

化 学

碱式碳酸铅单晶胶体纳米结构的 低温液相合成与表征

赵 丹 谭金山 郭培志 赵修松

(青岛大学纤维新材料与现代纺织国家重点实验室培育基地, 化学化工与环境学院, 青岛 266071)

摘 要 使用一种无表面活性剂辅助的室温合成方法, 通过反应物配比的简单调控, 实现了碱式碳酸铅单晶胶体纳米结构的简易合成。改用水热反应条件, 基于奥斯特瓦尔德熟化效应, 则合成出多边形片状碱式碳酸铅的单晶微纳结构, 并通过 XRD、FTIR、SEM 和 TEM 等手段对其进行表征。基于实验结果, 提出了该类微纳结构的形成机理。

关键词 纳米棒 胶体片状结构 水热合成 单晶

中图法分类号 O614.433; **文献标志码** B

Nanostructured materials have been attracted great interest due to their unique physical and chemical properties compared with their bulk materials^[1-3]. Many methods, such as chemical vapor deposition (CVD), hydrothermal synthesis, template method, coprecipitation and hydro-/thermolysis have been used to synthesis various nanostructures^[3-8]. Generally, these methods meet several disadvantages such as relative high temperature and long reaction time. Therefore, fabricating uniform nanostructured materials in a low cost and fast way under low or room temperature is believed to be an effective and energetic strategy to cater for such problems^[5-9].

Nanostructures with various morphologies of inorganic solids such as functional lead compounds have been synthesized using different methods due to their potential applications in energy storage, electronic nanodevices, and burn rate catalysts^[9-11]. For example, Yang et al reported the chemical vapor transport synthesis of lead chalcogenides nanowires, which showed

excellent thermoelectrical properties^[9]. Single crystal PbCO_3 nanoplates can be fabricated using block copolymers as crystal modifiers^[10]. Recently, pulse current deposition of PbO_2 thin film was performed on the substrate, which exhibited large specific capacitance and stable cycle performance^[11]. However, it is still a challenge to synthesize single crystal nanostructures of lead compounds in a facile template-free approach at low temperature or at room temperature.

In this work, single crystal nano-/colloidal structures of PbCO_3 and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ have been controllable synthesized via a simple precipitating method at low temperature through. The formation mechanism of the nanostructures was proposed based on the experimental results.

1 Experimental section

1.1 Synthesis of the nanostructures

In a typical synthesis, an aqueous 0.02 mol (or 0.06 mol) Na_2CO_3 solution was dropped into a 0.02 mol $\text{Pb}(\text{NO}_3)_2$ solution under stirring. And then the mixture was transferred to a 40-mL Teflon lined autoclave. Hydrothermal synthesis was carried out in an ov-

2009年9月24日收到

国家自然科学基金(20803037)和

“泰山学者”计划资助

第一作者简介: 赵 丹, 研究方向: 微纳结构材料制备与表征;

E-mail: pzguo@qdu.edu.cn。

en at 200°C for 24 h. The fresh precipitates and the products obtained after the hydrothermal treatments were collected by filtration, washed with distilled water and ethanol for several times each, and then dried in an oven at 60°C for 6 h.

1.2 Characterization

X-ray powder diffraction (XRD) measurements were performed using a Bruker D8 advanced X-ray diffractometer with a Cu K α radiation ($\lambda = 0.154\ 18\ \text{nm}$) from 10 to 80 degrees (2θ). Scanning electron microscopy (SEM) images were taken with a JSM—6390LV and JSM—840 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained with a JEM—2000EX transmission electron microscope. FTIR spectra are measured with a Nicolet 5 700 spectrophotometer.

2 Results and Discussion

Fig. 1 shows the XRD patterns of all the as-made products. It can be seen that mainly orthorhombic PbCO_3 (PDF, 05—0417) phases are obtained at room temperature when the Pb/CO_3 molar ratio in the reagents is 1:1 (fig. 1a). Meantime, a weak peak with 2θ degree of 27° is also observed (fig. 1a), which can be indexed to (015) peaks of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (PDF, 13—0131) phase. If the fresh precipitates go through a hydrothermal treatment, the phases are almost unchanged (fig. 1b). However, the XRD pattern of the products (fig. 1b) synthesized from the systems with the Pb/CO_3 molar ratio of 1:3 at room temperature can be well indexed to pure rhombohedral $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (PDF, 13—0131) phase. Furthermore, the rhombohedral phase of basic lead carbonate cannot be changed after the hydrothermal process.

SEM images reveal that the morphologies change greatly for the products synthesized from the systems with different Pb/CO_3 molar ratios at room temperature

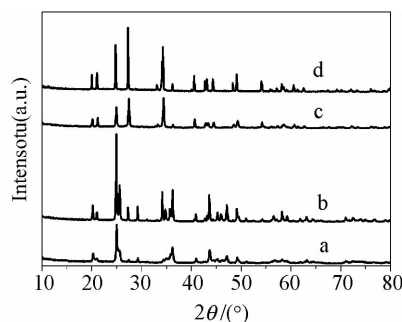


Fig. 1 XRD patterns of the products synthesized with the Pb/CO_3 molar ratios of 1:1 (a and b) and 1:3 (c and d) at room temperature (a and c) and 200°C (b and d), respectively.

(fig. 2a and b). For sample PbCO_3 synthesized at the molar ratio of 1:1, rod-like structures with diameters of (60 ~ 300) nm and lengths of (0.5 ~ 4) μm can be observed (fig. 2a). However, disk-like colloidal plates are obtained with the diameters of (100 ~ 300) nm for the $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ products synthesized at the molar ratio of 1:3 (fig. 2b). If the products are experi-

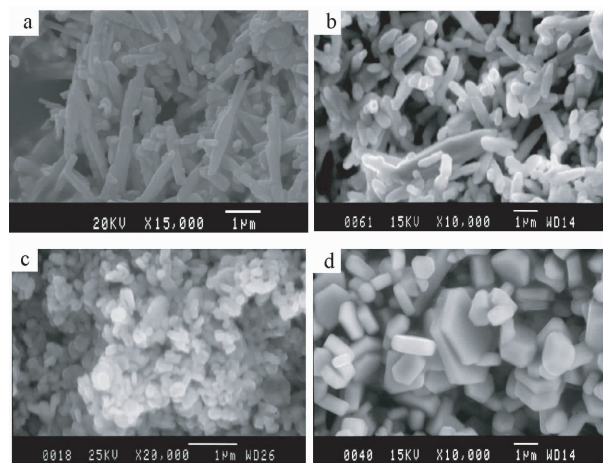


Fig. 2 SEM images of the PbCO_3 (a, b) and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (c, d) samples synthesized at room temperature (a, c) and 200°C (b and d).

enced a hydrothermal process, the morphology of PbCO_3 nanorods were almost unchanged (fig. 2c), while micro-scale polygonal plate structures with the diameters of about (1 ~ 3) μm and side lengths of about (200 ~ 400) nm for $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ can be obtained due

to the Ostwald ripening effect (fig. 2d)^[12].

TEM observations further confirm the rod-like structures of sample PbCO_3 (fig. 3a). The selected area electron diffraction (SAED) patterns shown in the insets of Fig. 3a can be identified as the $[002]$ zone axis projection of PbCO_3 phase. It is suggested that the orthorhombic PbCO_3 nanorod are single crystalline and grow with a preferred direction of $\langle 001 \rangle$. It can be seen from the TEM image (fig. 3b) that PbCO_3 nanorods are also single crystalline after the hydrothermal treatment. However, the diameters of the PbCO_3 nanorods increase compared with those synthesized at room temperature, which are induced to the effect of Ostwald ripening^[12]. Disk- or elliptical-like colloidal plates are observed from TEM images of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ products (fig. 3c). The hexagonal SAED patterns of one plate confirm the single crystal nature of the colloid structures and can be well indexed to the rhombohedral $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ phase for the (110) planes. Similar to those PbCO_3 samples, the sizes of the structures of basic lead carbonate are increased and the ED patterns also confirm that the micro-scale polygonal plate are single crystalline.

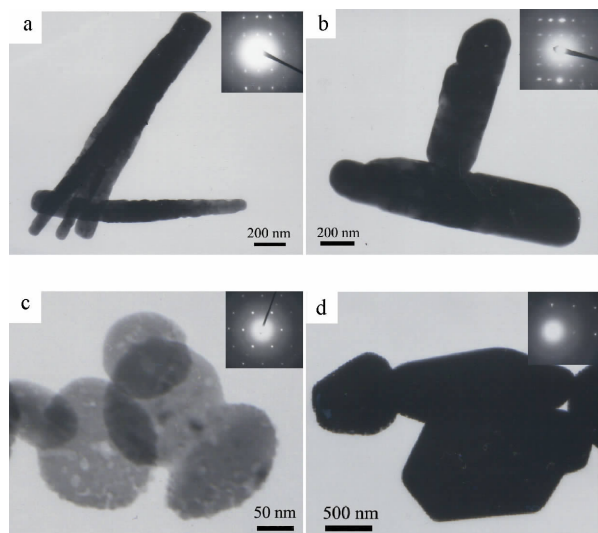


Fig. 3 TEM images of the products as used in fig. 2.

It can be seen that two absorption bands at $3\,435$ and $\sim 1\,630\text{ cm}^{-1}$ are appeared, denoting the existence of the adsorbed H_2O molecules onto the crystals. The vibration bands appeared at $\sim 1\,410$ and $\sim 680\text{ cm}^{-1}$, which can be ascribed to the absorption peaks of stretching and bending vibrations of CO_3^{2-} ions^[13,14], respectively, indicate the existence of the carboxyl group in the samples. However, obvious differences can be observed from the FTIR spectra. Compared to the FTIR spectra of the PbCO_3 samples (fig. 4a and 4b), a new peak at $3\,538\text{ cm}^{-1}$ appeared and the peak at 839 cm^{-1} disappeared in the spectra of the basic lead carbonate samples (fig. 4c and 4d), which are contributed to the stretching vibrations of hydroxyl group and the CO_3^{2-} ion, respectively^[13]. These results further indicated the formation of the $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ phase.

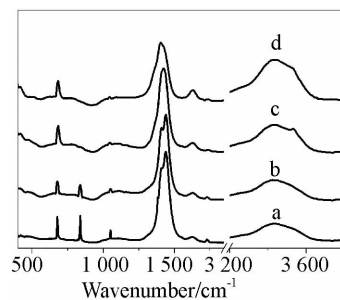
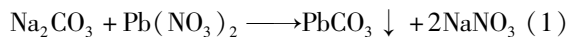


Fig. 4 FTIR spectra of the products as used in fig. 2.

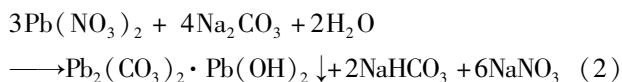
From the above results, it can be concluded that the morphology and the phases of lead compounds can be controlled through a simple synthesis method by changing the molar ratio of the reagents at room temperature or at an elevated temperature. When the Pb/CO_3 molar ratio was $1:1$, it is obvious that the following reaction [eq (1)] is occurred although few reagents reacted *via* eq (2) concomitant with Eq (1)^[15]. White products are formed and rod-like PbCO_3



nanostructures were obtained under such conditions. It is suggested that eq. (2) start firstly when the concentrated Na_2CO_3 solution was dropped into the $\text{Pb}(\text{NO}_3)_2$

Fig. 4 shows the FTIR spectra of all the samples.

solution^[15]. That eq. (2) was reacted should be contributed to the strong basic properties of aqueous Na_2CO_3 solutions due to the hydrolysis of carbonate ions^[15], which prevented the reaction of eq (1). And thus, single crystalline $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ colloidal plates could be obtained at room temperature.



It should be pointed out that the synthesis temperature is the key parameter that controlled the morphology and properties of the products. Although the phases of the products were unchanged when the fresh precipitates were experienced a hydrothermal treatment at 200°C , the morphology of PbCO_3 and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ change greatly and micro-scale rods and polygonal plates were obtained, respectively. It is suggested that the single crystal colloidal/nano-structures are formed due to the formation of large numbers of crystal nucleus at low temperature, while the micro-scale structures are formulated due to the effect of Ostwald ripening at high temperature^[12]. The controllable synthesis of these nanostructures at low temperature may help to fabricate single crystalline nanostructures of functional materials.

3 Conclusions

Single crystal nano- or colloidal structures of lead carbonate and basic lead carbonate have been controllable synthesized by a simple precipitating method through adjusting the molar ratio of $\text{Pb}(\text{NO}_3)_2$ to Na_2CO_3 at room temperature. However, micro-scale polygonal plate structures for $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ can be obtained due to the Ostwald ripening effect if the synthesis systems were underwent hydrothermal treatments. The strong basic nature of the solutions caused by the hydrolysis of carbonate ions contributes to the formation of lead carbonate and pure basic lead carbon-

ate phases.

References

- Burda C, Chen X B, Narayanan R, *et al.* Chemistry and properties of nanocrystals of different shapes. *Chem Rev*, 2005; 105:1025—1102
- Bratlie K M, Lee H, Komvopoulos K, *et al.* Platinum nanoparticle shape effects on benzene hydrogenation selectivity. *Nano Lett*, 2007; 7:3097—3101
- Kim D, Park J, An K, *et al.* Synthesis of hollow iron nanoframes. *J Am Chem Soc*, 2007; 129:5812—5813
- Wang X, Zhuang J, Peng Q, *et al.* A general strategy for nanocrystal synthesis. *Nature*, 2005; 437:121—124
- Xu Z, Stevenson G S, Lu C, *et al.* Stable suspension of layered double hydroxide nanoparticles in aqueous solution. *J Am Chem Soc*, 2006; 128:36—37
- Guo P, Tan J, Ji Q, *et al.* Hydrothermal synthesis and characterization of hexagonal γ -MnS single crystal nanorods in presence of biomolecule L-cysteine. *Chinese J Inorg Chem*, 2008; 24:1387—1392
- Tang C, Bando Y, Liu B, *et al.* Cerium oxide nanotubes prepared from cerium hydroxide nanotubes. *Adv Mater*, 2005; 17:3005—3009
- Guo P, Liu M, Nakahara H, *et al.* Controllable growth of straight nanorods and nanowires in the langmuir films of a bolaamphiphilic PAR derivative. *Chem Phys Chem*, 2006; 7:385—393
- Fardy M, Hochbaum A I, Goldberger J. *et al.* Synthesis and thermoelectrical characterization of lead chalcogenide nanowires. *Adv Mater*, 2007; 19:3047—3051
- Yu S, Colfen H, Antonietti M. Polymer-controlled morphosynthesis and mineralization of metal carbonate superstructures. *J Phys Chem B*, 2003; 107:7396—7405
- Yu N, Gao L. Electrodeposited PbO_2 thin film on Ti electrode for application in hybrid supercapacitor. *Electrochem Commun*, 2009; 11:220—222
- Madras G, McCoy B J. Temperature effects on the transition from nucleation and growth to Ostwald ripening. *Chem Eng Sci*, 2004; 59:2753—2766
- Bellamy L J. The infrared spectra of complex molecules, 2nd ed. London: Chapman and Hall, 1980
- Refat M S, Teleb S M, Sadeek S A. A novel method for preparation of cobalt(II) and lead(II) carbonates. *Spectrochim Acta A*, 2004; 60:2803—2805
- Chen Chunshou. Important inorganic chemistry reactions, 3rd. ed Shanghai: Shanghai Scientific & Technical Publishers, 1994

(下转第 7459 页)

4 结论

本文的研究结果表明,只要模拟抽样次数足够大,运用 ANSYS 软件与蒙特卡罗相结合的随机有限元法分析植物叶片的可靠性是可行的。

参 考 文 献

1 周智彬,李培军. 我国旱生植物的形态解剖学研究. 干旱区研究, 2002;19(1):35—39

2 von Ettinghausen C R. Die Blatt-skelette der dykotyledonen. Kaiserlich Königliche Hof-und Stattsdruckerei, Wien, 1861

3 Hickey L J. Classification of the architecture of dicotyledonous leaves.

Am J Bot, 1973;60:17—33

4 Klucking E P. Leaf venation patterns. J Cramer Berlin, 1986;1:1—256

5 王 洁,尹海丽. 蒙特卡罗方法的应用研究. 青岛理工大学学报, 2006;27(2):111—113

6 高 娟,罗奇峰,车 伟. 蒙特卡罗法理论及其在 ANSYS 中的实现. 青岛理工大学学报, 2008;29(4):18—21

7 Hidetoshi K, Masashi D, Kaori K. Venation pattern of butterbur leaf and its mechanical contribution. Journal of the Society of Materials Science. Japan, 2000;49(12):1318—1323

8 Balsamo R A, Bauer A M, Davis S D, *et al.* Leaf biomechanics, morphology, and anatomy of the deciduous mesophyte *Prunus serrulata* (Rosaceae) and the evergreen sclerophyllous shrub *Heteromeles arbutifolia*. American Journal of Botany, 2003;90(1):72—77

Reliability Analysis of Plant Leaves Using Monte Carlo Method

LIU Xi-feng, LIU Wang-yu

(School of Mechanical & Automotive Engineering, South China University of Technology, Guangzhou 510640, P. R. China)

[Abstract] In order to explore the close relationship between variable parameters of plant leaf and the reliability, a fresh plant leaf was picked and the coordinate clouding data of the plant leaf was got by the coordinate measuring machine. Then the data of the outlines and veins of plant leaf was selected and the simple model was built in ANSYS. Numerical simulation based Monte Carlo Method is carried out for the leaves affected by random wind load in the natural environment. The results indicate that the analysis of the reliability of plant leaves by ANSYS combined with the Monte Carlo method is feasible.

[Key words] plant leaf vein Monte Carlo method stress reliability

(上接第 7455 页)

Low-temperature Facile Synthesis and Characterization
of Single Crystal Colloid/Micro-structures of Basic Lead Carbonate

ZHAO Dan, TAN Jin-shan, GUO Pei-zhi, ZHAO Xiu-song

(Laboratory of New Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, College of Chemistry, Chemical Engineering and Environment, Qingdao University, Qingdao 266071, P. R. China)

[Abstract] Single crystal colloidal structures of basic lead carbonate ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) were controllable synthesized by a simple precipitating method through changing the molar ratios of $\text{Pb}(\text{NO}_3)_2$ to Na_2CO_3 at room temperature. However, micro-scale polygonal plate structures for $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ can be obtained due to the effect of the Ostwald ripening if the synthesis systems were underwent hydrothermal treatments at 200℃. The products are characterized by a series of techniques, such as XRD, SEM, TEM and FTIR. The formation mechanisms of the nanostructures are proposed based on the experimental results.

[Key words] nanorod colloidal plate hydrothermal synthesis single crystal