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Visible light induced hydrogen on the novel hetero-system $CuFe_2O_4/TiO_2$

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ABSTRACT

The hydrogen photo evolution has been successfully achieved over the new hetero-system $CuFe_2O_4/TiO_2$ and the activity is dependent on the synthesis method. The spinel $CuFe_2O_4$ is *p*-type semi conductor with activation energy of 0.21 eV. It has been prepared via a variety of techniques and the best performance is achieved on the catalyst elaborated by sol gel. The onset potential of the photocurrent ($-0.17\ V_{SCE}$) is slightly cathodic with respect to the flat band potential ($0\ V_{SCE}$) implying a small existence of surface states within the gap region. The photo induced minority carriers (electrons) react with H_2O molecules via TiO_2 interfacial mechanism. The intimate contact between $CuFe_2O_4$ and TiO_2 particles is necessary for H_2 liberation. The generated photovoltage is used to catalyze the reaction ($H_2O + S_2O_3^{2-} + 2OH^- \rightarrow 2H_2 + 2SO_3^{2-},\ \Delta G_R^\circ = -39.31$ kJ mol^{-1}) and the oxide approaches 100% stability to photo driven corrosion. The rate of H_2 evolution is found to be 15 μmol g^{-1} min^{-1} with a polychromatic power efficiency of 1.3%. Over time, a pronounced deceleration occurred. The competitive reduction of sulfite is therefore though to be the reason of the regression of the photoactivity.

1. Introduction

Concerning the availability of renewable energies, the solar power appears the most attractive owing to its renew ability [1]. The sun is an inexhaustible energetic source and it is interesting to develop specific experiments to a chosen goal i.e. either energetic or environmental [2]. However, because of its intermittence, the solar energy can only be useful if a convenient storage is developed [3]. Hydrogen is considered as a clean and sustainable substitute to fossil fuels [4]. Its production from cheap raw materials such as water remains a challenge which could offer an alternative to reduce of CO_2 emission, the main cause of the global warming. Various ways exist to decompose water into its constituents. The thermochemical splitting is one step process, but an appreciable quantity of hydrogen can be obtained when using only solar concentrators at temperatures exceeding 2500 K [5]. Moreover, the gas separation makes the process more difficult because the mixture must be quenched to preclude the gas recombination. On the other hand, the photochemical cycles were widely investigated in the past [6]. Nevertheless, the complexity of the chemical pathway increases with the number of sub processes yielding generally low conversion efficiencies. So, the interest seems to return to the water photoelectrolysis which remains one of the most promising ways to ensure energy storage under mild operating conditions. Absorption of energetic photons by *p*-type semiconductor (SC) generates electron/hole (e^-/h^+) pairs, the electrons migrate to the interface to reduce water into gaseous hydrogen whereas the holes move into the bulk to react with electron donor. However, the main hindrance limiting the utilization of oxides in photoelectrochemical (PEC) devices is the large forbidden band (E_g) which inhibits the absorption of the solar spectrum. The reason lies in the low energy of the valence band (VB), made up primarily of O^{2-}: *2p* orbitals. The recent research has been oriented toward materials whose electronic bands derive from cationic parentage [7]. The semiconductor is indeed the key element of PEC device and in order to approach the problem systematically, we have chosen to study materials with new band structure. Among oxides families, the spinels CuM_2O_4, where M is commonly *3d* metal, have not received a great attention as photocatalysts although they are low cost, possess a gap with *d–d* photo transitions and have relatively large absorption coefficients [8]. To get efficient hydrogen production, two conditions are required (i) a sufficient positive (resp. negative) flat band potential (V_{fb}), for *p*-type specimen (resp. *n*-type) and (ii) a gap E_g around the ideal value of ~1.4 eV needed for terrestrial applications. The reduction of the gap of CuM_2O_4 occurs at the expense of change of VB due to the non bonding t_{2g} orbitals, and decreases to approximately 2 eV [9]. However, in heterogeneous photocatalysis the electron exchange occurs isoenergetically and the large difference between the conduction band (CB) of $CuFe_2O_4$ and the redox couple H_2O/H_2 (~1 V) leads to a weak photoactivity.

Besides, TiO_2 based solar cells are inefficient under direct illumination where only 4% of the sunlight accounts for the UV radiation, resulting from low absorptivity. Some attempts to dope

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TiO_2 with foreign atoms have been made; the doping represents an interesting approach to shift the spectral photoresponse toward the visible region; but even this strategy requires a large bias although the gap is appreciably reduced. Another alternative would be the utilization of hetero-systems where little systematic work has been done because of the difficulty of adjusting the electronic bands of SCs. Encouraging progress has been made recently concerning the optimal matching as a means of separation of (e^-/h^+) pairs in colloidal suspensions by coupling narrow and wide band gap SCs [10]. To our knowledge, no papers dealing with the spinel based hetero-systems have been reported before now and the photoassisted catalysis is the first example wherein the water reduction has been investigated. $CuFe_2O_4$ is expected to be a good sensitizer considering the energetic position of CB of various SCs; its conduction band is pH insensitive whereas that of TiO_2 changes usually by -0.06 V pH^{-1}. We have exploited this property and we have successfully tested the new hetero-system $CuFe_2O_4/TiO_2$ for the water photo reduction which proceeds with low over-voltages[1] in alkaline electrolytes. The further advantage of $CuFe_2O_4$ is the direct band gap positioned near the optimal value of the sun spectrum and the high energy of CB, giving the photo electrons a strong reducing ability. Moreover, it is low cost and the constituent elements Cu and Fe are the most attractive if we take toxicity into account. TiO_2 has been chosen because (i) it is among the most water resisting in the whole pH range (ii) it has a complete transparency over the visible region (iii) it can be synthesized as active variety i.e. the anatase phase. Although it is not a general rule, the photocatalytic properties are mainly governed by the active surface and the performance increases with decreasing the crystallite dimension [11]. It is now well established that pure oxides with relatively large specific surface areas can be elaborated by sol gel. The method allows a lowering of the synthesis temperature as well as homogeneity of $CuFe_2O_4$ powder. The solid state reaction and the nitrate route are reported for a comparative purpose. The factors like the synthesis method, the mass concentration, the pH of the solution and the temperature are optimized.

2. Experimental

$CuFe_2O_4$ has been prepared through various methods:

2.1. Method A: solid state reaction

First, CuO (Prolabo, 99.9%) and Fe_2O_3 (Ventron, 99.9%) are heated respectively at 250 and 400 °C prior use. Then the synthesis is carried out by intensive grinding of the stoichiometric mixture in an agate mortar and firing at 850 °C. The process is repeated twice to get a single phase.

2.2. Method B: co precipitation

CuO and $Fe(NO_3)_3$, $9H_2O$ (Fluka, 99%) are used as starting materials. Stoichiometric amounts are dissolved in concentrated HNO_3 (9 N) and the solution is evaporated in a sand bath. The amorphous powder is fired 24 h in air at 850 °C with two intermediate regrindings.

2.3. Method C sol gel

$Cu(NO_3)_2$, $3H_2O$ (Merck, 99%)/$Fe(NO_3)_3$, $9H_2O$ (Merck, 99%) are dissolved in HNO_3 in which 4 g of agar and 400 mL of water are added and maintained 3 h at room temperature. The solution is then heated under stirring at 70 °C for 3 h. The gelation is proceeded gradually until a green gel is obtained, next dried at 120 °C (72 h). Finally, the powder is fired 900 °C during 16 h.

TiO_2 is synthesized according to the method described elsewhere [12] which consists of dissolving $Ti(OC_3H_7)_4$ in methanol/ethanol solution in a molar ratio (1/1/10). The solution is heated at 75 °C (3 h), after that water is added drop wise. The gel is dried overnight and heated at 450° (2 h, 3 °C min^{-1}). The synthesized products are characterized by X-ray diffraction (XRD). The data are collected for 10 s. at each 0.02° step over 2θ range (5–60°). Pellet dimensions, measured with a vernier and weighed in an analytical balance (10^{-4} g), are used to estimate the bulk density. UV–Visible spectrophotometer (Shimadzu 1800) is used for the optical measurements. The samples are prepared as suspension of powder using silicon oil. The Fourier transform infrared transmission spectrum (FT-IR) is recorded over the range (400–4000 cm^{-1}) with a Bio Rad-IR spectrometer, the routine KBr technique of sample separation is used. Particle size and morphology are observed by transmission electron microscopy (JEOL JSM-6360LV).

For PEC characterization, the powder is pressed under uniaxial pressure of 3 kbar into 13 mm diameter discs of ~1 mm thickness and sintered at 950 °C (compactness ~90%). The electrical contact with copper wire is made onto the backside of the pellet with silver paint. The electrode (0.85 cm^2) is encapsulated in a glass tube and isolated by epoxy resin. A standard three electrode cell is used for the intensity potential $J(V)$ characteristics including an emergency Pt electrode (Tacussel, 1 cm^2) and a saturated calomel electrode (SCE). The working electrode is illuminated by a 200 W halogen tungsten lamp through a flat window and the potentials are monitored by a Voltalab PGZ301 potentiostat (Radiometer Analytical). The extra pure KOH electrolyte (0.2 M) is continuously flushed with nitrogen and the experiments are performed at room temperature.

The photocatalytic tests are done in a double walled Pyrex reactor, equipped with a septum rubber. The concentration of the hetero-system $CuFe_2O_4/TiO_2$ is maintained at 1 g L^{-1}. The pH is adjusted to the desired value by adding KOH. Thiosulfate $S_2O_3^{2-}$ is used as reducing agent to preclude the photo driven corrosion. The solution is degassed in advance by nitrogen bubbling for 35 min under constant magnetic agitation. Unless otherwise noted, the tests are made at controlled temperature (50 ± 1 °C) by a thermo stated bath (Julabo). No temperature increase of the solution is observed during illumination. The light source comes from three tungsten lamps (200 W) symmetrically placed around the reactor. For the quantum efficiency (η), the light intensity (29 mW cm^{-2}, 2×10^{19} photons/s) is measured with a digital flux meter (Testo 545) without correction for solution absorbance. Evolved hydrogen is positively identified by gas chromatography and the amount is determined volumetrically in a water manometer. Blank runs are carried out in the dark and correction for pressure and temperature was run. The solutions are prepared from reagents of analytical quality in twice distilled water.

3. Results and discussion

3.1. Physical and photo electrochemical properties

At 850 °C, no additional XRD lines to the spinel $CuFe_2O_4$ (method C) referred to the starting oxides CuO and Fe_2O_3 are observed. At 900 °C, the pattern reveals a homogeneous single phase with a dark brown[2] color and a better crystallinity (Fig. 1). All the peaks index in the quadratic symmetry (SG: $I4_1/amd$, No. 141) with the lattice constants $a = 0.581$ and $c = 0.860$ nm, in agreement with

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[1] The over-voltage is the difference ($E_{CB} - E_{red}$) and is current independent.

[2] For interpretation of color in Fig. 6, the reader is referred to the web version of this article.