Preparation of Branched Gold Nanocrystals by an Electrochemical Method

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A simple electrochemical method is used for synthesis of branched gold nanocrystals in aqueous solution. The branched nanocrystals can be obtained by electrochemical reduction of $AuCl_4^-$ in the presence of PVP and a small amount of NaOH. The concentration of NaOH in the solution was found to have a profound influence of branch nanostructure formation.

Metal nanostructures have drawn considerable interest in the past years because of their application in catalysis, biosensing, optics, and magnetic devices where they have been exhibiting particular performance over their bulk counterparts.[1–3] Metal nanocrystals have been prepared by photochemical, electrochemical, biochemical, and thermochemical methods.[4–7] There are a great number of reports focusing on gold nanowires, nanocubes, and nanoplates, but a small number of reports on the preparation of branched gold nanocrystals in the past decade.[8–10] Chen et al. and Hao et al. reported the synthesis of a mixture of branched gold nanocrystals by using two different colloid chemical synthetic approaches.[11,12] Schatz and co-workers reported that branched gold nanocrystals were prepared by H_2O_2 in sodium citrate solution in the presence of BSPP.[13] Recently, Huang et al. synthesized branched gold nanocrystals by a seeding growth approach.[14]

Herein, we report an electrochemical procedure for preparing branched gold nanocrystals. We added small amounts of NaOH to our foregoing electrochemical synthesis approaches in aqueous solution.[15,16] To our surprise, the small amount of additives induced a dramatic change on the morphologies of the nanoparticles. In contrast with our foregoing approaches, a great number of branched nanocrystals instead of spheroid particles appeared in this approach. Typically, to 5 mL of 1×10^{-2} M of $HAuCl_4$ solution, were added 20 mL of 10 g/L PVP solution, and 1 mL of NaOH (0.1 mM) solution while stirring. The solution was purged by nitrogen. The electrochemical synthesis of branched gold nanocrystals was performed in a simple two-electrode cell. Two $1.0 \times 1.0\,cm^2$ platinum sheets being 5 cm apart were employed as electrolysis electrodes. The electrolysis was carried out in the galvanostatic manner at room temperature under stirring. The PVP serves as the stabilizer for nanocrystals to prevent their further growth. Electrolysis was used for a typical current density of $10\,mA/cm^2$ (working voltage 12 V) and a typical electrolysis time of 30 min.

The morphology of the nanocrystals obtained was first characterized by TEM (acceleration voltage 200 kV). A low-magnification image, shown in Figure 1a, demonstrates that the product was consisting of a large amount of branched structure in shape. A magnified image of an individual crystallite indicates that the nanocrystals comprised several branch structures radiating from the center, which can be seen in Figure 1b. The branched gold nanocrystals have sizes in the range of 40–80 nm in diameter. The corresponding selected area electron diffraction (SAED) (Figure 1c) patterns were obtained by focusing the electron beam on the nanoparticles on the TEM grid. The SAED pattern clearly displays that these particles have fcc structures.

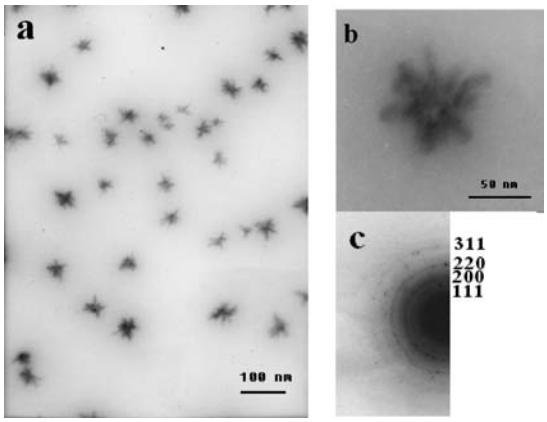

Figure 1. (a) Representative TEM image of the as-prepared gold nanocrystals. (b) High-magnification image of one branched nanocrystal. (c) Corresponding SAED pattern.

The EDS spectrum (Figure 2a) obtained shows only the peak corresponding to gold, which indicates that the particles are pure metallic Au (the peak of Cu comes from Cu grids). The optical properties of metal nanoparticles are highly dependent on the size and shape of the particles.[17] Figure 2b demonstrated an absorption spectrum of the as-prepared Au nanocrystals in aqueous solution. Different from the UV–vis spectra of spherical gold nanoparticles in solution that displayed surface plasmon resonance (SPR) bands located at about 520 nm, the UV–vis spectra collected on the resulting solution clearly show the SPR band being red-shifted to 570 nm. The red-shift effect of the branched nanocrystals is similar with gold nanorod.

The crystallinity of the gold nanocrystals was further confirmed by the corresponding XRD pattern (Figure 3). The four sharp peaks can be assigned to the {111}, {200}, {220}, and

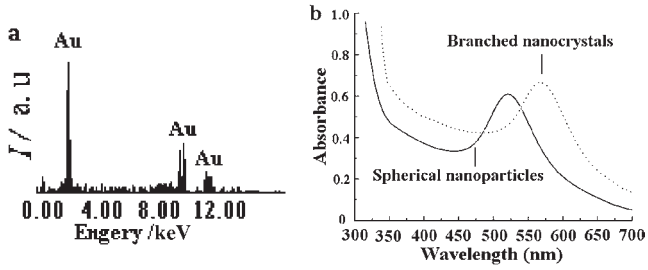

Figure 2. (a) EDS spectrum, (b) UV–vis spectrum of the branched gold nanocrystal.

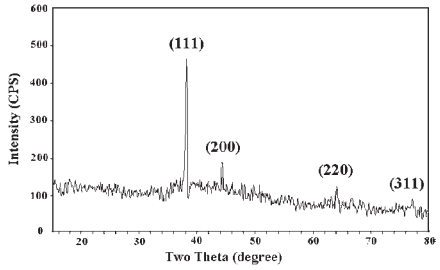

Figure 3. XRD pattern of the branched gold nanocrystal.

{311} diffraction peaks of metal gold, respectively, indicating that the product is composed of pure crystalline gold with fcc structure.

Referring to Figure 3, the Au lattice constant has been estimated to be $a = 4.0775$ Å, in agreement with the literature report ($a = 4.0768$ Å JCPDS, file No. 4-0784).[18] Also mentioned is that the intensity of the {111} plane is much higher than the other lattice planes. This structure feature is in according with previous report.[14]

In this synthesis, the addition of NaOH was critical to the formation of gold nanocrystals. When no NaOH was added, we only obtained a wine red colloidal gold solution. Figure 4a shows a typical TEM image of the gold product obtained in the absence of NaOH, under otherwise identical conditions. Clearly, the resulting gold product mainly consists of small spherical nanoparticles with no branched structure in shape. However, when 0.1 mM NaOH solution was added to the solution, the branched nanostructures were appeared (Figure 4b).

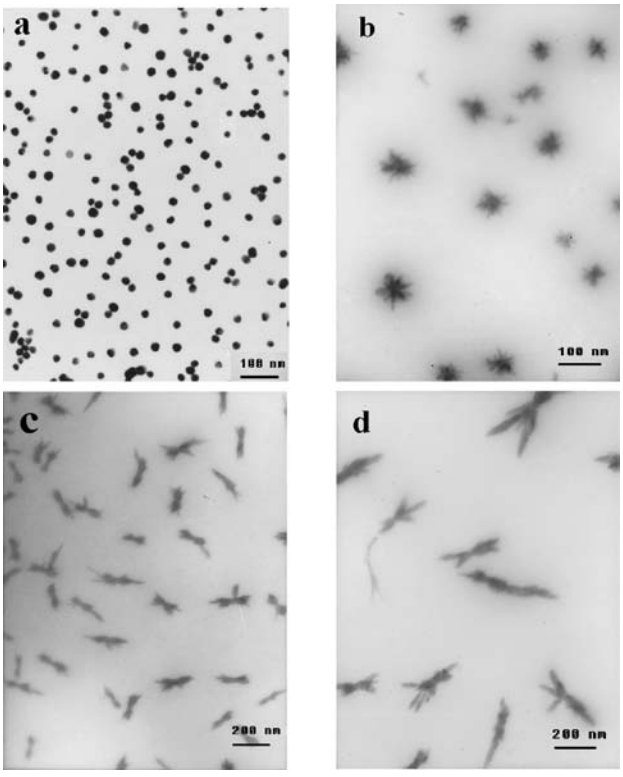

Figure 4. TEM images of gold products synthesized in the absence of NaOH (a) and in the presence of (b) 0.1 mM, (c) 0.5 mM, and (d) 2.0 mM NaOH.

When the NaOH concentration was increased to 0.5 mM (Figure 4c) and 2 mM (Figure 4d), the length of the gold nanocrystals were increased correspondingly. It can be also seen that the degree of branching of the resultant gold nanoparticles decreased when the concentrations of NaOH increased. It is suggested that nanocrystal growth direction of the branched gold nanoparticles was affected possibly by NaOH. However, it is not clear at the present time how the NaOH influences the growth of the gold nanocrystals, and the detailed mechanism requires further investigation.

Herein, branched gold nanocrystals were easily synthesized in solution through the addition of NaOH to a conventional electrochemical synthesis. In contrast to our previous work, we consider that NaOH plays an important role in the forming process of the branched structure. It is believed that large-scale shape-controlled gold nanocrystals will be conveniently produced through further optimization of this synthetic process and expected to find intriguing applications in fields such as catalysis, biosensor, recording media, and optics.

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