



## Visible light induced $\text{H}_2\text{PO}_4^-$ removal over $\text{CuAlO}_2$ catalyst

N. Benreguia<sup>a</sup>, S. Omeiri<sup>a,b</sup>, B. Bellal<sup>a</sup>, M. Trari<sup>a,\*</sup>

<sup>a</sup> Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry, (U.S.T.H.B), BP 32, 16111 Algiers, Algeria

<sup>b</sup> Centre of Research in Physical and Chemical analysis (CRAPC), BP 248 Algiers RP 16004, Algiers, Algeria

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### ABSTRACT

The delafossite  $\text{CuAlO}_2$  is successfully used for the visible light driven  $\text{H}_2\text{PO}_4^-$  reduction. It is prepared from the nitrates decomposition in order to increase the ratio of reaction surface per given mass.  $\text{CuAlO}_2$  is a narrow band gap semiconductor which exhibits a good chemical stability with a corrosion rate of  $1.70 \mu\text{mol year}^{-1}$  at neutral pH. The flat band potential ( $+0.25 \text{V}_{\text{SCE}}$ ) is determined from the Mott–Schottky characteristic. Hence, the conduction band, positioned at ( $-1.19 \text{V}_{\text{SCE}}$ ), lies below the  $\text{H}_2\text{PO}_4^-$  level yielding a spontaneous reduction under visible illumination. The photocatalytic process is investigated under mild conditions and 30% conversion occurs in less than  $\sim 6$  h with a quantum efficiency of  $\sim 0.04\%$  under full light. The concentration decreases by a factor of 39% after a second cycle. The photoactivity follows a first order kinetic with a rate constant of  $6.6 \times 10^{-2} \text{h}^{-1}$ . The possibility of identifying the reaction products via the intensity–potential characteristics is explored. The decrease of the conversion rate over illumination time is due to the competitive water reduction.

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### 1. Introduction

The photomineralization of organic molecules and photoelectrochemical (PEC) conversion of inorganic pollutants are major parts of the environmental protection [1]. The eutrophication is recognized as an environmental problem originating from the degradation of the aquatic medium by an excess supply of nutritive substances which increases the production of seaweed and aquatic plants. Algae grow in the presence of phosphate at a level as low as  $0.05 \text{mg L}^{-1}$  above which they disturb the ecosystem and become an increasing problem. The main source arises from fertilizers and industrial rejects [2,3]. Accordingly, the concentration of phosphate must be kept low and many techniques have been used for its removal, among which anion exchange and microfiltration [4]. However, such methods are high cost and often difficult to put in work. So, our research program has been oriented toward the broad pluridisciplinary field of the photoelectrochemistry and its application for the environmental protection [5]. A variety of inorganic compounds can be converted photocatalytically into less harmful forms over semiconductor (SC) aqueous suspensions. Most oxides investigated to date are chemically stable but have a valence band (VB) deriving from  $\text{O}^{2-} - 2p$  orbital, lying at  $\sim 7$  eV below vacuum. Hence, for narrow band gap SCs the conduction band (CB) is not negative enough to reduce inorganic species with useful rates. So, our choice has been directed toward oxides with new

band structure. The delafossites  $\text{Cu}^+\text{M}^{3+}\text{O}_2$ , where M is commonly a trivalent metal, are promising materials for the light energy conversion [6]. Among the congeners,  $\text{CuAlO}_2$  has attracted a great deal of attention in connection with the photocatalysis [7], thin solid films [8] and optoelectronic devices [9]. It possesses electronic bands deriving from Cu 3d orbital with high energetic position and this property has been exploited for the removal of heavy metals [10].  $\text{CuAlO}_2$  exhibits chemical inertness even in strong mineral acids such as aqua regia or perchloric acid. In addition, Cu and Al are by far the most attractive with regard to toxicity concern. On the other hand, the modern world needs a continual energy which can be supplied partially by the renewable energies sources. The sunlight is clean and its conversion can be accomplished through photocatalytic processes which may offer many advantages over their electrochemical counter parts. The photoactivity is intrinsically governed by the solid properties and is enhanced when the catalyst is elaborated by chemical way. Indeed, porous oxides are required in photocatalysis and the improved performance is attributed to the large active surface on which the adsorption occurs. Although attention has been paid to practical use of delafossites, to our knowledge there have been no papers in which the phosphate related compounds are photoelectrochemically converted. At neutral pH,  $\text{CuAlO}_2$ -CB is located below the potential of  $\text{H}_2\text{PO}_4^-$  and should allow a thermodynamically feasible reduction under illumination. Encouraging results have yet been obtained with the nitrate removal [11]. In extension, we report on the results of  $\text{CuAlO}_2$  as candidate to mediate the  $\text{H}_2\text{PO}_4^-$  reduction under soft conditions close to those encountered in the aquatic medium [12]. Given the fact that it has an optical gap ( $E_g$ ), near to the optimal value

\* Corresponding author. Tel.: +213 021 24 79 59; fax: +0213 21 24 80 08.  
E-mail address: [solarchemistry@gmail.com](mailto:solarchemistry@gmail.com) (M. Trari).

needed for terrestrial applications, and the foregoing characteristics,  $\text{CuAlO}_2$  seems promising for such objective.

## 2. Experimental

$\text{CuAlO}_2$  has been synthesized by chemical route which has succeeded in the preparation of delafossites [13].  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CuO}$  (pre-fired at  $400^\circ\text{C}$ ), both of purity greater than 99.5%, were used as starting reagents. The stoichiometric mixture was dissolved in  $\text{HNO}_3/\text{H}_2\text{O}$  (1/1) and the solution was evaporated and heated on a magnetic stirring hot plate until there were no  $\text{NO}_x$  fumes. The amorphous powder was fired at  $1020^\circ\text{C}$  in air with intermediate regrinding and furnace cooled. The end product exhibits a dark blue color and has been characterized by X-ray diffraction using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154178 \text{ nm}$ ). The specific surface area was measured by BET method using nitrogen gas as adsorbate at liquid nitrogen temperature on ASAP 2010 micromeritics apparatus. The determination of the crystallites distribution was performed by laser particle size analysis (Mastersizer 2000, Malvern).

The diffuse reflectance spectrum was recorded with a Carry 500 spectrophotometer attached to an integrating  $\text{MgO}$  sphere. Electrical contact onto the back side of sintered pellet was made with conductive silver paint; the pellet was encapsulated in a glass holder with epoxy resin. The titration of  $\text{Cu}^{2+}$ , for the corrosion test, was performed by atomic absorption (Perkin Elmer 2380). The PEC characterization has been performed in a “three-electrode-device”: the working electrode and a Pt counter electrode ( $\sim 1 \text{ cm}^2$ ); all the potentials were monitored by a potentiostat (Voltalab PGZ301, Radiometer) and given with respect to a saturated calomel electrode (SCE). A 200 W tungsten lamp whose spectrum peaks at 650 nm was used as light source. The point of zero zeta potential (pzpz) has been accurately determined by measuring the equilibrium pH of an aqueous powder solution. The free potential and the dark equilibrium time were determined by chrono-potentiometry.

The photocatalytic tests were carried out in a double walled Pyrex reactor. The powder (0.125 g) was dispersed in air equilibrated  $\text{H}_2\text{PO}_4^-$  electrolyte ( $200 \text{ cm}^3$ ) under magnetic agitation. The temperature was maintained at  $(25 \pm 2)^\circ\text{C}$  by using a thermostated bath (Julabo). The light source consisted of two tungsten lamps and the flux intensity was measured with a digital light meter (Testo 545) without correction for solution absorbance. The aliquots were periodically removed and the sample was separated by centrifugation,  $\text{H}_2\text{PO}_4^-$  reduction was followed by titration with KOH. In order to know whether the photoreduction occurs or not, blank tests were carried out in the dark. The amount of adsorbed  $\text{H}_2\text{PO}_4^-$  was checked by titration before and after keeping the powder in the working solution overnight. Pt rotating electrode (Radiometer analytical CVT 101 T) has been used for the identification of the end product through the intensity–potential  $J(V)$  characteristic. The quantum yield ( $\eta$ ) was calculated by dividing the number of converted  $\text{H}_2\text{PO}_4^-$  molecules by the photons rate integrated over the lamp spectrum.<sup>1</sup> The  $\text{H}_2\text{PO}_4^-$  conversion occurs in competition with the water reduction. The hydrogen in the outgoing gas was identified by gas chromatography (TCD Shimadzu IGC121 ML) containing two 4 m carbosieve B columns (1/8 inch, 100–200 meshes) and Ar as carrier gas. Sample was taken with a gas syringe for analysis. The amount was determined volumetrically thanks to a water manometer with an accuracy of 0.05 mL. The procedure and appa-

<sup>1</sup> The total energy  $E_t = \int_{\lambda_1}^{\lambda_2} hc\lambda^{-1}\phi d\lambda$ ,  $\phi$  being the incident light and  $\lambda_1$  and  $\lambda_2$  the extreme values of the lamp spectrum.

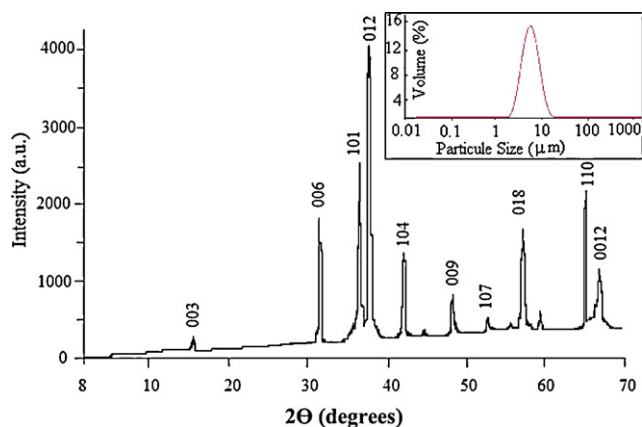


Fig. 1. Powder X-ray diffraction of the delafossite  $\text{CuAlO}_2$  elaborated by nitrate way. Inset: The particle size distribution.

ratu have been described elsewhere [14]. All the solutions were made up from analytical reagents grade and distilled water.

## 3. Results and discussion

### 3.1. Physical and photoelectrochemical properties

It is a known fact that the photoactivity is a surface phenomenon which depends on the physical properties of the powder (crystallite size and porosity) through the preparation technique. Large active surface and consequently fine granulometry are required for low mobility semiconductor delafossites and reducing the particle size should theoretically enhance the photo catalytic performance. To this end, the oxide was elaborated from the nitrates decomposition which has the advantage of producing submicron-sized particles with narrow particle size distribution (Fig. 1, Inset). The specific surface area  $4.82 \text{ m}^2 \text{ g}^{-1}$  was obtained from BET technique.  $\text{CuAlO}_2$  has been identified by X-ray diffraction (Fig. 1), all the peaks are indexed in a rhombohedral unit cell ( $R\bar{3}m$ ) with the lattice constants  $a = 0.2857 \text{ nm}$  and  $c = 1.6901 \text{ nm}$  in agreement with the JCPDS card No. 35-1401. It is worth mentioning that no peak belonging to the delafossite appears at  $700^\circ\text{C}$ ; the pattern shows only the reflections of the spinel  $\text{CuAl}_2\text{O}_4$  along with those of  $\text{CuO}$ .

Using a small size  $\text{M}^{3+}$  ion in the delafossites  $\text{CuMO}_2$  can be regarded as an approach to the visible light sensitization. The diffuse reflectance spectrum of  $\text{CuAlO}_2$  (Fig. 2) does not provide a clear cut absorption edge. The gap is evaluated using the wavelength at the absorption edge from the intersection of the straight line through the steep portion of the edge with the nearly horizon-

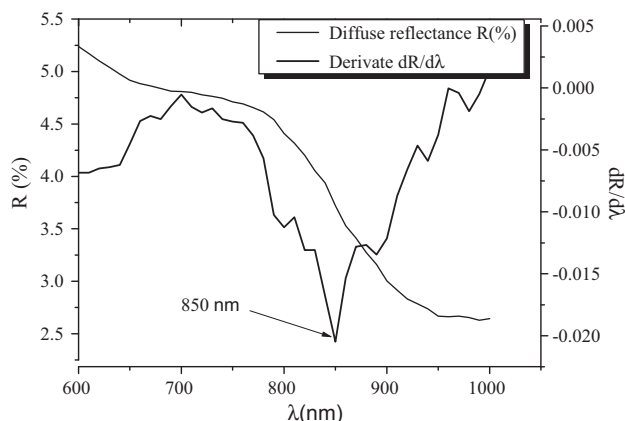


Fig. 2. The diffuse reflectance spectrum of  $\text{CuAlO}_2$  along with the derivative curve.

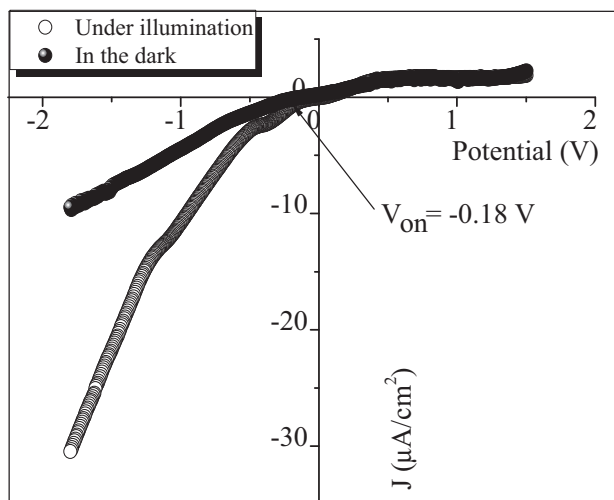


Fig. 3. The  $J(V)$  profiles of  $\text{CuAlO}_2$  in  $\text{KCl}$  (0.5M) electrolyte both in the dark and under illumination.

tal line; a precise value of 1.46 eV is obtained from the derivation curve. For practical applications, chemical stability test was carried out up to two months of continuous immersion in neutral solution. The dissolution rate, determined from dissolved copper by atomic absorption is found to be only  $1.70 \mu\text{mol year}^{-1}$ .

The slight deviation from the stoichiometry gives us the opportunity for characterizing  $\text{CuAlO}_2$  photoelectrochemically. The  $p$ -type conduction ( $\rho_{300\text{K}} = 1.2 \times 10^3 \Omega\text{-cm}$ ) evidenced from the positive thermopower ( $S_{300\text{K}} = 56 \mu\text{VK}^{-1}$ ), is ascribed to the oxidation of a small amount of  $\text{Cu}^+$  originating from intercalated oxygen in the layered lattice. In  $\text{CuMO}_2$ , the inter-ionic distance  $\text{Cu}^+ - \text{Cu}^+$  equal to the  $a$ -parameter, is large enough to host oxygen in the crystal structure. It has been shown that  $\text{O}^{2-}$  species intercalates reversibly in one step process [15], giving the formulation  $\text{CuAlO}_{2.03}$ . The  $J(V)$  characteristic shows a good electrochemical stability over a large potential range with a dark current ( $J_d$ ) less than  $2 \mu\text{A cm}^{-2}$ . Below  $\sim -0.8\text{V}$ ,  $J_d$  increases owing to the water reduction. The onset photocurrent potential ( $V_{\text{on}}$ ) is taken as that potential above which no photocurrent ( $J_{\text{ph}}$ ) could be observed and can be assimilated to the flat band potential  $V_{\text{fb}}$  (Fig. 3).  $J_{\text{ph}}$  appears at  $-0.125\text{V}$  and for potentials cathodic of  $-1\text{V}$ ; it is masked by  $\text{H}_2$ -evolution. However, the potential  $V_{\text{fb}}$  has been accurately deter-

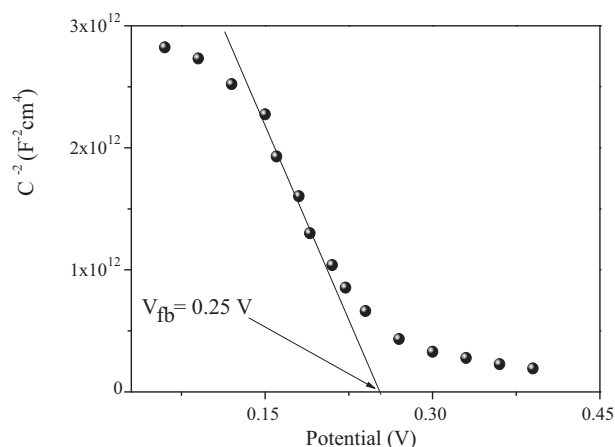


Fig. 4. The Mott-Schottky plot of  $\text{CuAlO}_2$  in  $\text{KH}_2\text{PO}_4$  electrolyte.

mined from the Mott-Schottky plot. The differential capacitance at the interface, approximated by a plate capacitor, is given by:

$$C^{-2} = \{0.5 \epsilon_0 \epsilon N_A\} \left\{ V_{\text{fb}} - V - \frac{kT}{e} \right\} \quad (1)$$

where all the symbols have their usual significations. The  $p$  type conductivity is confirmed by the negative slope. The potential  $V_{\text{fb}}$  ( $=+0.25\text{V}$ ), obtained by extrapolating the curve to  $C^{-2} = 0$  (Fig. 4), outlines the position of VB in the electrochemical scale. The PEC characterization permits to establish the energy band scheme of the junction (Fig. 5) which predicts from a thermodynamic point of view whether  $\text{H}_2\text{PO}_4^-$  and/or  $\text{H}_2\text{O}$  reductions occur or not. The PEC properties of  $\text{CuAlO}_2$  arise from  $\text{CuO}_3^{2-}$  entities; the crystal structure consists of close packed layers of  $\text{AlO}_6$  octahedra sharing common edges. Two adjacent sheets are connected to each other by bridged monovalent copper to form  $\{\text{O}-\text{Cu}-\text{O}\}^{2-}$  units parallel to the  $c$  axis. Both the electronic bands are made up of  $\text{Cu}-3d$  wave function; the lower filled  $t_{2g}$  orbital provides VB though being non bonding is separated by  $\sim 2\text{eV}$  from the lower lying  $\text{O}^{2-}-2p$  level whereas CB consists of empty hybridized  $\text{Cu}-dz^2/4s$  orbital with a high reducing ability.

### 3.2. Photo catalysis

Like most oxides,  $\text{CuAlO}_2$  shows a dark adsorption for inorganic ions and a transition time is needed before illumination. The pzzp,

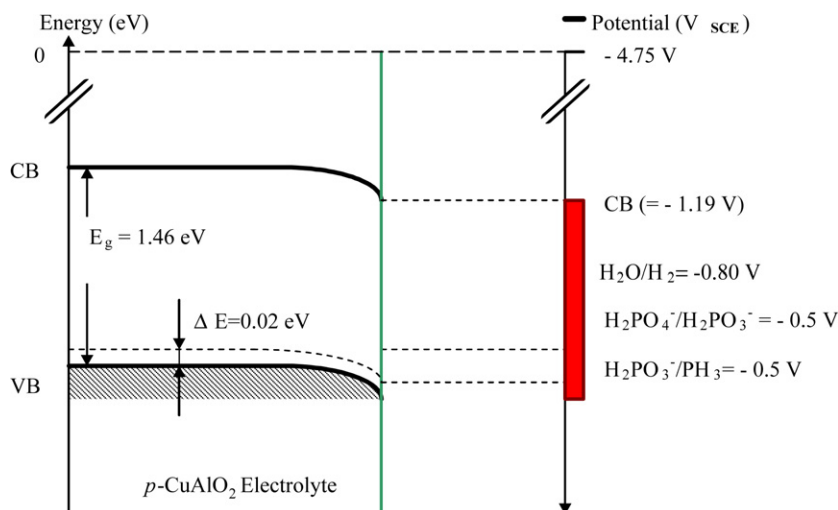


Fig. 5. Energy band diagram of the junction  $p\text{-CuAlO}_2/\text{KH}_2\text{PO}_4$  electrolyte.

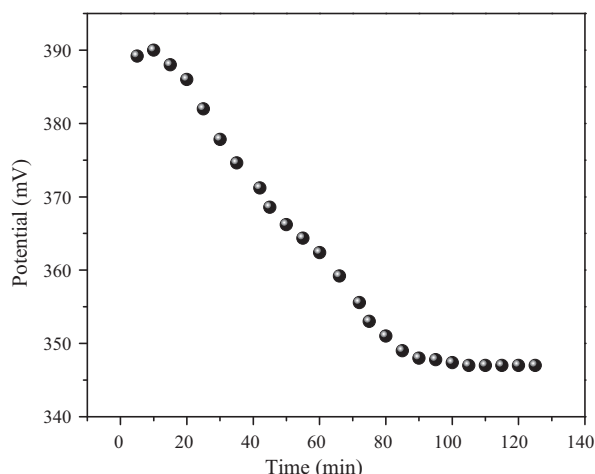
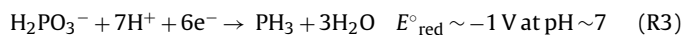
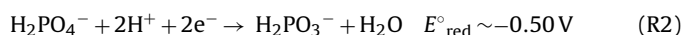
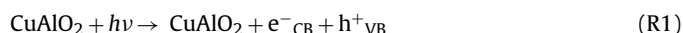


Fig. 6. Chronopotentiometric curve of CuAlO<sub>2</sub>/KH<sub>2</sub>PO<sub>4</sub> in the dark.

i.e. pH at which the total adsorbed charge on the surface is zero is found to be 7.89. Below pzzp, the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> species are attracted by the powder surface charged positively. So, the photocatalytic tests are performed at pH 6–7. The adsorption time (~2 h) and the equilibrium potential, assimilated to the free potential  $U_f$  (-0.348 V), are determined by chrono potentiometry (Fig. 6). In our case, the powder is kept in the dark overnight to ensure a complete H<sub>2</sub>PO<sub>4</sub><sup>-</sup> adsorption. The potential  $P$  of CuAlO<sub>2</sub>-CB (-1.19 V), calculated from the relation<sup>2</sup>:

$$P = V_{fb} + \frac{(\Delta E - E_g)}{e} \quad (2)$$

lies below both the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and H<sub>2</sub>O levels and provides a strong reducing power for the photoelectrons. The driving force ( $V_{fb} - E_{red}$ ) at the interface is expected to be less in the particle than can be induced in the electrode and the value needed to preclude the recombination process varies to some extent with the oxide being considered. For zero ( $e^-/h^+$ ) pairs recombination, Gerisher [16] proposed an optimal band bending of 0.35 V. In the presence of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, the space charge region is sufficiently depleted to exclude the recombination process. The potential  $U_f$  of CuAlO<sub>2</sub> is more negative than  $V_{fb}$  and this should promote the photoreduction in colloid systems. The possible reactions which occur at the interface CuAlO<sub>2</sub>/H<sub>2</sub>PO<sub>4</sub><sup>-</sup> electrolyte via CB process are the following:



The reaction (R2) could be involved owing to its potential, located above CuAlO<sub>2</sub>-CB. The reaction product has been identified by the  $J(V)$  characteristic of 6 h illuminated solution compared to a standard solution. The reaction consumes H<sup>+</sup> ions and should increase the pH. This hypothesis has found an experimental support and in unbuffered solution,  $\Delta(\text{pH})$  of ~+0.2 has been observed. However, such value is not large enough to draw a conclusion. H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is amphoteric, it predominates at neutral pHs and the hydrolysis must be taken into account:

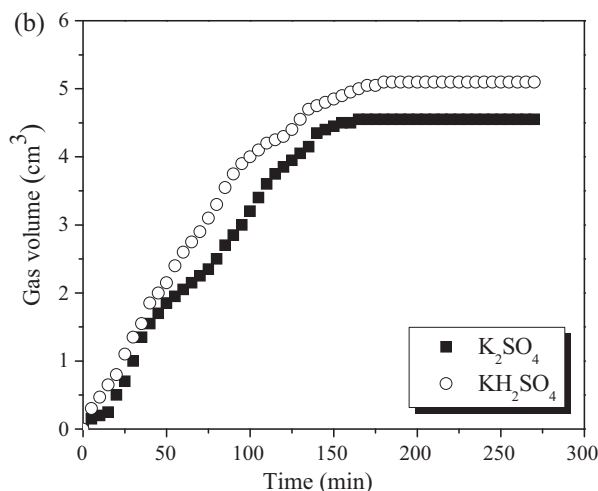
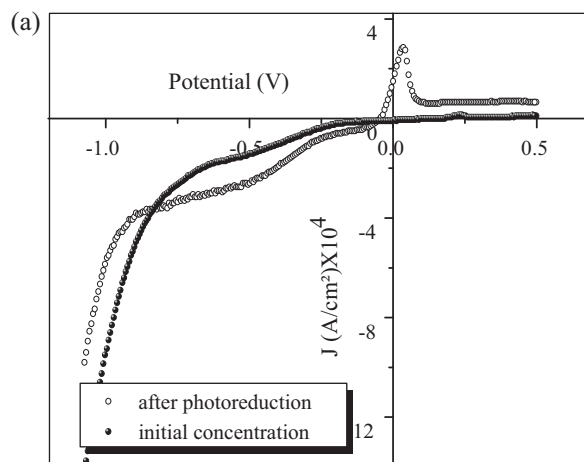
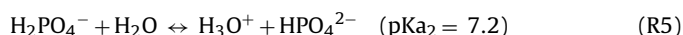


Fig. 7. (a)  $J(V)$  curves of the initial solution and after 5 h illumination. [KH<sub>2</sub>PO<sub>4</sub>] = 10<sup>-3</sup> M. (b) Evolution of evolved gas (H<sub>2</sub> and PH<sub>3</sub>) with illumination time for [KH<sub>2</sub>PO<sub>4</sub>] = 10<sup>-3</sup> M and [K<sub>2</sub>SO<sub>4</sub>] = 10<sup>-3</sup> M.

The solution is buffered through the mixture H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> but with a weak ability buffer. In such a case, the pH is accurately calculated from the relation [17]:

$$\text{pH} = -\log \sqrt{\frac{K_{a1}K_{a2}C_0 + K_{a1}K_w}{C_0 + K_{a1}}} \quad (3)$$

where  $C_0$  is the initial concentration of H<sub>2</sub>PO<sub>4</sub><sup>2-</sup> and  $K_w$  (= 10<sup>-14</sup>) the ionic product of water. The calculated pH is found to be 5.13. However, the fact that the pH stabilizes at 6, indicates that the reaction (R3) lies to the left hand side.

A rotating Pt electrode is useful in amperometric titrations, the reactants in a mixture behave independently of one another when the half potentials differ by at least 0.2 V. The apparition of a peak at ~0 V (Fig. 7a) is attributed to the electrochemical couple H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/H<sub>2</sub>PO<sub>3</sub><sup>-</sup>. It is helpful to mention that the orthophosphites are less soluble in water and can be extracted by precipitation. The fact that the volume of evolved gas is larger in the presence of KH<sub>2</sub>PO<sub>4</sub> indicates that in addition to hydrogen (see below), another gas probably PH<sub>3</sub> is produced in parallel. An interesting calculation consists to evaluate from saturation volumes the percentage of photoelectrons (89%) consumed for hydrogen formation.<sup>3</sup> On the

<sup>2</sup> The activation energy  $\Delta E$  (0.017 eV) has been determined from the conductivity measurements on sintered pellets.

<sup>3</sup> K<sub>2</sub>SO<sub>4</sub> is an indifferent salt and gives the solution an ionic conductivity, it does not participate in the reduction process owing to the positive potential of the couple S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/SO<sub>4</sub><sup>-</sup> (~1.6 V).

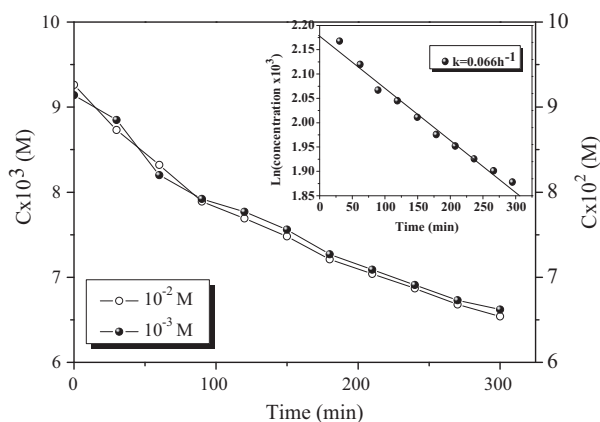


Fig. 8. Photoreduction of  $\text{KH}_2\text{PO}_4$  ( $10^{-2}$  M) on  $\text{CuAlO}_2$ . Inset: The plot of  $\ln C$  as a function of time for  $[\text{KH}_2\text{PO}_4] = 10^{-3}$  M.

other hand, the net tendency to saturation shows that the reactions (R2) and (R3) occur successively and the global kinetic is governed mainly by the latter. The absence of peak ascribed to the couple  $\text{H}_2\text{PO}_4^-/\text{PH}_3$  which should appear at  $-0.50$  V (depending on the molar ratio) lends a further support of the slowness of the  $\text{PH}_3$  formation. In addition, the decrease of  $\text{H}_2\text{PO}_4^-$  concentration ( $2.52 \times 10^{-4}$  M) should produce a volume of 6.2 mL knowing that  $\text{PH}_3$  is insoluble in water. However, the real volume (0.55 mL) at saturation deduced from Fig. 7b gives a degree of advancement of  $\sim 8\%$  for the reaction (R3). The conversion efficiency ( $\eta$ ) is defined as:

$$\eta = 2 \frac{(\text{number of } \text{H}_2\text{PO}_4^- \text{ converted})}{(\text{input number of photons})} \quad (4)$$

$\eta$  is calculated by dividing the number of converted  $\text{H}_2\text{PO}_4^-$  molecules by the photons rate integrated over the wavelengths range covering the lamp spectrum. Fig. 8 gives the time course of the reaction for two concentrations ( $10^{-3}$  and  $10^{-2}$  M). The fraction of converted  $\text{H}_2\text{PO}_4^-$  after 6 h attains  $\sim 30\%$  with  $\eta$  value of  $\sim 0.04\%$ . The plot of the logarithm of the concentration (Fig. 8 Inset) indicates a first order reaction with a rate constant of  $6.6 \times 10^{-2} \text{ h}^{-1}$ .

It is worth mentioning that with replacement of the catalyst by a new one and taking a concentration of  $0.7 \times 10^{-3}$  M (obtained from the first experiment), the concentration decreases down to  $3.01 \times 10^{-4}$  M, i.e. by a factor of 39%. The irreversibility of the electrochemical system  $\text{CuAlO}_2/\text{H}_2\text{PO}_4^-$  is due to the slow rate of electron transfer, a result corroborated by the small fill factor (Fig. 9) and caused by the low electron mobility in delafossites.

The  $\text{H}_2\text{PO}_4^-$  reduction takes place competitively with the  $\text{H}_2$ -evolution (R4) and is therefore the main reason for the regression in the photoactivity as evidenced by the bending over the curve (Fig. 7b). This is important for the solar energy conversion where a particular goal is desired. Sun is an inexhaustible energetic source and hydrogen is ideal for storing the solar energy. The potential at which the  $J_d$ -V curve intercepts the potential-axis  $\text{H}_2\text{O}/\text{H}_2$  varies as a function of the dissolved oxygen. In air equilibrated suspension, a value of  $\sim 1$  V is obtained by extrapolating a tangent line over the slope and prolonging it to the zero current. This competitiveness can be understood from the energy levels in the band diagram. Both the potentials of  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_2\text{O}$  depend on the pH and are sweeping respectively by  $-0.12$  and  $-0.06 \text{ V pH}^{-1}$  with respect to  $\text{CuAlO}_2$ -CB. The efficiency for  $\text{H}_2$  formation under the same conditions is found to be 0.28%.

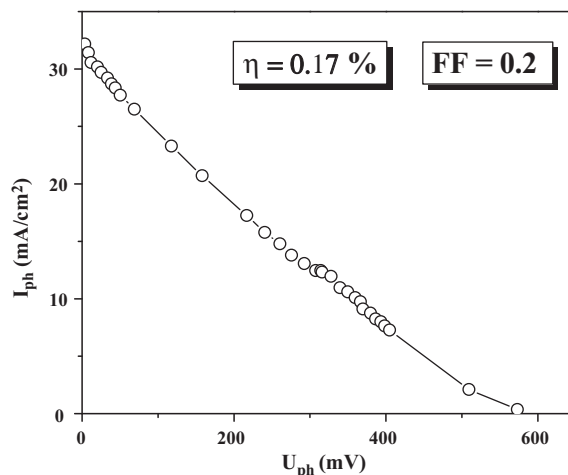


Fig. 9. Photocurrent photovoltage ( $J_{\text{ph}}-U_{\text{ph}}$ ) characteristic of  $\text{CuAlO}_2$  under a light intensity of  $21 \text{ mW cm}^{-2}$ .

#### 4. Conclusion

A new photo catalyst for  $\text{H}_2\text{PO}_4^-$  reduction has been synthesized and characterized photo electrochemically. The low cost delafossite  $\text{CuAlO}_2$  is a narrow band gap semiconductor, prepared from the nitrates decomposition in order to increase the surface-bulk ratio. Below pzzp, the surface is charged positively and shows  $\text{H}_2\text{PO}_4^-$  dark adsorption which favors the photo reduction process. The conduction band deriving from Cu: 3d orbital, provides a strong reducing power. It is pH-insensitive and appropriately positioned to induce the  $\text{H}_2\text{PO}_4^-$  reduction in neutral medium. Analysis of the end product was carried out by the intensity potential curves, readily identified by comparison with standards and the reduction follows a first order kinetic. The conversion tends to saturation because of the competitive water reduction, an issue of energetic concern.

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