

Hierarchical FeWO₄ Microcrystals: Solvothermal Synthesis and Their Photocatalytic and Magnetic Properties

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Received September 20, 2008

Highly hierarchical platelike FeWO₄ microcrystals have been synthesized by a simple solvothermal route using FeCl₃·6H₂O and Na₂WO₄·2H₂O as precursors, where ethylene glycol (EG) plays an important role as a capping agent in directing growth and self-assembly of such unique structures. In addition, a certain amount of CH₃COONa (NaAc) was necessary for the formation of such unique FeWO₄ microstructures. The photocatalytic property of as-synthesized hierarchical FeWO₄ microcrystals has been first studied, which shows excellent photocatalytic activity for the degradation of rhodamine B (RhB) under UV and visible light irradiation (modeling sunlight). Moreover, magnetic measurement indicates that hexangular FeWO₄ platelike microcrystals show a small ferromagnetic ordering at low temperature because of spin-canting of antiferromagnetic materials and surface spins of FeWO₄ nanoparticles.

Introduction

The fabrication of self-assembled hierarchical microstructures of inorganic materials with highly ordered architectures and well-defined physical properties by the bottom-up approach is of great interest to materials chemists, who explore their potential application in various fields such as magnetism, optics, and electronics fields.¹ In particular, the hierarchical assembly of solution-based nanobuilding blocks into various dimensional nanostructures with excellent properties has been reported in recent year,² such as CdSe terapods,³ branched ZnO microcrystals and dandelions,⁴ dendritic Pd nanostructures,⁵ spindle-like V₂O₅ bundles,⁶ snowflake-like α-Fe₂O₃ architectures,⁷ and so on.

Metal tungstates belong to an important family of inorganic functional materials with potential application in various fields and have been studied for many years.⁸ It has been proven that Bi₂WO₆ microstructures display enhanced visible-light-driven photocatalytic activities on decontamination,⁹ CdWO₄ and PbWO₄ can be used as scintillators

materials,¹⁰ and MnWO₄ is a promising material for humidity sensor and magnetic device applications.¹¹ In particular, the magnetic properties of FeWO₄ have been studied to explore their potential application in magnetism field.¹² Although FeWO₄ nanorods and nanocrystals have been prepared by the hydrothermal method or under refluxing conditions,^{12c,13} the synthesis of magnetic highly ordered self-assembled

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hierarchical hexagonal platelike FeWO₄ microcrystals and their excellent photocatalytic activity have not been reported so far.

Herein, we report an effective ethylene glycol (EG)-assisted solvothermal method to synthesize hierarchical platelike FeWO₄ microcrystals in high yield using FeCl₃·6H₂O and Na₂WO₄·2H₂O as precursors. The organic solvent EG played a key role as both a reducing agent and a structure-directing agent in driving such architectures assembly by oriented attachment of nanoparticles. In addition, the amount of CH₃COONa (NaAc) also influences the morphology of particles. The magnetic properties and photocatalytic activities of self-assembled hierarchical FeWO₄ microcrystals have been investigated.

Experimental Section

All chemicals were analytical grade and commercially available from Shanghai Chemical Reagent and used as received without further purification.

Synthesis of Self-Assembled Hierarchical Platelike FeWO₄ Microcrystals. In a typical experiment, FeCl₃·6H₂O (1 mmol) and Na₂WO₄·2H₂O (1 mmol) were respectively dissolved in 2.5 mL of distilled water. First, the Na₂WO₄·2H₂O solution was added dropwise to the FeCl₃·6H₂O solution with magnetic stirring; then, 10 mmol CH₃COONa (NaAc) was added to the above mixture with continuous stirring to dissolve NaAc completely. After that, 45 mL of glycol (EG) was added. Then, the solution was transferred to a Teflon-lined autoclave with a volume of 65 mL after they had been vigorously stirred for about 30 min. The autoclave was sealed and maintained at 200 °C for 12 h, which was done in a digital-type temperature-controlled oven, and was then cooled to room temperature naturally. The obtained products were filtered out and washed with absolute ethanol and distilled water several times to remove impurities, and they were dried at 60 °C for 4 h.

Characterization. The obtained samples were characterized on an (Philips X'Pert Pro Super) X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.541874 \text{ \AA}$). The morphology was examined with a JEOL JSM-6700F scanning electron microscope (SEM), a Hitachi (Tokyo, Japan) H-800 TEM at an accelerating voltage of 200 kV, and a high-resolution transmission electron microscope (HRTEM) (JEOL-2010) operated at an acceleration voltage of 200 kV. Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on the same HRTEM. The X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer using non-monochromatized Mg K α X-ray as the excitation source.

Photocatalytic Test. The photocatalytic activities of the FeWO₄ microcrystals were first evaluated by degradation of rhodamine B (RhB) in an aqueous solution under UV and visible light from a 300 W Xe lamp (modeling sunlight). The photocatalyst (30 mg) was poured in 100 mL of RhB aqueous solution ($1 \times 10^{-5} \text{ M}$) in a Pyrex reactor at room temperature under air. Before light was

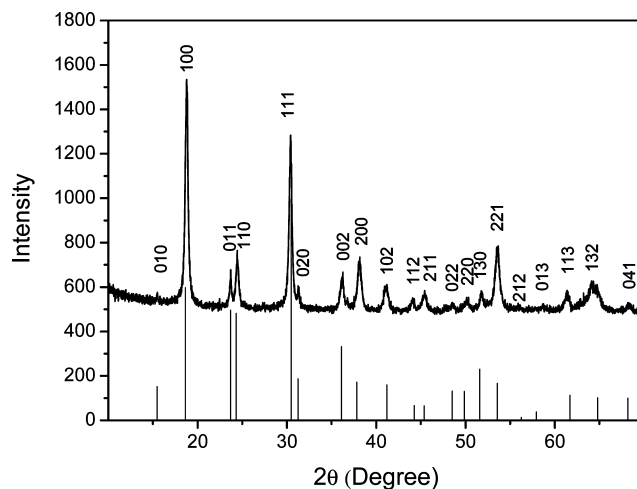


Figure 1. XRD pattern of the obtained FeWO₄ microcrystals aged at 200 °C for 12 h. [FeCl₃] = [Na₂WO₄] = 0.02 mol·L⁻¹, [NaAc] = 0.2 mol·L⁻¹, V_{H₂O}/V_{EG} 1:9. The standard pattern of ferberite is presented at the bottom.

turned on, the solution was continuously stirred for 15 min in the dark to ensure the establishment of an adsorption–desorption equilibrium. The concentration of RhB during the degradation was monitored by colorimetry using a UV–vis spectrometer (Shimadzu UV-2500 PC). Commercial TiO₂ (Degussa P25, Degussa) was adopted as the reference to compare the photocatalytic activity under the same experimental conditions.

Magnetic Measurement. The magnetic measurements on powder samples enclosed in a medical cap were carried out with a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS-XL, Quantum Design). The magnetization was measured under both zero field cooling (ZFC) and field cooling (FC) processes from 4 to 200 K under an applied field of 100 Oe. Magnetic–hysteresis loops were measured at 10 and 100 K separately under magnetic field up to 2 T.

Results and Discussion

Hierarchical platelike FeWO₄ microcrystals can be directly synthesized by a simple solvothermal process. The X-ray diffraction (XRD) pattern of as-prepared FeWO₄ microcrystals was shown in Figure 1. All reflection peaks can be indexed to a pure, well-crystalline, monoclinic phase of monoclinic FeWO₄ with lattice parameters of $a = 4.753 \text{ \AA}$, $b = 5.720 \text{ \AA}$, $c = 4.968 \text{ \AA}$ and $\beta = 90.8^\circ$, which are consistent with the reported values (Joint Committee on Powder Diffraction Standards (JCPDS), powder diffraction file no. 71–2390).

As shown in Figure 2a, the as-prepared product was composed of uniform platelike microcrystals with a diameter ranging from ca. 2.2 to 2.8 μm . The particles are very stable and cannot be broken into discrete individual nanoparticles even after ultrasonication for 60 min. Higher magnification images showed that each hexagonal plate with a thickness of ca. 300 nm was composed of six nearly equal petals and looked like a hexagonal symmetrically extended flower as a whole. As shown in Figure 2d, the hexagonal platelike microstructure was hierarchically assembled by slablike nanoparticles with an average size of ca. 60 nm.

The structure of the platelike FeWO₄ microstructures was further investigated by TEM and HRTEM observation. As

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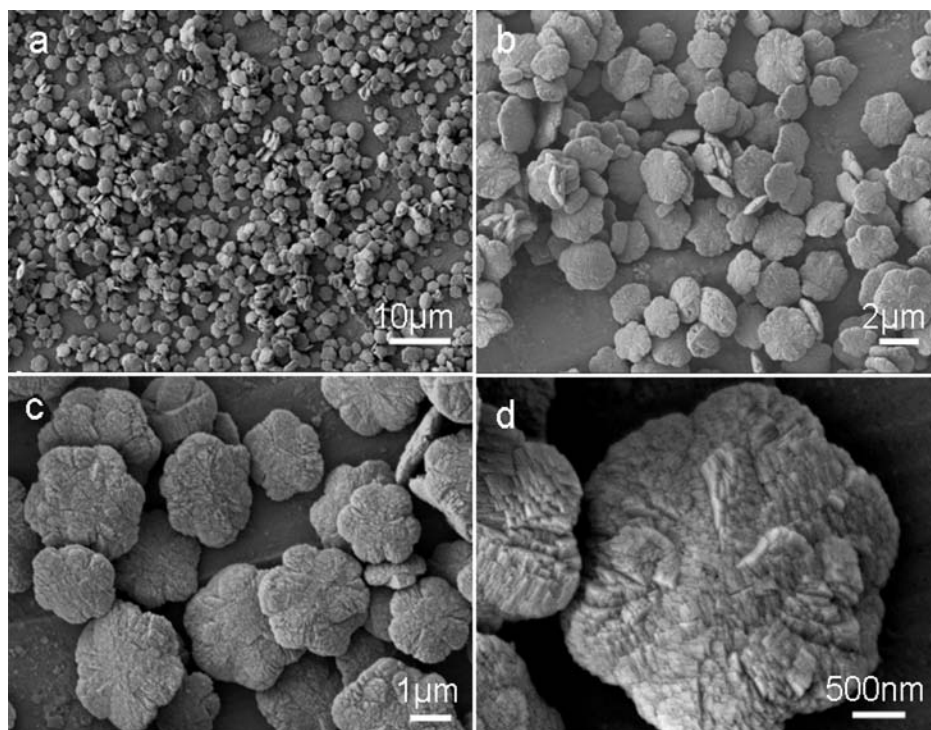


Figure 2. FESEM images of hierarchical platelike FeWO_4 microcrystals prepared by solvothermal process at 200 °C for 12 h. $[\text{FeCl}_3] = [\text{Na}_2\text{WO}_4] = 0.02 \text{ mol}\cdot\text{L}^{-1}$, $[\text{NaAc}] = 0.2 \text{ mol}\cdot\text{L}^{-1}$, $V_{\text{H}_2\text{O}}/V_{\text{EG}} 1:9$. (a) General review and (b,c,d) higher magnification images.

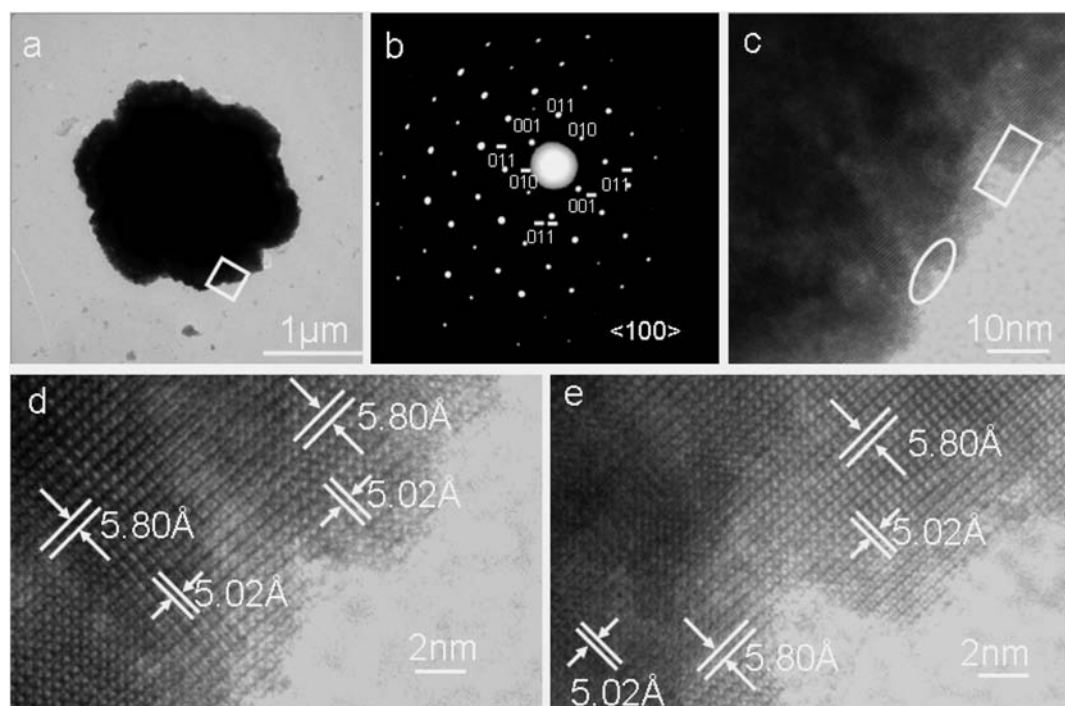


Figure 3. (a) TEM image of a typical hierarchical platelike FeWO_4 microcrystal, (b) selected area electron diffraction, and (c) HRTEM image taken on the typical FeWO_4 plate, and (d,e) enlarged HRTEM images of the two areas marked by the ellipse and rectangle, respectively.

shown in Figure 3a, a compact plate with rough surface made of aggregated nanoparticles could be observed. The selected area electron diffraction (SAED) pattern taken along the $[100]$ zone axis from the whole FeWO_4 plate is shown in Figure 3b and can be indexed as a monoclinic FeWO_4 phase. It is interesting that the nearly hexangular symmetric structure formed by self-assembly of single crystalline slablike nanoparticles also exhibits a single crystalline property, which

was confirmed by the SAED pattern. Figure 3c shows an HRTEM image in the area marked by square in Figure 3a. Figure 3d,e shows the enlarged lattice-resolved HRTEM images of the areas marked, respectively, by the white ellipse and rectangle in Figure 3c, indicating that the spacings of the observed lattice planes are approximately 5.80 and 5.02 Å, which are consistent with the spacings for the (010) and (001) planes of ferberite, respectively. The parallelism and

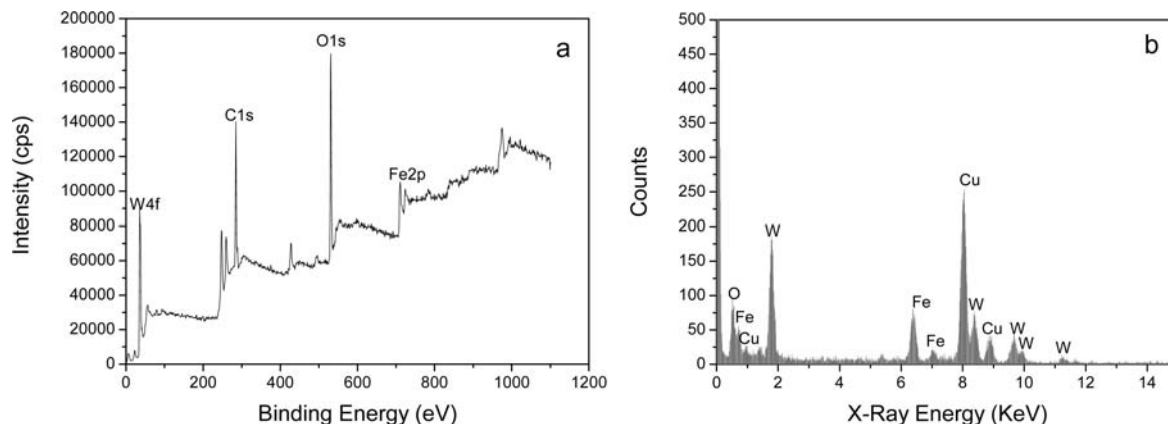


Figure 4. (a) XPS spectrum and (b) EDS spectrum of the prepared hierarchical platelike FeWO₄ microcrystals. The peaks of Cu originate from the Cu grid.

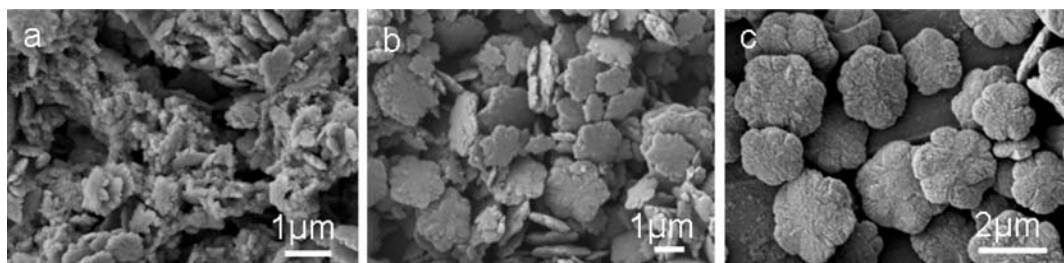


Figure 5. FESEM images of the obtained FeWO₄ particles after aging for different reaction time: (a) 4, (b) 5, and (c) 12 h, respectively.

overlap of the lattice fringes along the same crystallographic directions are based on the oriented attachment growth mechanism, which was proposed by Penn and Banfield¹⁴ as a new crystal growth mechanism involving attachment between two or more nanoparticles, followed by sharing a common crystallographic orientation and joining at the planar interface in an irreversible and highly oriented fashion.

The XPS spectrum in Figure 4a indicated that the main peak values at 35.11, 284.59, 530.34, and 710.45 eV can be readily assigned to the binding energies of W_{4f}, C_{1s}, O_{1s}, and Fe_{2p}, respectively. The quantitative analysis of the sample gives Fe, W, and O molar contents of 5.3, 6.1, and 27.3%, respectively. Elemental dispersive spectrum (EDS) analysis in Figure 4b indicates that the molar ratio of Fe/W/O is 1:1.12:3.94. Therefore, both the XPS and EDS results confirm that the self-assembled hierarchical platelike FeWO₄ microcrystals were composed of pure-phase FeWO₄.

A series of time-dependent experiments were performed to understand the formation process of self-assembled hierarchical platelike FeWO₄ microcrystals. The products obtained after different reaction time have been examined by the XRD patterns. (See Figure S1 in the Supporting Information.) Platelike nanoparticles and aggregates formed after the mixture was aged for 4 h (Figure 5a). After reaction for 5 h, more and more integrated platelike FeWO₄ architectures came into being with nanoparticles attached to their surface (Figure 5b). Finally, fully self-assembled symmetric hexangular FeWO₄ platelike microcrystals were obtained after reaction for 12 h (Figure 5c).

It is believed that EG is a general reducing agent with a relatively high boiling point, which has been widely used in the so-called polyol synthesis of monodisperse metal or metal oxide nanoparticles.¹⁵ As a nonaqueous solvent, EG has many characteristics similar to those of water such as small molecules and the ability to form hydrogen-bonded networks. Therefore, it can also be used as a cosolvent with water for the synthesis of highly hierarchical nanostructures.¹⁶ Moreover, EG functions as a soft template in directing the formation of complex microstructures.¹⁷ In the present reaction solution, EG may play triple roles in the synthesis of hierarchical platelike FeWO₄ microcrystals as a reducing agent, solvent, and crystal growth modifier. The Fe³⁺ cations were reduced to Fe²⁺ cations because of the reducing ability of EG, whereas different morphologies of hierarchical FeWO₄ microstructures were obtained by changing the volume ratio of H₂O and EG at certain levels. Multilayered FeWO₄ distorted round plates can be obtained when the volume ratio of H₂O/EG is 2:8 (Figure 6a,b). The multilayered cookie-like hierarchical FeWO₄ microcrystals were obtained while the volume ratio of H₂O/EG was 3:7, as shown in Figure 6c,d. Moreover, no precipitate was obtained if the volume ratio of H₂O/EG was 5:5. From the above experiments, it can be concluded that the volume of EG in mixed solvent is very important for the synthesis of hierarchical platelike FeWO₄ microcrystals. The reason may

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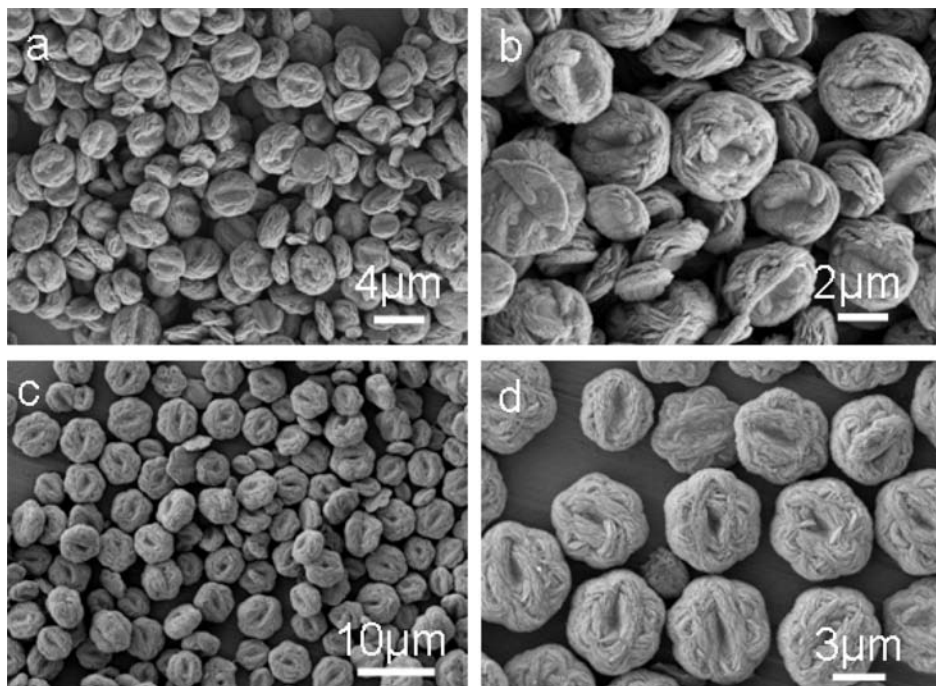


Figure 6. FESEM images of the prepared FeWO_4 microcrystals after aging at 200 °C for 12 h in media with different volume ratio of water and EG. (a,b) $V_{\text{H}_2\text{O}}/V_{\text{EG}}$ 2:8, (c,d) $V_{\text{H}_2\text{O}}/V_{\text{EG}}$ 3:7. $[\text{FeCl}_3] = [\text{Na}_2\text{WO}_4] = 0.02 \text{ mol}\cdot\text{L}^{-1}$, $[\text{NaAc}] = 0.2 \text{ mol}\cdot\text{L}^{-1}$.

be that different physical and chemical properties such as the viscosity and concentration of EG can affect the solubility, reactivity, and diffusion behavior of the reagents, which make EG selectively control the morphologies of final products as both a cosolvent and an organic additive in reaction solution.¹⁸ The XRD patterns showed that the obtained multilayered distorted round plates and the cookie-like particles can be indexed as pure FeWO_4 phase. (See Figure S2 in the Supporting Information).

Moreover, the morphology of FeWO_4 microcrystals can be varied by changing the concentration of NaAc in reaction solution. Because the hydrolysis of CH_3COO^- anions can produce OH^- anions in reaction solution¹⁹ and provide a basic environment for the formation of FeWO_4 microcrystals, the addition of various amounts of NaAc to the reaction solution leads to different alkaline reaction conditions. The precipitate was not formed when the concentration of NaAc was $<0.04 \text{ mol}\cdot\text{L}^{-1}$. The XRD patterns of the products obtained in the presence of 0.04 and 0.4 $\text{mol}\cdot\text{L}^{-1}$ NaAc, respectively, can be indexed to a pure monoclinic FeWO_4 phase. (See Figure S3 in the Supporting Information.) Disklike FeWO_4 microstructures with rough surface self-assembled by nanoparticles were produced by decreasing NaAc to $0.04 \text{ mol}\cdot\text{L}^{-1}$ (Figure 7a,b). When the concentration of NaAc was increased from 0.2 to 0.4 $\text{mol}\cdot\text{L}^{-1}$, more

hierarchical flowerlike architectures self-assembled by nanoparticles were prepared, as shown in Figure 7c,d. Therefore, it can be inferred that dissolution of enough NaAc in reaction solution during heat treatment will lead to a reasonable pH value, which is essential for the formation of such hierarchical FeWO_4 architectures. In addition, FeWO_4 microcrystals with different morphologies assembled by nanoparticles can be obtained by dosage of the same amounts of HCOONa , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{CH}_3\text{CH}_2\text{COONa}$, and $\text{NH}_3\cdot\text{H}_2\text{O}$ as alkaline source, respectively, in reaction solution, and maghemite was obtained while using NaOH and Na_2CO_3 as alkaline additive. (See Table S1 and Figures S4 and S5 in the Supporting Information.) From these comparative experiments, we may infer that NaAc is a better alkaline source for the fabrication of such hierarchical platelike FeWO_4 microcrystals than others.

However, compared with the hydrothermal synthesis of FeWO_4 nanorods growing along the [100] direction on the basis of the intrinsic structure of tungstate previously reported by our group,^{13b} FeWO_4 nanorods can also be obtained by using NaAc as alkaline source in pure water solution (Figures S6 and S7 in the Supporting Information), which implies that NaAc cannot change the intrinsic growth habit of FeWO_4 nanorod and EG played an important role in the fabrication of such self-assembled architectures.

A tiny amount of precipitates was obtained if the initial reactants were replaced by $\text{Fe}(\text{NO}_3)_3$ and Na_2WO_4 because of the strong oxidation effect of NO_3^- anions. Furthermore, only FeWO_4 nanocrystals can be prepared by using FeCl_2 and Na_2WO_4 as raw materials because of the direct production of FeWO_4 nanocrystals without directing and deoxidizing effects of EG in reaction solution. The results demonstrated that FeCl_3 is also essential for the formation of

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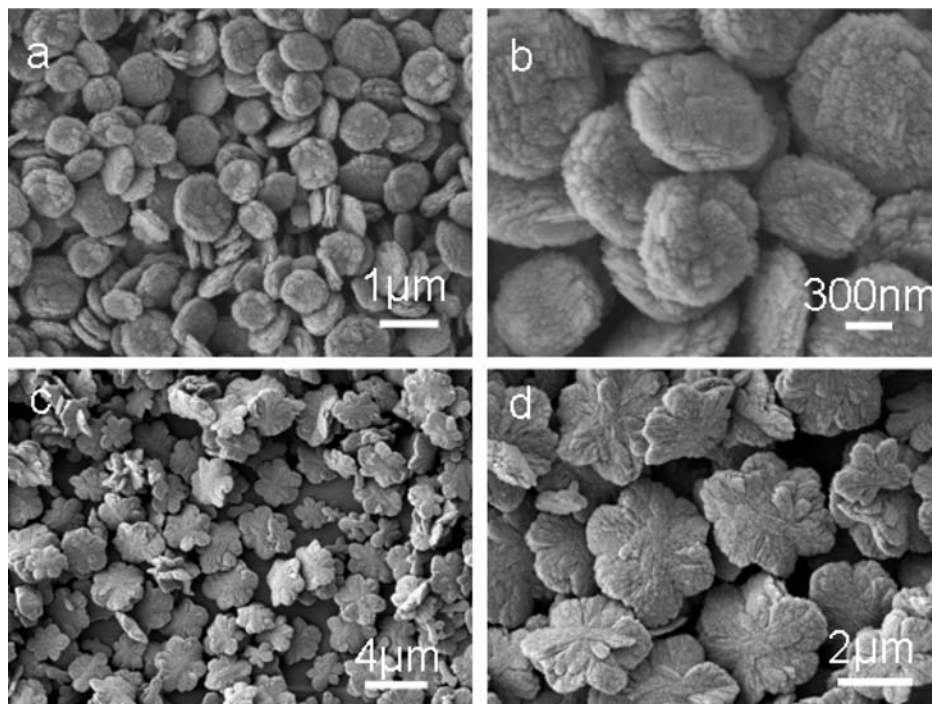
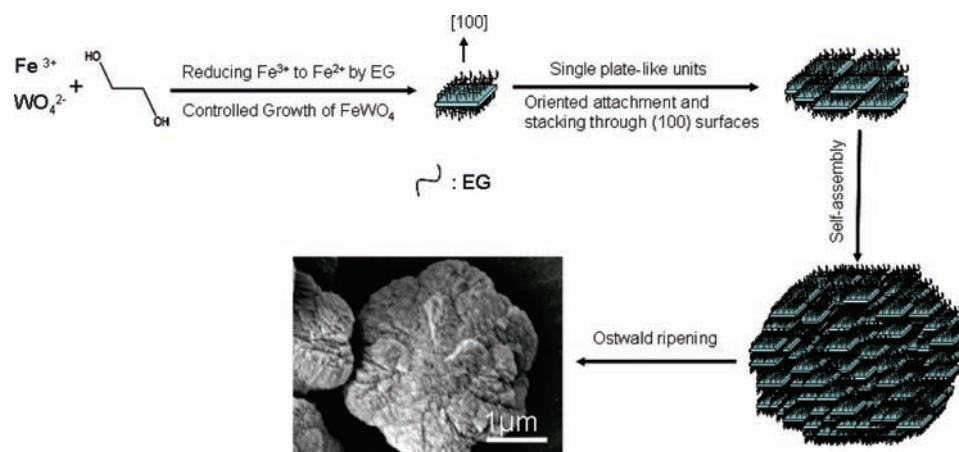


Figure 7. FESEM images of FeWO₄ microcrystals obtained for 12 h at 200 °C by using different concentration of NaAc. [FeCl₃] = [Na₂WO₄] = 0.02 mol·L⁻¹, V_{H₂O}/V_{EG} 1:9. (a,b) [NaAc] = 0.04 mol·L⁻¹, (c,d) [NaAc] = 0.4 mol·L⁻¹.

Scheme 1. Schematic Illustration of the Growth Process of Hierarchical Platelike FeWO₄ Microcrystals



hierarchical platelike FeWO₄ microcrystals. Because of slow releasing of Fe²⁺ through the reduction of Fe³⁺ by EG, it is more favorable for the formation of hierarchical structures than for the formation of FeWO₄ nanocrystals only through the direction precipitation from Fe²⁺ and WO₄²⁻. (See Figures S8 and S9 in the Supporting Information).

On the basis of the above experimental observation, a schematic illustration of the formation mechanism for the fabrication of hierarchical platelike FeWO₄ architectures is speculated, as shown in Scheme 1. First, the FeWO₄ slablike nanoparticles are quickly formed through the reduction of Fe³⁺ cations and stabilization on (100) crystal surface by EG. Then these slablike nanoparticles stacked through (100) surfaces by oriented attachment and self-assembly processes to form small sheetlike FeWO₄ microcrystals. With the reaction time prolonging, the small hexangular symmetric FeWO₄ sheetlike microcrystal further grew to platelike FeWO₄ microcrystals with nearly hexangular symmetry

through the Ostwald ripening process. In contrast with the growth habit of single crystallized FeWO₄ nanorods with preferential growth direction along [100] prepared in the absence of organic additives under hydrothermal condition,^{13b} the growth habit of such nearly hexangular symmetric FeWO₄ plates is very different from the previous case because of the emergence of EG in reaction solution. According to the structural features of FeWO₄ shown in Figure 8, the views along the planes indicate that more Fe atoms appear on the (100) plane than on the other two planes, and the comparison of views toward the planes shows that (001) and (010) planes are similar and contain the distorted quadrilateral net, but the (100) plane contains a puckered 6³ net along the plane, both indicating that the surface energy of (100) plane is different from those of (010) and (001) planes. The EG molecules have more chances to interact with the (100) plane and inhibit the growth of crystals along this face. The experimental results suggest that the most exposed

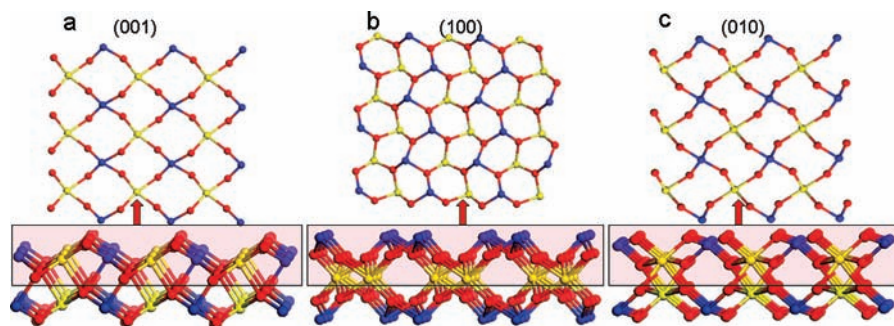


Figure 8. Views along the different directions of the crystal structure of FeWO_4 . (a) View along (bottom) and toward (up) the (001) plane, (b) view along (bottom) and toward (up) the (100) plane, and (c) view along (bottom) and toward (up) the (010) plane. Blue balls are W atoms; yellow balls are Fe atoms, and red balls are O atoms. (The model was calculated by Materials Studio software.)

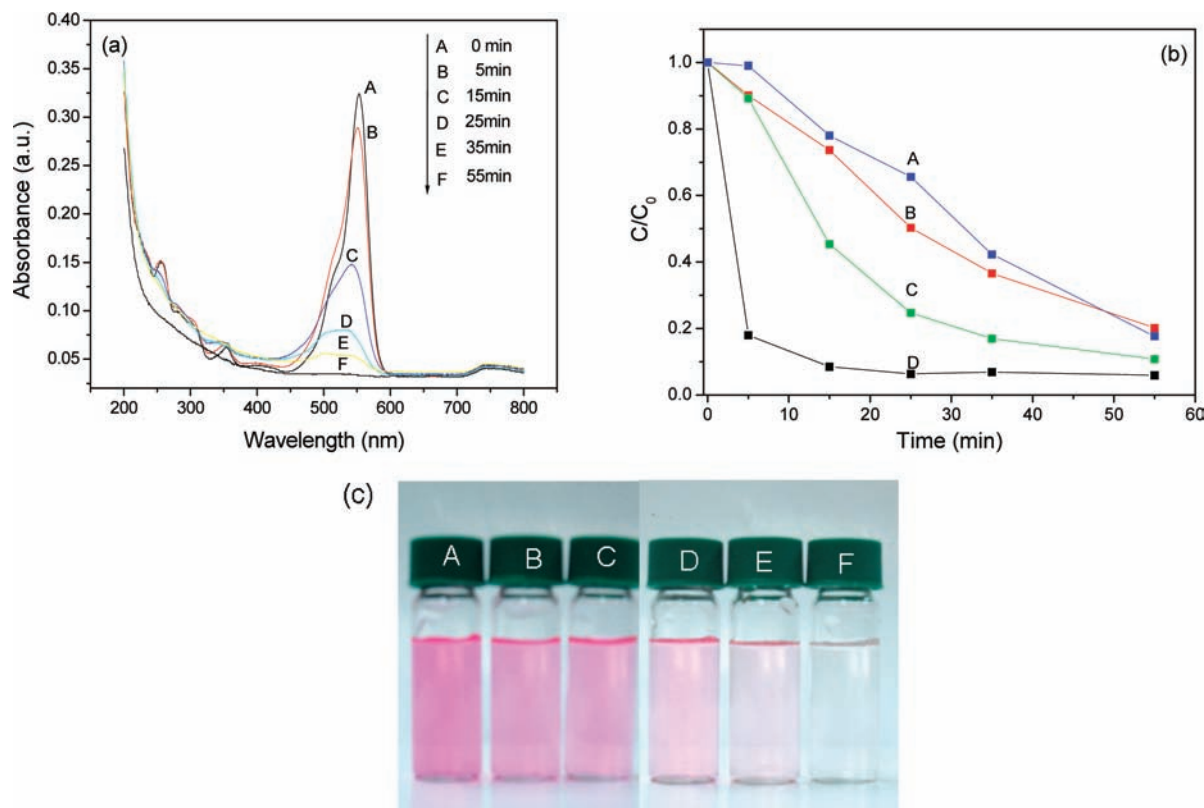


Figure 9. (a) Absorption spectra of the RhB solution (1.0×10^{-5} M, 100 mL) in the presence of 30 mg hexagonal symmetric FeWO_4 platelike microstructures under exposure to UV and visible light. (b) Photodegradation of RhB (1.0×10^{-5} M, 100 mL) using different samples as photocatalysts. Samples A–D correspond to (A) disklike FeWO_4 microcrystals obtained when the concentration of NaAc is 0.04 M, (B) FeWO_4 nanorods, (C) hierarchical platelike FeWO_4 microcrystals, and (D) TiO_2 (P-25) under UV and visible light illumination. (c) Time-dependent color change of RhB solution in the presence of hierarchical platelike FeWO_4 microstructures.

face in the slablike single crystal is found to be the (100) plane (Figures 2d and 3d), which is possibly due to the fact that the surface energy of the (100) plane of the slablike nanocrystals that self-assembled into the hexagonal symmetric plate by ordered aggregation of themselves is lower than that of (010) and (001) planes under the control of EG solvent.

To demonstrate the potential application of as-synthesized self-assembled hierarchical FeWO_4 microstructures in the degradation of organic contaminants, we have first investigated their photocatalytic activities by choosing the photocatalytic degradation of RhB as a model reaction. Figure 9a shows the temporal evolution of the spectra during the photodegradation of RhB (initial concentration: 10^{-5} M, 100 mL) in the presence of 30 mg FeWO_4 sample under UV

and visible light illumination (modeling sunlight). The absorption peaks at 553 nm corresponding to RhB diminished, and the intense pink color of the starting RhB solution gradually faded during the process of photodegradation by the hierarchical FeWO_4 microstructures as the exposure time was extended (Figure 9c). The adsorption peaks corresponding to RhB completely disappeared only after about 55 min, which shows the excellent photocatalytic activity of the hierarchical platelike FeWO_4 architectures. We also studied the degradation process of RhB by using FeWO_4 nanorods (obtained by hydrothermal synthesis) and disklike FeWO_4 microstructures prepared (obtained by using 2 mmol NaAc as alkaline source) as photocatalysts. The results of the RhB degradation of samples are shown in Figure 9b. It shows that the photocatalytic activity of hexagonal FeWO_4 mi-

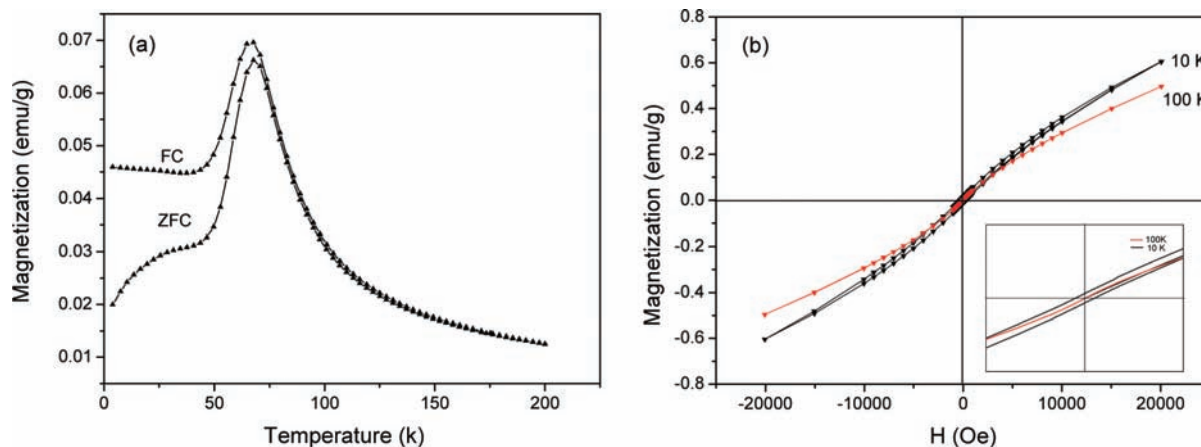


Figure 10. (a) Temperature dependence of magnetization curves measured with applied field of 100 Oe under FC and ZFC conditions. (b) Magnetization–hysteresis (M–H) loops measured at 10 and 100 K of hierarchical platelike FeWO₄ microcrystals. The inset of b shows an enlarged area of the center of the M–H loops.

microcrystals is the highest of three samples, which may be ascribed to higher photocatalytic activity of certain facets of hierarchical platelike FeWO₄ architectures than that of FeWO₄ nanorods and disklike FeWO₄ microcrystals. Moreover, the photocatalytic activity of FeWO₄ microstructure is comparable to photocatalytic ability of P25. However, more efforts need to be done on how to enhance the photocatalytic activity of hierarchical platelike FeWO₄ microcrystals to explore their application in photocatalytic degradation of water pollutants. The comparative experimental results demonstrated that the photocatalytic activity of the synthesized FeWO₄ is relative to their morphology, structure, and chemical synthesis method.

The magnetic properties of hierarchical platelike FeWO₄ microstructures obtained by adding 10 mmol NaAc to a mixed solution of water and EG ($V_{\text{H}_2\text{O}}/V_{\text{EG}}$ 1:9) were investigated by using a commercial SQUID magnetometer (Quantum Design, MPMS5XL). The temperature-dependent magnetization of such sample between 4 and 200 K was measured under ZFC and FC processes in the applied field of 100 Oe. The field dependence of magnetization curves of hierarchical platelike FeWO₄ microcrystals were measured at 10 and 100 K from 0 to 2 T and –2 to 0 T applied field.

The magnetization curves as a function of temperature of hierarchical platelike FeWO₄ architectures were shown in Figure 10a. It can be seen that the magnetization initially shows a monotonic increase with decreasing temperature from the beginning at 200 K down to 67.8 K (the FC magnetization curve), where a notable cusp is observed; then, the magnetization was decreased straight at temperature lower than 67.8 K. However, the magnetization in the ZFC process increased monotonously to the maximum at 67.8 K with increasing temperature at low temperature and then decreased with increasing temperature to 200 K, which has nearly the same trend as the FC curve besides a little difference that there was an irreversible diverge between FC and ZFC curves at temperatures much lower than the peak temperature. Therefore, it may be speculated that the main magnetic properties of the hexangular FeWO₄ platelike microstructure is antiferromagnetic at temperatures lower than 67.8 K with a small ferromagnetism at much lower

temperature, and the Néel temperature of such microcrystals is 67.8 K. It was reported that FeWO₄ crystal with magnetic cation Fe²⁺ belongs to antiferromagnetic materials with Néel temperature of 76 K;²⁰ we may infer that different preparation method and size effects of the microstructures lead to such difference in the measured Néel temperature.²¹ The field dependence of the magnetization curve of the hierarchical platelike FeWO₄ microcrystals measured at 10 K in Figure 10b shows a weak hysteresis with coercive force of 301.3 Oe and remnant magnetization of 1.35×10^{-2} emu/g, which further reveals the weak ferromagnetism of such sample in accordance with the results of the FC and ZFC curves, as shown in Figure 10a; whereas the M–H curve obtained at 100 K shows no hysteresis, which demonstrates the paramagnetic property of the hexangular FeWO₄ platelike microstructures at temperatures higher than their corresponding Néel temperature. The weak ferromagnetism of hexangular FeWO₄ plates at low temperature may be due to the spin-canting behavior of antiferromagnetic materials²² caused by a Dzyaloshinsky–Moriya (DM) interaction²³ and the uncompensated number of surface spins²⁴ of slablike FeWO₄ nanoparticles that self-assembled in hierarchical platelike FeWO₄ microstructures.

Conclusions

In summary, novel hierarchical platelike FeWO₄ architectures have been synthesized by a solvothermal route in an EG–water solvent system. EG plays a crucial role as an additive in the synthesis of such unique platelike FeWO₄ microcrystals that were formed through oriented attachment of nanobuilding blocks. The suitable amount of NaAc was essential for the formation of such hierarchical FeWO₄ microstructures. The photocatalytic property of the hierarchi-

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cal FeWO_4 architectures was first explored, showing excellent photocatalytic activity for degradation of rhodamine B (RhB) under exposure to UV and visible light irradiation. Magnetic measurement indicates that the T_N of hierarchical platelike FeWO_4 microcrystals is lower than that of the bulk FeWO_4 because of the size effects and a small ferromagnetic ordering that existed in FeWO_4 microstructures at low temperature caused by spin-canting of antiferromagnetic materials and surface spins of FeWO_4 nanoparticles. This unique FeWO_4 microstructure could find potential application in decontamination and magnetism field.

Acknowledgment. This work was supported by the National Science Foundation of China (nos. 50732006, 20621061, 20671085, 20701035), 2005CB623601, Anhui

Development Fund for Talent Personnel and Anhui Education Committee (2006Z027, ZD2007004-1), the Specialized Research Fund for the Doctoral Program (SRFDP) of Higher Education State Education Ministry, and the Partner-Group of the Chinese Academy of Sciences: The Max Planck Society.

Supporting Information Available: XRD patterns of FeWO_4 microcrystals and nanocrystals, products obtained by using different alkaline source in reaction solution, SEM images of FeWO_4 microcrystals, and TEM images of the FeWO_4 nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC801806R