Gemini Surfactant Directed Preparation and Photocatalysis of m-$BiVO_4$ Hierarchical Frameworks

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The m-$BiVO_4$ hierarchical frameworks were synthesized using a novel Gemini surfactant-monoalkylated disulfonated diphenyl oxide surfactant (C_{12}-MADS) as the structure-directing reagent and as-obtained m-$BiVO_4$ nanomaterials exhibited good photocatalysis for degradation of rhodamine B (RhB) under visible light.

The morphology control of nanocrystals with well-defined shapes is a key challenge in modern chemistry materials because the potential of relative properties of the nanocrystals are largely affected by the morphology.[1,2] Much admirable research on the morphology-control has been reported, including rods,[3] wires,[4] plates,[5] tubules,[3] dendrites,[6] and so on. Among them, the hierarchical frameworks have attracted intense interests due to their special significance in understanding the growth behavior of branched patterns, crystallography research and potential technological applications.[7] To obtain these tailored nanostructures, interest in using self-assembled organic additives to shape inorganic materials has increased, in which the organic additives are used as modifiers to affect and control the nucleation, growth, and structure of the nanocrystals. In previous reports, some double-hydrophilic block copolymers (DHBCs), consisting of a hydrophilic block that can chelated with the metal ions and the other hydrophilic block that promotes their own solubility in water, have been used as the effective modifiers to control the growth of inorganic nanostructures in aqueous solutions.[8]

In recent years, $BiVO_4$ has attracted considerable attention for its photocatalysis in both splitting water into hydrogen and oxygen and the degradation of organic pollutants, which are promising for solving present energy and environmental issues that confront mankind today.[9] As reported, the monoclinic scheelite $BiVO_4$ shows much higher photocatalytic activity under visible light irradiation over the other crystallographic forms, because m-$BiVO_4$ with a band gap of 2.4 eV can absorb visible light more widely than tetragonal $BiVO_4$ with a band gap of 2.9 eV.[10,11] Recently, Chen's group has prepared m-$BiVO_4$ nanosheets assisted by sodium dodecylbenzenesulfonate (SDBS) under hydrothermal condition and explored its coloristic and photocatalytic properties.[12] Most of the m-$BiVO_4$ nanomaterials prepared previously were only particles or sheets. There still remains a challenge to prepare m-$BiVO_4$ with hierarchical nanostructures. Herein, we reported a simple hydrothermal process to fabricate m-$BiVO_4$ frameworks using a novel Gemini surfactant-monoalkylated disulfonated diphenyl oxide surfactant (C_{12}-MADS) (Figure S1)[17] as structure-directing reagent. As desired, three-dimensions (3D) hierarchical frameworks of m-$BiVO_4$ have been obtained in a high yield. Moreover, as-obtained m-$BiVO_4$ nanomaterials exhibited good photocatalysis for degradation of rhodamine B (RhB) under visible light. To the best of our knowledge, it is the first report on the preparation and investigation of 3D hierarchical nanostructures of m-$BiVO_4$. Such a preparing route is interesting in understanding the self-assembly with building blocks and help to prepare functional nanomaterials with novel morphologies. Furthermore, the facile preparing method and good property reported here are of much significance in the preparation and future applications of nanomaterials.

In a typical preparation, 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved into dilute HNO_3 solution, and then 3 mmol MADS was added into the above solution which was stirred for about 2 h until a clear yellow solution formed. Finally, 2 mmol $Na_3VO_4 \cdot 12H_2O$ was added and the pH value of the solution was adjusted to 2 using 2.0 mol·L^{-1} NaOH solution under stirring. The final solution was transferred into a Teflon-sealed autoclave and maintained at 180 °C for 24 h. The bright yellow product was isolated by centrifugation, washed with distilled water and absolute ethanol for several times, and finally dried in a vacuum at 45 °C for 5 h.

The XRD pattern in Figure 1a reveals that the sample prepared at 180 °C for 24 h is the scheelite structure. All the diffraction peaks can be indexed as those of the end-centered monoclinic phase of scheelite structure with cell constants of $a = 5.197$ Å, $b = 5.096$ Å, and $c = 11.70$ Å as reported in JCPDS card No. 752480. The sharp and strong peaks indicate the high purity and good crystallinity of the sample. The mor-

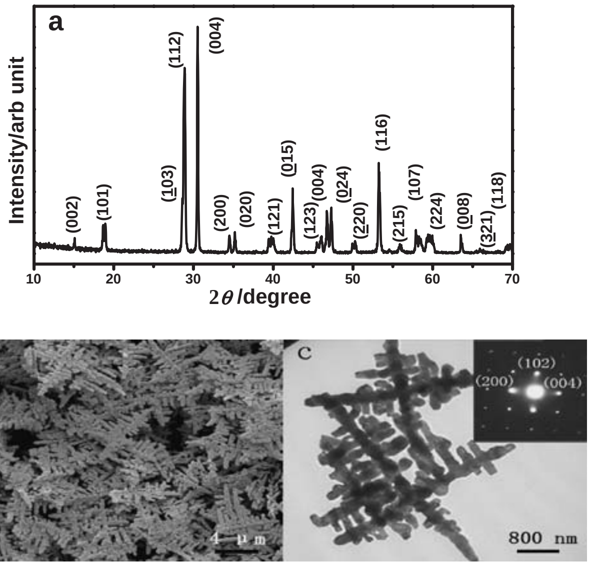

Figure 1. (a) XRD pattern of the m-$BiVO_4$ sample prepared at 180 °C for 24 h; (b) SEM and (c) TEM images of m-$BiVO_4$ frameworks and the ED pattern (inset c) taken from the trunk.

phologies and microstructures of m-BiVO$_4$ sample were illuminated by SEM and TEM images. A panoramic SEM image (Figure 1b) indicates the sample consists of a large scale of the 3D frameworks of m-BiVO$_4$ nanostructure. A magnified TEM image (Figure 1c) demonstrates a typical framework resembling morphologically to the crux, in which two stems are perpendicular and the branches on the major stems have symmetrical arrangement with a regular periodicity. The lengthes of the stems and the branches range from 2 to 6 μm and 100 to 500 nm, respectively. The selected area electron diffraction (SAED) pattern (inset of Figure 1c) reveals the well-aligned clear diffraction spots that can be indexed to the monoclinic structure of BiVO$_4$. The HR-TEM image of the framework (Figure S2)[17] indicates their single-crystalline character of both the stem and the branch. The calculated lattice constants of $d_1 = 2.9$ Å and $d_2 = 2.6$ Å are consistent with the literature data of $d(004) = 2.926$ Å and $d(200) = 2.592$ Å.

Since understanding the growth and evolution of the hierarchical nanostructure depends on the revelation of the intermediates involved in the growth process, the samples obtained at different stages of 10 min, 30 min, 45 min, and 3 h, were monitored by TEM and XRD (Figure S3),[17] respectively. When the reaction proceeded for 10 min, it is observed that many floccules (Figure S3a)[17] appeared and the XRD pattern (Figure S3a')[17] indicated that they are amorphous. When the reaction time was prolonged to 30 min, as observed from Figure S3b,[17] the amorphous floccules assembled into loose foursquare agglomerations with multilayer. Moreover, it is interestingly found that the embryos of the hierarchical frameworks of BiVO$_4$ have been formed in the loose foursquare agglomerations; the XRD pattern (Figure S3b')[17] of this sample indicated that the monoclinic BiVO$_4$ has crystallized at this stages. After 45 min, the foursquare agglomerations disappeared and the frameworks were shaped primarily (Figure S3c).[17] After a reaction time of 3 h, the main hierarchical frameworks were obtained (Figure S3d).[17] Finally, well-defined hierarchical m-BiVO$_4$ frameworks with good crystallization are obtained after 24 h. Thus, TEM images of the intermediates obtained at different stages reveal the evolvement from the amorphous floccules to the final hierarchical frameworks of m-BiVO$_4$, and the relevant XRD patterns display the gradual increase in the crystallinity of m-BiVO$_4$ samples. In addition, the SEM images of the intermediate obtained at the reaction stage of 30 min was designedly depicted in Figure S4,[17] clearly confirming that the loose foursquare agglomerations with multilayer were assemble by the floccules and the embryo of the hierarchical frameworks of BiVO$_4$ have been gestated in the loose foursquare agglomerations. A proposed mechanism based on time-dependent comparative experiments can be illuminated as Scheme S5.[17]

One of the most important applications of m-BiVO$_4$ material is used as photocatalyst under the irradiation of visible light.[13,14] Previously, most of researches have been focused on its ability of splitting water into O$_2$,[9,11] but few of them are related to the degradation of organic contaminants.[15,16] The photocatalytic activities of m-BiVO$_4$ frameworks were investigated by degradation of RhB dye in water solution under visible light irradiation to demonstrate the degradation of organic pollutants. Figure 2 shows the UV–vis absorption spectrum of an aqueous solution of RhB (initial concentration: 1.0×10^{-5} M, 100 mL) in the presence of the BiVO$_4$ frameworks sample (80 mg) under visible light irradiation. The peaks of RhB gradually weakened and the color of the solution gradually lightened as the exposure time extended. During this process, the intense pink color of the starting RhB solution almost faded completely with the exposure time increasing to 50 min. The change in concentration of RhB under different situations was plotted in Figure S6.

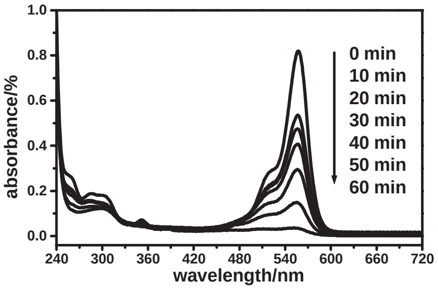

Figure 2. Absorption spectrum of the RhB solution in the presence of m-BiVO$_4$ frameworks under visible light.

In summary, we have developed a one-step hydrothermal process for preparation of hierarchical frameworks of m-BiVO$_4$ materials assisted by a novel Gemini surfactant-MADS via the Ostwald ripening during the crystallization period. In addition, as-obtained m-BiVO$_4$ nanostructures exhibit a much higher photocatalytic activity for degradation of RhB under visible irradiation, suggesting the potential future applications in degradation organic contaminations by visible light.

References and Notes

1 J. Hu, L. S. Li, W. Yang, L. Manna, L. W. Wang, A. P. Alivisatos, *Science* **2001**, *292*, 2060.
2 Y. W. Jun, Y. Y. Jung, J. Cheon, *J. Am. Chem. Soc.* **2002**, *124*, 615.
3 B. Zhang, W. Dai, X. C. Ye, F. Zuo, Y. Xie, *Angew. Chem., Int. Ed.* **2006**, *45*, 2571.
4 Y. J. Xiong, Y. Xie, Z. Q. Li, C. Z. Wu, *Chem.—Eur. J.* **2003**, *9*, 1645.
5 Q. R. Zhao, Z. G. Zhang, T. Dong, Y. Xie, *J. Phys. Chem. B* **2006**, *110*, 15152.
6 Z. C. Wu, C. Pan, Z. Y. Yao, Q. R. Zhao, Y. Xie, *Cryst. Growth Des.* **2006**, *6*, 1717.
7 T. Vicsek, *Fractal Growth Phenomena*, 2nd ed., World Scientific, Singapore, **1992**.
8 H. Cölfen, *Macromol. Rapid Commun.* **2001**, *22*, 219.
9 A. Kudo, K. Omori, H. Kato, *J. Am. Chem. Soc.* **1999**, *121*, 11459.
10 S. Tokunaga, H. Kato, A. Kudo, *Chem. Mater.* **2001**, *13*, 4624.
11 J. Q. Yu, A. Kudo, *Adv. Funct. Mater.* **2006**, *16*, 2163.
12 L. Zhang, D. R. Chen, X. L. Jiao, *J. Phys. Chem. B* **2006**, *110*, 2668.
13 A. Kudo, K. Ueda, H. Kato, I. Mikami, *Catal. Lett.* **1998**, *53*, 229.
14 S. Kohtani, J. Hiro, N. Yamamoto, A. Kudo, K. Tokumura, R. Nakagaki, *Catal. Commun.* **2005**, *6*, 185.
15 B. P. Xie, H. X. Zhang, P. X. Cai, R. L. Qiu, Y. Xiong, *Chemosphere* **2006**, *63*, 956.
16 L. Zhou, W. Z. Wang, S. W. Liu, L. S. Zhang, H. L. Xu, W. Zhu, *J. Mol. Catal. A: Chem.* **2006**, *252*, 120.
17 Supporting Informations available on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.

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