A Facile Chemical Solution Route to Convert Bulk Cuprous Iodide into Nanoparticles

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CuI nanoparticles were fabricated from conventional CuI powders in micrometer size. Acetonitrile was used as a dispersing agent to dissolve CuI powders. With acetonitrile evaporated, poly-2-vinylpyrolidine (PVP) in the solution could effectively restrict CuI particle growth, prevent them from aggregation, and result in the formation of CuI nanoparticles embedded in the polymer matrix.

Nanometer-sized particles have been attracting great interest because of their novel electronic and optical properties related to their quantum-scale dimensions.[1,2] A large number of liquid-phase synthetic routes have been achieved in reducing the size of inorganic particles and obtaining various materials in nanometer scales.[3] Cuprous iodide (CuI) is an important functional material. Its low-temperature (below 350 °C) γ-phase is one of p-type semiconductors, whose direct fundamental band gap is up to 3.1 eV. Until now, many approaches have been provided to prepare CuI nanoparticles in different dimension.[4–7] Most strategies related to solution routes commonly involve the introduction of suitable surfactants or stabilizing agents to the reaction between copper cations (2+) and iodine anions for the formation of CuI particles. These growth moderators could significantly restrict the size of prepared CuI particles owing to the strong binding of their functional groups at the particle surface or their highly effective dispersive action.

The aim of this work is to prepare CuI nanoparticles directly from conventional bulk CuI powders through a unique and simple liquid-phase method. The key issue is the utilization of good solubility of CuI in acetonitrile at room temperature. It is well known that CuI is a water insoluble solid. Its good solubility in acetonitrile is ascribed to the formation of CuI–acetonitrile adducts,[8] which will re-crystallize into bulk CuI when acetonitrile is volatilized.[9] Nano-particulate CuI thin film was obtained in dye sensitized solid-state solar-cell structure through this route by using organic thiocyanate as crystal growth inhibitors. It was suggested that monolayer coverage should be formed around the crystallites in the film, thus to restrict the average crystallite size.[10] In this letter, based on the dissolution–recrystallization process of CuI/acetonitrile system, CuI nanoparticles was fabricated by using PVP as a protective agent in CuI acetonitrile solution. The synthetic route for CuI nanoparticles is schematically presented in Figure 1.

All the chemicals used were analytical grade, purchased from Wako Pure Chemical Industries, Ltd., Japan. In a typical experiment, 95 mg of CuI (0.5 mmol) powder in micrometer size was dissolved in 10 mL moisture-free acetonitrile by ultrasonic mixing at 15 °C. A transparent pale-yellow solution was obtained, followed by adding 29 mg of PVP (PVP K30, $M_w = 58,000$) with mechanical stirring for one minute. The color of solution was changed into shallow green. The resultant solution was evaporated under decompression at 30 °C to remove the acetonitrile solvent. The residual solid products were washed with distilled water and ethanol several times, dried in vacuum at 15 °C for 2 h, and stored in the dark. For comparison, polyethylene oxide (PEO) was also introduced into CuI acetonitrile solution and CuI particles were deposited by the same procedure mentioned above.

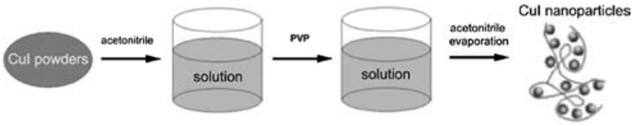

Figure 1. Scheme for the preparation of CuI nanoparticles in PVP.

In Figure 2 data a and b show the XRD patterns of CuI products obtained without and with PVP in the solution when entirely removing acetonitrile, respectively. Both patterns present similar diffraction peak positions, which can be well indexed to the CuI crystal planes of a face-centered cubic (fcc) structure (JCPDS card No. 83-1105). The diffraction peaks in datum b is obviously broadened relative to those in datum a, indicating that the grain size of CuI particles significantly reduces in the presence of PVP. The average particle size calculated from Scherrer's equation is estimated to be 10 nm in this case. Datum c exhibits XRD pattern of CuI particles prepared with PEO, from which no obvious broadening of the peaks could be detected.

FT-IR spectra were measured to examine the components of the prepared CuI samples. For CuI particles directly deposited from acetonitrile solution, no vibration bands from organic molecules could be observed. Especially the characteristic band related to C≡N stretching vibration mode could not be found in the range of 2000–2200 cm^{-1}. This confirms that CuI is the only residue after the decomposition of CuI–acetonitrile adducts. As for CuI nanoparticles deposited with PVP, a strong band at 1654 cm^{-1} related to C=O stretching vibration from amide group and other C–C vibrations could be clearly detected. All

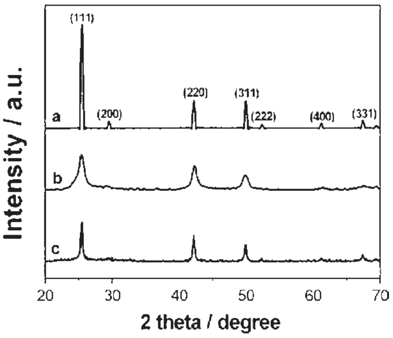

Figure 2. XRD patterns of the CuI particles prepared from acetonitrile solution without PVP (a), with PVP (b), and with PEO (c).

these absorption peaks well agree with those of pure PVP. Therefore, even if PVP is a polymer with good water-solubility, it can't be totally removed from this sample by repetitious water washing. This result demonstrates that some polymer PVP can strongly encapsulate around the particles, i.e. the prepared CuI nanoparticles are embedded in the polymer matrix.

SEM images of CuI particles directly deposited from acetonitrile solution are shown in Figures 3a and 3b, in which large CuI grains with the size from 15 to 30 µm could be clearly observed. These grains exhibit perfect crystal shape, which is well consistent with the high crystallinity acquired from XRD results (datum a in Figure 2). Figure 3c shows a typical TEM photograph of CuI particles precipitated from acetonitrile solution containing PVP, in which obvious difference in grain morphology could be found. It can be seen that the sample consists of many individual CuI nanoparticles. Besides, there is relatively low contrast around the specimen boundary (between two arrows), which further confirms the existence of polymer matrix. Figure 3d shows the high-resolution TEM image of CuI nanoparticles embedded in the PVP matrix. The corresponding selected area electron diffraction (SAED) pattern in its inset supports the presence of polycrystalline CuI. All the particles in Figure 3d are nearly spherical and the average diameter is ca. 10 nm, agreeing with the size calculated from XRD data. The marked interplanar spacing is about 0.36 nm, corresponding to (111) crystal planes of γ-CuI. The above results demonstrate that PVP can play an effective role in controlling the size of CuI particles when they are deposited from acetonitrile solution.

One possible explanation for the formation of CuI nanoparticles embedded in PVP induced by the removal of acetonitrile is as follows. In solution there is much acetonitrile, which strongly solvates CuI particles, reduces the Cu–I bond, and leads to the formation of CuI–acetonitrile adducts whose coordination originates from a significant π anti-bonding from cuprous to nitrogen.[8] Therefore, the bonding of nitrogen in PVP functional groups to cuprous ion is suppressed. However, acetonitrile serves as a reasonably good ligand for cuprous ion only at high concentrations. During the evaporation of acetonitrile, the decrease of acetonitrile will improve the coordination interaction between cuprous ions and nitrogen atom from PVP. At the same time, the residual cuprous and iodine ions in the solution are strongly inclined to reunite to CuI particles. So the competitive reaction of iodine ions and PVP with cuprous ions will happen. In this process, PVP can be abundantly adsorbed on the particle surface of produced CuI and acts as a terminating agent to restrict the particle growth. Moreover, PVP can also prevent the produced particles from congregating due to its long chain structure. These ensure the formation of PVP-encapsulated CuI nanoparticles. Since PVP also reacts with cuprous ion to form the Cu^+-related complex, formation of some by-products cannot be avoided in the present reaction mode. The formed Cu^+-related complex is usually easy to be dissolved in ethanol, so most of them can be removed by repetitious washing.

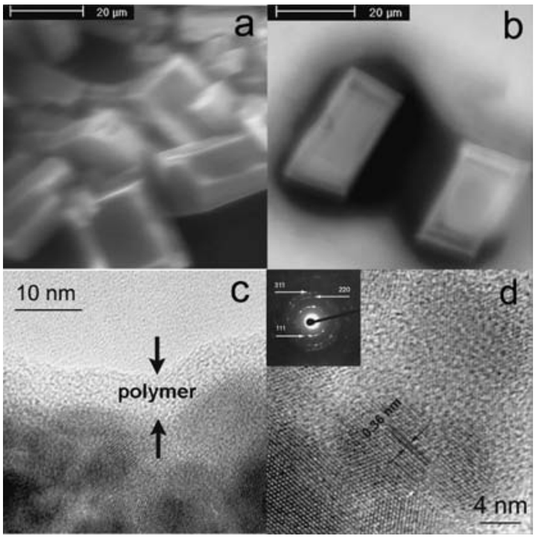

Figure 3. (a, b) SEM images of CuI particles deposited from acetonitrile solution without PVP, (c) TEM image of CuI nanoparticles prepared with PVP, (d) High-resolution TEM image of CuI nanoparticles embedded in PVP. Inset is the corresponding SAED pattern of Figure 3d.

When the amount of PVP in the solution is increased, the size of prepared CuI particles will gradually reduce. The average particle size will decrease to 6 nm by adding 290 mg of PVP in 10 mL acetonitrile while keeping the amount of CuI unchanged. It is noted that when PEO takes place of PVP in the solution, no CuI nanoparticles could be obtained even if the amount of PEO is added up to 290 mg, as reflected in datum c of Figure 2. This might result from the quite weak coordination interaction between oxygen atom in PEO and cuprous ion. As a result, though PEO is a quite good stabilizer for many other systems, it is unable to effectively compete with iodine ions and form an adsorption layer to reduce the size of the produced CuI particles.

In summary, we have succeeded in fabricating CuI nanoparticles embedded in PVP matrix by a facile and low-cost method. The mechanism of the formation of nanoparticles was also suggested. This method is expected to be feasible for preparing other cuprous halide nanoparticles.

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