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Short communication

Microwave-assisted synthesis of CdF_2 nanoflakes in ionic liquid

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Abstract

Cadmium fluoride (CdF_2) nanoflakes have been successfully synthesized using an ionic liquid (1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [BMIM]BF_4) under microwave heating for 10 min. Not only did the ionic liquid act as the reaction medium in this route but also as an efficient fluridizer for the formation of CdF_2 species. The crystal phase, size and morphology of as-prepared nanomaterials were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

Keywords: B. Electron microscopy; B. X-ray methods; A. Microwave processing; Ionic liquid

1. Introduction

Cadmium fluoride is an ionic crystal with fluoride structure with the space group O_h^5 (Fm-3m) at ambient conditions [1]. This compound has been the subject of several experimental and theoretical studies recently due in part to its visible and ultraviolet light transparency [2], and semiconductivity after doping and thermal treatment [3]. Crude CdF_2 has been traditionally obtained from cadmium carbonate when treated with aqueous hydrofluoric acid [4]. The question arised, however, to what extent the toxicity and acute causticity of aqueous hydrofluoric acid brought the new seeking for an alteration.

Room-temperature ionic liquids (RTILs) have developed to a focal point of interest in both academia and industry in the past few decades due to their advantages such as the thermal stability, the ability to dissolve a variety of materials and most important, the negligible vapor pressure [5]. Considered as environmentally benign solvents, ionic liquids have a growing number of applications such as chemical reactions [6], catalysis [7], electrochemistry [8] and separation [9]. They have also been applied to the inorganic field [10]. Meanwhile, ionic liquids are excellent microwave-absorbing agents due to their thermal stability, high ionic conductivity and polarizability, and thus leading to a high heating rate and a significantly shortened reaction time. Recently, the microwave-assisted ionic liquid (MAIL) method has been applied in the synthesis of Te nanowires and nanorods [11], flower-like ZnO [12], etc. In all these cases, fluorides were not obtained under microwave irradiation, and ionic liquids acted as the reaction media to modify crystals, and/or tune granule sizes or morphologies. In the current article, we focus on the formation of CdF_2 species through the reaction of an ionic liquid ([BMIM]BF_4) with cadmium hydroxide ($Cd(OH)_2$) under microwave radiation. This novel route may offer a universal pathway towards other metal fluorides nanostructures.

2. Experimental

Ionic liquid [BMIM]BF_4 was synthesized according to previous literature [13]. $Cd(OH)_2$ powders were prepared through the reaction of cadmium nitrate with aqueous NaOH. All other chemicals were of analytical grade and used as received without further purification. In a typical synthetic procedure, 50 mg of $Cd(OH)_2$ powder was added into a 10-ml reaction tube containing 5 ml of ionic liquid [BMIM]BF_4, and the resulting mixture was microwave-heated with 100% power in a domestic microwave oven (National, IEC-705, 700W) for 10 min. Then microwave heating was terminated and the solution was allowed to cool to room temperature. The products were separated by centrifugation, washed with distilled water and absolute ethanol in sequence, and then dried in a vacuum at 60 °C for 4 h. X-ray diffraction (XRD) patterns of the sample

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were collected on a Philips-PW3040/60 X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm). TEM images were carried out on a JEOL-2010 transmission electron microscope at an accelerating voltage of 200 kV. Samples for TEM measurements were prepared by placing a drop of dilute alcohol suspension of products onto a carbon-coated copper grid and allowing the alcohol to evaporate in air.

3. Results and discussion

X-ray diffraction (XRD) pattern of the sample, recorded in the 2θ range of 10–90° with a scanning step of 0.02°, is shown in Fig. 1. It can be seen from Fig. 1 that all of the diffraction peaks can be well indexed to the cubic CdF_2 with a lattice parameter $a = 0.539$ nm, which is consistent with the value reported previously (JCPDS Cards 75-0226). No characteristic peaks of potential impurities are detected in the XRD pattern based on this standard card. The morphological characteristic of CdF_2 species was further investigated by transmission electron microscopy (TEM). A representative image in Fig. 2 illustrates that the sample consists of nanometer-sized structures with a typical laminar morphology. Although these flakes are slightly agglomerated, the boundaries are clearly distinguishable.

In the current reaction, ionic liquid [BMIM]BF_4 serves as the source of the fluoride ions. As mentioned above, the ionic liquid is a good suspector of the microwave radiation because of its ionic nature, and its boiling temperature is thus reached within a very short time. When the ionic liquid exceeds its boiling temperature as a result of superheating, the BF_4^- anions undergo fast hydrolysis in the presence of transition metal salts with hydration water molecules under microwave superheating [14,15]. The overall reaction may be simplified as follows [16]:

$$BF_4^- + H_2O \overset{\text{Microwave}}{\longrightarrow} BF_3{}^{\bullet}H_2O + F^-$$

The fluoride ions react with the metal ions, giving an insoluble metal fluoride. In parallel, the cations of ionic liquid [BMIM]BF_4 decompose to form carbon [15].

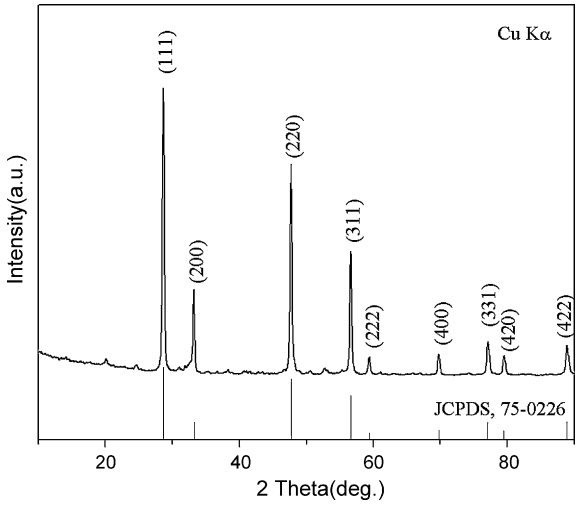

Fig. 1. XRD pattern of as-prepared CdF_2 species. Peaks were indexed according to JCPDS card (75-0226).

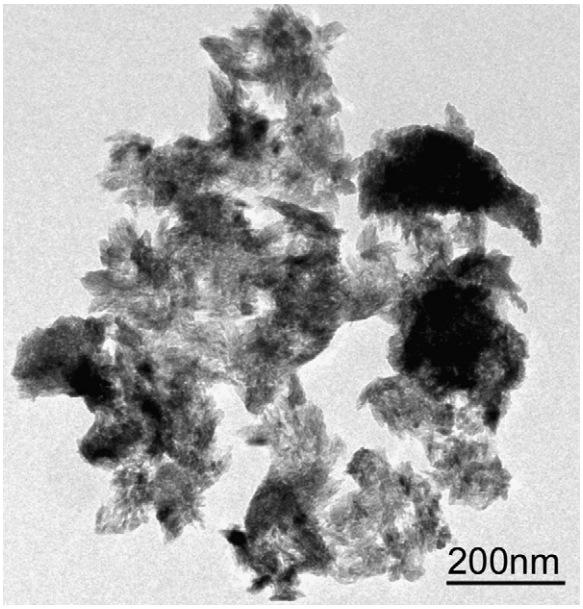

Fig. 2. TEM image of as-prepared CdF_2 nanoflakes.

4. Conclusions

A microwave-assisted ionic liquid method for the synthesis of CdF_2 nanoflakes was developed. The ionic liquid [BMIM]BF_4 acted as the solvent and an efficient fluridizer under microwave superheating has favored the formation of CdF_2 nanostructures. This method is facile, green and ecologically friendly. We expect that this method may be extended to synthesize nanostructures of other fluorides.

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References

[1] W. Hayes, Crystals with the Fluorite Structure, Clarendon Press, Oxford, 1974.
[2] R.L. MacDonald, R.A. Linke, G.E. Devlin, M. Mizuta, Confirmation of the local nature of the plasma grating photorefractive effect, Opt. Lett. 20 (1995) 1322–1324.
[3] S.A. Kazanskii, D.S. Rumyantsev, A.I. Ryskin, Ionized donor pairs and microwave and far-infrared absorption in semiconducting CdF_2, Phys. Rev. B 56 (2002) 165214.
[4] M. Rubenstein, H. Banks, Color centers in cadmium fluoride, J. Electrochem. Soc. 106 (1959) 404–409.
[5] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–2084.
[6] P. Wasserscheid, W. Keim, Ionic liquids—new "solutions" for transition metal catalysis, Angew. Chem. Int. Ed. 39 (2000) 3772–3789.
[7] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Ionic liquid (molten salt) phase organometallic catalysis, Chem. Rev. 102 (2002) 3667–3692.
[8] J. Fuller, R.T. Carkin, R.A. Osteryoung, The room temperature ionic liquid 1-ethyl-3-methylimidaz-olium tetrafluoroborate: electrochemical

couples and physical properties, J. Electrochem. Soc. 144 (1997) 3881–3886.
[9] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Green processing using ionic liquids and CO_2, Nature 399 (1999) 28–29.
[10] M. Antonietti, D.B. Kuang, B. Smarsly, Y. Zhou, Ionic liquids for the convenient synthesis of functional nanoparticles and other inorganic nanostructures, Angew. Chem. Int. Ed. 43 (2004) 4988–4992.
[11] Y.J. Zhu, W.W. Wang, R.J. Qi, X.L. Hu, Microwave-assisted synthesis of single-crystalline tellurium nanorods and nanowires in ionic liquids, Angew. Chem. Int. Ed. 43 (2004) 1410–1414.
[12] W.W. Wang, Y.J. Zhu, Shape-controlled synthesis of zinc oxide by microwave heating using an imidazolium salt, Inorg. Chem. Commun. 7 (2004) 1003–1005.
[13] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for ''clean'' liquid–liquid extraction, Chem. Commun. (1998) 1765–1766.
[14] D.M. Fox, J.W. Gilman, H.C. De Long, P.C. Trulove, TGA decomposition kinetics of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate and the thermal effects of contaminants, J. Chem. Thermodyn. 37 (2005) 900–905.
[15] D.S. Jacob, L. Bitton, J. Grinblat, I. Felner, Y. Koltypin, A. Gedanken, Are ionic liquids really a boon for the synthesis of inorganic materials? A general method for the fabrication of nanosized metal fluorides, Chem. Mater. 18 (2006) 3162–3168.
[16] R.J. Gillespi, J.S. Hartman, ^{1}H and ^{19}F nuclear magnetic resonance spectra of the adduct $BF_3{\bullet}H_2O$, Can. J. Chem. 45 (1967) 859–863.