



p-Type CaFe_2O_4 semiconductor nanorods controllably synthesized by molten salt method

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ABSTRACT

Pure phase, regular shape and well crystallized nanorods of p-type semiconductor CaFe_2O_4 have been fabricated for the first time by a facile molten salt assisted method, as confirmed by XRD, TEM, SEM and HRTEM. UV–vis diffuse reflectance spectra and Mott–Schottky plots show that the band structure of the CaFe_2O_4 nanorods is narrower than that of the CaFe_2O_4 nanoparticles synthesized by conventional method. The enhancement of the visible-light absorption is due to narrowness of the band gap in CaFe_2O_4 nanorods. The appropriate ratio between the molten salt and the CaFe_2O_4 precursors plays an important role in inhibiting the growth of the crystals along the (201) plane to give the desired nanorod morphology. This work not only demonstrates that highly pure p-type CaFe_2O_4 semiconductor with tunable band structure and morphology could be obtained using the molten salt strategy, but also affirms that the bandgap of a semiconductor may be tunable by monitoring the growth of a particular crystal plane. Furthermore, the facile eutectic molten salt method developed in this work may be further extended to fabricate some other semiconductor nanomaterials with a diversity of morphologies.

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1. Introduction

Efficient separation of photogenerated charges serves as the driving force for the photocatalytic reactions, which is crucial for achieving high photocatalytic activity [1]. Fabrication of p–n junction photocatalysts is one of the ideal approaches to separate photogenerated charges [2,3]. Unfortunately, though various kinds of n-type semiconductors have been well studied, p-type semiconductors are still rare in study, nevertheless to say fabrication of efficient p–n junction photocatalysts. In order to develop p–n junction photocatalysts, it is necessary to develop and study p-type semiconductors [4].

CaFe_2O_4 is a p-type semiconductor (with band gap $\sim 2.0\text{ eV}$) composed of earth-abundant elements. Because it is inexpensive and environmentally friendly, CaFe_2O_4 has been widely investigated for various applications, such as pigments [5], absorbent of hydrogen sulfide for hot-gas cleaning [6], heterogeneous catalyst

[7,8], photocatalyst for CO_2 reduction and degradation of pollutants [9–13] as well as photocathode material for photoelectrochemical hydrogen production [14–18]. However, controllable synthesis of highly pure CaFe_2O_4 crystals with specific morphology has not been reported so far. It is well known that the nanomaterials with specific morphologies, such as nanowires [19], nanorods [20] and nanobelts [21], may give remarkably different physical and chemical properties compared to the corresponding nanoparticle counterparts [22,23]. Tailor control of the morphology may render exposure of high-reactive crystal facets [24–26], well-aligned nano-architecture to provide short or fast pathway for transfer of charge carriers at a particular directions [27–30], and efficient inhibition of photogenerated charge recombination to lead to enhanced photocatalytic and photovoltaic performances [31–33].

The morphology control of calcium ferrite-type compounds still remains a great challenge. For the preparation of CaFe_2O_4 without regular shape, solid-state reaction and polymerizable complex are the two commonly used methods [13,34–37]. However, to the best of our knowledge, there have been no reports on the controllable synthesis of CaFe_2O_4 nanomaterials with regular morphology. Here, we report for the first time that well defined CaFe_2O_4 nanorod crystals could be synthesized via a facile polymerizable

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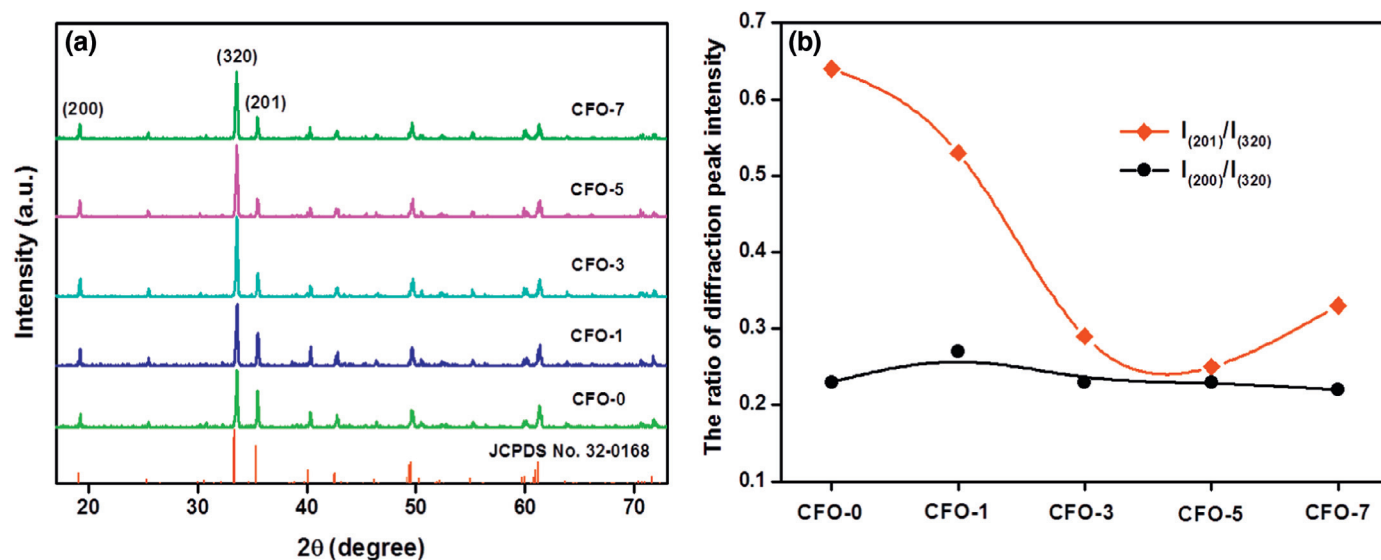


Fig. 1. (a) XRD patterns of CaFe_2O_4 samples synthesized with different amounts of molten salt, and (b) the relative intensity ratios of the diffraction peaks (201)/(320) and (200)/(320).

complex method in a eutectic mixture of NaCl and KCl molten salt. The introduction of the molten salt gives great benefit in nanorod morphology control by inhibiting the growth of the specific crystal plane.

2. Experimental

2.1. Preparation of the materials

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%) were purchased from Aladdin Industrial Corporation. Ethylene glycol ($\geq 99.0\%$), citric acid ($\geq 99.5\%$), NaCl ($\geq 99.5\%$) and KCl ($\geq 99.5\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were used as received without further purification.

CaFe_2O_4 nanorods were prepared by polymerizable complex method in a molten salt of NaCl and KCl mixture. In a typical experiment, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (4.723 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (16.160 g) were stirred and dissolved in deionized water (20 mL) containing citric acid (8.406 g) at room temperature, followed by addition of ethylene glycol (8 mL) to yield a transparent solution. The reaction mixture was dried at 80°C for 12 h to evaporate water. Subsequent polyesterification at 130°C for 12 h followed by pyrolysis at 350°C for 2 h gave solid CaFe_2O_4 precursor, which was divided into several portions and blended with NaCl and KCl (molten salt) in the molar ratios of 1:0:0, 1:1:1, 1:3:3, 1:5:5 and 1:7:7. The thoroughly ground samples were then loaded into a high purity alumina crucibles and heated in air at 900°C for 5 h in a muffle furnace. After washed with boiling deionized water for several times to remove any residual salt, the products were dried in an oven at 80°C overnight. The final products prepared as the above molar ratios of CaFe_2O_4 precursor to molten salt components are denoted as CFO-0, CFO-1, CFO-3, CFO-5 and CFO-7, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT-2200 diffractometer equipped with a $\text{CuK}\alpha$ radiation source operating at a voltage of 40 kV and a current of 20 mA. The morphologies of the samples were examined by scanning electron microscopy (SEM) on a Hitachi SU-8020 cold field emission instrument. High-resolution transmission electron microscopy (HRTEM)

images were taken on a JEOL JEM-2100 microscope at 200 kV. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a UV-vis spectrophotometer (JASCO V-750) equipped with an integrating BaSO_4 sphere. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out on a Diamond TG/DTA apparatus.

The Mott-Schottky plots were measured in a conventional three-electrode glass cell mode on an electrochemical workstation (CHI660A, Shanghai Chenhua Instruments, China). The thin films of the CaFe_2O_4 samples prepared by electrophoretic deposition method were used as the working electrodes. Pt plate and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. A 0.5 M Na_2SO_4 solution was used as the electrolyte.

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1(a) shows the XRD patterns of the synthesized CaFe_2O_4 samples. It can be seen that all of the samples exhibit diffraction peaks corresponding to the orthorhombic phase CaFe_2O_4 (JCPDS-32-0168). No observation of significant impurity peaks is an indication that the synthesized CaFe_2O_4 samples are in high quality. For comparison, the (320) peak was used as the internal standard to normalize all of the XRD patterns and the peak intensity ratios of (201)/(320) and (200)/(320) are plotted as shown in Fig. 1(b). No obvious changes in (200)/(320) intensity ratio are observed for all five samples, indicating that molten salt does not affect the growth of the CaFe_2O_4 on this direction. However, it is evident that the intensity ratio of (201)/(320) dramatically decreases with the increase of the molten salt. Increasing the amounts of the added molten salt during synthesis by decreasing the CaFe_2O_4 precursor/NaCl/KCl molar ratio from 1:0:0 to 1:7:7 results in the decrease of the (201)/(320) intensity ratio from 0.64 for CFO-0 to the minimum value of 0.25 for CFO-5. This strongly suggests that the growth of the CaFe_2O_4 crystals along the (201) plane is largely inhibited with the increase of the amount of the NaCl-KCl molten salt. Furthermore, such inhibition of crystal growth towards a particular direction seems to have optimal conditions, as is evident from the trend that further increase in

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