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VISIBLE LIGHT INDUCED HYDROGEN EVOLUTION ON COPPER OXIDE DEPOSITED ON ZINC OXIDE SYNTHESIZED BY THE HYDROTHERMAL METHOD

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ABSTRACT

The hetero-junction CuO/ZnO synthesized by hydrothermal route and characterized by thermal analysis, FTIR spectroscopy, X-ray diffraction, scanning electron microscopy, diffuse reflectance and electrical conductivity. As expected, the X-ray diffraction shows mixed phases i.e. CuO (tenorite) and ZnO wurtzite. The specific surface area is in the range (17-23 m^2 / g) while the crystallite size lies between 31 and 41 nm. The curves $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) indicate direct optical transitions at 3.1 eV for ZnO, and an indirect transition 1.41 eV for CuO. The electrical conductivity of CuO is found to increase with raising temperature, indicating a semiconductor behavior.

Keywords: photocatalysis, hetero-junction, CuO/ZnO, hydrothermal.

1. INTRODUCTION

During the last two decades, a great deal of research has been focused on the synthesis of different nanostructures, which help in the understanding of the phenomena of growing nanomaterial. In this respect, several nanostructures of oxide semiconductors with potential applications in the energy supply and environmental protection have been explored. Among the candidates, ZnO is considered to be a popular and promising material for the nanoscale based devices due to its direct band gap of ~ 3.4 eV and high exciton binding energy of 60 meV. ZnO nanostructures are used in the development of light emitting diodes (LEDs), piezoelectric transducers, gas sensors and dye-sensitized solar cells. As research on the fabrication of ZnO is maturing and the pronounced effect of the morphology of ZnO, nanostructures has been debated. It is crucial to have a controlled morphology of the nanostructures for specific applications, due to its backbone role in the performance of solar devices. Several methods have been reported for the synthesis of ZnO nanostructures, either by physical or chemical approaches. Moreover, more works are devoted in the synthesis of well align ZnO nanostructures. The oriented ZnO morphology is highly demanded for the technological devices. The solvothermal technique has been widely applied for preparing ZnO nanostructures by autoclaving at temperatures between 100 and 200 °C from alkaline zinc salts solutions in alcoholic media often in the presence of different additives and/or reaction conditions (Liu et al., 2003) obtained monodispersed, highly crystalline ZnO nanorods by adding ethylene diamine to the reaction mixture. (Cheng et al., 2000) demonstrated the importance of alcohol (methanol or ethanol) in the preparation of one-dimensional ZnO nanostructures, by producing them directly by autoclaving zinc acetylacetonate and NaOH in an alcoholic medium without any other additive. This occurs, for instance, in some hydrothermal reactions using cetyl-trimethyl-ammonium bromide (CTAB) as additive. As reported by (Li et al.,2008), the hydrothermal heating at 130 °C of an alkaline solution of zinc acetate with CTAB leads to arrays of nanorods in the form of flower-like structures formed by tapered ZnO nanorods with diameter decreasing from 400 nm at the base, down to 80 nm at the top. However, the same reaction conducted in the range (150–180 °C) produces cabbage-like ZnO structures, built up by overlapping bi-dimensional ZnO nanosheets. On the other hand, (Qiu et al.,2010) reported that the hydrothermal treatment of zinc acetate and urea in the presence of CTAB leads to superstructures of meso/micro-porous ZnO nanoplates. The variety of morphologies of ZnO nanostructures, obtained by controlling the solvothermal reaction conditions, is mainly due to different surfaces structures of the wurzite ZnO with different growth rates that could induce anisotropic growth (Wang et al.,2004). The Wurzite ZnO is a polar crystal with a certain iconicity formed by alternately stacking crystal planes, charged positively (Zn^{2+}) and negatively (O^{2-}) (Wang et al.,2003). Recently, nanocomposites based on ZnO have been studied and demonstrated with a higher photocatalytic activity due to the effective transfer of the charge carriers (Zhang et al.,2012). As an important *p*-type narrow band gap semi-conductor, CuO has been applied to improve the photocatalytic activity of some wide band gap semiconductors (Li et al 2010, Belhadi et al 2015).

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In this work we have synthesized three solids namely CuO, ZnO and hetero-junctions CuO/ZnO by hydrothermal route. They were characterized by TGA, XRD, FTIR spectroscopy, and UV-Visible spectroscopy and electrical conductivity.

2. MATERIAL AND METHODS

2.1. SAMPLE PREPARATION

Cu $(NO_3)_2$, $3H_2O$ is dissolved in 200 ml of an aqueous solution of $NaHCO_3$ of concentration 0.1 mol / l, then NaOH solution is added slowly with constant stirring until reach a pH 10. The mixture is stirred for 2 h, put in the autoclave at 150 ° C for 24 h. The precipitate is separated by centrifugation, washed with distilled water, then dried in an oven at 100 ° C overnight. The powder is calcined at 370 ° C for 4 h with a heating rate of 5 ° C/min. The support ZnO is synthesized from $Zn(NO_3)_2$, $6H_2O$ at pH ~ 10, the solution is evaporated and heated at 380 °C (4 h, 5 °C mn^{-1}). The hetero-junction 5% CuO/ZnO was prepared by impregnation of ZnO with an appropriate concentration of $Cu(NO_3)_2$, $3H_2O$; the suspension is agitated for 2 h. The mixture was transferred into a Teflon-lined stainless steel autoclave. The crystallization was performed at 80 °C under autogenous pressure for 24 h. The powders are heated at 380 °C for 4 h and furnace cooled.

2.2. Catalysts characterization

TGA is performed in a commercial thermo balance (Perkin Elmer STA 6000). The phases are identified by XRD using Cu Kα radiation (λ= 0.154178 nm). The sample (100 mg) is dissolved in 20 mL of aqua regia (2.5 mL HCl/7.5 mL HNO_3), and the resulting solution is analysed by atomic absorption spectroscopy (AAS, Varian SpectrAA) in the frequency range (190–900 nm). The diffuse reflectance spectra are recorded with a UV–VIS Cary 500 spectrophotometer.

For the photo electrochemical (PEC) characterization, the powder is pressed into dense pellets (Ø = 13 mm, thickness ~ 1 mm) and sintered at 600 °C (compactness ~ 75%). A copper wire is fixed on the back pellet with silver paint and isolated with epoxy resin in a glass tube. The electrochemical measurements are carried out in a standard Pyrex cell under N_2 atmosphere and shielded from daylight by an opaque box. The electrode surface is polished with fine emery papers under water flow. Pt electrode serves as emergency electrode, and the potentials are controlled with a PGZ301 potentiostat and reported with respect to a saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1. Thermal and structural properties

The combined DTA/TGA plots of representative samples are shown in Fig. 1. The TGA curve presents a first loss due to a well-defined plateau for the last step, indicating the phase formation. However, in light of the DTA plot, three major weight losses are easily identified. The first one occurring at ~ 100 °C reflects the loss of physically adsorbed surface water which begins at ~ 90°C. The weight losses starting at 200 and at 250 °C are due to the decomposition of Cu- and Zn-nitrates respectively. The end products have been identified as CuO and ZnO.

The Thermal method produces homogeneous powder with narrow size distributions (Cheng et al.,2000). By contrast, the synthesis of oxides by ceramic route requires high temperatures and produces irregular particles with large crystallites size and consequently low active surface. The purity of the hetero-junction is checked by XRD, which indicates mixed phases. Although the low temperature synthesis, the XRD lines (Fig. 2) are fairly narrow indicating a good crystallinity of CuO (Tenorite JCPDS card N°: 05-0661) and ZnO (Wurtzite JCPDS card N°: 36-1451). No secondary phase is detected. The crystallite dimension of CuO (Table I) is evaluated from the full width at half maximum ($D= K\lambda/\beta\cos\theta$), where K = 0.94 is the shape factor and β (radian) the broadening of the intense XRD peak (111). The average sizes of the hetero-junctions is 41 nm, whereas the sizes of ZnO and CuO are ~ 30 and 57 nm, respectively, indicating nano-morphological aspect. The concentrations of copper, determined by AAS, are very close to the nominal ones (Table 1).

The characteristic peaks of CuO/ZnO are also identified by the Fourier transform infrared spectroscopy (figure not shown); the spectra are very similar much except CuO. The peak at 517 cm^{-1} corresponds to Zn–O bond, while the band at 1626 cm-1 is assigned to O–H bending vibrations because of absorbed water when the sample is handled in air. The peak at 1423 cm^{-1} is ascribed to the O–H stretching mode, these results are similar to that reported in the literature (Li et al., 2008).

Table 1: Characterization of the oxides

Oxides	Cu theo(%)	Cu real(%)	d (nm)	Ssp (m^2/g)
CuO			57	17
5%CuO/ZnO	5	4.25	41	18
ZnO			30	23

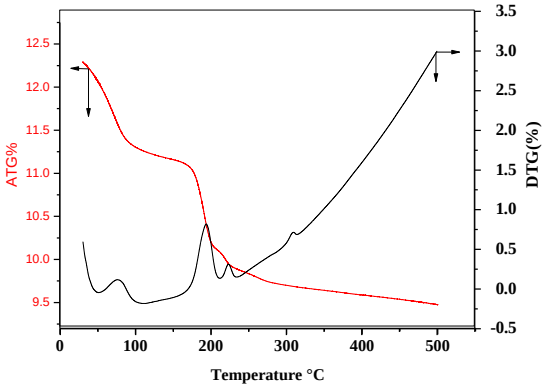

Fig. 1: Thermogravimetric profiles of CuO/ZnO

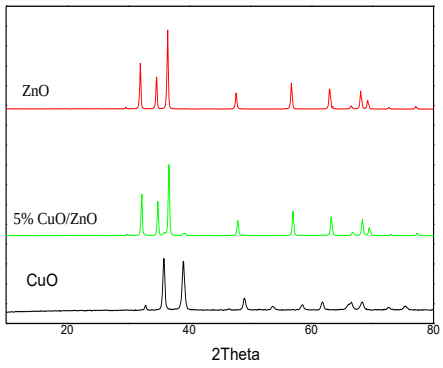

Fig. 2 : XRD patterns of CuO, ZnO, and 5%CuO / ZnO

3.2. Optical and photo-electrochemical properties

The optical properties are important in photocatalysis. CuO crystallizes in the NaCl structure with two interpenetrating face-centred cubic lattices; the oxygen crystal field splits the Cu^{2+}: *3d* orbital into two sets of orbitals; a value of 1.50 eV is obtained from the plot $(\alpha h\nu)^2$ versus the incident photons ($h\nu$), in agreement with the literature data (Qiu et al.,2010).

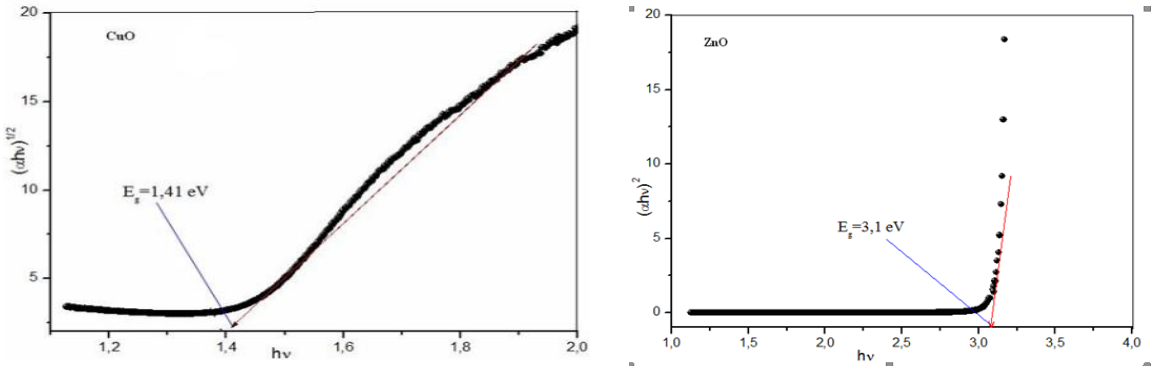

Fig. 3: Determination of the indirect and direct optical transitions of CuO and ZnO.

The relationship between the absorption coefficient (α) and the energy ($h\nu$) is expressed by (Wang et al., 2003) :

$$(\alpha h\nu)^n = A\,(h\nu - E_g)$$

A is a constant and n= 2 and 0.5 for direct and indirect transition respectively.
Figures 4a and 4b represent $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as function of $h\nu$ of CuO and ZnO, respectively. The direct and indirect transitions are evaluated by extrapolating the linear region at the steeply increasing curve of the plots to the hv axis. The obtained values of 1.41 and 3.1 eV are in good agreement with those reported in the literature (Chen et all.,2004 ; Wei et all.,2013).

3.3. Application

The curves of H_2 production for 5% CuO/ZnO as a function of the time under visible light have the nearly same shape, with a maximum (V= 2.4 mL) at 60 mn (Fig. 4).

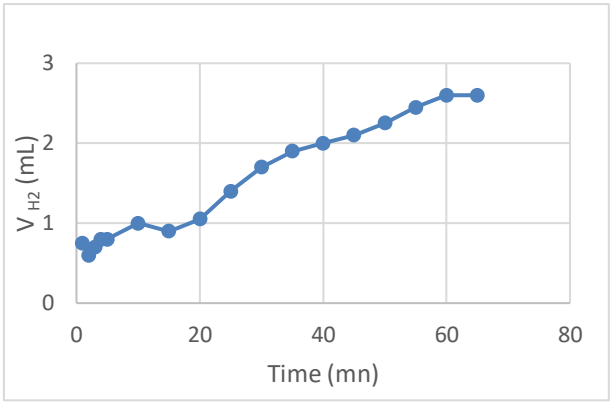

Fig. 4. Evaluation of the quantity of hydrogen produced in presence of 5% CuO /ZnO

4. CONCLUSION

The hetero-junction p-CuO/n-ZnO is prepared by impregnation / hydrothermal method at low temperature, not exceeding 400 °C to preclude the formation of secondary phases and to obtain small crystallites size. We note that the conductivity of the sensitizer CuO increases with temperature indicating a semiconductor material studied behavior. The synthetized oxides were successfully applied for the H_2 production under visible light. The hetero-junction has been successfully tested for the dyes degradation and the results will be reported very soon.

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