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CuMnO₂, a novel hydrogen photoevolution catalyst

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Abstract

Photocatalytic hydrogen production induced under illumination using a new oxide CuMnO₂ has been studied. The applied catalyst was without noble metal. The hydrogen was generated from aqueous solution containing either S²⁻ or SO₃²⁻. The conduction band of CuMnO₂, with a value of -0.88 V/SCE, allows a spontaneous hydrogen formation. The highest hydrogen evolution rate was 0.95×10^{-2} ml mg⁻¹ h⁻¹ on the crednerite CuMnO₂-E obtained by exchange reaction with SO₃²⁻ as hole scavenger. When S²⁻ was used, the hydrogen production reaches a saturation attributed to the competitive reduction of yellow polysulfides S_n²⁻ as well as their strong light absorption in the visible region. There was no photoactivity observed below pH 12.

Keywords: Crednerite; Photocatalysis; Hydrogen; Polysulfide; p/n-photochemical diode

1. Introduction

Photoassisted hydrogen production induced by illumination of a suspension of small particles of semiconducting oxides continue to attract great attention as an alternative route of storing solar energy and has been the subject of many investigations [1–4]. Reported efficiencies of pure semiconductor particles remain indeed low. The hydrogen evolution in the cathodic process can be highly enhanced by loading with noble metals, leading to a great simplification of the system. The set functions as a microphotoelectrochemical cell. A particular advantage of such systems is that the electron hole pairs induced by irradiation quickly reach different parts of the surface. In this state they react with suitable redox couple before they recombine.

Semiconductor oxides are commonly believed to have a good chemical stability. However, the main factor limiting their use in photoelectrolysis of water is their large band gap.

Their photosensitivity is limited to the UV region and does not make efficient use of the solar spectrum. The explanation for this phenomenon is that the valence band formed mainly by deep O²⁻:2p orbitals lies far below the O₂/H₂O redox level whereas the conduction band is primarily made from cationic orbitals. Several strategies to overcome this inconvenience were reported [5,6]. One of them is the creation of a low-lying valence band made from 3d orbital of transition metals. This approach is illustrated with the ternary oxide CuMnO₂ where copper array provides both valence and conduction bands. The d-levels of Cu(I) are known to split into a filled d-level of 1 eV above the O²⁻:2p orbitals and empty levels, forming the conduction band located above the H₂O/H₂ levels.

Photoelectrochemical properties are extended to other purposes such as photodegradation of pollutants to less harmful forms and photocatalysis [7,8].

Hydrogen sulfide H₂S is a widespread waste product. It is present in petrol-related industry and natural gas in non-neglected amounts. Hydrogen sulfide decomposition using photocatalysts can provide an interesting alternative way of converting it into less harmful products such as polysulfides S_n²⁻ and hydrogen, which otherwise requires a succession of complex steps [9]. Moreover, hydrogen is highly valued as an energy source and an important chemical feedstock for organic synthesis [10].

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CuMnO₂ occurs mostly as p-type material and exhibited a direct band gap of 1.23 eV close to the ideal value required for photoelectrochemical applications. It is a potentially suitable candidate for conversion of light to chemical energy because of its good chemical stability in alkaline electrolytes [11] and its sufficiently positive flat band potential. H₂ evolves at a much higher potential than is expected usually in the dark.

Improvement in the performance may be induced by combining suitable n-type photoanode and p-type photocathode and when higher conversion efficiencies are obtained [12].

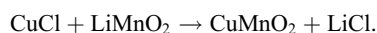
In the present paper, we report on photocatalytic hydrogen production from p-CuMnO₂/n-Cu₂O suspended in an alkaline solution containing either S²⁻ or SO₃²⁻ as holes scavengers.

2. Experimental

All of the reagents used in this work were of an analytical grade and were used without further pretreatment.

Pure CuMnO₂ and doped CuCa_{0.03}Mn_{0.97}O₂ were prepared by solid-state reaction from *stoichiometric* amounts of binary oxides Cu₂O, Mn₂O₃ and CaO. The starting oxides were homogenized, pressed into pellets and placed into a quartz tube. The tube was evacuated to a pressure of 2×10^{-5} Torr and sealed. The tube was heated at 960°C. The same procedure was repeated until the reaction was complete i.e. a single phase was detected by the X-ray diffraction. Then a black sintered powder was obtained. Pure CuMnO₂ was labeled as CuMnO₂-D.

In order to obtain a powder with a higher specific surface, a second synthesis method has been adopted. CuMnO₂ was obtained from LiMnO₂ via Cu → Li exchange (CuMnO₂-E) in molten chloride CuCl:



The reagents were pressed and heated in an evacuated quartz tube for 5 days at 590°C, CuMnO₂ was recovered by leaching with water.

LiMnO₂ was obtained by heating a mixture of Li₂CO₃ and Mn₂O₃ at 880°C in a pure argon atmosphere. A 5% weight excess of carbonate was added. The oxidation state of manganese has been confirmed by iodometric titration and was found to be 3 ± 0.01 .

The specific areas were determined in the means of BET isotherms measured using N₂ at 77 K (Coultronics Model 2100 E).

Electrochemical measurements were performed in 1 M KOH (pH = 13.4) using “three electrode device”: the Ca-doped CuMnO₂, 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 *I*–*V* characteristics were recorded with a PRT 20-2X Tacussel potentiostat

under 85 mW cm⁻² light intensity from a 250 W Oriel (model 66183) tungsten-halogen lamp.

For photoactivity, typically 50 mg of catalyst powder were suspended in 40 ml of an alkaline solution in a water cooled double walled Pyrex reactor thermostated at $30 \pm 1^\circ\text{C}$. A 500 W halogen lamp (General Electric Company) was employed as the light source. The solution was purged with pure nitrogen for 15 min prior to illumination to remove dissolved oxygen. The evolved gas was identified as hydrogen by gas chromatography using Ar as carrier gas. The volume of hydrogen evolved was collected in a water manometer and determined volumetrically.

Blank tests, carried out in the same conditions, showed that no hydrogen was detected when the catalyst was maintained in the dark.

3. Results and discussion

The X-ray powder pattern of all CuMnO₂, taken with Cu k_α radiation, revealed a well-crystallized single phase with the space group C2/m (Fig. 1). The unit cell parameters were in good agreement with our previous results [13]. The crystallite sizes determination by X-ray diffraction were made using the line broadening technique, it varies from 43 nm to 36 nm for CuMnO₂-D and CuMnO₂-E, respectively.

The pure and doped oxides, as prepared, were low mobile p-type semiconductors from the results of thermoelectric power [14]. More detailed investigations regarding the photoelectrochemical behavior are currently under way and the results will be reported elsewhere along with the optical properties. The oxides showed a long-term stability in basic medium (KOH 1 M). Indeed, after irradiation for 3 h, the X-ray diffraction did not show any change or foreign impurities.

3.1. Photoelectrochemistry

Undoped CuMnO₂ had a room temperature resistivity ρ of $\sim 10^5 \Omega \text{ cm}$ and the electrical resistivity of Ca-doped CuMnO₂ did not decrease significantly ($0.6 \times 10^4 \Omega \text{ cm}$) unlike the isotype oxides CuMO₂ (M = Al, Fe or Cr), in which ρ decreased by five orders of magnitude [6]. Photoelectrochemical characterization was done with calcium-doped CuMnO₂ in 1 M KOH at a potential sweep rate of 2.5 mV s⁻¹ (Fig. 2). The photocurrent *i*_{ph} started flowing at a potential *V*_{on} of +0.15 V and increased towards cathodic potential. This phenomenon is characteristic of a p-type semiconductivity. It was also observed that *i*_{ph} increased slowly without reaching a saturation value. This behavior is ascribed to the resistive nature of CuMnO₂ and the recombination of charge carriers took place at the grain boundaries that results in low quantum efficiency.

The photocurrent onset potential can be reasonably likened to the flat band potential *V*_{fb}. The photogenerated electrons and holes are separated in the depletion layer *W*.

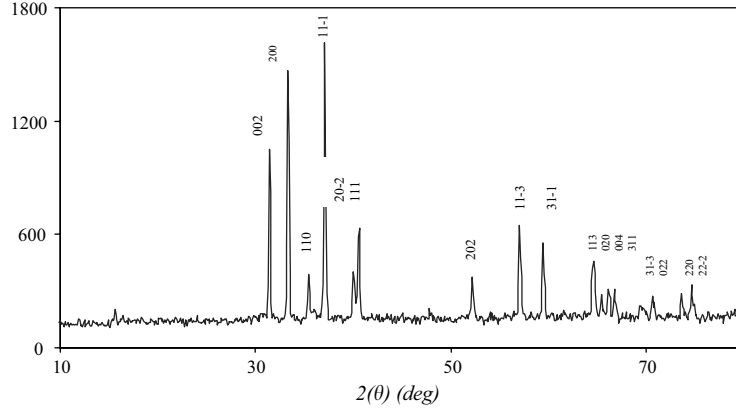


Fig. 1. XRD spectra of CuMnO₂ catalysts prepared by direct solid-state reaction into a quartz tube at 960 °C.

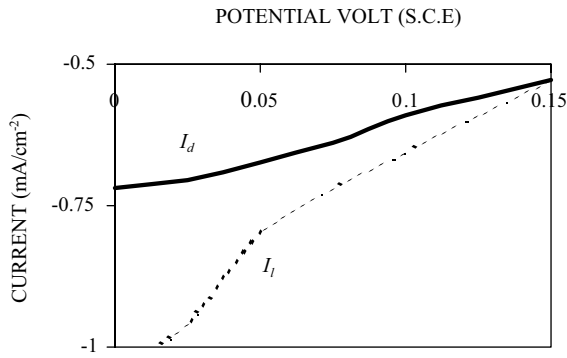


Fig. 2. The instantaneous photocurrent I_i and the dark current I_d of CuMn_{0.97}Ca_{0.03}O₂ as a function of sample potential V (SCE). Electrolyte: 1 M KOH, pH = 13.4, N₂ flushed.

V_{fb} was almost pH independent. The position of the valence band can be predicted from the relation [15]:

$$D = 4.75 + e V_{fb} + 0.056(\text{pH} - \text{pH}_{\text{pzzp}}) + \Delta E$$

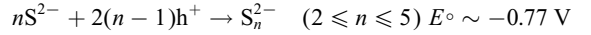
pH_{pzzp} is the pH at the point of zero zeta potential (pzzp), in our case, $\text{pH} - \text{pH}_{\text{pzzp}} = 1.2$. ΔE is the separation between the Fermi level and the valence band that was determined from electrical measurement (~ 0.1 eV) [14]. The valence band edge was therefore: 5.1 ± 0.1 eV below the vacuum level. This value is close to that observed with the isostructural oxides CuCrO₂ and CuFeO₂ [6]. This is due to the fact that the valence band is made up of mainly Cu-3d orbitals.

3.2. Photoactivity

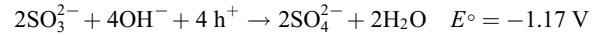
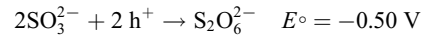
The electrons transfer occurs across the interface when levels of similar energy exist on both sides of the interface depending on V_{fb} and the potential E° of the redox couple. On the other hand, to avoid the recombination which takes place in operating conditions, a band bending of about 0.5 V is recommended [16]. The p-CuMnO₂ photocathode is com-

bined to the n-Cu₂O photoanode² and the whole system acts as a p/n microphotoelectrolysis cell in a short circuit configuration. The Fermi level, being equal throughout the whole system for load conditions remains high enough for electrons in the conduction band to reduce water to gaseous hydrogen. Absorption of light promotes electrons in the conduction band, where the potential (-0.88 V) is sufficient to liberate hydrogen. At the same time, holes in the valence band, located at 0.35 V, move into the bulk towards the n-Cu₂O photoanode where they are transferred to reduced species X^{2-} ($=S^{2-}$ or SO_3^{2-}). Sulfide S^{2-} and sulfite SO_3^{2-} are particularly favorable as hole scavengers. According to the main redox reactions the result is as follows:

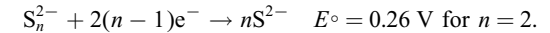
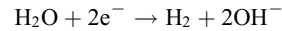
Photoanode³ n-Cu₂O:



or



Photocathode p-CuMnO₂:



The standard redox potential of SO_3^{2-}/SO_4^{2-} couple in base (pH = 13.4) is -1.17 V while that of $SO_3^{2-}/S_2O_6^{2-}$ is -0.50 whatever the pH value. Electron-hole recombination depends on the degree of the band bending within the semiconductor.

² Unreacted Cu₂O was detectable by chemical analysis. CuMnO₂ soaked 24 h in 50% NH₄OH leaves the solution blue due to the formation of the aqua complex $Cu(NH_3)_n^{2+}$. On the other hand, the I - V plot of sintered Cu₂O at 960 °C under static vacuum (evacuated silica tube) showed n-type semiconductivity under illumination [17].

³ The precipitation of sulfur is prevented in strong alkaline solution and preliminary experiments showed that it stays dissolved in the form of polysulfides S_n^{2-} ($n = 2 \rightarrow 5$).

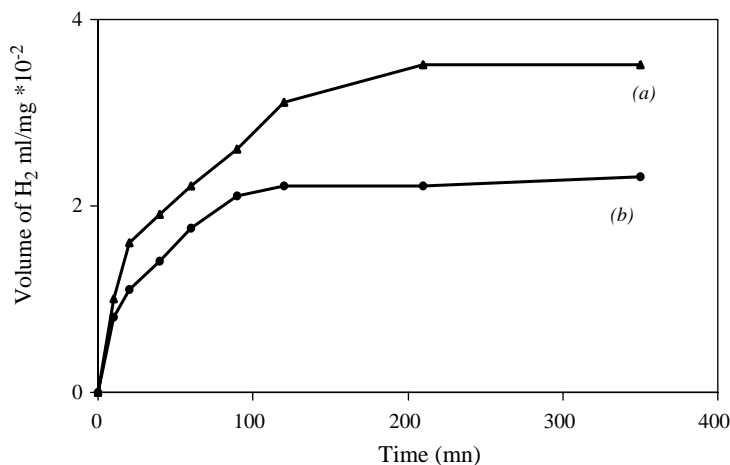


Fig. 3. Hydrogen evolved [$\text{ml}(\text{mg catalyst})^{-1}$] vs illumination time for (a) $\text{CuMnO}_2\text{-E}$ (b) $\text{CuMnO}_2\text{-D}$. (40 ml of S^{2-} 0.1 M/KOH 1 M solution, 50 mg of catalyst, $\text{pH} = 13.4$).

In the case of S^{2-} , the volume of H_2 increases monotonically with a rate formation of $10^{-2} \text{ ml h}^{-1} \text{ mg}^{-1}$ ($\text{CuMnO}_2\text{-D}$) (Fig. 3). Simultaneously, the color of the solution turns yellow. The more hydrogen released the more yellow hydrogen solution is. For a hydrogen volume of $\sim 0.15 \text{ ml}$, the transmittance of the solution decreases by $\sim 25\%$. This behavior is ascribed to the increasing concentration of yellow polysulfides S_n^{2-} . These ions function like optical filters and lower the transmission of light falling on the dispersed catalyst. Moreover, S_n^{2-} are reduced in competition with water molecules when their concentration attains a critical value. This dual behavior explains the saturated value of H_2 -liberation reached beyond three hours.

$\text{CuMnO}_2\text{-E}$, synthesized at lower temperature (590°C), has a higher specific surface and improves the hydrogen production by about 30% compared to $\text{CuMnO}_2\text{-D}$. Electrons photogenerated within $L_D + W$ of the interface have a high probability of diffusing in the electric field layer. They are separated; and then reduce H_2O molecules to hydrogen. L_D is the hole diffusion length and W is the depletion layer thickness.⁴ For a constant mass of powder catalyst, the number of particles is higher than that of $\text{CuMnO}_2\text{-E}$. Each particle behaves as a p/n microphotochemical diode, and therefore leads to an increase in hydrogen production (Table 1).

No hydrogen evolved below $\text{pH} 12$. This value coincides somewhat with the second pK_a value of the diacid H_2S ($\text{pK}_a = 11.96$ [18]) showing that the determining parameter of H_2 evolution was mainly the concentration of S^{2-} free ions. Below $\text{pH} 12$, toxic H_2S vapors were highly detected and the concentration could not be controlled.

⁴ No data relative to the dielectric constant ϵ of the new oxide CuMnO_2 , are available in the literature, therefore the length W cannot be known.

The oxidation of sulfite SO_3^{2-} led SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$, quantitative analysis was not performed. At the beginning, the volume of released H_2 increases monotonically as long as the concentration of SO_3^{2-} remains high. The lessening of H_2 formation over time can also be attributed to the fact that we work with a buffered solution ($\text{pH} = 13.5$) as well as to the back reactions resulting from the irradiation of p/n-photochemical diode in a basic thiosulfate solution (Fig. 4). However, it should be taken into account that the system has not been optimized for the concentration of SO_3^{2-} and the pH . It would be expected that applying higher concentration of SO_3^{2-} allowed to obtain a higher efficiency of light conversion to chemical energy of hydrogen. Preliminary results relative to other delafossite oxide showed a maximal efficiency at around $\text{pH} = 8$ [19].

4. Conclusion

H_2 evolution under visible light was accomplished using the new active catalyst CuMnO_2 which did not require any noble metal or external bias. This oxide has a direct band gap of 1.23 eV, close to the ideal value required for photoelectrochemical applications. It is stable towards photocorrosion in aqueous alkaline medium in the presence of suitable redox couples such as S^{2-} and SO_3^{2-} . The I - V characteristics were used to establish the type of semi-conductivity, the negative direction of i_{ph} confirms the p-type character.

p- CuMnO_2 is combined to n- Cu_2O in 1 M KOH containing either S^{2-} or SO_3^{2-} , the whole system acts as a p/n microphotochemical diode. The conduction band potential lies at -0.88 V , sufficient to reduce water molecules even in a highly alkaline solution. In parallel, sulfides are oxidized to colored polysulfides S_n^{2-} . When their concentration increases, S_n^{2-} ions compete with the reduction of

Table 1
Some physical properties of CuMnO₂

Sample preparation	Specific mass mass (g cm ⁻³)	Specific area (m ² g ⁻¹)	V_{fb} (V SCE ⁻¹)	$H_2(\text{ml mg}^{-1}) \times 10^{-2}$ after 4 h	
CuMnO ₂ -D	5.324	1.10	+0.15	2.3 ^a	2.48 ^b
CuMnO ₂ -E	5.281	2.38	—	3.5	3.8

^a Volume obtained in 1 M KOH, 0.1 M S²⁻

^b Volume obtained in 1 M KOH, 0.1 M SO₃²⁻

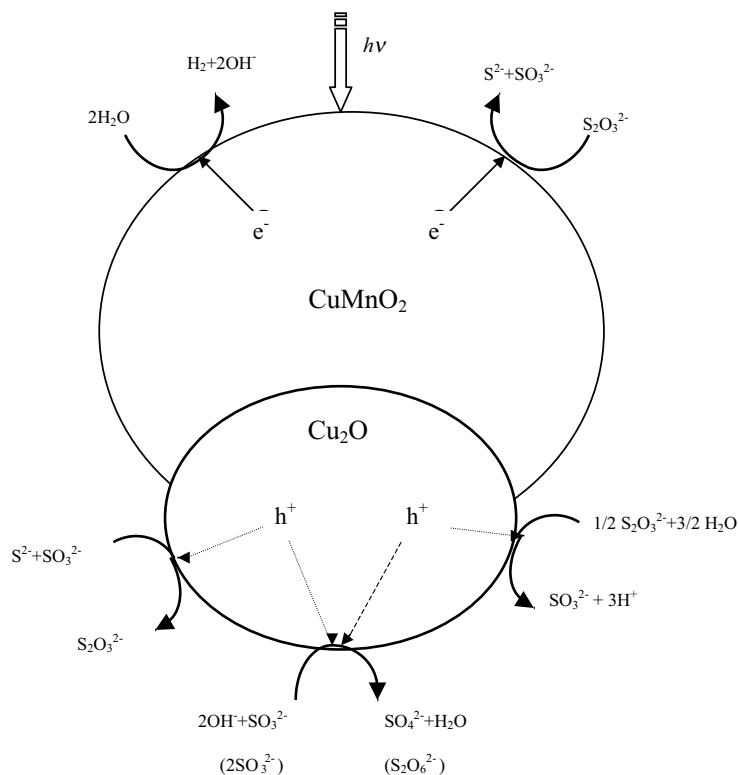


Fig. 4. Main path of photocatalytic reactions on n-Cu₂O/p-CuMnO₂ photochemical diode particle using thiosulfate ions as the electron donor.

water and lower the hydrogen formation. In addition, formation of S_n²⁻ resulted in a yellow solution which allowed fewer photons to enter. The specific surface of CuMnO₂ powders has a determining influence on their photocatalytic properties. The higher specific area implies a higher number of crystallites, each crystallite acts like a p/n microphotochemical. The sulfide concentration is a determining factor for H₂ formation and no photoactivity was observed below pH 12. H₂S is a waste product in the petroleum industry and can be converted photoelectrochemically over CuMnO₂ into less harmful forms. Additionally, the photodegradation of H₂S can constitute an attractive energy-storing process that could provide an alternative to water splitting for high purity H₂ generation from solar energy.

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