



Preparation of p-type AgCrO_2 nanocrystals through low-temperature hydrothermal method and the potential application in p-type dye-sensitized solar cell



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ARTICLE INFO

Article history:

Received 10 February 2015

Received in revised form 9 April 2015

Accepted 11 April 2015

Available online 20 April 2015

Keywords:

Hydrothermal synthesis

p-type semiconductor

Delafossite oxide

Photocathode

Dye-sensitized solar cell

ABSTRACT

The synthesis of nano-sized ternary delafossite oxides with pure crystal phases is of great challenge. We present a novel hydrothermal method for the synthesis of AgCrO_2 nanocrystals with ultrafine size of 10–20 nm at relatively low temperature range (190–230 °C). It is the first time to report that AgCrO_2 nanocrystals can be hydrothermally synthesized at such a low temperature (190 °C) and applied as photocathode in dye sensitized solar cells (DSSCs). The as-synthesized AgCrO_2 nanoproductions, including their crystal phases, morphologies, element compositions, valence state information, thermal stability, electrical and optical properties, have been systematically studied. This facile method employed metal nitrates (AgNO_3 and $\text{Cr}(\text{NO}_3)_3$) as the starting materials and NaOH as the mineralizer, where $\text{Cr}(\text{NO}_3)_3$ undertook the dual functions of Cr^{3+} source material and weak reducing reagent. The in-situ oxidation–reduction reaction between Cr^{3+} and $\text{Ag}^+/\text{Cu}^{2+}$ during the hydrothermal crystal growth is the noteworthy feature of this general method. The crystal formation mechanism disclosed in the synthesis of chromium based delafossite oxides will certainly be benefit for the preparation of other delafossite oxides.

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1. Introduction

The crystal structure of delafossite oxides, deriving their name from the mineral CuFeO_2 , was first confirmed by Pabst in 1946 [1]. The delafossite structure is constructed from alternate layers of two-dimensional close-packed copper cations with linear $\text{O}-\text{Cu}^+-\text{O}$ bonds and slightly distorted edge shared Fe^{3+}O_6 octahedras [2]. To date, numerous delafossite oxides (AMO_2 , A = Ag or Cu, M = B, Al, Ga, In, Fe, Cr, Sc, Y, etc.) have been reported to serve important roles in diverse applications, such as photovoltaics, transparent photodiode, catalysts, batteries, ferroelectrics and so on [2,3]. The most attractive features of delafossite oxides should rest with their high p-type conductivity and optical transparency, which have been firstly discovered in CuAlO_2 by Hisono et al. and well explained by the “chemical modulation of valance band” theory [4]. Recently, several groups including ours started the applications of delafossite oxides nanocrystalline as the photocathode materials in p-type dye-sensitized solar cells (DSSCs), in

replacement of conventional NiO, and several successful examples include CuAlO_2 [5,6], CuGaO_2 [7–10] and CuCrO_2 [11–14]. As reflected in all of the previous works [10–14], size control of the delafossite nanocrystals are critical for the high performance of p-type DSSCs [15,16].

Generally, delafossite oxides powders could be prepared through high temperature solid-state reactions [17–19], cation exchange reactions [19–23], and hydrothermal synthesis [7–14]. However, it is very difficult to synthesize nano-sized crystals of delafossite oxides, which largely restricts their application fields. To the best of our knowledge, only a few literatures focused on the synthesis of nano-sized delafossite oxides; the successful examples are not exceeding CuAlO_2 [24], CuGaO_2 [7–10,25] and CuCrO_2 [11–14,26]. Though, more copper based delafossite oxides (CuAlO_2 , CuCrO_2 , CuFeO_2 , CuScO_2 and so on) could be synthesized readily via high temperature solid-state reactions under N_2 or Ar atmosphere at 800–1200 °C [2], avoiding the valence for the monovalent copper (Cu^+) being oxidized into bivalent Cu^{2+} , the higher temperature usually led to excessive growth of big delafossite crystals. Compared with the copper based delafossites, the synthesis of silver based delafossites is even more difficult. The related reports

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for the synthesis of silver based delafossite oxides are much fewer. The inherent cause is suggested to derive from the fact that, the simple binary oxide of silver (Ag_2O) is easy to decompose at a temperature of $\sim 300^\circ\text{C}$, which limits the preparation of silver based delafossites through solid-state reactions. Therefore, it becomes a reasonable choice to synthesize silver based delafossite oxides at low-temperature and/or closed reaction systems [2,27]. For example, AgCrO_2 crystals with an average size of around $1\ \mu\text{m}$ have been synthesized through cation exchange reactions, by heating LiCrO_2 , KNO_3 and AgNO_3 at 350°C in an evacuated silica tube for 4 days [19,21]. Recently, AgCrO_2 crystals with an average size of $2\ \mu\text{m}$ have been prepared under a critical hydrothermal condition (400°C , $40\ \text{MPa}$) [27]. Note that, those reported processes are complicated and include tough conditions; to synthesize nano-sized silver based delafossite oxides still remains as great challenge.

In this work, delafossite AgCrO_2 nanocrystals with ultrafine sizes of $10\text{--}20\ \text{nm}$ have been synthesized for the first time via a low temperature hydrothermal method, and its potential as photocathode in p-type DSSC has been primarily examined. The synthesis parameters effecting on the crystal phases and morphologies have been studied. The element composition and valence state information, thermal stability, electrical and optical properties of AgCrO_2 nanocrystals have been systematically investigated. At last, a general crystal formation mechanism for the hydrothermal synthesis of chromium based delafossite oxides (AgCrO_2 and CuCrO_2 nanocrystals) based on the in-situ oxidation–reduction reactions have been proposed.

2. Experimental section

All of the chemicals in these experiments without special notification were purchased from Sigma Aldrich with analytical grade and used without further purification. In a typical hydrothermal synthesis, certain amounts of reactants were dissolved in deionized water, and the obtained solution was transferred into a Teflon-lined autoclave. The sealed autoclave was maintained at $190\text{--}230^\circ\text{C}$ for reaction. After the reaction finished, the autoclaves were naturally cooled to room temperature. Finally, the obtained precipitate was washed for several times in a centrifugal cleaning machine and was finally stored in absolute alcohol solution for further use.

Powder X-ray diffraction patterns were collected at room temperature by using a Panalytical X'pert Pro diffractometer (XRD, $\text{Cu K}\alpha$ radiation). A field emission scanning electron microscope (FESEM) system (Hitachi-S-4800) coupled with energy dispersive X-ray spectroscopy (EDX) and a transmission electron microscope (FETEM, Tecnai G2 F30) were used to observe the microstructure and determine the composition of the as-synthesized nanocrystals. The thermal stability of nanocrystals was investigated by a differential scanning calorimeters-thermo gravimetric analyzer (DSC-TG, Diamond TG/DTA, Perkin–Elmer Instruments), these samples were heated in air from room temperature to 800 or 1000°C at a heating rate of $10^\circ\text{C min}^{-1}$. The ultraviolet–visible–near infrared (UV–vis–NIR) spectra of films were recorded on a Perkin–Elmer UV/Vis spectrophotometer (UV–vis, Model Lambda 950) in the wavelength range of $300\text{--}800\ \text{nm}$. Hall effect measurements were done on a Hall effect analysis system (Accent HL 5500 PC), of which the samples were prepared by the powder pellet method, using Ag coating at four contact points to decrease the contact resistance. X-ray photoelectron spectroscopy measurements (XPS) were performed with a physical electronics surface analysis equipment (Model PHI 5600), and the C (1s) line (at $285.0\ \text{eV}$) corresponding to the surface adventitious carbon (C–C line bond) has been used as the reference binding energy. By using a mask with a size of $4.5 \times 4.5\ \text{mm}^2$ to prevent the scattering of light, the solar cells were tested using a solar simulator with an AM 1.5 G filter (Oriel, model 91192) at a light intensity of $100\ \text{mW cm}^{-2}$, and calibrated using a standard silicon reference cell.

3. Results and discussion

3.1. Hydrothermal synthesis of AgCrO_2 nanocrystals

AgCrO_2 nanocrystals were prepared similarly to our previously hydrothermal procedure for $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ ($x = 0, 0.05, 0.10$) [11,12]. At first, $15\ \text{mMol Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $15\ \text{mMol AgNO}_3$ were dissolved in $70\ \text{ml}$ deionized water at room temperature, $2.40\ \text{g}$ NaOH was added to the above solution and stirred for $10\ \text{min}$.

After reaching a homogeneous state, the solution was loaded into a $100\ \text{ml}$ Teflon-lined autoclave, which was sealed and maintained at $190\text{--}230^\circ\text{C}$ for $60\ \text{h}$. After the reaction finished, the obtained yellow green precipitate was washed with diluted nitric acid, deionized water and absolute alcohol in sequence for several times, and then stored in absolute alcohol solution. Finally, about $2.0\ \text{g}$ nano-sized AgCrO_2 product could be gained from each reaction.

Fig. 1 shows the XRD patterns and morphologies of AgCrO_2 nanocrystals prepared at different reaction temperature (190°C , 210°C and 230°C). Fig. 1a shows that all of the diffraction peaks can be indexed to delafossite AgCrO_2 (JCPDS File Card No. 70-1703) with the hexagonal $R3m$ crystal structure, and no impurity phase can be detected. The full width at half maximum of the XRD patterns becomes wider as the reaction temperature decreases, which reflects the crystal size decreases. By applying the Scherrer equation to the broadened diffraction peaks, the average crystal sizes at different synthesis temperatures of 190°C , 210°C and 230°C were calculated to be $18.4\ \text{nm}$, $15.9\ \text{nm}$ and $14.1\ \text{nm}$, respectively. This result is consistent with their corresponding SEM and TEM images in Fig. 1b–d. From TEM images, the nanocrystals are with the hexagonal nanoplates morphology. The observed diameters of the nanoplates obtained at 230°C , 210°C and 190°C are $15\text{--}50\ \text{nm}$, $15\text{--}30\ \text{nm}$ and $10\text{--}30\ \text{nm}$, respectively, while their thicknesses are much thinner. From these, it is known that the decreased reaction temperature leads to slower crystal growth rate, and therefore smaller crystal size of the nano-products.

Furthermore, the SEM–EDS mapping results of AgCrO_2 nanocrystals are shown in Fig. 2, to reduce the measurement errors caused by absorption of water molecules on the sample surface, the AgCrO_2 was analyzed after annealing at 120°C for $2\ \text{h}$ in vacuum. It can be observed that all of the Ag, Cr and O elements are homogeneously distributed (Fig. 2a–c), the elementary percentages of Ag ($25.75\ \text{at.}\%$), Cr ($26.88\ \text{at.}\%$), O ($47.37\ \text{at.}\%$) are nearly consistent with their source materials' concentrations in the hydrothermal precursor and close to the stoichiometric proportion of AgCrO_2 (Ag: Cr: O = 1: 1.04: 1.84, see Fig. 2e). In addition, the elemental chemical states of the AgCrO_2 crystals have been investigated by XPS. The corresponding results are shown in Fig. 3. The peaks located at near $368.5\ \text{eV}$ (Ag 3d 5/2) and $373.9\ \text{eV}$ (Ag 3d 3/2) shown in Fig. 3a confirm the monovalent state of silver element (Ag^+) in the samples [20]. The peaks located at near $576.3\ \text{eV}$ and $585.8\ \text{eV}$ (Fig. 3b) are corresponding to the binding energies of Cr 2p 3/2 and Cr 2p 1/2, which confirm the trivalent state of chromium element (Cr^{3+}) in the samples [12,26].

3.2. Thermal stability of AgCrO_2 nanocrystals

From the thermogravimetric (TG) curve shown in Fig. 4a, the initial weight losses of AgCrO_2 samples are suggested to be due to the evaporation of chemically combined water of crystallization and the variation of oxygen vacancy in the sample. The sharp mass decrease from the temperature of above 400°C should be due to AgCrO_2 decomposition in air at the temperature. Fig. 4b shows the diffraction patterns of AgCrO_2 samples sintered in air at 350°C , 400°C , 500°C , and 550°C for $1\ \text{h}$, respectively. The diffraction peaks of the AgCrO_2 powder sintered at 350°C should be identified as pure AgCrO_2 crystal phase; whilst for the AgCrO_2 powder sintered at 550°C , the diffraction peaks owing to the newly generated by-products of Ag (JCPDS File Card No. 65-8428) and Cr_2O_3 (*, JCPDS File Card No. 38-1479) could be clearly identified. The appearance of Cr_2O_3 inside the AgCrO_2 powders sintered at the temperatures of $>400^\circ\text{C}$ suggests that the decomposition of AgCrO_2 occurs. This phenomenon is consistent well with the TG analysis result. It is suggested that the following chemical reaction

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