Synthesis of Well-dispersed CuI Nanoparticles from an Available Solution Precursor

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A convenient liquid-phase route was proposed to synthesize well-dispersed CuI nanoparticles from Cu^+–DMF solution precursor, which was prepared by dissolving bulk CuI in DMF. When water was gradually added, nanoscaled CuI was produced through the decomposition of the complex formed in this solution. A passivation layer of Cu^+–DMF adsorbed on the particle surface was suggested to be responsible for the nanoparticle formation.

In the past decades, fabrication of novel nanomaterials has been one of the fundamental focusing points of chemical research.[1–3] Hereinto, a variety of liquid-phase preparative techniques have been fully built up to synthesize inorganic semiconductor nanoparticles such as coprecipitation, sol–gel processing, microemulsions, hydrothermal methods, solvo-thermal methods, template syntheses, biomimetic syntheses, and so on.[3] Despite the exciting developments, finding new routes suitable for facile scale-up synthesis and flexible experimental processing is still a current challenge to meet the demand of applications in the near future.

As a wide band gap p-type semiconductor, low-temperature (below 350 °C) γ-phase CuI has exhibited many potentials in the design of dye-sensitized solid-state solar cells, room-temperature blue-emitting devices, field emission displays, and vacuum fluorescent displays.[4–6] Besides, CuI is also a traditional and important catalyst for synthesis of many organic compounds. Recently, we have reported a facile preparation of CuI nanoparticles embedded in a polymer matrix.[7] In this letter, we provide another simple route to synthesize CuI nanoparticles from a solution precursor. This solution can be readily acquired by dissolving bulk CuI in dimethyl formamide (DMF). Compared with the previous polymer-approach, CuI nanoparticles prepared by the present strategy show better dispersion in the suspension.

In a typical preparation procedure, 95 mg (0.5 mmol) of CuI was firstly dissolved in 5 mL of acetonitrile under ultrasonic stirring to facilitate its dissolution in DMF. Then 10 mL of DMF was added into this transparent pale-yellow solution. The resulting mixture was evaporated at 25 °C to remove the acetonitrile (boiling point is 81.1 °C), and a brilliant green solution was obtained. Subsequently, 10 mL of water was slowly dripped into the above solution under mechanical stirring. The transparent green color of the solution gradually faded and turned to cloudy, indicating the formation of many ultrafine white particles. These particles were collected by centrifugal separation and purified by repeated centrifugation and decantation in ethanol for the following analysis. The sample was characterized by UV–vis absorption spectroscopy (Hitachi U-3210), X-ray diffraction (XRD: Rigaku RINT/DMAX-2000) using Cu Kα_1 radiation ($\lambda = 0.154056$ nm), Fourier transform infrared spectroscopy (FT-IR: HORIBA FT-210), scanning electron microscopy (SEM: Philips XL-20LaB6) and transmission electron microscopy (TEM: Hitachi H-8100) operated at 200 kV. The sample for TEM measurement was prepared by placing a drop of the obtained CuI colloid suspension onto the carbon-coated copper grid and dried at 25 °C.

UV–vis absorption spectrum of the CuI/DMF solution is shown in curve 1 of Figure 1a, in which a shoulder is observed around 370 nm. This absorption is likely to the charge-transfer band of the Cu^+-related complex in this solution.[8] With the addition of water step by step, the intensity of the shoulder quickly reduced. At the same time, an absorption peak at 406 nm grew and saturated when 10 mL of water was added, as exhibited from curves 2 to 7 in Figure 1a. The peak position of 406 nm agrees well with the previously reported direct band gap energy of CuI (3.06 eV).[9] The above absorption change demonstrates that water can decompose the complex in the solution and induce the formation of CuI simultaneously.

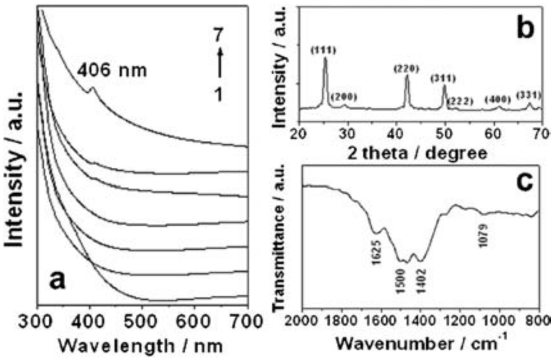

Figure 1. (a) UV–vis absorption spectra of 0.5 mmol of CuI in 10 mL of DMF before and after water addition: 1) 0 mL, 2) 1 mL, 3) 2 mL, 4) 3 mL, 5) 4 mL, 6) 5 mL, and 7) 10 mL. (b) XRD pattern of CuI particles. (C) FT-IR spectrum of CuI particles.

The XRD pattern (Figure 1b) reveals that the obtained particles possess a face-centered cubic (fcc) structure, and all of the peaks match well with the Bragg reflections of the standard fcc structure of CuI (JCPDS card No. 83-1105). The diffraction peaks are obviously broadened because of the size effect. The average particle size is calculated to be 10.8 nm by using the Debye–Scherrer formula. However, this size cannot lead to any blue shift of the absorption peak (curve 7 in Figure 1a), since CuI has a small Bohr exciton radius of 1.5 nm.[10]

The characteristic of the particle surface was studied by FT-IR spectrum, as shown in Figure 1c. It can be found that the peaks attributed to C=O, C–N, and C–H stretching vibrations from DMF locate at 1625, 1500, and 1402 cm^{-1}, respectively. Compared to those of pure DMF, the peak of C=O vibration shifts toward low-energy side from 1660 to 1625 cm^{-1} and that of C–N vibration shifts from 1520 to 1500 cm^{-1}. These results suggest that DMF molecules are coordinated to CuI particle surface.

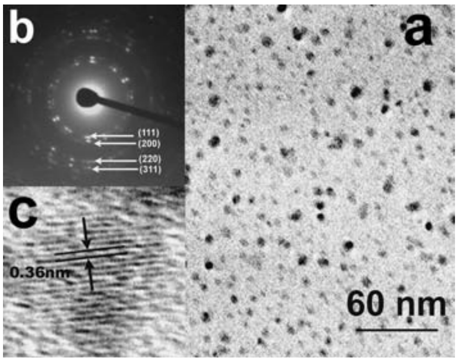

Figure 2. (a) TEM image of the as-prepared CuI nanoparticles. (b) Corresponding SAED pattern. (c) HRTEM image of an isolated CuI nanoparticle.

Figure 2a shows the TEM image of the CuI sample, in which well-dispersed nanoparticles can be clearly observed. Most of the particles are of spherical shape in the size range from 8 to 12 nm, agreeing with the calculated value from XRD. The related selected area electron diffraction pattern (SAED) in Figure 2b reveals the formation of crystalline CuI particles. Indexing of the SAED pattern is attributed to (111), (200), (220), and (311) planes of the fcc crystalline phase of CuI nanoparticles. The multiple lattice fringes in the high-resolution TEM image (Figure 2c) suggest the high crystallinity of the particles. The spacing of 0.36 nm between adjacent lattice planes corresponds to (111) crystal planes of CuI.

To understand the formation mechanism of CuI nanoparticles in this case, it is necessary to inspect the reason why CuI can be dissolved in DMF. It is well known that the lifetime of free Cu^+ in water is usually very short. However, its relative stability can be strongly influenced by the nature of anions or other ligands present. Measuring mass spectrum of CuI/DMF solution, we detected an intense signal at m/z 355.9, which could be assigned to the species of $[Cu(DMF)_4]^+$. In view of this condition, iodine ion (I^-) might act as a counter anion of this complex. So the role of DMF in this system appears to be a stabilizing agent for Cu^+. From the present experimental data, we cannot verify whether this inferred complex is the only species in this system. However, on the basis of results from absorption spectra and mass analysis, it is reasonable to suppose that the $[Cu(DMF)_4]^+$ is the preferential species in this system. After water is added in the above solution, this complex is decomposed to form small CuI particles. Nevertheless, DMF in the solution is still capable of reacting with the particle surfaces to form a layer of Cu^+–DMF capping each particle, which prevents them from further aggregating. The observed colloid stability is possibly attributed to this surface passivation. A similar phenomenon was reported on the synthesis of CdS in dimethyl sulfoxide (DMSO), in which the capping of a Cd^{2+}–DMSO complex was proven to bring about the formation of CdS nanoparticles.[11]

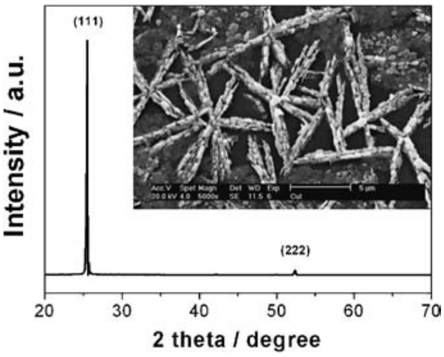

Figure 3. XRD pattern of CuI deposited on a glass substrate from CuI/DMF solution at 100 °C. Inset is the SEM image of the CuI crystals.

For further studying the role of DMF in CuI particle growth, 1.0 mL of CuI/DMF solution was placed on a glass substrate and evaporated at 100 °C in the air. Figure 3 shows the XRD pattern of the solid products on the substrate, in which two peaks assigned to (111) and (222) planes in cubic CuI were observed. Interestingly, the deposited CuI on the substrate is highly oriented (compare Figure 1b), the reason of which has been discussed elsewhere.[12] According to the ultranarrow (111) FWHM linewidth ($<0.1°$), this CuI sample is supposed to hold a large size of high crystallinity. The inset of Figure 3 exhibits the SEM image of the deposited particles. The dendrite structure is composed of large CuI crystals in the size of several microns. FT-IR measurement shows no vibrations related to DMF, indicating that all DMF-related complexes have been decomposed and no DMF exist in this sample. Therefore, CuI nanoparticles could not be formed in the absence of the Cu^+–DMF passivation layer on particle surface.

In conclusion, we have prepared well-dispersed CuI nanoparticles by a very simple liquid-phase route from CuI/DMF solution. Formation of nanoparticles was attributable to the Cu^+–DMF passivation layer on particle surface. This method may be extended to other kinds of nanoparticles' fabrication.

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