Ionic Liquid-mediated Preparation Strategy for CuCl Nanocrystal

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(Received December 28, 2006; CL-061520; E-mail: sky50@zjnu.cn)

CuCl was obtained through a novel route in the absence of concentrated acid or additives. The formation of nanocrystal CuCl was confirmed by XRD, SEM, TEM, and EDX studies. In this paper, an ecologically and environmentally friendly preparation route of CuCl nanocrystal was proposed.

Nanomaterials have unique physical, optical, electrical, magnetic, and biological properties and have attracted much attention in extending their structures and applications in the past decade. In general, nanomaterials are synthesized in rigorous conditions or through adding varieties of organic solvents or using morphological templates. A common disadvantage of these methods is environmental unfriendly because of using various additives or templates. Therefore, it is interesting to find an efficiently and ecologically benign route or some "green" solvents to synthesize nanomaterials.

Room temperature ionic liquids (RTILs), which are liquid organic salts at ambient temperature, can dissolve many organic/inorganic materials with the advantages of negligible vapor pressure, thermo/chemical stabilities, wide electric window, etc. Thus, RTILs have got applications in organic synthesis,[1–4] electrochemistry,[5–7] and separation.[8–10] Their applications in inorganic field, however, are still in infancy. From theoretical points, RTILs can be used as both solvents and morphological templates at the same time and can be recovered after the reactions. Therefore, RTILs as an alternative recyclable and environmentally benign medium are promising to be used in synthesizing inorganic nanomaterials. So far, there have only been a few reports on its applications in the areas of metal nanoparticles, ordered metal oxides, and solvents/templates for material preparation.[11–17]

Copper(I) chloride (CuCl) is extensively used as a catalyst in the organic synthesis, and as a desulfurizing, decolorizing and deodorizing agent in the petroleum industry.[18] The traditional synthesis of CuCl, however, is via reducing copper(II) by using different reduction agents and quantity of acid, which has already caused a big problem in the environment. Therefore, it is significant to find a new synthetic methodology for CuCl. In this paper, CuCl nanocrystal was prepared through an ecologically and environmentally friendly route in ionic liquid and characterized by XRD, SEM, TEM, and EDX, respectively. The room temperature ionic liquid (IL), 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM]^+BF_4^-$, was synthesized according to the literature[19] and used as medium in this work. In a typical synthetic procedure, 0.74 g (5.5 mmol) of $CuCl_2$ and 0.32 g (5 mmol) of Cu powders were added into a vial with 1 mL of $[BMIM]^+BF_4^-$. The mixture was stirred mildly at 75 °C for 6 h and then allowed to cool to room temperature (Scheme 1). The product was collected by centrifugation, washed several times with diluted hydrochloric acid (0.1 M), and dried at 75 °C in vacuum. X-ray diffraction (XRD) patterns of the sample were collected on a Philips-PW3040/60 X-ray diffractometer with Kα radiation ($\lambda = 0.15418$ nm). The morphologies and elemental analysis were conducted by the HITACHI S-4800 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX), respectively. The crystallite sizes were performed on a JEOL-2010 transmission electron microscope (TEM) at an accelerating voltage of 200 kV.

$$CuCl_2 + Cu \xrightarrow[\text{magnetic stirring}\ 75\,^\circ\mathrm{C}]{\text{IL}} 2CuCl$$

Scheme 1.

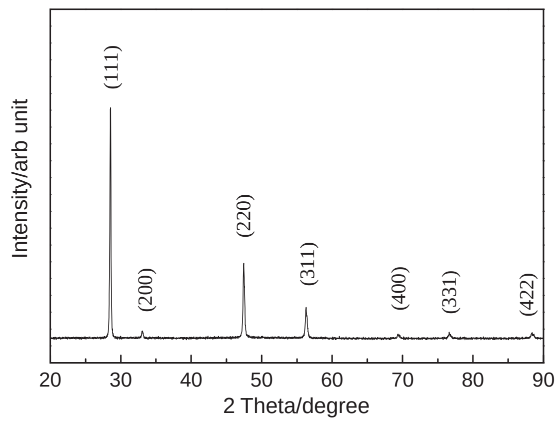

Figure 1. XRD pattern of the as-prepared CuCl sample in $[BMIM]^+BF_4^-$.

Figure 1 shows the XRD pattern of the as-prepared CuCl sample in $[BMIM]^+BF_4^-$. All diffraction peaks of the sample can be well indexed to the cubic crystal with a lattice parameters $a = 0.5414$ nm, which is consistent with the standard card (JCPDS card No. 77-2383). Characteristic peaks at 2θ angles of 28.54, 33.06, 47.45, 56.33, 69.36, 76.63, and 88.41° can be assigned to scattering from the (111), (200), (220), (311), (400), (331), and (422) planes of the CuCl crystal, and no characteristic peaks of impurity such as $CuCl_2$ or Cu are detected in the XRD pattern, indicating that the pure CuCl nanocrystal can be successfully obtained in $[BMIM]^+BF_4^-$. In addition, the sharp diffraction peaks reveal the good crystallinity of the CuCl sample.

Figure 2 and Figure 3 show the SEM and TEM images of CuCl nanocrystal prepared in $[BMIM]^+BF_4^-$, respectively. It can be seen from Figure 2 and Figure 3 that the as-prepared sample is approximately spherical with the diameter of ca. 20 nm.

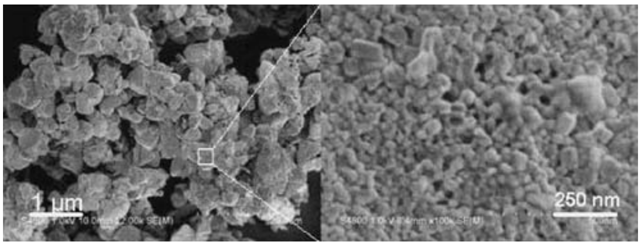

Figure 2. SEM images of CuCl nanocrystal obtained in $[BMIM]^{+}BF_4^{-}$ (left: low magnification, $\times 2000$ (times); right: high magnification, $\times 10000$ (times)).

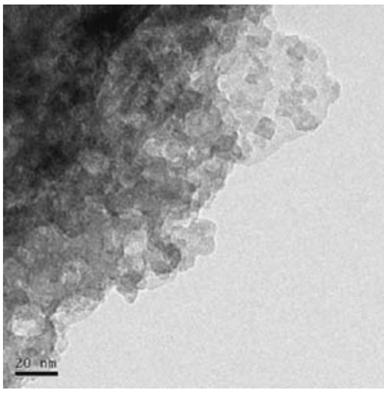

Figure 3. TEM images of CuCl nanocrystal obtained in $[BMIM]^{+}BF_4^{-}$.

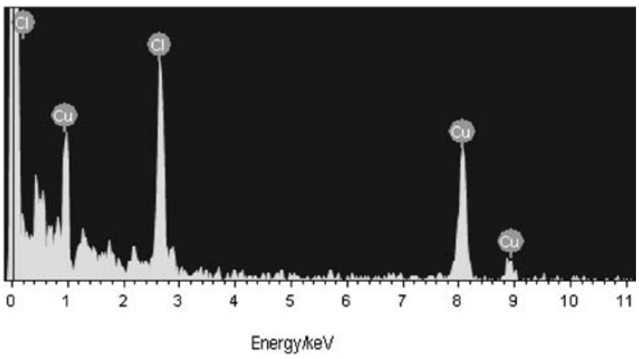

Figure 4. EDX spectrum of CuCl nanocrystal obtained in $[BMIM]^{+}BF_4^{-}$.

EDX spectrum of the as-prepared CuCl shown in Figure 4 confirms that the sample is composed of Cu and Cl atoms, and the ratio of Cu/Cl is agreed with the desired composition.

All the evidences here indicate that the ionic liquid has a unique function in the reaction. A possible mechanism can be proposed as follows: (i) in our experiment, IL was used as reactive medium owing to its high surface activity, and $CuCl_2$ and Cu can disperse in IL which forms thousands of tiny reactors; (ii) RTILs really had polarity, however, their low interfacial tension made the inorganic species have a high nucleation ratio, which propelled the formation of the nanocrystal; (iii) it is known that Cu^{II} ($\varphi_{Cu2+/Cu+}/V = +0.17$) and Cu can not react to form Cu^{I} ($\varphi_{Cu+/Cu}/V = +0.521$) in aqueous systems, whereas IL here acted as both a nonaqueous medium and an electrical conductor drove the above reaction. Therefore, this work made it possible to get CuCl avoiding the environmental problems caused by the usage of concentrated hydrochloric acid or organic solvent consumed in the traditional method, which could be considered as an example of preparing CuCl in a green method and expected to extend to prepare other inorganic compounds which are unstable in aqueous systems.

In conclusion, CuCl nanocrystal was prepared using ionic liquid as medium. XRD, SEM, TEM, and EDX results indicated the formation of cubic CuCl nanocrystal. Compared with the traditional preparation methodology, this route was environmentally and ecologically friendly. The probable formation mechanism of CuCl nanocrystal was proposed as well. This strategy was expected to extend to prepare other composites which were unstable in aqueous systems.

This work was supported by the National Science Foundation of Zhejiang Province [Y404358].

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Published on the web (Advance View) April 14, 2007; doi:10.1246/cl.2007.642