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$CuAlO_2/TiO_2$ heterojunction applied to visible light H_2 production

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Abstract

$CuAlO_2/TiO_2$ heterojunction was prepared and studied for its potential application as dispersed photoelectrode capable to generate H_2 under visible light. Transport properties of delafossite $CuAlO_2$, i.e. thermoelectric power and electrical conductivity were studied and correlated to an optical and photoelectrochemical characterization to establish energetic diagram of the heterosystem $CuAlO_2/TiO_2$. The valence and the conduction bands were estimated to be respectively of −0.05 and of −1.34 V/SCE, which permit electron injection from activated $CuAlO_2$ to an activated TiO_2. This fact permitted a physical separation of charge carriers. Photocatalytic experiment performed using S^{2-} and $S_2O_3{}^{2-}$ showed efficiency respectively of 5265 and 60 μmol and then after 40 min of irradiation by visible light. The ideal heterojunction composition was $CuAlO_2$ (300 mg)/TiO_2 (75 mg). In all cases, the heterosystem was found to be more efficient than $CuAlO_2$ alone whatever the conditions. The optimal pH value was estimated to be of 11.

Keywords: Heterojunction; $CuAlO_2$; TiO_2; H_2-photoproduction; Delafossite

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1. Introduction

Solar hydrogen production using semiconductor (SC) materials continue to attract much attention since the first reports on this innovation in the beginning of the 1970s [1–3]. As it is well admitted, hydrogen energy is one of the most serious candidates to replace the fossil fuel [4]. In addition, hydrogen is renewable, it possesses one of the highest energy capacity per unit mass and does not produce any pollutant during combustion [5]. The development of water photoelectrolysis technology is intimely connected to the development of materials [6]. Two types of materials are usually used for such applications: (i) wide band gap SC such as TiO_2, which has the advantage of high stability toward photocorrosion and can split water simultaneously into H_2 and O_2. However, they absorb only the UV light and are of little practical use in regard to solar emission, which contain less than 4% of UV irradiation. (ii) Narrow band gap SC such as CdS absorbs visible light and is very attractive for solar energy conversion. Nevertheless, this type of SCs has commonly a subject of photocorrosion and is challenged to be stabilised for long term of utilisation in aqueous electrolytes.

Recently, very interesting SC crystallizing in the delafossite structure ($CuAlO_2$) has been developed for solar to hydrogen conversion under visible light [7]. $CuAlO_2$ is a very stable material, even in strong acidic electrolytes such as HCl, $HClO_4$ or aqua regia and then for long periods of time. Preliminary investigations of $CuAlO_2$ properties and photocatalytic performance showed that this material is able to generate hydrogen under visible light. However, their performances remain moderated and suffer of a charge carrier lost by recombination and then even by using holes scavenger such as S^{2-} or $S_2O_3{}^{2-}$ [7].

Noble metal or noble metal oxide such Pt, Au, Ag and RuO_2 are commonly used to prevent charge carrier recombination by their act as electron accumulators which facilitate charge separation and electron transfer [8–10]. However, it should be noted that these materials are costly and they are not easily recovered after use. Recently, some heterojunctions based on the coupling of narrow and wide band gap SCs have been developed [11,12]. The synergy between the properties of each group of materials resulted on an increasing of photocatalytic activity of composite materials under visible illumination [13,14]. The physic that takes place for this photoelectrode configuration can be applied for an oxidation process (advanced oxidation process (AOP)),

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as well as for a reduction process (H_2 photoproduction from water).

The aim of this work is to progress our knowledge on some physico-chemical properties of $CuAlO_2$ and to improve its photocatalytic performance by their use in the presence of TiO_2.

2. Experimental

2.1. Heterojunction preparation

$CuAlO_2$ was prepared by dissolving stoichiometric amounts of $Al(NO_3)_3\cdot 9H_2O$ (Merck, >98%) and CuO (Riedel-deHaën, 98%) in concentrated HNO_3 solution. The obtained solution was dehydrated by heating over flame until it became a black precipitate. After grinding in mortar, the powder was calcined at 900 °C for 18 h. TiO_2 was purchased from Degussa (TiO_2-P25) and used as received. The heterojunction $CuAlO_2/TiO_2$ was obtained by directly mixing both catalysts during photocatalytic experiment.

2.2. Materials characterization

Powder X-ray diffraction (XRD) patterns of $CuAlO_2$ and TiO_2 were obtained with a Philips diffractometer equipped with a monochromated high intensity Cu Kα in the scan range 2θ between 20° and 80°.

Absorption and reflectance spectra of pure SCs were recorded with a Cary 500 UV-VIS-NIR spectrophotometer equipped with an integrated sphere. $BaSO_4$ was used as a reference to measure all samples. The spectra were recorded at room temperature in air in the range of 300–2000 nm enabling the study of the spectral properties of these materials.

The transport properties of $CuAlO_2$ were studied by measuring the dc electrical resistivity ρ by the two-terminal method and the thermopower data S ($=\Delta V/\Delta T$) were obtained using an equipment described elsewhere [15]. $CuAlO_2$ was used in the form of compactness-sintered pellets heated in the same conditions as their preparation. A compactness of 83% was obtained.

Electrochemical measurements were performed in 1 M KOH (pH 13) using a “three electrode device”: the $CuAlO_2$, a large platinum counter electrode and a saturated calomel reference electrode (SCE) to which all potentials were quoted. The electrolyte was continuously flushed with pure nitrogen gas. The intensity–potential $J(V)$ characteristics were recorded with a PRT 20-2X Tacussel potentiostat. A 200 W Oriel (model 66183) tungsten–halogen lamp was used as a light source. The light intensity of 74 mW cm^{-2} was estimated by a light-meters to attain the surface of the working electrode.

Photocatalytic experiments were carried out in a closed system equipped with a Pyrex double wall reactor connected to a thermostatic bath, whose temperature was fixed at 50 ± 0.1 °C. The closed system was connected to a water manometer. The detailed assembly was reported previously [16]. Typically for each experiment, powder catalyst is suspended by magnetic stirring in 200 ml of aqueous S^{2-} or $S_2O_3{}^{2-}$ (0.025 M) solution and submitted to three tungsten lamps each one of 200 W. Prior to irradiation, the mixture is flushed with N_2 for 30 min to remove dissolved oxygen from the electrolyte. Qualitative H_2 identification has been made using gas chromatography techniques in which a molecular sieve 13× column and an Ar as gas carrier were used.

3. Results and discussion

The X-ray powder pattern of $CuAlO_2$ revealed a well-crystallized single phase with the space group $R3m$, according to the JSPDS No. 35-1401. The unit cell parameters ($a = 0.2855$ nm and $b = 1.6947$ nm) are in good agreement with our previous results [7]. The crystallite size was determined according to the Scherrer equation using the full-width at half-maximum (FWHM) of the peak presenting the highest intensity (0 2 1). The crystallite size was estimated to be 29 nm. This value is smaller than that obtained for $CuAlO_2$ prepared by a solid-state reaction at 1150 °C [7]. The XRD pattern of commercial TiO_2-P25 reveled, as it is well known a mixture of anatase and rutile phases with a major composition on anatase.

Diffuse reflectance spectroscopy was used to determine the optical properties of pure $CuAlO_2$. Indeed, the band gap was determined by plotting $(\alpha h\nu)^n$ versus $h\nu$ and extrapolating the linear portion which intercept the energy axes $h\nu$. α is the absorption coefficient, which depend on the wavelength, n can take the value 1/2 or 2, respectively, for indirect and direct optical transition. It should be noted that α is proportional to $\ln[(R_{\max} - R_{\min})/(R - R_{\min})]$, where reflectance decreased from $R_{\max}$ to $R_{\min}$ due to the semiconductor absorption. R is the intermediate for any intermediate energy photons [17]. As presented in Fig. 1, indirect optical transition was observed at 1.29 eV and corresponds to the band gap energy. This value is inferior to that observed by others by about 0.4 eV [7,18] probably due to the decreasing of the particle size, generated from the preparation method which can induce an optical shifting of the band gap [19]. This result suggested that $CuAlO_2$ (1.29 eV) is more adequate for solar light harvesting contrary to TiO_2, which possesses a band gap of 3.2 eV as it is well known.

The study of the thermopower effect demonstrates that $CuAlO_2$ is p-type SC due to the positive coefficient $S_{303\,K}$

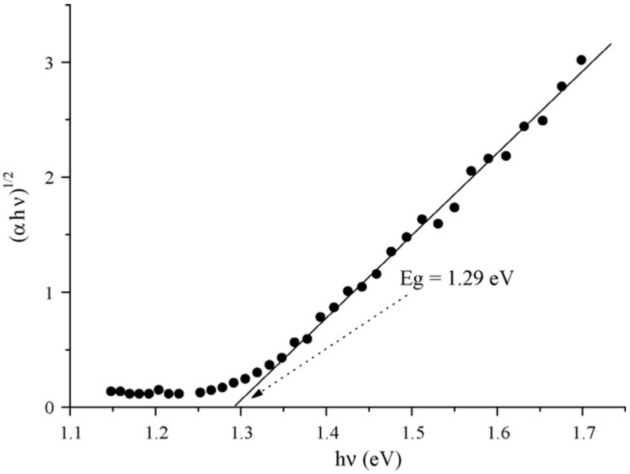

Fig. 1. Indirect band gap transitions of $CuAlO_2$.