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Cu_2O precipitation-assisted with ultrasound and microwave radiation for photocatalytic hydrogen production

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ABSTRACT

Copper oxides are considered efficient photocatalysts for H_2 generation. In addition, due to their interesting properties such as surface plasmon resonance, they are applied in photo-induced reactions. In heterogeneous photocatalysis, CuO and Cu_2O are the main oxides based in copper that are used as catalysts in water splitting. In this work, Cu_2O is prepared by precipitation method assisted with ultrasound and microwave radiation at 80 °C. For the Cu_2O synthesis, the use of glucose is proposed as a reducing agent due to its abundance in nature, non-toxicity, and low cost. According to the results obtained, the highest glucose concentration and the suspension exposure to microwave irradiation promote the formation of Cu_2O particles with low and homogeneous particle size and a convenient position of their conduction and valence band to produce H_2. The highest H_2 generation using Cu_2O under the aforementioned experimental conditions is 78 μmol g_{cat}^{-1}. Additionally, the effect of adding glucose in the photocatalytic reaction is studied in order to provide more electrons to the reaction due to its effect as a hole scavenger, which inhibits the recombination of the electron and hole, promoting a higher H_2 production (400 μmol g_{cat}^{-1}).

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Introduction

Recently, the pollution levels in the environment have been increasing at alarming rates, so much so that it is necessary to act and propose alternative technologies to mitigate pollution levels. The use of hydrogen as fuel is one of the best alternatives that have been proposed to replace fossil fuels. There are several advantages from the use of hydrogen as a fuel, for example; it is a potential emission-free fuel and it can be produced using renewable energy which can reverse the high pollution levels recorded daily. Among the options for H_2 production, photocatalytic water splitting is an attractive reaction due to its low-cost, clean, and sustainable process that requires solar light and a semiconductor with a conduction band edge more negative than the required potential for

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$H^+ \rightarrow H_2$. When a semiconductor material is irradiated with energy equal or higher than its band gap, electrons and holes are generated in the conduction and valence bands, respectively. Photogenerated electrons can reduce hydrogen ions to form hydrogen and photogenerated holes participate in oxygen generation [1,2]. Several semiconductor compounds have been proposed as photocatalysts in order to produce hydrogen from water splitting. The photocatalysts proposed in this area are classified into four groups: 1. d^0 metal (Ti^{4+}, Zr^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, and Mo^{6+}) oxide, 2. d^{10} metal (Cu^{+1}, In^{3+}, Ga^{3+}, Ge^{4+}, Sn^{4+}, and Sb^{5+}) oxide, 3. f^0 metal (Ce^{4+}) oxide, and 4. An additional small group of non-oxide photocatalyst (ZnS, CdSe, GaN, G_3N_4, AgBr, C_3N_4) has been proposed [3]. Some materials can be used as co-catalysts (Cu, Ag, Pt, Pd, RuO_2, Ni, etc) to avoid fast recombination between photogenerated charges, since these materials can act as electrons and hole traps [1]. Copper oxide (d^{10} metal) represents an alternative photocatalyst which can be activated with visible light to be used in the photo-induced process [4]. Copper (Cu) is one of the most abundant metals on Earth, it is cheap, and it has high electrical conductivity. In addition, copper exhibits plasmonic properties related to an enhancement in the photocatalytic activity due to the Schottky junction and its surface plasmon resonance (SPR) [5]. It is reported that this effect forces the electrons and holes moving in different directions to minimize their recombination.

In heterogeneous photocatalysis, CuO and Cu_2O are the main oxides based in copper that have been used as a catalyst in water splitting [6,7]. CuO (black) and Cu_2O (reddish) oxides are p-type semiconductors with direct band gaps (<2 eV) [8]. In addition, the potential of the conduction band (CB) of Cu_2O is negative enough, to carry out the reduction of H^+ to H_2. On the other hand, Montini and collaborators have made an extensive study in the application of Cu_xO_y (x, y = 0, 1, 2) thin films, specially as CuO photocatalysts for H_2 production [9,10]. Particularly, they have found a direct correlation between the morphology and a possible upward shift in the conduction band of CuO for photocatalytic H_2 production [9], and with the exposition of the crystallographic plane (−111) of CuO [10], which confirms the possibility for the application of CuO particles.

In literature, there are several reports of Cu_2O obtained by different synthesis methods as powders and thin films, which are summarized in Table 1.

In Cu_2O synthesis it is necessary to add a reducing agent, which generally is an organic molecule to reduce the precursor of copper ($Cu^{2+} \rightarrow Cu^{1+}$) [11–36]. The most common reducing agents are ascorbic acid ($C_6H_8O_6$), ethylene glycol, and sodium tartrate ($Na_2C_4H_4O_6$). However, the latter compound has a strong chelating effect between copper and tartrate ions, which limits the diffusion of the copper to the reaction medium. In addition, the use of other molecules as a reducing agent has been proposed, such as TMEDA, hydroxylamine hydrochloride, related to high costs and a long procedure to remove them from the final product. As an alternative of these compounds, glucose ($C_6H_{12}O_6$) is an excellent reducing agent, which has numerous advantages; for example, it is ecofriendly, abundant as biomass residue, and is related to low costs [38,39]. Regarding the synthesis method, there are several reports which proposed the use of a sonochemical method to produce homogeneous particles with a narrow distribution size for photocatalytic, catalytic, and adsorptive applications. Also, the use of microwaves to assist precipitation is of high interest due to the rapid transfer of energy, heating homogeneity, rapid phase formation and a small particle size being able to obtain materials with unique properties [40,41]. The use of microwaves has been recently employed in the synthesis of Cu_2O for its application as a photocatalyst and gas sensor [28,29]. However, the synthesis of Cu_2O by microwave and its application as a photocatalyst for H_2 generation has not been reported so far. Regarding the sonochemical synthesis of Cu_2O, there are two reports in which the material has been employed as a photocatalyst and photoelectrocatalyst for H_2 production [11,25].

In the paper herein, the preparation of Cu_2O by precipitation assisted by ultrasound and microwave methods is proposed to promote homogeneous heating and the formation of particles with both a low and closed distribution size. Cu_2O samples were tested as catalyst in the photocatalytic hydrogen production.

Experimental

Synthesis of Cu_2O

Cu_2O was prepared by precipitation assisted with ultrasound and microwave radiation. This method consists in the preparation of two solutions. In the first one, 0.003 mol of copper acetate ($Cu(CO_2CH_3)_2$) (98% Aldrich) was dissolved in 40 mL of deionized water at 50 °C. A second solution of 0.6 mol of NaOH (99% Fermont) was prepared and added to the copper solution with vigorous stirring at 80 °C. The resulting brown suspension was maintained at 80 °C for 2 h and then different amounts of glucose ($C_6H_6O_{12}$) (99% Aldrich) were added to obtain a molar ratio of 1:0, 1:0.5, 1:1, and 1:1.5 regarding copper acetate. The resulting mixture was stirring vigorously for 2 h and, after this time, we obtained a red solution. On the other hand, this mixture was exposed to different energy sources (ultrasound and microwave) to study their effect on the physical properties developed by Cu_2O. The mixture was exposed to ultrasound radiation employing a cavitation field generated by a 150 W Hielscher's UP200Ht ultrasonic processor for 1 h. The temperature at the end of the ultrasound treatment was 80 °C ± 5 °C. Alternatively, the mixture was exposed to microwave radiation, using a 150 W MARS-6 programmable microwave and a temperature of 80 °C for the same time (1 h). The resulting mixtures obtained were centrifuged and washed with deionized water and ethanol in order to remove the by-products generated during the synthesis process. Finally, the powders were dried at 80 °C. Fig. 1 shows a scheme of the Cu_2O synthesis by precipitation assisted by different energy sources. The samples obtained will be hereinafter referred to as Cu-*x*/y, where *x* is the molar relation of copper acetate and glucose and y refers to the synthesis method P = precipitation, US = ultrasound, and MW = microwave.

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