



Preparation and properties of mixed metal oxides based layered double hydroxide as anode materials for dye-sensitized solar cell



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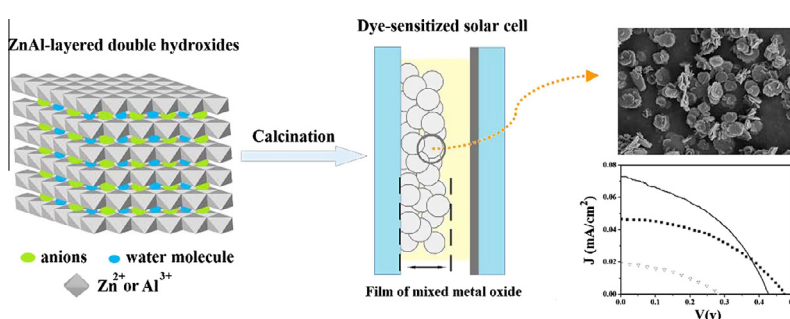
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HIGHLIGHTS

- Prepare the DSSC using the ZnAl-LDH as the precursor.
- Mixed metal oxides based LDH were used as anode materials of the DSSC.
- The band gap of the MMO from ZnAl-LDH is similar to that of the pure ZnO.
- The specific surface area of MMO is slightly lower at high calcinated temperature.
- The best efficiency of the corresponding solar cells was 0.0129%.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a new simple approach has been developed for the preparation of anode materials for dye-sensitized solar cell by a facile calcination method using the layered double hydroxide (LDH) as a precursor. The ZnAl-LDH with molar ratio Zn:Al = 3:1 is prepared by urea method. The mixed metal oxides (MMO) are prepared by calcining the LDH at different temperatures and a series of dye-sensitized solar cells (DSSC) are assembled by the corresponding oxides and the dye Ruthenizer 535-bisTBA (N719). The basic parameters are investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric and differential thermal analysis (TG-DTA), nitrogen sorption analysis and UV-Vis absorption spectrum. The band gap of the MMO (about 3.13 eV) obtained from ZnAl-LDH is similar to that of the pure ZnO (about 3.2 eV). The photovoltaic behaviors of solar cells are characterized and the best efficiency is 0.0129% when the calcining temperature is 500 °C.

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1. Introduction

The layered double hydroxides (LDH) are a large class of important layered anionic clays with two metallic ions, which octahedrally coordinated in the sheets. The LDHs are generally formulated as $[M_1^{II}_x M_2^{III}_x (OH)_2] (A^{n-})_{x/n} \cdot mH_2O$ (where M^{II} and M^{III} represent divalent and trivalent metallic ions, respectively; A is

interlayer anion; $n-$ is charge on interlayer ion) [1–3]. The net positive charges, due to the existence of divalent and trivalent ions in the brucite-type layers, are balanced by the intercalation of interlayer anions [4–6]. LDH particles usually consist of small crystalline plates [7,8]. Thanks to the diversity of the gallery anions LDH shows many promising properties for a wide range of applications, such as degradation of environmental pollutants, photo-response, photo catalysts and drug delivery [9–13].

The increasing concern about detrimental environmental impacts related to the use of fossil fuels has aroused the

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development of alternative renewable energy sources [14,15]. Thermal treatment of LDH can lead to the collapse of the layered structure and the formation of the mixed metal oxides (MMO) with high specific surface area. The MMO has garnered great interests as a promising visible light photocatalyst for solar energy conversion and it also shows the applications for lithium-ion batteries due to its high specific surface area [10,16–18]. With the well-established synthesis methods of LDH, finely dispersed bimetal oxides can be obtained from the LDH by calcination because of the uniform distribution of the cations in the brucite layers of LDH. The MMO is considered to be a good electrode material to make the dye-sensitized solar cell (DSSC) because it has similar injection efficiency, photoresponse and band gap energy as ZnO and TiO₂, the most widely used model electrode materials for the DSSC [19]. The MMO shows great potential in manufacture on a large scale because of the low cost, high purity and good quality control [20–22]. This manuscript presents the preparation and photovoltaic application of the MMO derived from calcination of ZnAl-LDH, it will become a new approach for the preparation of anode materials for the DSSC by a facile calcination method using the LDH as a precursor.

2. Experimental

2.1. Preparation of the ZnAl-LDH

The ZnAl-LDH was prepared by the urea decomposition method [23,24]. The molar concentration of the Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O solution is Zn²⁺ + Al³⁺ = 0.15 M and the molar ratio of the Zn²⁺ to Al³⁺ is 3. The salt solution was mixed with the urea solution under the condition that [urea]/[NO₃⁻] is 3. The obtained mixture will be heated in a three-neck flask for 24 h at 100 °C. The formed solids were filtered, washed by the deionized water and dried at 80 °C for 24 h. All chemicals were purchased from Sinopharm Group Co., Ltd. and were used directly without any further purification.

2.2. Preparation of the MMO

The dried ZnAl-LDH was grinded in a silica mortar and calcined in a muffle furnace with a heating rate of 5 °C/min to the target temperatures (500 °C, 600 °C and 700 °C, respectively), after which the temperature was maintained for 60 min, and then naturally cooled down to room temperature. The MMOs obtained at different calcination temperatures (500 °C, 600 °C and 700 °C) were designated as ZA-500, ZA-600 and ZA-700, respectively, they were grinded in an agate mortar before further characterizations.

2.3. Preparation of DSSC

In our experiment, the freshly-cleaned transparent conductive glass (FTO) was used as the electrode and the Pt electrode was used as the counter electrode. A paste of composite oxides (working electrode, 10 wt%) was obtained by dispersing the corresponding MMO in an ethylcellulose/terpineol solution [25]. The paste layer (0.5 cm × 0.5 cm) spread onto FTO was sintered in a muffle furnace at 450 °C for 30 min. After being cooled down to 50 °C, the film was immersed into the dye solution for 24 h. The commercial dye Ruthenizer 535-bisTBA (N719, from Solaronix) was used here as the sensitizing agent. The molar concentration of the dye solution which was used for preparing the solar cells was 5 × 10⁻⁴ mol/L. The electrode was then assembled with the counter-electrode using the double-sided adhesive polymer film that acts as the separator and sealing element. The two electrodes were held together by hot melting the adhesive polymer film at 120 °C while applying

gentle pressure to the electrodes. Electrolyte solution (0.5 M lithium iodide, 0.05 M iodine and 0.4 M 4-tert-butylpyridine in acetonitrile) was fully absorbed into the electrodes by capillarity.

2.4. Characterization

The XRD patterns were recorded using a Rigaku D/MAX-rA X-ray diffractometer with Cu K α radiation ($\gamma = 0.15418$ nm). The samples were scanned for 2θ values ranging from 3° to 70° with a scan speed of 1°/min. The optical measurements were performed using a UV–vis diffuse reflectance spectrophotometer (Shimadzu, UV-2550) with the integration sphere diffuse reflectance attachment. Thermogravimetric and differential thermal analysis (TG–DTA) were carried out in air using a SDTQ600 comprehensive thermal analyzer with a heating rate of 10 °C/min. Micro-morphology was obtained with an S-4800 high resolution scanning electron microscopy (SEM). The textural properties of MMO obtained at different calcination temperatures were investigated by the nitrogen sorption analysis using a Quadrasorb SI-MP system (Quantachrome, USA). The Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distribution and the specific surface areas of the MMOs are calculated by the BET method. The photovoltaic behavior was characterized under simulated AM 1.5 sunlight with an output power of 100 mW/cm⁻² using a Solar Simulator (Solsim, Luzchem Research) with a 300 W Xenon Lamp Power Supply (XE300BF, Luzchem Research) as the light source.

3. Results and discussion

Fig. 1(a) illustrates the XRD pattern for the ZnAl-LDH. The XRD pattern showed the basal peaks of planes hkl (003) and (006) and non-basal peaks (012), (015), (018), (110) and (113) similar to the brucite structure Mg(OH)₂, in consistent with the typical structure of LDH. Fig. 1(b) shows that the peaks of ZnAl-LDH fully disappeared after calcination. The calcination of the LDH samples resulted in the MMOs with strong peak reflections of the ZnO (JCPDS No. 89-1397), and it also shows the weak peak reflections of ZnAl₂O₄ (JCPDS No. 05-0669). This fact clearly presents that the heat treatment destroys the layered structure of the ZnAl-LDH and the crystalline phase of the LDH converted to the ZnO and ZnAl₂O₄. The diffraction peaks of ZnO in ZA-700 sample were much sharper than those of ZA-500, which indicates a higher crystalline of ZnO was obtained at a high temperature. From Fig. 1(b), the diffraction peaks of the ZnAl₂O₄ can be discerned at 700 °C. It was found that the reflections of the ZnAl₂O₄ spinel structure became visible when the ZnAl-LDH was treated at 600 °C [23]. As the formation of the ZnAl₂O₄ in the MMO will decrease the efficiency of the DSSC due to its low electronic mobility, the calcination temperature higher than 700 °C was not used in this study.

The UV–vis absorption spectra of ZA-500, ZA-600, and ZA-700 are shown in the Fig. 2(a). Each MMO shows a strong UV absorbance band when the wavelength is less than 400 nm, which is the characteristic band gap of the ZnO and ZnAl₂O₄. This result supports our analysis of XRD patterns above. The UV–vis absorption spectra shows redshift indicating that the composition of the MMOs changed when the calcining temperature increased from 600 °C to 700 °C. All the MMOs exhibited a band gap of about 3.13 eV, which is similar to the band gap of the titanium oxide and zinc oxide (3.2 eV) [25,26].

Fig. 2(b) shows the TG–DTA curves of ZnAl-LDH. The weight loss before 180 °C (10%) corresponds to the removal of water from the surface and the interlayer, where the first endothermic peak around 115 °C is caused by removal of water from interlayer and external surface and the second sharp endothermic peak at 180 °C is due to the decomposition of carbonate anions and the

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