time-consuming, and multi-step procedures to fabricate onto the surface of metal substrates. Hence, the synthesis of NPs with well-defined structures and in large quantities on the metal surface remains challenging tasks. The face-centered Cu (*fcc*) copper with a full *d*-band is regarded as an ideal alternative material for prototypically nonmagnetic materials and metallic conductors. Anisotropic properties for Cu NPs are mentioned in very few reports because its stability of the synthesized shapes is not guaranteed.[15] To the best of our knowledge, the Cu NPs with anisotropic structures are particularly rare even though the Cu deposition on Au single-crystal electrodes has been extensively studied.[16] In this communication, we present a sophisticated single-step electrodeposition approach for preparation of surface-confined Cu NPs supported on a Au substrate. Free-standing pyramidal Cu NPs have been synthesized in large quantities (over 70%) on Au surface through systematically exploring electrodeposition parameters.

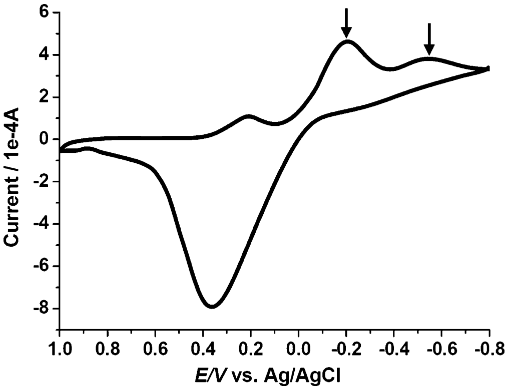

Figure 1. Cyclic voltammograms of Cu/DBSA solution at scan rate of 0.05 V s^{-1}. Arrows indicate the Cu(II)/Cu(I) and Cu(I)/Cu(0) reduction potentials in the course of reduction scans.

Pyramidal Cu NPs were synthesized on a cleaned Au substrate (99.999%; 1 × 0.5 cm) by immersing it in copper ion containing solution. The solution was prepared from 0.029 g of copper(II) tetrafluorobrorate hydrate ($Cu(BF_4)_2 \cdot xH_2O$, Aldrich, MW 237.15) and 0.087 g of dodecylbenzene sulfonic acid sodium salt (DBSA, Fluka, MW 348.48) used as precursor and capping reagent, respectively. Electrical treatments were carried out on the CH Instruments 672A electrochemical system with a three-electrode system at room temperature. It consisted of a bare Au substrate as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The deposition potential was accordingly controlled in the range of −0.6 to −0.8 V at a scan rate of 0.05 V s^{-1}, and the deposition time was 200 s. After deposition, the electrodes were rinsed with copious amounts of Milli-Q water (18 M·Ω resistivity; Millipore System) to remove the residual capping reagent.

Cyclic voltammetry was employed to screen the electrodeposition parameters for electro-crystallization of metallic Cu pyramids. Figure 1 explores the cyclic voltammogram of DBSA/$Cu(BF_4)_2$ solution exhibiting two peaks at −0.20 and −0.55 V versus Ag/AgCl in the course of reduction scan, attributed to the reduction process of Cu(II)/Cu(I) and Cu(I)/Cu(0), respectively,[17] and the peak at 0.25 V is caused by the reduction of DBSA. Thus, the deposition potential was accordingly controlled in the range of −0.6 to −0.8 V at a scan rate of 0.05 V s^{-1}.

The morphology of Cu NPs depends on the ratio of the concentration of surfactant/precusor and deposition time in

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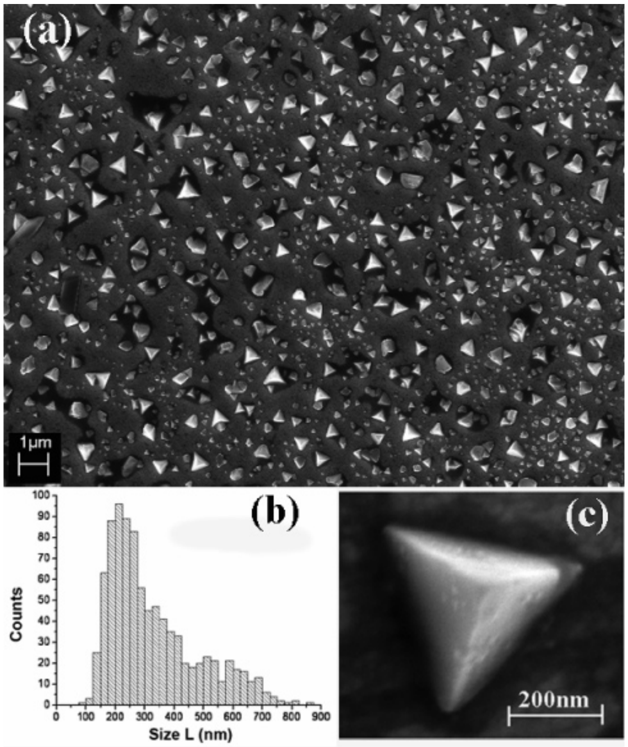

Figure 2. (a) FESEM images of Cu pyramids on gold substrates. The electrodeposition potential was controlled between −0.6 and −0.8 V vs Ag/AgCl at scan rate of 0.05 V s^{-1}. (b) Size distribution of Cu pyramids. (c) FESEM image of one of the developed particles.

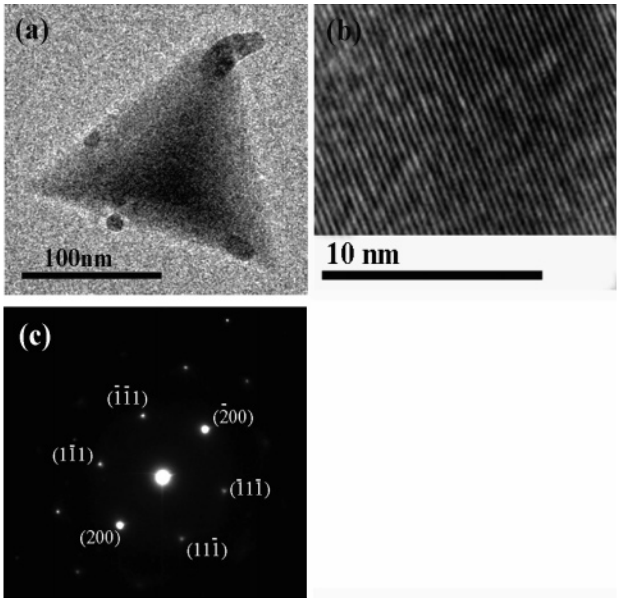

Figure 3. HRTEM of (a) morphology of one of as-electrodeposited pyramidal Cu NPs; (b) lattice image of the (111) diffraction plane; (c) selected area electron diffraction patterns of pyramidal Cu NPs.

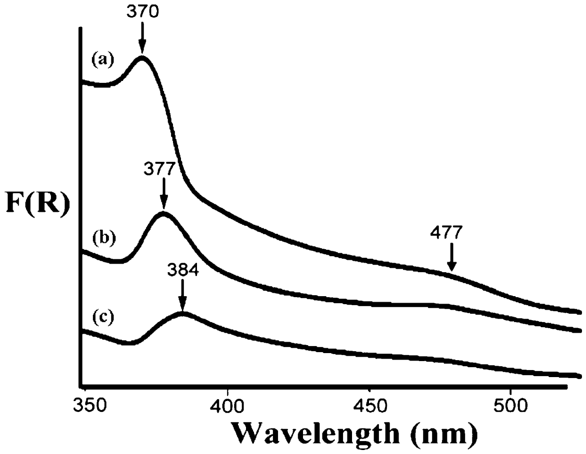

Figure 4. UV−Vis diffuse reflectance spectra of the yield of (a) 20% (deposition time = 800 s), (b) 40% (400 s), (c) 70% (200 s) of Cu pyramids on gold substrate. The relative reflectance of a film, $F(R)$, is given by the Kubelka−Munk equation [$F(R) = (1 - R)^2/2R$, where R is the ratio of the reflected intensities of the sample and a gold film standard].

our experimental method. We monitored the weight ratio of DBSA/Cu^{2+} from 1 to 5 and the deposition time from 200 to 800 s to investigate the influence on pyramidal architectures. With a weight ratio of 3 and a depostion time of 200 s, we can obtain the optimal condition to synthesize free-standing pyramidal Cu NPs. The as-deposited Cu NPs were characterized by FESEM (TOPCON ABT-1150S); 70% of the particles are pyramidal shape (the corresponding SEM image is shown in Figure 2a). The size distribution histograms of Cu pyramids (Figure 2b) show that the edge sizes of the pyramids are in the range of 100−800 nm, with a major distribution at 220 nm. In viewing an individual, well-defined pyramidal Cu (Figure 2c), we were capable of observing small NPs with with nearly fully developed pyramidal shape bearing on the {111} faces of pyramids of copper. This implies that the pyramidal Cu NPs should be crystalline, which offers a great opportinity for further growth of these smaller pyramids. Furthermore, energy-dispersive X-ray (EDX) analysis shows that carbon and oxygen atoms are absent in as-deposited products, only the signal of Cu is obtained. This implies that the pyramid Cu NPs do not possess DBSA capping agent, and they may be metallic Cu rather than metal oxides on the gold surface. Details of the structure can be observed in high-resolution transition electron microscopy (HRTEM, JEOL JEM-2010) images. The produced pyramidal Cu NPs were transferred from Au substrate to Milli-Q water by sonicating for 12 h and then are spotted by placing a drop of the solution onto a carbon film covered with a copper grid and evaporating the drop in air. Figure 3 shows the image of an individual pyramidal Cu NP with edge length of 180 nm and its corresponding selected area electron diffraction (ED) pattern. Its corresponding lattice image is depicted in Figure 3b. The space between the diffraction planes is ca. 0.23 nm, which corresponds to the space between (111) planes ($d_{111} = 0.21$) in face-center cubic (*fcc*) Cu (a = 3.615 Å, JCPDS No. 3-2838). Figure 3c is a typical selected-area electron diffraction (SAED) pattern of the pyramid. The ED pattern taken along the [011] zone axis shows two fringes with plane distances of 2.035 and 1.881 Å, which is consistent with the *fcc* metal Cu (111) and (200), respectively.[18] The ED pattern also confirms that the pyramids are single-crystal metallic Cu.

It is commonly accepted that the interplay between the faceting tendency of the capping agent and the growth kinetics could affect the formation of various shapes.[19,20] We suggest that DBSA molecures appeal to bind more strongly

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to the {100} than the {111} planes. Therefore, pyramidal Cu NPs covered with the {111} family of planes could be obtained.

The study of optical properties of copper pyramidal nanostructures is very interesting because of their unique shape. The optical absorption properties for these pyramids on gold surface were conducted by means of UV−Vis diffuse reflectance spectroscopy (DRS). Figure 4 shows that the DRS spectra of copper pyramids displayed two plasmon bands[5] at 384 and 477 nm, entirely different from the typical optical density at 575 nm of spherical NPs.[16] In addition, it was also found that the optical spectra show gradually red-shifts from 370 to 384 nm while the distribution of pyramids increased from 20% to 70%.

In summary, high yields of the fabrication of free-standing metallic, pyramidal copper nanostructures on gold substrate can be produced through the micelle electrodeposition method. Our current method provides a versatile and facile pathway to fabricate anisotropic nanomaterials with novel architectures. Controlling the shape of copper particles could open up tremendous possibilities for exploiting the highly sensitive, real-time electrode-based sensor for chemical and biological species as well as catalytic conversion of hydrocarbons and alcohols for fuel cells. Besides, the copper pyramidal tips may be useful for scanning probe applications.[21,22]

Acknowledgment. This work was supported by the National Science Council of Taiwan (NSC 95-2627-M-005-001; NSC 95-2752-M-005-001-PAE; NSC-95-2120-M007-002).

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