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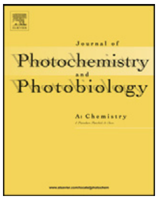

Visible-light-driven photocatalytic hydrogen production over dye-sensitized β-$BiTaO_4$

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ABSTRACT

β-$BiTaO_4$ photosensitized with methylene blue, methyl orange, alizarine and eriochrome black T in order to extend its photoresponse into a visible region and the photocatalytic activity was evaluated for each sensitized material under visible light irradiation. The results demonstrate that β-$BiTaO_4$–methylene blue presented photocatalytic activity with respect to hydrogen production, which opens up prospects for improving systems that are able to drive photocatalytic reaction with visible light illumination to make effective use of solar light (~45% of visible light) to produce hydrogen from water.

1. Introduction

Semiconductor-mediated photocatalytic processes have been widely investigated in recent years as potentially efficient, economic and environmentally friendly methods for hydrogen production. Since 1972, after the pioneering work of Fujishima and Honda [1], who discovered that water can be photoelectrochemically decomposed into hydrogen and oxygen using a semiconductor (TiO_2) electrode under UV irradiation, a large number of metal oxides has been reported to have photocatalytic activity for water splitting. Nowadays, research efforts have attempted mainly to extend the photosensitivity of semiconductor photocatalysts toward the visible light region in order to fully harvest solar energy, since it accounts for approximately 43% of the incoming solar energy spectrum against only about 3% of UV light.

Several strategies for the development of visible-light-driven photocatalysts have been tested, such as dye sensitization, band gap modification by nonmetals doping and transition metal doping and co-doping [2,3]. Dye sensitization has been demonstrated as a useful tool to induce visible light photocatalysis on the surface of wide band gap semiconductors. The conceptual mechanism [4] of photocatalytic hydrogen production over dye-sensitized metal oxide semiconductor is based on light excitation of the dye sensitizer molecule (S) followed by electron injection into the conduction band of metal oxide, leading to the oxidized form of the dye (S^+). The excited electrons in conduction band migrate to the metal attached on semiconductor where water is reduced to achieve hydrogen. At the same time, the original form of the dye is regenerate by a sacrificial electron donor.

It is known that the positions of the valence band and conduction band are critical variable in determining the feasibility of semiconductor for hydrogen production. In the last decades a lot of attention was devoted to study bismuth niobates and tantalates. These materials are envisaged as interesting photocatalysts for eliminating organic pollutants from domestic or industrial effluents [5], as well as for producing H_2 by the photocatalytic decomposition of water under UV light irradiation [6]. Recently, we prepared nano-sized triclinic $BiTaO_4$ (known as type β polymorph, stable at high temperatures) by polymeric precursor method with BET surface area of $3.31\,m^2\,g^{-1}$ [7,8]. It is seven times much higher than surface area of $BiTaO_4$ obtained from solid state reaction. The band gap have also been estimated to be 2.65 and 2.45 eV using photoacoustic spectroscopic (PAS) method and density functional theory (DFT) calculations, respectively, as well as the positions of reduction and oxidation levels with respect to vacuum level were identified. Results showed that the energy level for water reduction (H^+/H_2) exist 0.5 eV lower than the conduction band (CB), thus leading to inject electrons into the solution phase for hydrogen production. Oxidation level (O_2/H_2O) exists about 0.7 eV higher the valence band (VB), so the holes can spontaneously transfer to the oxidizing potential of the water splitting with oxidation power 0.7 eV, which confirms that $BiTaO_4$ can be a good photocatalyst for hydrogen production. However, despite the narrow band gap energy

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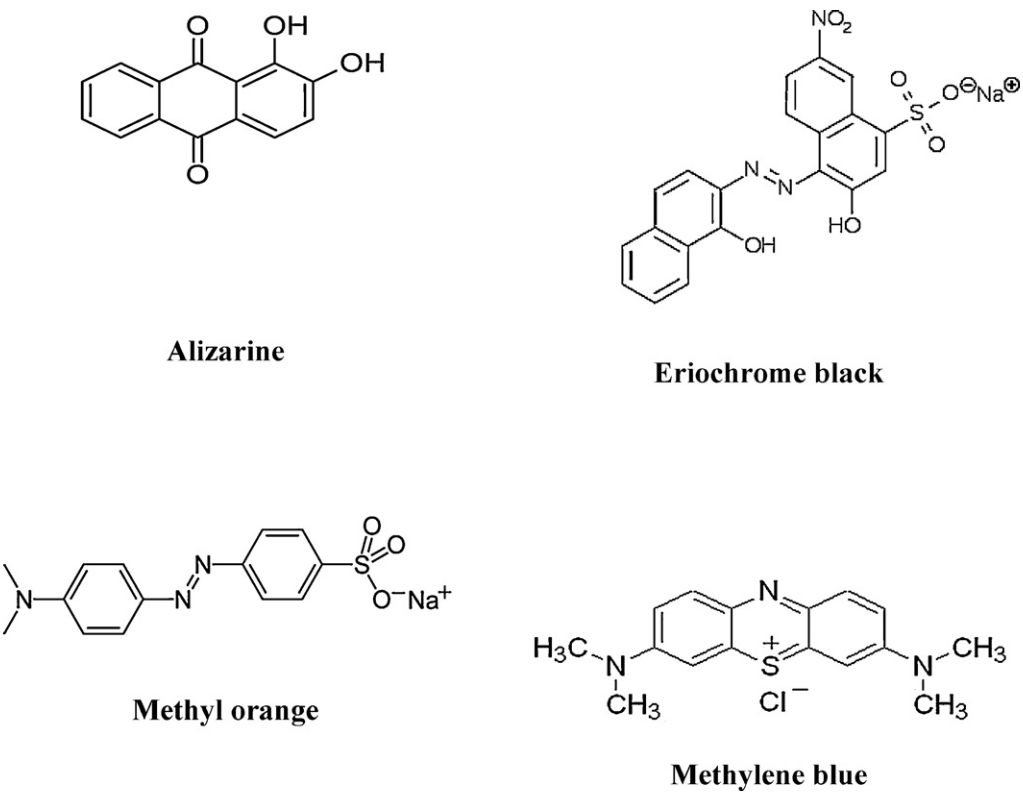

Fig. 1. Molecular structures of organic dyes.

(Eg < 3 eV) and the suitable VB and CB position, no photocatalytic activity is observed above 400 nm, probably due to the too low absorption intensity of β-$BiTaO_4$ in the visible region.

In this work we submitted $BiTaO_4$ to a photosensitization process to extend its photoresponse into a visible region and the photocatalytic activity was evaluated for each sensitized material under visible light irradiation. In order to accomplish the photosensitization, several cationic, anionic and neutral organic dyes, such as methylene blue, methyl orange, alizarine and eriochrome black T (Fig. 1), have been employed as photosensitizers.

Before sensitization, it was performed a previous study about hydrolysis reactions on the $BiTaO_4$ surface suspended in water in order to identify the optimum pH to promote the complete adsorption of dye on the $BiTaO_4$ surface. Metal oxide particles suspensions behave as if they were simple diprotic acids. In general, hydroxyl groups on the metal oxide surface are involved in the follow acid–base equilibrium:

$$>\mathrm{MOH_2}^+ = >\mathrm{MOH} + \mathrm{H}^+, \quad Ka_1 \qquad (1)$$

$$>\mathrm{MOH} = >\mathrm{MO}^- + \mathrm{H}^+, \quad Ka_2 \qquad (2)$$

The pH of zero point of charge (pHZPC) is given by one half of the sum of the two surface pK_as [9]. At high pH, under conditions in which the $\mathrm{pH} > \mathrm{pH_{ZPC}}$, the metal oxide surface become negative ($>\mathrm{MO}^-$) and the interactions with cationic dye will be favored, while anionic dye will be favored at low pH under conditions in which $\mathrm{pH} < \mathrm{pH_{ZPC}}$, where the surface is positively charged ($>\mathrm{MOH_2}^+$).

2. Experimental

2.1. $BiTaO_4$ preparation

$BiTaO_4$ was prepared by the citrate method according to reference [7]. In a typical synthesis, bismuth citrate and tantalum pentachloride ($TaCl_5$) are used as starting materials and citric acid and ethylene glycol as chelating agent and reaction medium, respectively. All reagents used in the entire procedure were of analytical grade.

2.2. Characterization

The powder obtained was characterized by X-ray diffraction (Shimadzu XRD6000), using CuK_α, Ni-filtered radiation, and scanning rate of 2° $2\theta\,\mathrm{min}^{-1}$, in a 2θ range of 5–80°, at 35 kV and 15 mA. The average crystalline sizes were calculated from the X-ray line broadening at $2\theta = 32.06°$ using the Debye–Scherrer equation [7,10]. The PAS experiments were performed using a spectrometer consisting of a 1000 W xenon arc lamp whose beam was modulated by a mechanical chopper (SRS, model SR540). This technique is able to give the absorption spectrum of a given sample directly.

2.3. Point of zero charge

The point of zero charge of $BiTaO_4$ was determined by the solid addition method according to the procedure described by Vieira et al. [11]. To a series of 50 mL of cylindrical flasks were transferred 10 mL of solution with pH varying of 1–12 and the initial pH values of each solution was adjusted by adding either 1.0 mol L^{-1} of hydrochloric acid or sodium hydroxide. The initial pH ($\mathrm{pH_o}$) of the solutions were then accurately measured and 0.040 g of $BiTaO_4$ was added to each flask, which was securely sealed immediately. The suspensions were then manually shaken, allowed to equilibrate for 24 h with intermittent manual shaking and the pH values of the supernatant were measured ($\mathrm{pH_f}$). The difference between the initial and final pH value, $\Delta\mathrm{pH} = \mathrm{pH_o} - \mathrm{pH_f}$, was plotted against $\mathrm{pH_o}$ and the point of intersection of the resulting null ΔpH corresponds to the point zero charge, $\mathrm{pH_{PZC}}$.