doi:10.1246/cl.2011.68

Unusual Synthesis of Highly (111) Oriented Crystalline CuI

Jing Li, Hongxiao Zhao,* Huimin Jia, Like Zhang, Yuanhao Gao, and Zhi Zheng*
Institute of Surface Micro and Nano Materials, Xuchang University, Xuchang, Henan 461000, P. R. China

(Received September 21, 2010; CL-100808; E-mail: zhaoxiao@xcu.edu.cn, zzheng@xcu.edu.cn)

Highly (111) oriented γ-CuI crystals were successfully synthesized by a microwave-assisted method using $Cu(NO_3)_2 \cdot 3H_2O$ and I_2 as raw materials in an ethanol solution, in which ethanol plays an important role as both the solvent and reducing agent. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A possible reaction mechanism was proposed and discussed the results from gas chromatography–mass spectrometry (GC–MS).

Cuprous iodide is a water-insoluble solid and has three crystalline phases (α, β, and γ).[1–3] γ-CuI is usually obtained at low temperature (below 350 °C) and is one of a few kinds of p-type large band gap materials with zincblende structure. It is an important additive for the production of white conducting polymeric fibers and a powerful heterogeneous catalyst in many organic reactions.[4–7] In recent years, it has been found that γ-CuI has potential applications in superionic conductors[8,9] and in solid-state dye-sensitized solar cells.[10–15] Therefore, a large number of reports[16–19] have demonstrated that CuI can increase device efficiency, and the morphology of γ-CuI can affect electron-optic micro/nanodevices made of cuprous iodide. Consequently, considerable efforts[20–22] have been made to fabricate micro–nanoscale γ-CuI materials with different morphology.

Various techniques have been developed to prepare CuI materials, such as hydrothermal,[23] surface-etching,[24] sonochemical,[25] pulse laser deposition,[26–28] and precipitation methods.[29] Copper(II) salt or Cu foil are usually used as copper sources. When copper(II) salt is used, iodide ion is used as iodine source accompanying by adding a certain reducing agent. To the best of our knowledge, there has been no report of CuI synthesized using copper(II) salt and iodine as starting materials.

Purely from the standpoint of electron transfer, it is impossible to form CuI from copper(II) salt and iodine because both copper(II) salt and iodine are electron acceptors, and there is no electron donor during the reaction. In the present reaction design, we adopt ethanol as reductive solvent that has the capacity to provide electrons. Furthermore, considering that microwave-assisted synthesis is a fast, simple, and efficient method,[30–35] we employ microwave irradiation to fabricate γ-CuI crystals by using copper(II) nitrate and iodine in an ethanol solution, in which ethanol plays a key role as both the reaction media and reducer. The formation process of γ-CuI crystals is discussed supported by GC-MS data. This is likely to be the first report of the synthesis of CuI using copper(II) salt and iodine as raw materials.

The synthesis of CuI was carried out by a microwave-assisted method. Typically, 0.25 g of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.45 g of I_2 were separately dissolved in 10 mL of anhydrous ethanol. The two solutions were mixed and the resultant solution was subsequently transferred to a flask with a condenser tube. The flask was placed in a microwave oven and maintained at 100 mA for 20 min. Then, the flask was air-cooled to room temperature. The resulting suspension was separated by centrifugation, and the precipitate was washed with anhydrous ethanol. Finally, the resultant materials were dried at 60 °C in a vacuum oven.

Absolute ethanol was treated by microwave heating before use. Other reagents were used as received. Absolute ethanol, ethanolic $Cu(NO_3)_2$, ethanolic I_2, and ethanolic solution of $Cu(NO_3)_2$ and I_2 were microwave heated under the above conditions for GC-MS testing.

The samples were characterized by XRD (Bruker D8 Advance diffractometer) using Cu Kα radiation source and SEM (Zeiss EVO LS-15). The solutions were investigated by GC–MS (Agilent Technologies 5975C/7890A GC-MS System).

A typical XRD pattern of the resultant micro CuI is shown in Figure 1. It is evident that the products are pure γ-CuI because all the diffraction peaks can be indexed to γ-CuI and match well with the peaks of standards (JCPDS file No. 6-246, space group: $F\bar{4}3m$ (No. 216)). No peaks of any other phases or impurities can be observed, confirming the purity of the synthesized γ-CuI materials. In addition, it is easily seen that the peak at 25.6° assigned to the (111) plane of CuI is very strong, which indicates that the as-synthesized materials were highly oriented perpendicularly to the [111] crystal axis. Therefore, the prepared CuI is of high crystallinity, which can also be verified by the ultra-narrow (111) full width at half-maximum line width (<0.1°).[6]

Figure 2 shows the SEM images of the as-prepared micro CuI. CuI in the size of 2.5–8 µm can be clearly identified. It also shows that the shape of CuI are not very uniform and that the products are mainly composed of flat materials with an average thickness of 1.5 µm.

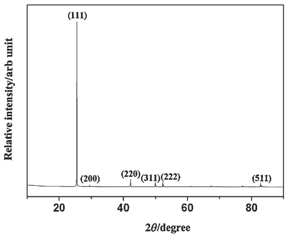

Figure 1. XRD pattern of CuI.

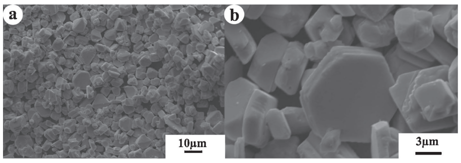

Figure 2. SEM images of CuI.

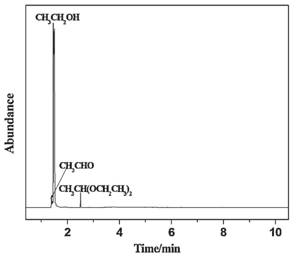

Figure 3. GC-MS of the microwave-treated solutions of I_2, $Cu(NO_3)_2$, and ethanol.

It is impossible to form CuI from copper(II) salt and iodine only through electron transfer. It can be supposed that the solvent ethanol also attends the reaction. First, ethanol loses two electrons to form acetaldehyde, accompanying by the transfer of electrons to I_2 to form I^- and Cu^{2+} to obtain Cu^+. Then, CuI is formed from Cu^+ and I^-. The process can be described by the following equations:

$$2Cu^{2+} + CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2Cu^+ \quad (1)$$

$$CH_3CH_2OH + I_2 \rightarrow CH_3CHO + 2HI \quad (2)$$

$$Cu^+ + I^- \rightarrow CuI \quad (3)$$

A side reaction also takes place in the presence of ethanol, shown as follows

$$2CH_3CH_2OH + CH_3CHO \rightarrow CH_3CH(OCH_2CH_3)_2 + H_2O \quad (4)$$

$$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O \quad (5)$$

In order to clarify the process, the remaining solutions after microwave heating were tested by GC-MS (Most GC-MS and MS spectra for each GC peak are given in Supporting Information (SI)[36]). First of all, ethanol that was microwave heated before use was selected to conduct a blank test. From SI-Figure 1,[36] it can be seen that there was only ethanol peak present in the remaining solution after microwave treatment, indicating that no other reaction can take place during the microwave exposure. However, ethanol, acetal, and iodoethane could be produced in solutions of I_2 and ethanol by microwave heating (as shown in SI-Figure 2[36]), implying that I^- and certain amount of acetaldehyde were brought out, and all side reactions we predicted happened during the course of reaction. It was clearly seen that acetaldehyde and acetal were present from SI-Figure 3,[36] showing that plenty of acetaldehyde was formed and that the side reaction shown in eq 4 takes place during microwave heating solutions of $Cu(NO_3)_2$ and ethanol. From Figure 3, it can be seen that during the reactions of $Cu(NO_3)_2$ and I_2 in ethanol solutions plenty of I^- was resumed by reaction with Cu^+ and that it produced very little iodoethane which cannot be detected. All these results demonstrate that the process is reasonable and that during the formation of CuI ethanol plays a key role as both the solvent and reducing agent.

In conclusion, highly (111) oriented micro CuI was synthesized by a microwave-assisted method using $Cu(NO_3)_2 \cdot 3H_2O$ and I_2. A formation mechanism of CuI was also proposed and discussed. We demonstrated that the ethanol acted not only as the common solvent but also played the key role as the reducing agent. This unusual reaction predicts further use of ethanol to synthesize other metal iodides.

This work was supported by National Natural Science Foundation of China (Grant No. 20873118), Program for New Century Excellent Talents in University (Grant No. NCET-08-0665), Henan Province Science and Technology Key Project (Grant No. 082102230036), and Natural Science Foundation of Henan Province, China (Grant No. 2008B150019).

References and Notes

1 C. E. Mohn, S. Stølen, S. Hull, *J. Phys.: Condens. Matter* **2009**, *21*, 335403.
2 G. S. Hsiao, M. G. Anderson, S. Gorer, D. Harris, R. M. Penner, *J. Am. Chem. Soc.* **1997**, *119*, 1439.
3 J. G. Pan, S. Y. Yang, Y. B. Li, L. Han, X. Li, Y. J. Cui, *Cryst. Growth Des.* **2009**, *9*, 3825.
4 B. Mallesham, B. M. Rajesh, P. R. Reddy, D. Srinivas, S. Trehan, *Org. Lett.* **2003**, *5*, 963.
5 J.-H. Li, J.-L. Li, D.-P. Wang, S.-F. Pi, Y.-X. Xie, M.-B. Zhang, X.-C. Hu, *J. Org. Chem.* **2007**, *72*, 2053.
6 X. A. Xie, Y. Chen, D. W. Ma, *J. Am. Chem. Soc.* **2006**, *128*, 16050.
7 A. V. Kel'in, V. Gevorgyan, *J. Org. Chem.* **2002**, *67*, 95.
8 S. Y. Gao, Z. D. Li, S. X. Yang, K. Jiang, Y. Li, H. B. Zeng, L. Li, H. Q. Wang, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2080.
9 Y. Y. Zhou, M. K. lü, G. J. Zhou, S. M. Wang, S. F. Wang, *Mater. Lett.* **2006**, *60*, 2184.
10 B. V. Andryushechkin, K. N. Eltsov, V. M. Shevlyuga, *Surf. Sci.* **2004**, *566–568*, 203.
11 Y. Yang, X. F. Li, B. Zhao, H. L. Chen, X. M. Bao, *Chem. Phys. Lett.* **2004**, *387*, 400.
12 R. George, J. A. Harrington, *Opt. Eng.* **2006**, *45*, 055004.
13 Z. Zheng, A. R. Liu, S. M. Wang, B. J. Huang, K. W. Wong, X. T. Zhang, S. K. Hark, W. M. Lau, *J. Mater. Chem.* **2008**, *18*, 852.
14 Y. Y. Xu, D. R. Chen, X. L. Jiao, *Mater. Lett.* **2009**, *63*, 1859.
15 T. H. Wei, T. C. Wen, L. C. Hwang, S. C. Lee, W. Y. Chou, S. J. Hu, J. H. Wang, *Opt. Mater.* **2006**, *28*, 569.
16 X. Li, M. X. Wan, *Cryst. Growth Des.* **2006**, *6*, 2661.
17 Y. Yang, Q. M. Gao, *Langmuir* **2005**, *21*, 6866.
18 B. R. Sankapal, A. Ennaoui, T. Guminskaya, T. Dittrich, W. Bohne, J. Röhrich, E. Strub, M. C. Lux-Steiner, *Thin Solid Films* **2005**, *480–481*, 142.
19 H. Iimori, S. Yamane, T. Kitamura, K. Murakoshi, A. Imanishi, Y. Nakato, *J. Phys. Chem. C* **2008**, *112*, 11586.
20 C. H. B. Ng, W. Y. Fan, *J. Phys. Chem. C* **2007**, *111*, 9166.
21 M. Gu, P. Gao, X.-L. Liu, S.-M. Huang, B. Liu, C. Ni, R.-K. Xu, J.-M. Ning, *Mater. Res. Bull.* **2010**, *45*, 636.
22 P. Gao, M. Gu, X. Lin-Liu, *Cryst. Res. Technol.* **2008**, *43*, 496.
23 W.-J. Li, E.-W. Shi, *Cryst. Res. Technol.* **2002**, *37*, 1041.
24 X. L. Hu, J. C. Yu, J. M. Gong, Q. Li, *Cryst. Growth Des.* **2007**, *7*, 262.
25 B. J. Huang, Z. Zheng, F. L. Yang, Y. G. Zhang, D. P. Pu, H. X. Zhao, D. P. Li, *Solid State Ionics* **2008**, *179*, 2006.
26 P. M. Sirimanne, M. Rusop, T. Shirata, T. Soga, T. Jimbo, *Chem. Phys. Lett.* **2002**, *366*, 485.
27 P. M. Sirimanne, T. Soga, T. Jimbo, *J. Lumin.* **2003**, *105*, 105.
28 P. M. Sirimanne, M. Rusop, T. Shirata, T. Soga, T. Jimbo, *Mater. Chem. Phys.* **2003**, *80*, 461.
29 Y. Y. Xu, D. R. Chen, X. L. Jiao, L. Ba, *J. Phys. Chem. C* **2007**, *111*, 6.
30 B. Martin, H. Sekljic, C. Chassaing, *Org. Lett.* **2003**, *5*, 1851.
31 Z. G. Li, H. Huang, H. B. Sun, H. L. Jiang, H. Liu, *J. Comb. Chem.* **2008**, *10*, 484.
32 R. Hoogenboom, B. C. Moore, U. S. Schubert, *J. Org. Chem.* **2006**, *71*, 4903.
33 K. Lee, S. Myung, Y.-K. Sun, *Chem. Mater.* **2007**, *19*, 2727.
34 R. Harpeness, A. Gedanken, *Langmuir* **2004**, *20*, 3431.
35 W. Schumacher, A. Nagy, W. J. Waldman, P. K. Dutta, *J. Phys. Chem. C* **2009**, *113*, 12132.
36 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.