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Letter

Synthesis of $La_{1-x}Fe_xVO_4$ solid solutions and their photocatalytic activity

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ABSTRACT

Nanocrystalline $La_{1-x}Fe_xVO_4$ ($x = 0, 0.05, 0.10, 0.20$) solid solution powders were successfully synthesized via a low-temperature molten salt method. The products were characterized using powder X-ray diffraction (XRD), transmission electron microscopy (TEM). The results show a gradual phase transformation from monoclinic to tetragonal-phase with the increase of x value, accompanied by a remarkable morphology variation from nearly spherical nanoparticles to nanorods, nanosheets. Fe^{3+} doped $LaVO_4$ can be fully stabilized in tetragonal-phase at $x = 0.20$, whereas only a monoclinic-phase can be obtained without adding Fe^{3+}. The followed photocatalytic degradation data present that the metastable tetragonal-phase exhibits higher photocatalytic activity than the monoclinic.

1. Introduction

Rare earth compounds of stoichiometric RBO_4, where R is a rare earth and B is transition element, are well known for their wide range of physical/chemical properties. Among these materials, lanthanide orthovanadate ($LaVO_4$) is an important rare earth compound which has been applied as laser host materials [1], catalysts [2], and luminescent materials [3] due to its unique electronic structure and the numerous transition modes involving the 4f shell of rare earth ions [4–6]. Generally, $LaVO_4$ crystallizes in two polymorphs, namely, monoclinic monazite and tetragonal zircon type. As reported previously, the monoclinic-phase $LaVO_4$ is neither a suitable host for luminescent activators [7,8], nor a promising catalyst [2] owing to its monazite structure compared to other orthovanadates. Nevertheless, the tetragonal-phase $LaVO_4$ possesses potential excellent properties, as revealed by some researchers [9] though it is difficult to be prepared by conventional methods. A variety of methods have been explored for preparing $LaVO_4$ or $LaVO_4$ solid solutions: the traditional solid-state reaction [10], sol–gel method [11], and hydrothermal process [3,12,13], etc. Moreover, the controlled phase-transition could be realized in the hydrothermal process [13] by tuning pH value of the growth solution. However, there have still existed in above approaches such drawbacks as either needing high calcining temperature and long holding time, or using complicated manipulation like repeatedly crushing-calcining for the complete reaction between reactants, or consuming a large amount of organic agents, and requiring specific equipment. Although a series of orthovanadates with nominal compositions $La_{1-x}Fe_xVO_4$ can be synthesized by the traditional solid-state reaction [14], their products, in practice, are either monoclinic $LaVO_4$ (triclinic $FeVO_4$) or a mixture of both of them. No tetragonal-phase can be obtained. Here, we report on alternative method for preparing $La_{1-x}Fe_xVO_4$ solid solutions, under a molten salt medium condition, both the monoclinic-phase and the tetragonal can be successfully prepared at a synthetic temperature of not exceeding 450 °C. It fully exhibits unique advantages of the molten salt method such as simple facilities, easy manipulation, and environmentally friendly process [15–17]. The photocatalytic degradation data of the as-prepared samples also confirm the superior photocatalytic performance of the tetragonal-phase $La_{1-x}Fe_xVO_4$ solid solution over that of the monoclinic $LaVO_4$.

2. Experimental

2.1. Synthesis of $La_{1-x}Fe_xVO_4$ Solid Solutions

Well-crystallized $La_{1-x}Fe_xVO_4$ solid solutions ($x = 0, 0.05, 0.10, 0.20$) were prepared via a low-temperature molten salt method, the whole process can be described as follows: analytical grade $NaVO_3 \cdot 2H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ were used as starting materials. Appropriate amounts of metal nitrates and $NaVO_3 \cdot 2H_2O$ were separately weighed according to the nominal composition of $La_{1-x}Fe_xVO_4$ ($x = 0, 0.05, 0.10, 0.20$), and then dissolved in distilled water to form aqueous solutions. Fox each x, 3 aqueous solutions respectively contained La^{3+}, Fe^{3+}, and VO_3^- ions were mixed together with strongly magnetic stirring at room temperature, and the pH value of the mixed solution was adjusted to 10.5 by

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adding ammonia water; a precipitate could be obtained. The precipitate was filtered, washed with distilled water for several times, and then dried in an oven at 60 °C for 3 h to obtain $La_{1-x}Fe_xVO_4$ precursor. The precursor was well mixed by milling in absolute ethanol with $LiNO_3$ whose melting point is 253 °C [18], where the weight ratio of the salt to the precursor were selected as 8:1. The obtained mixture was put into an alumina crucible and calcined at 450 °C for 6 h. The product was dissolved in hot distilled water, and then filtered and thoroughly washed with distilled water for several times, and finally dried at 60 °C for 3 h.

2.2. Characterization

X-ray diffraction measurement was performed at room temperature by using an X-ray powder diffractometer (XRD, D8ADVANCE, Bruker, Germany) with Cu K_α radiation ($\lambda = 1.5406$ Å). A transmission electron microscope (TEM, JEM-1200 EX, JEOL Ltd., Japan) was used to observe the particle size and morphology of the as-prepared powders.

2.3. Photocatalytic degradation evaluation

The photocatalytic activity of the typical samples was evaluated by comparing the degradation rates of Rhodamine B in aqueous solution under UV-light irradiation. 0.50 g of sample was added into a Pyrex glass beaker containing Rhodamine B aqueous solution (20 mg/L, 500 ml). Before UV-light irradiation, the suspension was stirred for 1 h under atmosphere by an air pump in a dark box. Then, it was irradiated using a 400W high pressure Hg lamp (with a major emission at about 365 nm) and continuously stirred. The reaction temperature was kept at 25 ± 2 °C by a cooling water system. The periodic interval was set 10 min. 5 ml was taken from the suspension every time, and centrifuged to obtain filtrates, which were finally analyzed by a spectrophotometer (722-E, Shanghai spectrum Instrument Co. Ltd., China) at its maximum absorption wavelength of 554 nm.

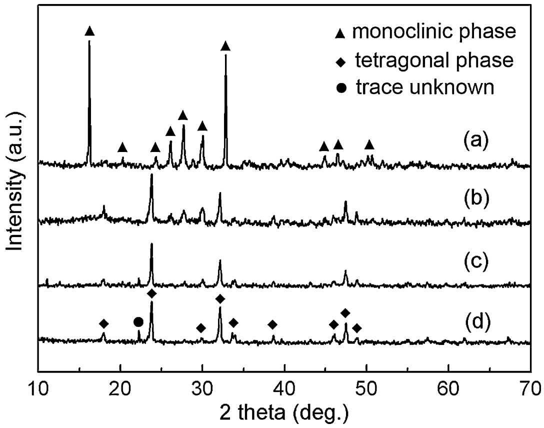

Fig. 1. XRD patterns of $La_{1-x}Fe_xVO_4$ samples with different values of x: (a) 0; (b) 0.05; (c) 0.10; and (d) 0.20. (Calcining temperature: 450 °C; holding time: 6 h; and the weight ratio of the salt to the precursor: 8:1).

3. Results and discussion

3.1. X-Ray diffraction analysis

Fig. 1 shows XRD patterns of $La_{1-x}Fe_xVO_4$ ($x = 0$, 0.05, 0.10, 0.20) samples obtained by the molten salt method at 450 °C. Obvi-

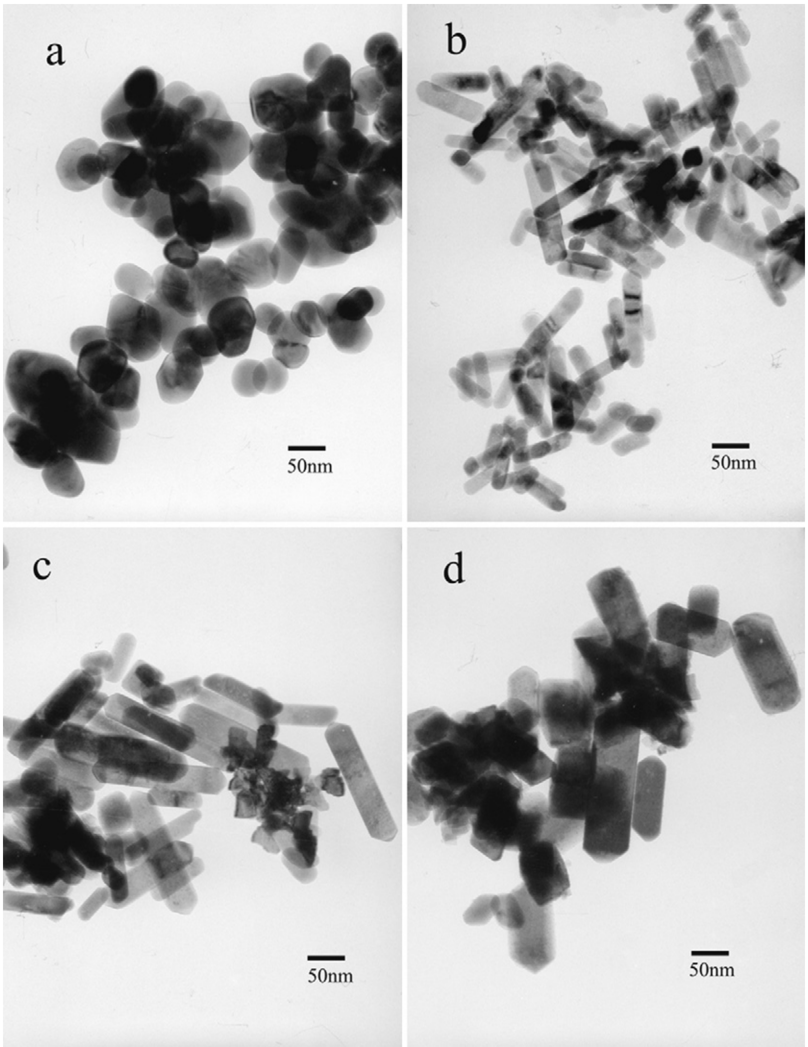

Fig. 2. TEM images of $La_{1-x}Fe_xVO_4$ samples with different values of x: (a) 0; (b) 0.05; (c) 0.10; and (d) 0.20.

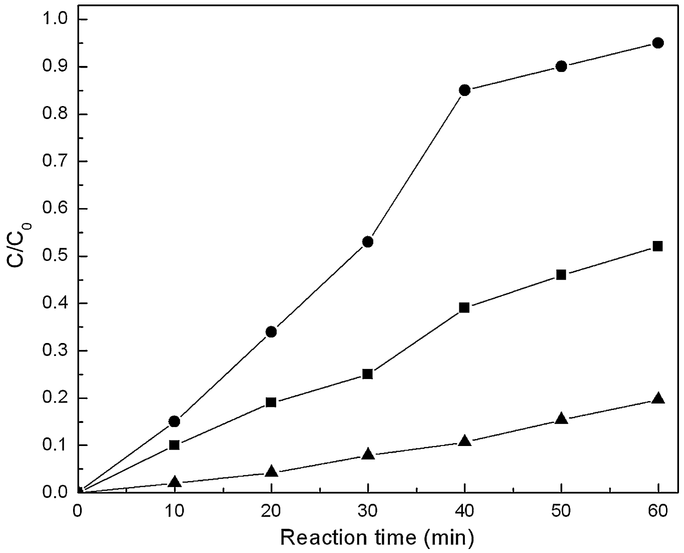

Fig. 3. Photocatalytic degradation rates of typical $La_{1-x}Fe_xVO_4$ samples ($x = 0, 0.20$) and Rhodamine B blank solution: (●) $La_{0.80}Fe_{0.20}VO_4$; (■) $LaVO_4$; and (▲) Rhodamine B solution.

ously, at $x = 0$ (Fig. 1(a)), the XRD pattern of the as-prepared sample matches well with the reported data of monoclinic-phase $LaVO_4$ (JCPDS: 50-0367). Likewise, Fig. 1(d) presents a XRD pattern which can be ascribed to tetragonal-phase $LaVO_4$ (JCPDS: 32-0504) at $x = 0.20$. It means, without adding Fe^{3+}, only monoclinic-phase $LaVO_4$ can be obtained; whereas at $x = 0.20$, Fe^{3+} can fully stabilize $LaVO_4$ in metastable tetragonal-phase, which, in practice, is a Fe^{3+} doping solid solution ($La_{0.80}Fe_{0.20}VO_4$). Fig. 1(b) and (c) ($x = 0.05$, 0.10) is situated in a transition state from monoclinic-phase to the tetragonal. Both of them are a mixture of the monoclinic-phase and tetragonal one. Moreover, with the increase of x value, the monoclinic-phase in quantity gradually declines, at $x = 0.20$, it completely disappears. Compared with our results, the traditional solid-state reaction route shows its obvious limitation: e.g. tetragonal-phase $La_{1-x}Fe_xVO_4$[14] or $La_{1-x}Ce_xVO_4$ [10] solid solution cannot be formed in the whole x range.

3.2. *TEM observation*

Fig. 2 presents TEM images of above $La_{1-x}Fe_xVO_4$ samples. The monoclinic-phase $LaVO_4$ ($x = 0$) nanoparticles have homogeneous and nearly spherical morphology, and their particle size is ca. 50 nm (Fig. 2(a)). With x value increasing, the mixtures ($x = 0.05$, 0.10) of monoclinic-phase and tetragonal-phase are nanorods of 10–30 nm width and 30–200 nm length with perfectly crystallized morphology (Fig. 2(b) and (c)). At $x = 0.20$, well-crystallized nanosheets with ca. 50 nm width and 100–200 nm length can be formed, as shown in Fig. 2(d). The preferred orientation growth should be attributed to the phase transformation of $LaVO_4$ matrix solid solutions ($La_{1-x}Fe_xVO_4$) from m-phase to t-phase. The similar results can also be found in the reference [13], where the selected-control hydrothermal synthesis of $LaVO_4$ was reported. Though m-phase $LaVO_4$ particles have nearly spherical morphology (pH = 2.5), further increasing pH value leads to the formation of t-phase $LaVO_4$, e.g. at pH = 4.5, well-crystallized nanorods with the preferred orientation growth can be successfully obtained.

The results suggest that Fe^{3+} doping in $LaVO_4$ matrix would promote the preferred orientation growth of $La_{1-x}Fe_xVO_4$ solid solutions besides stabilizing the tetragonal-phase.

3.3. *Photocatalytic activity analysis*

Fig. 3 gives the photocatalytic degradation data of Rhodamine B aqueous solution under UV-light irradiation by two typical samples ($x = 0$, and $x = 0.20$); simultaneously, the degradation rate of Rhodamine B blank solution (without adding any catalyst) is also plotted in Fig. 3 for comparison. The monoclinic-phase $LaVO_4$ nanoparticles show a poor photocatalytic activity. Within 60 min, about 52% photodegradation rate can be achieved, i.e. only a little higher than that of the blank solution. However, $La_{0.80}Fe_{0.20}VO_4$ solid solution with the pure tetragonal-phase exhibits much higher photocatalytic activity than the monoclinic $LaVO_4$; within the same time of 60 min, its photogradation rate reaches over 95%. The superior photocatalytic activity of the tetragonal-phase over the monoclinic-phase can also be found in the other references [19], which was further confirmed in present study.

4. Conclusion

Homogeneous and well-crystallized nanocrystalline $La_{1-x}Fe_xVO_4$ solid solutions can be synthesized at 450 °C by a low-temperature molten salt method. Their phase composition can be easily tuned by varying x value. At $x = 0$, only a monoclinic-phase can be obtained, whereas pure tetragonal-phase can be prepared even at $x = 0.20$. The mixtures of both monoclinic-phase and tetragonal-phase appear in a range of $0 < x < 0.20$. Fe^{3+} doping in $LaVO_4$ matrix can not only stabilize $La_{1-x}Fe_xVO_4$ solid solution in metastable tetragonal-phase at a relatively low-temperature (450 °C) but also favor their preferred orientation growth. The tetragonal-phase solid solution exhibits much higher photocatalytic activity than the monoclinic.

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