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Room-Temperature Synthesis of Hierarchical CuSCN Nanocrystals Using an Ionic Liquid Precursor

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Abstract

High-quality hierarchical CuSCN microcrystals assembled by nanoplates were successfully synthesized via a metathesis reaction between SCN⁻ ions and CuCl in ionic liquid [Bmim]SCN. The as-obtained samples were characterized by the X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that [Bmim]SCN played multiple roles during the formation process of hierarchical CuSCN microcrystals. This method is an effective and ecologically benign route to synthesize the hierarchical CuSCN microcrystals, without pollutant, heating and complicated equipment. This method is expected to be extended to synthesize other functional inorganic materials.

Keywords: CuSCN, Hierarchical nanostructures, Ionic liquids, Nanocrystals, Crystal Growth

Introduction

In recent years, room temperature ionic liquids (RTILs) have attracted great attention in the synthesis of inorganic nanomaterials due to their unique characteristics, such as negligible vapor pressure, thermal stability and wide electrochemical window.^[1] Various IL-involved techniques, such as electrosynthesis,^[2] hydro/solvothermal synthesis,^[3-6] ionothermal synthesis,^[7-9] controlled solvent evaporation process,^[10] microwave-assisted ionic liquid method^[11] and sol-gel method,^[12] have been used to synthesize different inorganic nanomaterials. Furthermore, physicochemical properties of RTILs strongly depend on the species of cations and anions, the alternation of anions allows finely tuning the physicochemical properties of ILs, such as viscosity, dissolving ability, hydrophobicity and melting points.^[13] Thus, these features provide possibilities in designing RTILs for specific reaction systems.^[14, 15]

Recently, CuSCN has received increasing attention due to its potential application in photovoltaic cells, which is considered as one of the most green energy devices and intensively researched.^[16-18] Furthermore, CuSCN has also been widely used in various organic synthesis reactions as catalysts.^[19] To date, much work has focused on the preparation of the CuSCN thin films.^[20-24] However, there is rare report on the synthesis of CuSCN materials.^[22, 23]

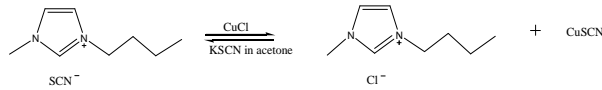
Herein, we report an environment-friendly route to synthesize hierarchical CuSCN microcrystals by translating CuCl into CuSCN in ionic liquid [Bmim]SCN at room temperature. Our as-used route has four remarkable merits: First, reaction media is nonvolatile and recyclable; Secondly, the reaction is proceeded at room temperature, without additional heating; Thirdly, the reaction does not give rise to organic contamination; Lastly, the reaction is versatile to gain more nanomaterials by exchange of the reactant and the anion of ionic liquid, for example, Br⁻, I⁻ can replace the SCN⁻; silver halide can replace the cuprous chloride. In summary, the present method will provide an effective and benign route to synthesize functional inorganic nanomaterials.

Experimental Section

Synthesis of CuSCN microcrystals

All reagents are analytical grade and used without further purification. The ionic liquid 1-n-butyl-3-ethylimidazolium thiocyanate ([Bmim]SCN) was synthesized according to the reference.^[28] In a typical synthesis of CuSCN nanocrystals, 0.1g CuCl was added into 10 mL ionic liquid [Bmim]SCN under magnetic stirring at room temperature. The reaction was maintained for 10 h. The product was collected by centrifugation and washed with ethanol

and distilled water several times, and dried in vacuum at 60 °C. Moreover, the by-product BmimCl can be translated into [Bmim]SCN by adding a litter KSCN in acetone. The whole experiment procedure is illustrated in Scheme 1.



Scheme 1 Translation process of [Bmim]SCN from [Bmim]Cl.

Characterization

The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu K_{α} source ($\lambda = 0.15406$ nm). The scanning electron microscopy (SEM) images were taken with a JEOLJSM-6700F field emission scanning electron microscope (15 kV).

Results and Discussion

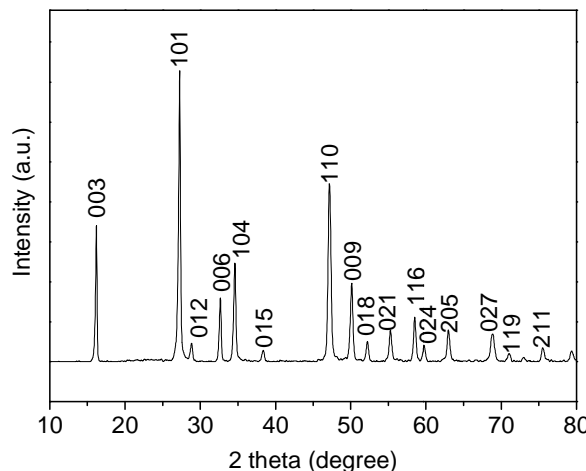


Fig. 1 XRD pattern of hierarchical CuSCN microcrystals.

Fig. 1 shows the XRD pattern of the as-prepared CuSCN products in [Bmim]SCN. All diffraction peaks in Fig. 1 could be well indexed to the rhombohedral crystal, which is consistent with the standard card (JCPDS card No. 29-0581). Characteristic peaks at 2θ angles of 16.16, 27.22, 28.83, 32.64, 34.58, 38.37, 47.07, 49.82, 52.20, 55.26, 58.48, 59.73, 62.30, 68.94, 70.97, and 75.44 can be assigned to scattering from the (003), (101), (012), (006), (104), (015), (110), (009), (018), (021), (116), (024), (205), (027), (119) and (211) planes of the CuSCN crystal, and no characteristic peaks of impurity such as CuSCN are detected in the XRD pattern, indicating that pure CuSCN microcrystals could be successfully obtained from [Bmim]SCN. In addition, sharp diffraction peaks in the pattern reveal the good crystallinity of the as-prepared CuSCN sample.

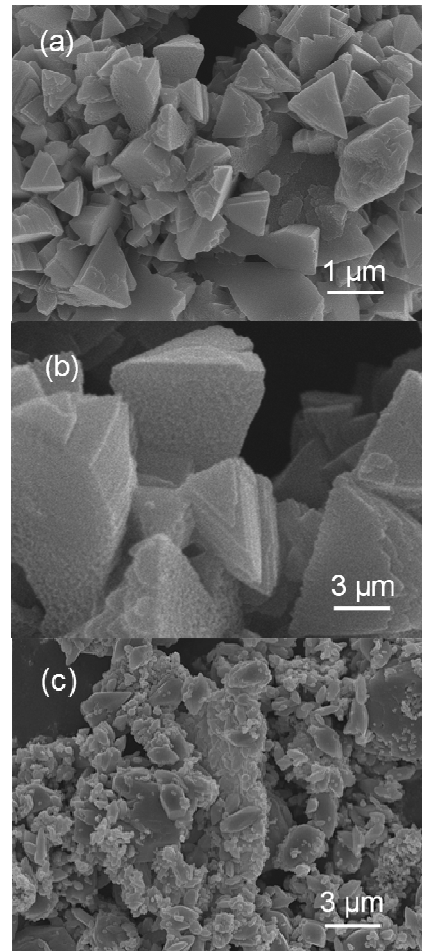


Fig. 2 SEM images of CuSCN synthesized in: (a and b) [Bmim]SCN and (c) distilled water.

The morphologies of the as-prepared samples were investigated by SEM. Fig. 2a and b show SEM images of the CuSCN nanocrystals, from which one can find that the as-prepared CuSCN microcrystals are consisted of nanoplates, which are aligned together, face to face, along the pillar. Although the size and shape of the CuSCN microcrystals are different, the individual CuSCN microcrystal is regular.

The reaction mechanism is based on the metathesis reaction between SCN ions and CuCl. As we know that the $K_{sp}CuSCN$ (4.8×10^{-15}) is largely lower to $K_{sp}CuCl$ (1.2×10^{-6}), so the reaction is readily thermodynamically favored. In order to determine the role of [Bmim]SCN, we conducted the experiment in water at the same conditions with the same amount of KSCN. The as-obtained sample is composed of irregular particles, as shown in Fig. 2c. Based on above-mentioned results, we speculate that [Bmim]SCN plays a crucial role in determining the nucleation and growth of CuSCN microcrystals. However, the formation mechanism of hierarchical

CuSCN nanocrystals assembled nanoplates needs further investigation.

Conclusion

In conclusion, hierarchical CuSCN microcrystals have been successfully prepared via a metathesis reaction in the ionic liquid at room temperature. Possible formation mechanism was rationally proposed. This route is demonstrated to be effective and ecologically benign, and expected to be extended to prepare other functional inorganic materials. Moreover, the as-prepared hierarchical CuSCN microcrystals are expected to be promising materials for photovoltaic cells.

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