



Letter

Ionic liquid-assisted synthesis of transition metal oxalates via one-step solid-state reaction

Hao Luo^a, Dingbing Zou^a, Lingang Zhou^a, Taokai Ying^{a,b,*}^a College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, PR China^b Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, PR China

ARTICLE INFO

Article history:

Received 9 December 2008

Received in revised form 28 January 2009

Accepted 25 February 2009

Available online 14 March 2009

Keywords:

Inorganic materials

Solid state reaction

X-ray diffraction

Scanning electron microscopy

ABSTRACT

Transition metal oxalates ($\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Cu, Ni, Mn, Co, Zn}$)) were prepared in ionic liquids (ILs) (1-butyl-3-methylimidazolium chloride [BMIM]Cl) by conventional one-step solid-state reaction at room temperature. $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ submicrometer cubes, $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ nanorods, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanoparticles are obtained. The structure and morphology of products were characterized by means of X-ray powder diffraction (XRD), infrared spectrum (IR), scanning electron microscope (SEM) and transmission electron microscopy (TEM). XRD and IR studies indicated that every product is well-crystallized phase with high purity. The SEM and TEM images showed that the morphology of the samples ranged from submicrometer cubes to nanoparticles for different metal. It was predicted that ionic liquids is utilized as both template and medium which play a crucial role in the formation of transition metal oxalates with different morphologies.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Over the past decades, room temperature ionic liquids (ILs) have attracted increasing interest in the context of green synthesis because of their unique chemical and physical properties of non-volatility, non-flammability, thermal stability, and controlled miscibility [1,2]. Recently, many efficient approaches to novel micro/nanostructures by selecting suitable ILs reaction systems have been reported. In our group we have been working on the applications of ionic liquids in controlling synthesis of inorganic metal oxides and sulfides for some time [3–5].

Currently, the most common approaches to metal oxalates are reverse-micellar route [6–11], solvothermal reaction [12] sol-gel process [13], microwave-assisted solution approach [14] and one-step solid-state reaction [15]. As a simple method for fabricating nanomaterials at room temperature, one-step solid-state reaction has attracted considerable interest because complex process control, high reaction temperature or long synthesis time should not be required any more [15–22]. Though it was reported that metal oxalates have been synthesized using ILs as templates [12,14], to the best of our knowledge, there has been no report on the prepara-

tion of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ using pure ILs as the reaction medium. Herein, we report a route for synthesis of metal oxalates $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ submicrometer cubes, $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ nanorods, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ nanoparticles in the presence of ionic liquid ([BMIM]Cl) via one-step solid-state reaction at room temperature.

2. Experimental

The transition metal acetates ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) are analytical pure reagents (AR) and purchased and used without further purification. The ionic liquid ([BMIM]Cl) was synthesized according to the literature [23].

In a typical synthesis, 2 mmol of $\text{M}(\text{CH}_3\text{COO})_2$ ($\text{M} = \text{Cu, Ni, Mn, Co, Zn}$) was weighed and ground for about 5 min in agate mortar at room temperature, then 0.35 g of [BMIM]Cl (2 mmol) was added. After mixing completely, 2 mmol of solid $\text{H}_2\text{C}_2\text{O}_4$ was added to the mixture, which was ground for 50 min. After grinding, the mixture was washed in ultrasonic bath with distilled water and absolute ethanol three times respectively. Finally, the product was dried in air at room temperature. The ILs was collected for purification and reused.

The XRD (X-ray powder diffraction) patterns were recorded by a Holland Philips X'Pert (PW3040/60) using Cu ($\text{K}\alpha$) radiation ($\lambda = 0.15418 \text{ nm}$) operating at 40 kV and 40 mA with 2θ ranging from 10° to 70° . IR was recorded on a Nicolet Nexus 670 spectrometer in the range of $3800\text{--}540 \text{ cm}^{-1}$ using KBr pellets. The SEM (scanning electron microscope) images were taken with Japan Hitachi S-4800 field-emission scanning electron microscope. The TEM (transmission electron microscopy) images were taken with a JEOL-2010 transmission electron microscope at an accelerating voltage of 200 kV.

* Corresponding author at: College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, PR China. Tel.: +86 579 82282780; fax: +86 579 82282269.

E-mail address: sky50@zjnu.cn (T. Ying).

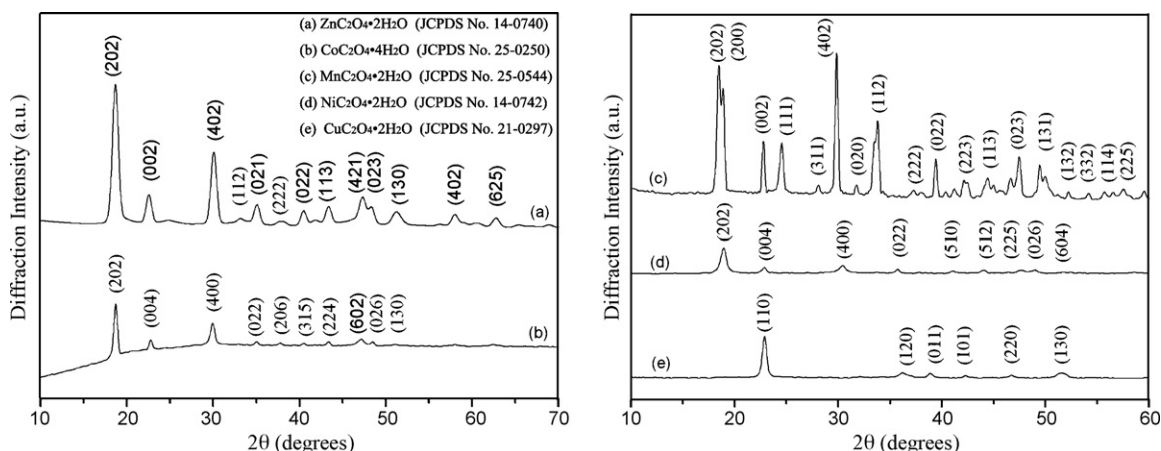


Fig. 1. XRD patterns of oxalates synthesized in [BMIM]Cl via one-step solid-state reaction: (a) $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (b) $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$; (c) $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (d) $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (e) $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

3. Results and discussion

Fig. 1 shows the XRD patterns of oxalates samples prepared by one-step solid-state reaction in [BMIM]Cl. Single phase of well crystallized $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 1a), $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (Fig. 1b), $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 1c), $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 1d), and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Fig. 1e) were obtained [11,14,24–26]. No characteristic peaks of impurity phases ([BMIM]Cl) are present, indicating the high purity of the products.

Fig. 2 shows IR spectra of metal oxalates synthesized via one-step solid-state reaction utilizing [BMIM]Cl. The IR spectra displayed bands at 3424 (s/br), 1625 (vs), 1380 (m), 1328 (s), 825 (m), 727 (s) (except e) and 621 (m) cm^{-1} . These bands are assigned [13,27,28] to $\nu(\text{O-H})$, $\nu_{\text{as}}(\text{C=O})$, $\nu_{\text{sym}}(\text{C-O}) + \nu(\text{C-C})$, $\nu_{\text{sym}}(\text{C-O}) + \delta(\text{O-C=O})$, $\nu(\text{O-M-O})$, $\delta(\text{O-C=O}) + \nu(\text{M-O})$ and $\nu(\text{O-M-O})$. The imidazolium $\nu(\text{C-H})$ stretching between 3200 and 3000 cm^{-1} [29] disappears completely.

The size and morphologies of oxalates were observed by SEM and TEM (Fig. 3). Fig. 3(a) shows that the $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are sub-microcubes with diameters of 0.8–1.5 μm . Fig. 3(b) shows that the $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ are nanorods with diameters of about 100 nm

and lengths up to several micrometers. And morphologies of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are submicrocubes with diameters of 0.5–1.0 μm (Fig. 3(c)). From Fig. 3(d and e), it can be seen that $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ consist of nanoparticles with diameters of about 12–20 nm which are shorter than those of products [15].

Ye et al. have reported the synthesis of nanospheres (10–60 nm) of transition metal oxalates utilizing one-step solid-state reaction at ambient temperatures without using any surfactant [15]. Wang and Zhu have successfully synthesized $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ nanorods, with diameters of about 50 nm and lengths up to several micrometers, by a simple microwave-assisted solution approach using an ionic liquid 1-*n*-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM]BF₄) aqueous solution [14]. They predicted that both the [BMIM]BF₄ and microwave heating play an important role in the formation of cobalt oxalate nanorods. In this paper, however, different morphologies were observed using different transition metal acetates reacting with oxalic acid in ILs. For example, cobalt oxalate nanorods also are obtained without microwave heating. It is indicated that the [BMIM]Cl plays an important role in the formation of $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ nanorods except microwave heating. Further more, transition metal oxalates submicrometer cubes and nanoparticles are obtained.

Sonalika Vaidya et al. [9] have reported the formation of nickel oxalate nanospheres, nanocubes, and nanorods by reverse-micellar route. And they suggested that the cationic surfactant is critical to the rod formation since nonionic surfactants produced either cubes or spheres, and the surfactants and solvents in reverse micelles play a major role in controlling the size and morphology of the product. Nakashima and Kimizuka [30] concluded the ILs could form many micro-sized droplets in the solution under proper experimental conditions. In our experiment, the reaction mechanism responsible for the formation of metal oxalates submicrometer cubes, nanorods, nanoparticles can be explained as follows. The [BMIM]Cl consists of [BMIM]⁺ cation, which could imbibe the crystal water of acetate to form droplets. Ionic liquids are non-volatile, highly polar solvents that dissolve several organic, inorganic and metallorganic compounds. Then the acetate is dissolved in droplets. When $\text{H}_2\text{C}_2\text{O}_4$ was added, the surface charge on the nanorods also plays an important role in the anisotropic growth of the nanorods. The rodlike morphology could be modified by changing the different acetates [9]. Electrical percolation and rate constant for exchange of material between droplets is different. For example [BMIM]Cl provides a greater barrier to interdroplet exchange when $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were prepared, leading to small sized particles. Based on the experimental results, the ILs acted as both reaction medium and surfactant.

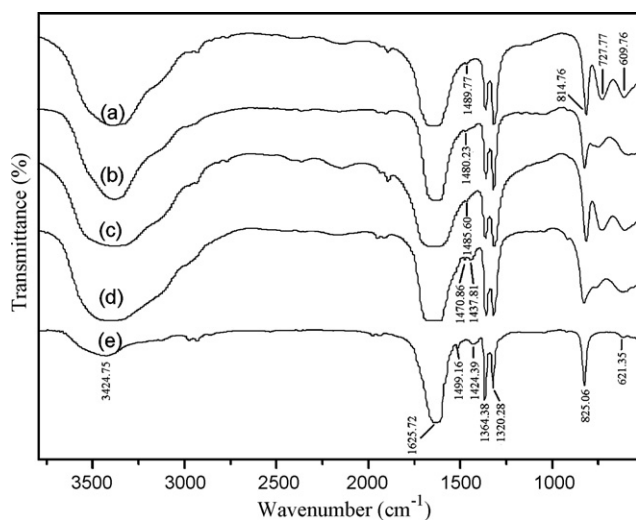


Fig. 2. FT-IR spectra of oxalates synthesized in [BMIM]Cl via one-step solid-state reaction: (a) $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (b) $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$; (c) $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (d) $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; (e) $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

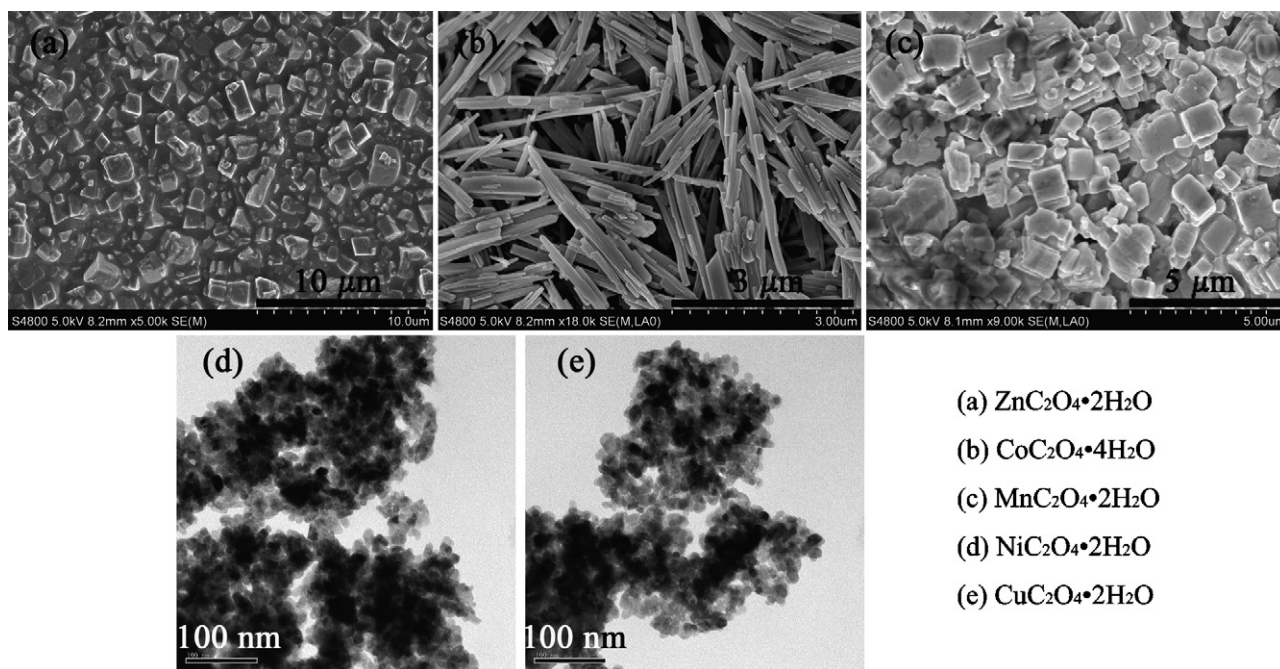


Fig. 3. SEM images of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{CoC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; and TEM images of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ synthesized in [BMIM]Cl via one-step solid-state reaction.

4. Conclusions

In conclusion, transition metal oxalates submicrometer cubes, nanorods and nanoparticles have been successfully synthesized by ionic liquid-assisted one-step solid-state reaction at room temperature within short reaction time. On the one hand, the strategy described here is expected to prepare transition metal sulfides and carbonates. On the other hand, the reclaiming and reusing of ILs for the subsequent reactions has bright future in the development of clean manufacturing processes.

Acknowledgment

This research was financially supported by National Science Foundation of Zhejiang province of China (no. Y404358).

References

- [1] H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, Inc., Indianapolis, 2005.
- [2] T. Welton, *Chem. Rev.* 99 (1999) 2071–2084.
- [3] H. Luo, C. Xu, D.B. Zou, L. Wang, T.K. Ying, *Mater. Lett.* 62 (2008) 3558–3560.
- [4] C. Xu, L. Wang, D.B. Zou, T.K. Ying, *Mater. Lett.* 62 (2008) 3181–3184.
- [5] D.B. Zou, C. Xu, H. Luo, L. Wang, T.K. Ying, *Mater. Lett.* 62 (2008) 1976–1978.
- [6] T. Ahmad, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, *J. Mater. Chem.* 14 (2004) 3406–3410.
- [7] T. Ahmad, R. Chopra, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, *J. Nanosci. Nanotechnol.* 5 (2005) 1840–1845.
- [8] T. Ahmad, S. Vaidya, N. Sarkar, S. Ghosh, A.K. Ganguli, *Nanotechnology* 17 (2006) 1236–1240.
- [9] S. Vaidya, P. Rastogi, S. Agarwal, S.K. Gupta, T. Ahmad, A.M. Antonelli, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, *J. Phys. Chem. C* 112 (2008) 12610–12615.
- [10] J. Ahmed, T. Ahmad, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, *J. Colloid Interface Sci.* 321 (2008) 434–441.
- [11] X. Zheng, G.H. He, X.C. Li, H.J. Liu, *Chem. Ind. Eng. Prog.* 26 (2007) 1159–1165.
- [12] M.Y. Li, W.S. Dong, C.L. Liu, Z.T. Liu, F.Q. Lin, *J. Cryst. Growth* 310 (2008) 4628–4634.
- [13] A.S. Khan, T.C. Devore, W.F. Reed, *J. Cryst. Growth* 35 (1976) 337–339.
- [14] W.W. Wang, Y.J. Zhu, *Mater. Res. Bull.* 40 (2005) 1929–1935.
- [15] X.R. Ye, D.Z. Jia, J.Q. Yu, X.Q. Xin, Z.L. Xue, *Adv. Mater.* 11 (1999) 941–942.
- [16] E.G. Gillan, R.B. Kaner, *Chem. Mater.* 8 (1996) 333–343.
- [17] W.Z. Wang, Y.J. Zhan, G.H. Wang, *Chem. Commun.* (2001) 727–728.
- [18] W.Z. Wang, Y.K. Liu, Y.J. Zhan, C.L. Zheng, *Mater. Res. Bull.* 36 (2001) 1977–1984.
- [19] F. Li, H.G. Zheng, D.Z. Jia, X.Q. Xin, Z.L. Xue, *Mater. Lett.* 53 (2002) 282–286.
- [20] Y.L. Cao, D.Z. Jia, L. Liu, J.M. Luo, *Chin. J. Chem.* 22 (2004) 1288–1290.
- [21] Z.P. Sun, L. Liu, L. Zhang, D.Z. Jia, *Nanotechnology* 17 (2006) 2266–2270.
- [22] L. Wang, B. Zhao, L.X. Chang, W.J. Zheng, *Sci. China Ser. B Chem.* 50 (2007) 224–229.
- [23] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem. Commun.* (1998) 1765–1766.
- [24] B. Donkova, D. Mehandjiev, *Thermochim. Acta* 421 (2004) 141–149.
- [25] B. Malecka, A. Malecki, E. Drozd-Ciesla, L. Tortet, P. Llewellyn, F. Rouquerol, *Thermochim. Acta* 466 (2007) 57–62.
- [26] B. Donkova, D. Mehandjiev, *J. Mater. Sci.* 40 (2005) 3881–3886.
- [27] S.P. Goel, P.N. Mehrotra, *J. Therm. Anal.* 30 (1985) 145–151.
- [28] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 1970.
- [29] Y. Zhou, M. Antonietti, *J. Am. Chem. Soc.* 125 (2003) 14960–14961.
- [30] T. Nakashima, N. Kimizuka, *J. Am. Chem. Soc.* 125 (2003) 6386–6387.