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Crystal structural, optical properties and mott-schottky plots of p-type Ca doped $CuFeO_2$ nanoplates

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ABSTRACT

We first report a facile hydrothermal method to synthesize Ca doped 3R-$CuFeO_2$ nanoplates with 100–400 × 15–40 nm^2 at 100 °C for 24 h. The Ca dopants have a significant effect on the crystal structure of $CuFeO_2$, as our investigation shows clearly that the Ca^{2+} ions were successfully doped into the $CuFeO_2$ lattice and substituted Cu^+ ion, resulting in the formation of $Cu_{1-2x}Ca_xFeO_2$ solid solution of a rhombohedral 3 R structure. Furthermore, the calculated direct bandgap energies of (Ca doped) $CuFeO_2$ nanoplates were estimated to be 3.20–3.40 eV, and the optical bandgaps decreased with increasing concentration of Ca dopant. The mott-schottky anaylsis results indicated that (Ca doped) $CuFeO_2$ nanoplates have a p-type semiconductor behavior, and the carrier density of these $CuFeO_2$ based nanoplates around 10^{20} cm^{-3}, which also decreased with increasing concentration of Ca dopant due to the Ca^{2+} ion replacement of a part of Cu^+ ions.

1. Introduction

In the past two decades, Cu-based delafossite ternary oxides $CuMO_2$ (M = Al, Cr, Fe, Ga, Mn and so on) have received immense attractions [1–4], since the first discovery of p-type conductivity on $CuAlO_2$ thin films by Kawazoe H. et al. [1]. These p-type delafossite oxides semiconductors have been widely used in several technological fields such as transparent conducting oxides [5,6], luminescent materials [7], catalysts [8,9], batteries [10–12], ferroelectrics [13,14], thermoelectric [15,16] and so on. The crystal structure of delafossite oxides, deriving their name from the mineral $CuFeO_2$, which can be described as sheets of edge-shared FeO_6 octahedra alternating stacked with close-packed Cu-ion layers, and the hexagonal 2 H (space group P63/mmc) and the rhombohedral 3 R (space group R3m) structures can be formed depending on the stacking of these layers [3]. Recently, $CuFeO_2$ is a well-known p-type semiconductor presenting an appropriate absorption properties, favorable stability, and relatively high conductivity, and it is exclusively made of atoms abundant in the earth's crust. Recently, several different applications of $CuFeO_2$ were reported in the literatures such as anode material for batteries [10,12], active layer *p-n* heterojunction diodes [17,18], photocatalyst for the reduction of cadmium and carbon dioxide [19,20], and antiviral materials [21]. It was also investigated as photocathodes in photoelectrochemical cells for water splitting and hydrogen evolution reaction [22,23].

Several methods including solid state reactions [4,24], sol-gel techniques [25,26] and hydrothermal methods [27–30] were proposed to synthesize delafossite oxides $CuMO_2$. However, both the solid state reaction and sol-gel method need a post-treatment at high temperature (900–1200 °C). These energy intensive methods usually cause the crystal size of delafossite oxides around micron scale. To lower the vast energy consumed during the material synthesis, many works reported the preparation of delafossite oxides through hydrothermal method, and the synthesis temperature can be dramatically reduced to 300 °C or below [27–30]. The advantages of hydrothermal method compared with other techniques include low process temperature, low cost and rapid growth rates of crystals. But it still remains a great challenge to synthesize $CuFeO_2$ crystals by a low temperature

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method, especially desirable for obtaining nano-sized crystals. For example, M. M. Moharam and coworkers demonstrated hydrothermal synthesis of 3R-$CuFeO_2$ at 280 °C within 96 h, and the particle sizes around 1–5 μm [29]. M. Miyauchi and coworkers explored an even lower temperature hydrothermal synthesis of 2H-$CuFeO_2$ crystals at 180 °C within 24 h, but the crystal size was bigger than 4 μm [21]. Very recently, Melanie John and coworkers investigated a low temperature synthesis method to obtain pure delafossite $CuFeO_2$ (a mixture of 3R- and 2H-$CuFeO_2$) at 70 °C solely by precipitation and ageing, and the crystal size of $CuFeO_2$ around 200–400 nm [31,32].

In 2012, several groups including ours started to apply $CuMO_2$ nanocrystals (including $CuAlO_2$ [28,33], $CuCrO_2$ [34–39], $CuGaO_2$ [40–44], $CuFeO_2$ [45], $CuMnO_2$ [46] and $AgCrO_2$ [47]) as photocathode materials in photoelectric devices (such as dye-sensitized solar cells). Most of these delafossite oxides were prepared through a facile hydrothermal method, with the synthesis temperature around 200 °C. However, the disadvantage of low electrical conductivity usually lead to delafossite oxides based photoelectric devices displayed a poor performance, such as $AgCrO_2$ and $CuCr_{1-x}Ga_xO_2$ based dye sensitized solar cells [39,47]. A great deal of efforts have been focused on employing the impurity doping method to as increase the carrier density and mobility in recent years, which is desirable for controlling the electrical properties of delafossite oxides. [48–54]. It is already known that introduction of some divalent species (Ca or Mg) into the delafossite oxides could effectively increase the electrical conductivity of materials, such as $CuYO_2$ [48], $CuCrO_2$ [49,50], $CuAlO_2$ [51,52], $CuGaO_2$ [53], and $CuFeO_2$ [54]. In our earlier work, we first reported hydrothermal synthesis of $CuFeO_2$ crystals at 100 °C, and obtained a mixture of 3R- and 2H-$CuFeO_2$ nanocrystals with an average size of 100–300 nm [45]. Herein, we further synthesized Ca doped $CuFeO_2$ nanoplates ($100–400 \times 15–40\ nm^2$) with a 3 R structure through a single step hydrothermal reaction at 100 °C for 24 h. Moreover, the crystal phases and morphologies, chemical compositions and chemical states of elements, optical properties and Mott-schottky plots of these Ca doped $CuFeO_2$ nanoplates were studied in detail.

2. Experimental

2.1. Preparation of Ca doped $CuFeO_2$ nanoplates

All chemicals (analytical grade) in these experiments were purchased from Sigma Aldrich and used as received. Ca doped $CuFeO_2$ nanocrystals were prepared according to our previous hydrothermal procedure for Mg/Ga doped $CuCrO_2$ nanocrystals [36,39]. Typically, 15 mmol $Cu(NO_3)_2{\cdot}3H_2O$, 15x mmol $Ca(NO_3)_2{\cdot}4H_2O$ (x = 0, 0.05, 0.10) and 15 mmol $FeCl_2{\cdot}4H_2O$ were dissolved in 70 ml deionized water at room temperature. 4.40 g NaOH was added to the above solution and stirred for 10–20 min. Then, the solution was loaded into a 100 ml Teflon-lined autoclave. After the reaction was kept at 100 °C for 24 h, the obtained reddish brown precipitate was washed with deionized water and absolute alcohol in sequence for several times, and then stored in absolute alcohol solution. For Mott-schottky analysis, (Ca doped) $CuFeO_2$ films were prepared through a modified doctor blade method [55], and the paste was consisting of 0.50 g (Ca doped) $CuFeO_2$ nanocrystals and 10 ml absolute alcohol. Then the freshly obtained (Ca doped) $CuFeO_2$ films were dried on a hot plate at temperature of 100 °C for 1 h to remove the ethanol.

2.2. Materials characterization

Powder X-ray diffraction patterns were collected at room temperature by using a Panalytical X'pert Pro diffractometer (XRD, Cu Kα radiation). A field emission scanning electron microscope (FESEM, Hitachi, S4800) coupled with an energy dispersive X-ray spectroscopy (EDX) were used to observe the microstructure and to determine the composition of samples. The transmission electron microscope (TEM, Tecnai G2 F30) was employed to observe the microstructure of Ca doped $CuFeO_2$ nanocrystals. The surface chemical status was analysed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000), and the C (1s) line (at 285.0 eV) corresponding to the surface adventitious carbon (C—C line bond) has been used as reference binding energy. The UV-vis-NIR spectroscopy of films was recorded on a Perkin-Elmer UV/Vis spectrophotometer (UV-vis, model Lambda 750S) in the wavelength range of 200–800 nm. The Mott-Schottky curves were recorded by an electrochemical analyzer (CHI760E, Shanghai). The bias voltage for the Mott-Schottky measurements was scanned form −1.00 to 1.20 V vs. Ag/AgCl (saturated Ag/AgCl reference electrode) in dark at a frequency of 1000 Hz, using 1.0 M NaOH as the electrolyte.

3. Results and discussion

3.1. Hydrothermal synthesis of Ca doped $CuFeO_2$ nanocrystals

Ca doped $CuFeO_2$ nanocrystals were prepared via a similar hydrothermal method modified from our previous reports on the preparation of delafossite oxides [36,39,45]. Different reaction parameters like the Ca dopants (0, 5% and 10%) and the synthesis temperatures (100 °C, 120 °C and 140 °C) were examined to evaluate the effects on structural and morphology of $CuFeO_2$ crystals. Experimental details are summarized in Table 1.

The powder X-ray diffraction patterns of freshly obtained samples were collected at room temperature. Fig. 1 exhibits the diffraction peaks of undoped $CuFeO_2$ could be indexed as two structural polytypes of $CuFeO_2$, 3R-$CuFeO_2$ (JCPDS card No. 39-0246) and 2H-$CuFeO_2$ (*, JCPDS card No. 79-1546), respectively. Although both 3R- and 2H-$CuFeO_2$ have several similar diffraction peaks (located at 15.5°, 31.2°, and 65.1°.), we can identify these two crystal phases by the characteristic diffraction peaks located at 35.0° (2H), 37.6° (2H), 34.5°(3R), 35.7°(3R), and 40.2°(3R). The morphology of SEM image is consistent well with XRD result as shown in Fig. 2a. All $CuFeO_2$ crystals displayed hexagonal and rhombohedral morphologies, and the size for major crystal phases of 3R-$CuFeO_2$ was around 300–500 nm, which is similar to our earlier report [45]. More interesting, we got pure 3R-$CuFeO_2$ crystals after Ca doped, and the diffraction peaks of Ca doped $CuFeO_2$ could be indexed as pure 3R-$CuFeO_2$ (JCPDS card No. 39-0246) from Fig. 1. No impurity or 2H-$CuFeO_2$ could be detected. Furthermore, the lower intensity and broader width of diffraction peaks for Ca doped $CuFeO_2$, indicated the nano-sized crystal of these Ca doped $CuFeO_2$ samples. The SEM image in Fig. 2b confirmed the smaller size of 10% Ca doped $CuFeO_2$ in comparison to that of undoped one, although the uneven distributed crystal size ranged from 50 to 500 nm. The inset SEM image in Fig. 2b showed the typical size of 10% Ca doped 3R-$CuFeO_2$ with a length of 200–300 nm and a thickness of 20–30 nm. Moreover, the 5% Ca doped $CuFeO_2$ also displayed a typical morphology of delafossite structure with hexagonal plates, and the diameters of 5% Ca doped

Table 1
Details of the reaction conditions employed to synthesize Ca doped $CuFeO_2$ nanocrystals.

Ca dopant (%)	Temperature (°C)	NaOH (g)	Phase composition
0	100	4.40	2H-, 3R-$CuFeO_2$
5	100	4.40	3R-$CuFeO_2$
10	100	4.40	3R-$CuFeO_2$
5	120	4.40	3R-$CuFeO_2$
5	140	4.40	3R-$CuFeO_2$