The Cu²⁺ reduction and H₂ evolution on the hetero-system CuFeO₂/ZnO under visible light

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Received: 28 March 2019 / Accepted: 30 April 2020 / Published online: 12 May 2020
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Abstract

The hetero-system CuFeO₂/ZnO was successfully used in the Cu²⁺ reduction under visible light irradiation; it was conducted with varying some important factors such as the initial Cu²⁺ concentration, mass ratio CuFeO₂/ZnO and light flux. The Cu²⁺ reduction obeys to a first-order kinetic with a half-life of 60 min. The regression in the reduction rate over time is due to the competitive hydrogen evolution. Indeed, the electrons are transferred to water via Cu²⁺ clusters. Also as application, the H₂ evolution is successfully achieved with an evolution rate of 3.42 μmol (g catalyst)⁻¹ min⁻¹ and a quantum yield of 0.5%. The hydrogen is facilitated through generated bifunctional hetero-system because of the low H₂ overvoltage on copper.

Keywords CuFeO₂/ZnO · Cu²⁺ reduction · Hydrogen · Visible light · Hetero-system · Photocatalysis

Introduction

The mankind is living in an environment with toxic compounds including heavy metals (Tack et al. 2017; Boulaiche et al. 2019). They are fatal for the human health, and the World Health Organization (WHO) has drastically reduced their concentrations in water (Liang et al. 2015). Unlike organic molecules, metals are persistent and non-biodegradable; they appear in water through industrial activities and accumulate in living organisms. Therefore, their elimination is a concern worldwide and the effluents must be treated at the source before being released in the aquatic medium.

Conventionally, the treatment includes physical methods such as the ions exchange, reverse osmosis, adsorption and

electro-reduction (Abbas et al. 2014; Azoudj et al. 2018; Quibén et al. 2018; Yeddou Mezenner et al. 2017). However, such methods remain high cost and some of them are inefficient at low concentrations. Therefore, an effective treatment is required and the photocatalysis provides an efficient method for the water depollution (Bagtache et al. 2018). The technique is based on the excitation of a semiconductor (SC) by energetic photons ($h\nu > E_g$), E_g being the optical gap. The generated electron/hole (e^-/h^+) pairs are used to degrade organic pollutant via radicals O₂^{·-} and 'OH and/or to reduce water to hydrogen (Bagtache et al. 2016) and metals ions into less harmful forms (Cherifi et al. 2019; Saïen and Azizi 2015). The subject is pertinent to the environmental protection, and one of the challenges in photo-electrochemical (PEC) devices is the reduction of the material cost. In this respect, the delafossites Cu⁺M³⁺O₂, where *M* denotes 3*d* metal, have attracted a great deal of attention as photocatalysts (Bellal et al. 2009), and among the candidates, CuFeO₂ absorbs over the whole solar spectrum and is water resistant (Omeiri et al. 2008; Bassaid et al. 2009). In addition, Fe is attractive with regard to toxicity concern. On the other hand, copper is an oligo-element but becomes toxic above a threshold concentration of 1 ppm.

The photoactivity is a surface phenomenon and depends on the morphology of the powder. Large active surfaces are needed for low polaron oxides like CuFeO₂ because of the low diffusion length of the minority carriers (Bassaid et al. 2009). On the other hand, the photocatalytic performance

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13201-020-01220-4>) contains supplementary material, which is available to authorized users.

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can be significantly improved on hetero-systems because they produce an optimal band bending at the interface semiconductor/electrolyte (Derbal et al. 2008; Qin et al. 2019). Hence, the visible light is not converted with ZnO and affords a poor PEC activity but ZnO can be used as Electron Bridge between CuFeO₂ and Cu²⁺ and favors the separation of (e⁻/h⁺) pairs. Moreover, ZnO has attracted a great attention as window material owing to its light transparency for the visible light.

Herein, we prepared for the first time the hetero-system CuFeO₂/ZnO by nitrate route. We report for CuFeO₂ and ZnO the flat band potential (E_{fb}), the chemical stability, the optical gap and the position of their conduction bands. These characterizations make it possible to draw the energetic diagram of CuFeO₂/ZnO which was used for the Cu²⁺ reduction. Many parameters are studied like the initial Cu²⁺ concentration, the mass ratio of CuFeO₂/ZnO, stirring speed and light intensity. Also the tri-functional system CuFeO₂/ZnO/Cu was evaluated for the hydrogen production under visible light.

Experimental

The preparation procedure of CuFeO₂ was reported elsewhere (Omeiri et al. 2008). ZnO is prepared by dehydration and denitrification of Zn(NO₃)₂·6H₂O (Panreac, 98%) at 200 °C; then, the powder is heat-treated at 400 °C. The phases were identified by X-ray diffraction (XRD) using Cu K_α radiation ($\lambda = 0.15406$ nm).

The optical gap was determined by using a Jasco V-650 spectrophotometer attached to an integrating sphere. The data were collected in the range (190–900 nm), and BaSO₄ was used as standard.

CuFeO₂ pellets pressed under a pressure of 5 kbar and sintered at 950 °C exhibit a density of ~80%. A copper wire was attached to the back pellet with silver cement to insure an ohmic contact. The pellet was enrobed in a glass tube with epoxy resin leaving a cross section of 0.5 cm². The electrode was polished with alumina paste and thoroughly washed with distilled water. The electrochemical study was conducted in a standard cell; the emergency electrode consists of a platinum flag sealed in a soft glass and cleaned in HNO₃ (65%). The potential of the working electrode was monitored by a PGZ 301 potentiostat (radiometer analytical); it was given with respect to a saturated calomel electrode (SCE) and uncorrected for the junction potentials. Because of the *p*-type behavior of CuFeO₂, the potential was ramped from +1 V toward cathodic direction at a scan rate of 5 mV s⁻¹ in CuSO₄ electrolyte.

The photocatalytic tests were done in a double-walled reactor (500 mL total capacity) at atmospheric pressure; the temperature was regulated at 25 °C. Typically, 200 mg of the

catalyst was dispersed in 200 mL of Cu²⁺ solution, prepared from CuSO₄ (Merck). The amount of adsorbed Cu²⁺ was evaluated by titration after keeping the powder in solution overnight. A tungsten lamp (200 W, Sonelec, Algeria) with a maximum emission at 620 nm was used as light source. The aliquots were removed at regular time intervals, and the precipitate was separated by centrifugation (5000 rpm, 15 min). The aliquots were withdrawn at periodic time for the Cu²⁺ titration. After vigorous centrifugation, the analysis was carried out by inductively coupled plasma (ICP, Varian Vista-Pro-CCD and Simultaneous ICP-OES). The concentration was determined by interpolation from a calibration plot.

Evolved hydrogen was evaluated volumetrically; hydrogen rises to the top of the vial and displaces the solution up the graduate tube. Distilled water (~0.8 Ω cm) was used in all experiments.

Results and discussion

The co-precipitation has succeeded in the synthesis of homogeneous delafossites; the technique consumes less energy and time and produces submicron-sized grains with increased active surface areas (Omeiri et al. 2008). The heat treatment gave a dark phase and CuFeO₂ nano-crystallites (~40 nm) were obtained from the full width t half maxim (FWHM). All XRD peaks are assigned to CuFeO₂ (Fig. 1) and indexed in a hexagonal structure (SG: R $\bar{3}m$), JCPDS card N° (39-0246) with the cell constants: $a = 303.3$ nm, $c = 1713.6$ nm. The structure defects affect the electrical properties, and the delafossites exhibit *p*-type SCs because of the oxygen incorporation in the layered crystal lattice (Abdi et al. 2018).

ZnO obtained from nitrate decomposition crystallizes in the wurtzite structure with a hexagonal symmetry (SG: P 6 $\bar{3}mc$); the lattice constant, $a = 0.324552$ nm, $c = 0.520640$ nm, agree with the JCPDS N° 36-1451 as shown in inset (Fig. 1). The gap (E_g) of CuFeO₂ (Fig. 2) is determined from the diffuse reflectance spectrum by using the Pankov relation (Kabouche et al. 2017)

$$(\alpha h\nu)^m = \text{Const} \times (h\nu - E_g), \quad (1)$$

where m is equal to 0.5 and 2 for indirect and direct allowed transition, respectively. The oxide is a narrow band gap semiconductor with E_g value of 1.32 eV, close to the optimal value for the solar energy conversion and assigned to *d*–*d* transition of Cu⁺ linearly coordinated. The potential of photoelectrons in the conduction band (-0.92 V_{SCE}) is negative enough to reduce Cu²⁺ into elemental state. ZnO has band gap energy of $E_g = 3.2$ eV (Helaïli et al. 2010) and is active under visible light, but its spectral photoresponse is extended to visible region in the hetero-system.

Fig. 1 The XRD pattern of ZnO prepared by chemical route. Inset: the pattern of the delafossite CuFeO₂ synthesized by co-precipitation

Fig. 2 The direct optical transition of CuFeO₂

The photocatalysis needs not only a gap of ~ 1.5 eV but also a matching of electronic bands with the redox couples. In this respect, the energy electronic bands are determined from the capacitance measurements. The dark current is low, and the capacity of the space charge region gives an accurate value of the flat band potential (E_{fb}). The value of -0.71 V obtained for ZnO is provided from the intercept of the potential-axis at $C^{-2}=0$ of the capacitance given by the relation (Fig. 3b):

$$C^{-2} = (2/\epsilon\epsilon_0 N_D) \{E - E_{fb} - kT/e\}. \quad (2)$$

Fig. 3 **a** The Mott–Schottky plots in Na₂SO₄ (0.1 M, pH $\sim$ 7) solution of: **a** *p*-CuFeO₂; inset: the photocurrent onset potential (V_{on}); **b** *n*-ZnO

The symbols have their usual significations. The positive slope of ZnO is characteristic of *n*-type conduction (Fig. 3b). On the contrary, CuFeO₂ shows *p*-type behavior with E_{fb} value of +0.36 eV (Fig. 3a).

As noticed above, the photoactivity is dependent on the conditions of preparation and the improved performance is due to increased active surface area of ZnO on which the Cu²⁺ adsorption occurs. The adsorption on ZnO is pH dependent and is pronounced below pzc (= 7.23) where the Cu²⁺ ions are attracted by ZnO surface, negatively charged; the equilibrium dark is reached after ~ 2 h. However, to ensure a total adsorption, the suspension was kept overnight in the dark.

The Cu²⁺ reduction is non-spontaneous, and the light is used for its reduction. In addition, the free potential of *p*-CuFeO₂ is more negative than the potential E_{fb} and there is no need to apply an additional voltage to drive the uphill reaction as it occurs under cathodic polarization. The energy diagram (Fig. 4), drawn from the optical and electrochemical characterizations at pH ~ 7, shows that Cu²⁺ has a potential above ZnO-CB and can be reduced spontaneously upon illumination on the hetero-system *p*-CuFeO₂/*n*-ZnO.

CuFeO₂ works as electrons reservoir; its illumination excites electrons to the conduction band which are injected into ZnO-CB acting as electro-catalytic centers for the

charge transfer to adsorbed Cu²⁺. The reduction no longer holds if the potential of the couple Cu²⁺/Cu is located outside the forbidden band of ZnO.

The reduction is optimized with respect to the catalyst dose, Cu²⁺ concentration and light intensity. The concentration of copper in industrial effluents can reach 10 ppm or more. Therefore, it is of interest to study the photoactivity as a function of Cu²⁺ concentration (C_o). As expected, clearly shows that the Cu²⁺ reduction decreases with augmenting C_o (Fig. 5). At low concentrations, the number of the photocatalytic sites is greater than Cu²⁺ ions and the photoactivity increases linearly with raising C_o until occupation of all sites. The photons flux was maintained constant (6.96×10^{18} photons s⁻¹) and increasing C_o decelerates the photoactivity because of the saturation of photo-electrochemical sites of ZnO. Water reduction on Cu clusters also accounts for the regression of the activity (see below).

The influence of the mass ratio (CuFeO₂/ZnO) on the photoactivity is illustrated in Fig. 6. As expected, the activity increases with augmenting the mass of the sensitizer CuFeO₂ which and the best performance is obtained for a ratio of 1, this is simply due to the increasing number of photo-electrochemical sites with a higher receptive surface for incident photons. It slightly decreases when further

Fig. 4 Energy diagram of the hetero-system *p*-CuFeO₂/*n*-ZnO

Fig. 5 Percentage of Cu^{2+} reduction versus initial pollutant concentration

Fig. 6 Percentage of photo-reduction against the mass ratio of $\text{CuFeO}_2\text{-ZnO}$ in the hetero-system

CuFeO_2 is added. The light scattering also accounts for the decreased activity.

The amount of deposited copper depends on the light flux (Fig. 7). A linear behavior is observed at small intensities, and the plot deviates from linearity above 9 mW cm^{-2} . The plateau region at high intensities indicates that the number of incident photons exceeds that of catalytic sites and the reduction becomes kinetically governed by the electrons transport in CuFeO_2 . Indeed, the rate of the overall reaction is determined by the electron flow within $\text{CuFeO}_2\text{-CB}$ whose width does not exceed $\sim 2 \text{ eV}$. Therefore, the electrons with a low mobility ($\sim 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and a small diffusion length are rate determining step (Yong and Ling 2014; Abbasi and Arvand 2018). So it is interesting to work under direct sunlight where the diffuse nature of the sun allows low investment and where solar concentrators are not needed; the Cu^{2+} reduction follows a first-order kinetic

with a half-life of 40 min (Fig. 8). The Cu-photodeposition occurs after 160 min and the quantum yield, determined by the number of deposited Cu divided by the number of photons ($P = 6.96 \times 10^{18} \text{ photons s}^{-1}$) is found to be 0.36%

Light catalysis results in the deposition of ultra-fine Cu particles onto ZnO and over time; the Cu^{2+} reduction slows down because of the competitive water discharge. Indeed, the ZnO catalyst modified by Cu photodeposition gives heterogeneous surface and offers active sites for the water reduction into hydrogen where the electrons are channeled toward Cu sites. It is tempting to postulate the in situ photodeposition of Cu over ZnO leads to a better ohmic contact $\text{CuFeO}_2/\text{ZnO}/\text{Cu}$ and Cu deposits are grown by electrocrystallization.

The interfacial charge transfer occurs easily through the generated hetero-junction because of the low H_2 over potential on Cu-sites. This can be easily understood in terms of energy

Fig. 7 Percentage of Cu^{2+} reduction versus the light flux on the hetero-system $\text{CuFeO}_2\text{--ZnO}$

Fig. 8 The kinetic of Cu^{2+} reduction on the hetero-system $\text{CuFeO}_2\text{--ZnO}$. Inset: the plot $\ln C_t/C_0$ versus time

levels of CB--CuFeO_2 , Cu^{2+} and H_2O . The potential of the couple $\text{H}_2\text{O}/\text{H}_2$ can be positioned anywhere and the value at which the $J_d(E)$ curve intercepts the potential-axis depends on the oxygen partial pressure. In air-equilibrated suspension, a potential -0.70 V is obtained by extrapolating a tangent line over the slope and prolonging it to the zero current (Fig. not shown). The volume of evolved gas remains weak until ~ 40 min, and this means that at the beginning, the photoelectrons are consumed to reduce Cu^{2+} . Once, the Cu-clusters are formed they trigger the H_2 liberation. The quantum yield η (H_2) of H_2 -formation for a maximal volume $V(\text{H}_2)$ ($=2.64$ mL) at saturation time t ($=140$ min):

$$\eta(\%) = \frac{100 \times N \times V \times 1240}{\lambda \times P \times V_m \times t \times S}, \quad (3)$$

where N is the Avogadro number, λ the average wave lamp of the lamp spectrum, V_m the molar volume, P the flux intensity, and S the surface area of the reactor. A value of 0.5% was obtained under optimized conditions (see SM 1). Work is continuing and preliminary tests on spinel Ni^{2+} deposition have been conclusive and the results will be communicated very soon.

Conclusion

The choice of CuFeO_2 for the Cu^{2+} deposition is motivated by the light absorption in the visible IR regions, low cost and chemical stability over the whole pH range and the environmental friendless characteristic. However, its conduction band has a high energy for electron transfer and ZnO was

used as electron bridge. The enhanced activity is attributed to the increased active surface area of ZnO on which Cu^{2+} is adsorbed.

Photocatalysis results in the deposition of ultra-fine Cu particles onto ZnO, providing an ohmic contact where the interfacial charge transfer occurs with small activation energy.

The hydrogen evolution is obtained after Cu-photodeposition dispersed in fine clusters over ZnO. The hetero-junction $\text{CuFeO}_2/\text{ZnO}/\text{Cu}$ became photocatalytically active for the hydrogen evolution which takes place competitively with Cu^{2+} reduction and therefore seems to be the main reason in the regression of the Cu^{2+} conversion as over illumination time.

Acknowledgements The financial support of the work was provided by the Faculty of Chemistry. The authors are grateful to Dr. R. Laib for his technical assistance in the X-ray diffraction.

Compliance with ethical standards

Conflict of interest The authors attest that there are not conflict of interest financial, personal or other relationships with other people, laboratories or organizations worldwide.

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