Journal of Photochemistry and Photobiology A: Chemistry 243 (2012) 61–64

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

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

D.L.S. Maia [a], I. Pepe [b], A. Ferreira da Silva [b], L.A. Silva [a,c,*]

[a] Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, Salvador 40170-290, Bahia, Brazil
[b] Instituto de Física Universidade Federal da Bahia, Campus de Ondina, Salvador 40170-290, Bahia, Brazil
[c] Instituto Nacional de Ciência e Tecnologia, INCT, de Energia e Ambiente, Universidade Federal da Bahia, 40170-290 Salvador-BA, Brazil

ARTICLE INFO

Article history:
Received 12 March 2012
Accepted 14 June 2012
Available online 23 June 2012

Keywords:
Bismuth tantalate
Dye-sensitized photocatalyst
Visible light
Hydrogen production

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

* Corresponding author at: Instituto de Química, Universidade Federal da Bahia, 40170-290 Salvador-BA, Brazil. Tel.: +55 71 3283 6881.
E-mail address: las@ufba.br (L.A. Silva).

1010-6030/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochem.2012.06.008

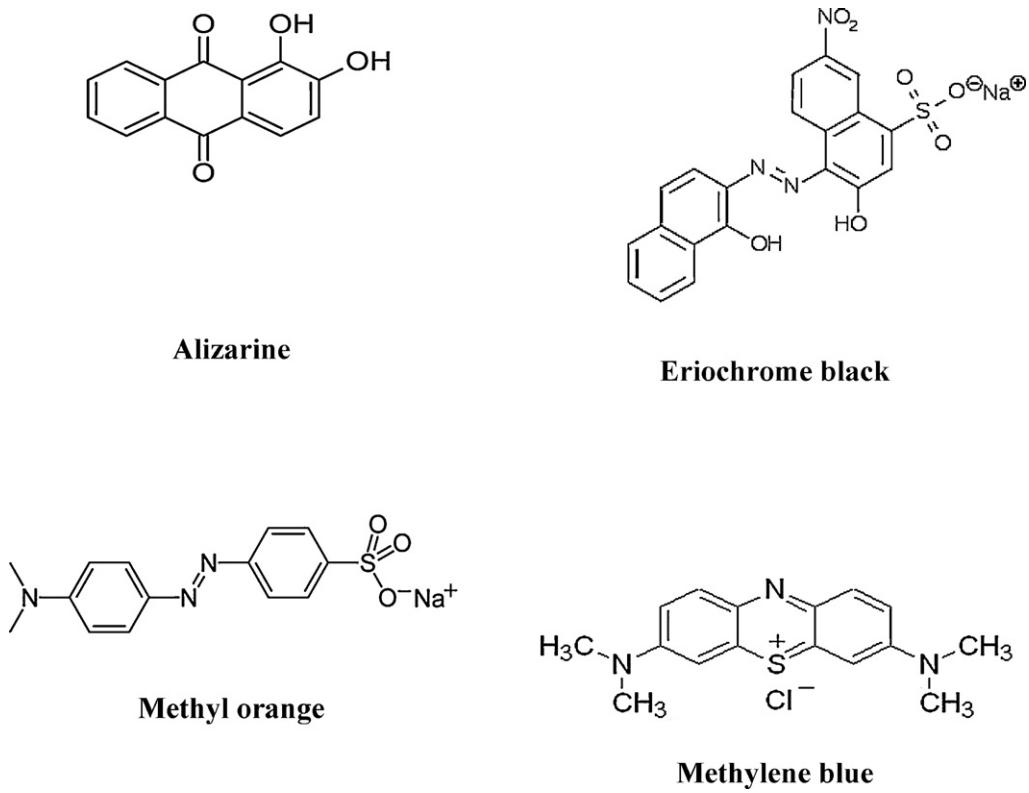

Fig. 1. Molecular structures of organic dyes.

(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:

$$>MOH_2^+ = >MOH + H^+, \quad Ka_1 \tag{1}$$

$$>MOH = >MO^- + H^+, \quad Ka_2 \tag{2}$$

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 pH > pH_{ZPC}, the metal oxide surface become negative ($>MO^-$) and the interactions with cationic dye will be favored, while anionic dye will be favored at low pH under conditions in which pH < pH_{ZPC}, where the surface is positively charged ($>MOH_2^+$).

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° $2\theta\,min^{-1}$, 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 (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 (pH_f). The difference between the initial and final pH value, $\Delta pH = pH_o - pH_f$, was plotted against pH_o and the point of intersection of the resulting null ΔpH corresponds to the point zero charge, pH_{PZC}.

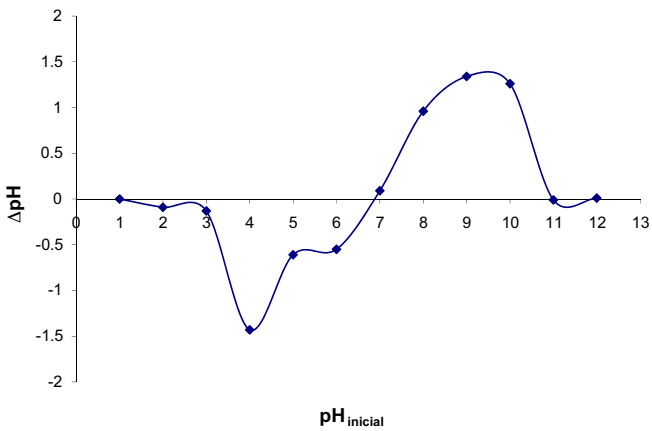

Fig. 2. Point zero charge of β-$BiTaO_4$.

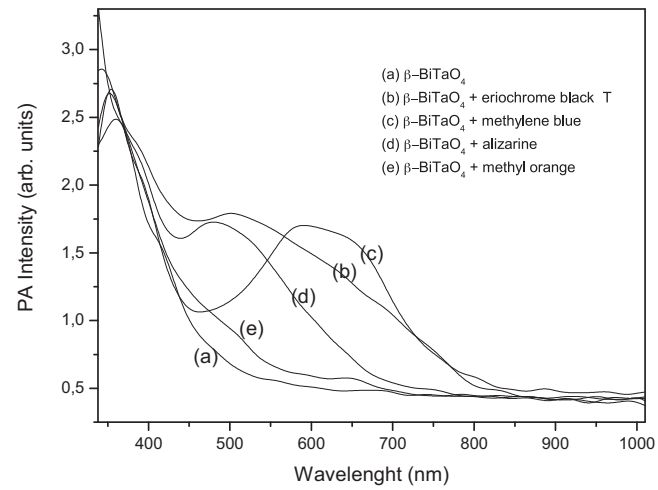

Fig. 3. Photoacoustic spectra of pure and photosensitized β-$BiTaO_4$.

2.4. Dye absorption

0.8 g of material was added to 40 mL of the organic dye with concentration of 10^{-4} mol L^{-1} in appropriate pH. The mixture remained under agitation for 24 h then centrifuged 4 times with deionized water, once with ethanol and dried at room temperature.

2.5. Photocatalytic reactions

A high-pressure 500 W Hg–Xe arc lamp was used as the light source for the photocatalytic reactions. The collimated light beam was passed through an IR filter, a focusing lens and a 418 nm cutoff filter before reaching the photocatalytic cell, which was air cooled to maintain a constant temperature. Before each experiment, the photocatalytic cell was purged with argon for 30 min to eliminate O_2. Hydrogen gas evolution was measured by gas chromatography SHIMADZU (GC2014) with thermal conductivity detection (TCD) and flame ionization detector (FID) with methanator. Because He and H_2 have similar conductivity values, argon was used as a carrier gas.

In a typical photolysis experiment, 60 mg of a target sensitized $BiTaO_4$ was dispersed in an aqueous solution (total volume = 60 mL) containing 30% isopropanol and 40 μL of 8% H_2PtCl_6 (~0.3 wt.% Pt), with pH adjusted to the adsorption pH by the addition of 1.5 mL of buffer solution (fenate, pH 9.3, for cationic dyes and acetate, pH 4, for anionic and neutral dyes). Metallic platinum was deposited *in situ* on the photocatalyst surface by the photodecomposition of $PtCl_6^{2-}$. The photocatalytic cell was equipped with argon gas inlet/outlet tubes, which serve to collect and transfer gaseous products to the analytical system.

3. Results and discussion

Pure triclinic phase of $BiTaO_4$, known as high-temperature β-type is obtained and confirmed by X-ray diffraction (XRD) by comparison with the pattern (PDF 16-0906). The crystallite size of β-$BiTaO_4$ was estimated in 47 nm by Scherrer's equation from XRD data.

The pH of zero point of charge, pHzpc, was determined by solid addition method to be 7 (Fig. 2). In very simple terms, a pHzpc of 7 for $BiTaO_4$ implies that interactions with cationic dye will be favored for adsorption at high pH (pH > pHzpc), while anionic dye will be favored at low pH (pH < pHzpc). In Fig. 2 one can see a minimum in the curve at pH 4, which represents an increase in solution pH after metal oxide contact, indicating the surface protonation and maximum positive charge. Under this condition, the anionic dyes were adsorbed. On the other hand, the maximum in the curve at pH 9.3 indicates a decrease in solution pH, as a consequence of the surface deprotonation, yielding a maximum negative charge on metal oxide surface. Under this condition cationic dyes are adsorbed on β-$BiTaO_4$ surface.

UV–vis photoacoustic spectra of pure and photosensitized β-$BiTaO_4$ in Fig. 3 show clearly the absorption band of the dyes in each case. In the case of alizarine, neutral dye, the adsorption was tested in both pH 4 and 9.3. Alizarine deprotonation takes place in pH 11–13, yielding an anionic dye. Meanwhile, the optimum pH to adsorb anionic dye is pH 4, where the metal oxide surface is positively charged. Photoacoustic spectra reveal that dye adsorption takes place at pH 4, which means a better interaction between alizarine and positive surface, indicating that alizarine behaves as an anionic dye, probably due to the high electronic density of the oxygen atom in the *p*-quinone group.

The hydrogen production rate, as well CO and CO_2 evolution, was measured from an aqueous solution containing isopropanol (30%) as sacrificial reagent under visible light irradiation ($\lambda \geq 418$ nm) for each target photocatalyst. The results demonstrate that only β-$BiTaO_4$–methylene blue presented photocatalytic activity with respect to hydrogen production.

Fig. 4 shows the profile of hydrogen, CO and CO_2 evolution as a function of time for β-$BiTaO_4$–methylene blue photocatalyst. The kinetic curve display an apparent induction period of 4 h before the evolution of hydrogen started, but an immediate production of CO and CO_2 is observed. The induction period for hydrogen production could be associated with either Pt^{IV} photo-reduction to Pt^0, which plays role as a co-catalyst for hydrogen reduction, as CO adsorption on Pt. A mechanism proposed for photocatalytic alcohols reforming reaction on Pd/TiO_2 [12,13] and Pt/CdS, Pt/TiO_2/CdS and Pt/CdS/TiO_2 [14] based on alcohol decomposition to gas phase hydrogen, an organic moiety and adsorbed CO on the metal as the initiation of the process. According to this proposition, the reaction stops after very little hydrogen has evolved due to blockage of the surface with CO, even at ultralow concentrations, which is strongly held and has a self-poisoning. This proposition must be considered here since it was observed CO evolution in the beginning of the irradiation, followed by decrease until CO concentration remain constant, while CO_2 concentration increases in this period. It is evidence that CO was continuously removed as CO_2 by an active oxygen species, leaving a vacant site on the metal. After virtually suppression of CO evolution, we observed a hydrogen production. The CO evolution was also observed by Zou and Arakawa [6] from

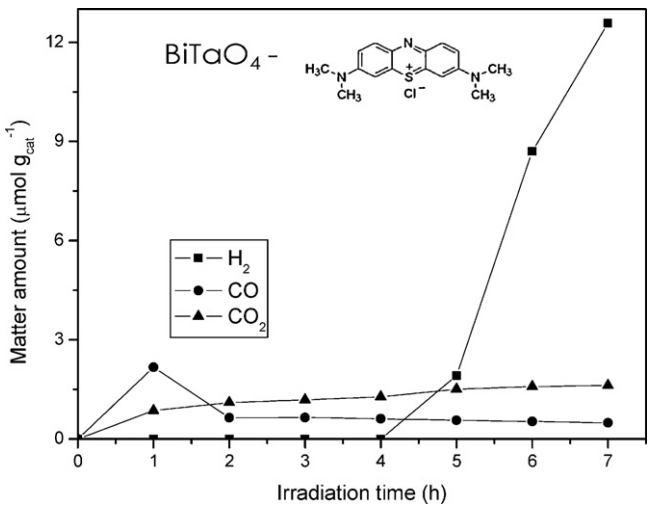

Fig. 4. Profile of hydrogen, CO and CO_2 evolution over β-$BiTaO_4$–methylene blue photocatalyst ($\lambda \geq 418$ nm) as a function of time.

CH_3OH/H_2O solution with pure $BiTaO_4$ under UV irradiation as the oxidation product, but in this case, the CO evolution increases with illumination time as does hydrogen evolution. Nevertheless, the rate of CO evolution is much lower than that of H_2 evolution.

Our results are still lower than those obtained by Zou and Arakawa [6] from pure $BiTaO_4$ irradiated with UV light but open 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.

4. Conclusions

The hydrolysis reactions on the β-$BiTaO_4$ surface suspended in water result in charged surface particles, it makes easier the dyes adsorption. The employed adsorption method demonstrated to be efficient, with complete adsorption of dye on the β-$BiTaO_4$ surface under the optimum pH conditions. β-$BiTaO_4$–methylene blue presented photocatalytic activity with respect to hydrogen production, but an apparent induction period of 4 h before the evolution of hydrogen was observed, mainly due to blockage of the surface with CO. However, CO was continuously removed as CO_2, leaving a vacant site on the metal co-catalyst to produce hydrogen.

Acknowledgements

Authors wish to thank CNPq, FINEP and FAPESB for financial support.

References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[2] K. Maeda, K. Domen, Journal of Physical Chemistry C 111 (2007) 7851.
[3] S. Rehman, R. Ullah, A.M. Butt, N.D. Gohar, Journal of Hazardous Materials 170 (2009) 560.
[4] R. Abe, K. Sayama, H. Arakawa, Journal of Photochemistry and Photobiology A: Chemistry 166 (2004) 115.
[5] C.Y. Lee, R. Macquart, Q. Zhou, B.J. Kennedy, Journal of Solid State Chemistry 174 (2003) 310–318.
[6] Zou, H. Arakawa, Journal of Materials Research 17 (2002) 1446.
[7] C.G. Almeida, H.M.C. Andrade, A.J.S. Mascarenhas, L.A. Silva, Materials Letters 64 (2010) 1088.
[8] J. Nisar, L.A. Silva, C.G. Almeida, A.J.S. Mascarenhas, B. Wang, C.M. Araujo, R. Ahuja, I. PEPE, J.S. Almeida, A. Ferreira da Silva, Study of electronic and optical properties of the $BiTaO_4$ for photocatalysis, Physica Status Solidi C, Current Topics in Solid State, http://dx.doi.org/10.1002/pssc.201100654, in press.
[9] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chemical Reviews 95 (1995) 69.
[10] T.B.F. Guimarães, I. Pepe, A. Ferreira da Silva, A.S. Mangrich, J.B. de Andrade, L.A. Silva, Journal of Alloys and Compounds 481 (2009) 654.
[11] A.P. Vieira, S.A.A. Santana, C.W.B. Bezerra, H.A.S. Silva, J.A.P. Chaves, J.C.P. de Melo, E.C. da Silva Filho, C. Airoldi, Journal of Hazardous Materials 166 (2009) 1272.
[12] M. Bowker, P.R. Davies, L.S. Al-Mazroai, Catalysis Letters 128 (2009) 253.
[13] M. Bowker, Green Chemistry 13 (2011) 2235.
[14] M.O. Melo, L.A. Silva, Journal of Photochemistry and Photobiology A: Chemistry 226 (2011) 36.