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Synthesis of copper nanorods using electrochemical methods

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Abstract: Copper nanorods were synthesized using controlled-current electrochemical methods. The surfactants in the electrolyte served as both a templates and stabilizers during the synthesis procedure. TEM images show that the products consist mainly of nanosized rod-like structures. The current density applied during the electrodeposition was found to have an effect on the shape and yield of the copper nanorods.

Keywords: copper nanorods, electrochemical, template, microemulsion.

INTRODUCTION

There is significant interest and ongoing research in the preparation and application of nanometer sized materials. The physical and chemical properties of these matenals are quite different from those of the bulk phase due to the high surface area to volume ratio. Their distinctive electronic, magnetic, and optical properties contribute attractive prospects in the design of new electronic and optical devices, information storage, gas sensors, *etc*.[1]

Metal nanoparticles are of interest due to their special properties in many aspects, such as catalysis,[2–4] template for assembly of nano-sized materials,[5] *etc*. Their properties and applications are strongly dependent on their shapes.[6,7] Of all the methodologies developed for the production of metal nanoparticles, on either a physical or chemical basis, the electrochemical method[8–10] offers an simple alternative means for high yield production of nanoparticles. Wang's group has synthesized gold nanorods *via* an an electrochemical method by introducing a shape-reducing co-surfactant into the electrolyte.[11,12] The surfactants they used were employed as both the supporting electrolyte and the stabilizer for the resulting cylindrical Au nanoparticles. The mechanisms of particle-growth when using the electrochemical technique and the mixed cationic surfactant system are not fully understood. Yet it is generally considered to be a template method with a dynamic micelle system serving as the template.[12] M. B. Mohamed *et al.* reported the effect of temperature on the gold nanorods produced by this electrochemical method.[13] They found that the mean aspect ratio of the nanorods in solution decreases with increasing temperature while the average width remains constant.

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Micromulsions find application in enhanced oil recovery, as well as in the pharmaceuticals and cosmetic industries. Water-in-oil microemulsions have been extensively used as microreactors to prepare monodisperse nanosized particles, such as metal, metal borides and metal oxides.[14] Pileni *et al.* reported the synthesis of copper nanorods by using reverse micelles as templates.[15]

The previous electrochemical synthesis method using a surfactant as the template was limited to Au nanorods.[11–13] Recently, we extended the method to a more active metal, *i.e.*, copper. In this paper, attempts to prepare copper nanorods using a new experiment system are reported. TEM results show that the product consists of nanorods with a mean diameter of 30 nm and length of up to 1 μm. The effect of the current density applied in the experiment on the shape of the product is also reported in this communication.

EXPERIMENTAL

A two-electrode cell was used for the electrodeposition. A copper plate (1.2×1.2 cm^2) was used as the anode and a platinum plate (1.5×1.5 cm^2) as the cathode. Both the electrodes were immersed in an electrolyte consisting of a hydrophilic cationic surfactant, 0.08 mol dm^{-3} hexadecyltrimethylammonium bromide (C_{16}TABr), and a hydrophobic cationic co-surfactant, 0.01 mol dm^{-3} tetrabutylammonium bromide (TC_4ABr). The glass electrochemical cell was then placed in an ultrasonic cleaner.

Controlled-current electrolysis was used throughout the experiments at two different current densities: 0.14 mA cm^{-2} and 0.3 mA cm^{-2}. The typical electrolysis time was 30 minutes. The synthesis was performed under an ultrasonication at a controlled temperature, 38 ± 2 ºC. The surface of the copper electrode was polished with emery papers and ultrasonically cleaned first in ethanol and then in water before the experiment. Immediately before the electrolysis, 0.2 mL of acetone and 0.16 mL of cyclohexane were added into 10 mL of electrolyte solution. Acetone was used to loosen the micellar framework and cyclohexane was necessary for enhancing the formation of elongated rodlike C_{16}TABr micelle.[11] After several minutes of electrolysis, the white solution turned a light red color, which indicates the formation of colloidal copper nanostructures. During the synthesis procedure, the bulk copper anode was converted into copper nanorods, probably at the interfacial region of the surfactants in the electrolyte, which allows the production of the resulting cylindrical structure.

Transmission electron microscope (TEM) data were acquired on a Hitachi H-800 TEM operated at 100 kV acceleration voltage. Samples containing Cu nanorods were prepared by dip coating the colloidal solutions on formvar/carbon film Cu grids.

RESULTS AND DISCUSSION

Typical TEM morphologies of the products are shown in Figs. 1–3. It can be seen that the products mainly consist of rod-like structures.

Figure 1 and Fig. 2 show nanorods obtained under a controlled current of 0.14 mA cm^{-2}. Figure 1 is an overall image of the products. The mean transverse diameter of a Cu nanorod is equal to *ca*. 30 nm, while the mean longitudinal length varies from 400 nm to 1 μm. The two typical copper nanorods shown in Fig. 2 are about 30 nm in diameter. A higher yield of nanorods was obtained at a current density of 0.3 mA cm^{-2}. The shape of the nanorods (Fig. 3) obtained at this current density are different from those obtained at a current density of 0.14 mA cm^{-2}, (Fig. 1). There is evidence that the current applied during the production plays and important role in the synthesis of copper nanorod by this method.

A microemulsion is a thermodynamically stable dispersion of two immiscible liquids consisting of microdomains of one or both liquids stabilized by an interfacial film of sur-

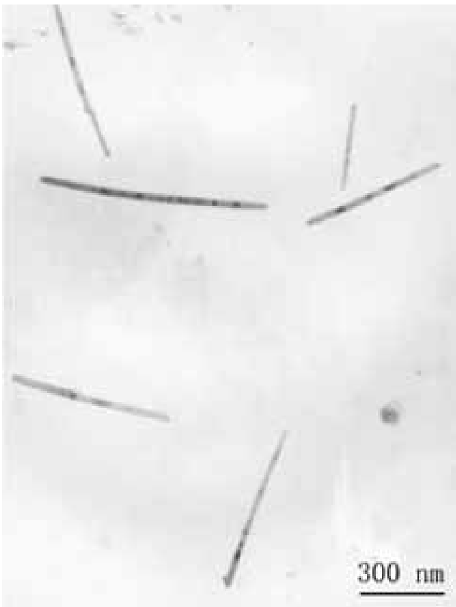

Fig. 1. TEM images of Cu nanorods obtained at a constant current of 0.14 mA cm^{-2} for 30 min. Mean diameter 30 nm. Mean lingth 500 nm.

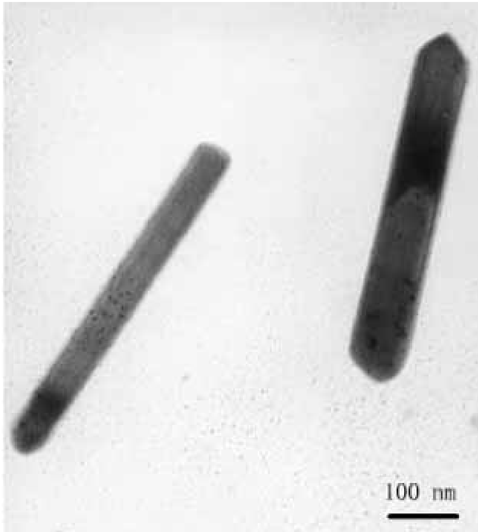

Fig. 2. Morphologies of two as-prepared Cu nanorods obtained at a constant current of 0.14 mA cm^{-2} for 30 min.

Fig. 3. TEM images of Cui nanorods obtained at a constant current of 0.3 mA cm^{-2} for 30 min.

face active molecules. The microstructure of a quaternary microemulsion CTAB/*n*-pentanol/*n*-hexane/water has been investigated in detail.[16] In such a system, the water-in-oil microemulsion acts as a microreactor. The system used in this work was a five-componenet system: CTAB/CT_4ABr/acetone/cyclohexane/water, which is more complicated than the one previously discussed. Under continuous ultrasonication, the cyclohexane phase was dispersed as small droplets surrounded by a monolayer of surfactant in the continuous liquid phase. The copper nanoparticles can then move into the small droplets. The role of acetone is to facilitate the incorporation of cylindrical-shaped-inducing co-surfactant into the CTAB micellar framework. Cyclohexane then acts as a stabilizer to protect the copper from further reaction.

As a result, copper nanorods have been successfully synthesized using a simple but efficient electrochemical method. Further experiments are to be carried out to investigate other factors controlling the shape of the obtained nano-materilas. High yields of the product should also be achieved by carefully controlling the experiment conditions.

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ИЗВОД

СИНТЕЗА НАНОШТАПИЋА ОД БАКРА ЕЛЕТРОХЕМИЈСКИМ ПУТЕМ

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Наноштапићи од бакра добивени су коришћењем електрохемијске методе контролисане струје. Површински активна средства у електролиту током синтетске процедуре служе једновремено и као калуп и као стабилизатор. Слике добијене електронским микроскопом показују да је производ углавном материјал који има штапићасту структуру. Примењене густине струја током електрохемијског таложења имају утицаја и на облик и на принос бакарних наноштапића.

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