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Bi_2InTaO_7 compounds as promising photocatalysts for marine plankton removal

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The removal of marine plankton, red (*Amphidium carterae*), and green (*Tetraselmis suecica*) tide algae, by heterogeneous photocatalysis was carried out using pyrochlore-type semiconductors. The semiconductor, Bi_2InTaO_7, was prepared by the sol-gel method and a solid state reaction. The XRD patterns evidence formation of the pyrochlore phase in the sol-gel materials calcined at low temperatures (600-800 ºC). Nanostructured sol-gel materials were observed by SEM. The sol-gel preparation allowed the formation of the pyrochlore-type compound with specific surface areas (7-13 m^2g^{-1}) higher than the solid obtained by solid state preparation (< 5 m^2g^{-1}). Band gap (*Eg*) values between 2.1-2.7 eV determined by UV-Vis spectroscopy were obtained. Bi_2InTaO_7 photocatalysts prepared by the sol-gel method were able to eliminate *Tetraselmis suecica* and *Amphidium carterae* algae totally after 50 minutes of UV-irradiation, whereas Bi_2InTaO_7 by solid state preparation needed more than 1 h.

Key words: Pyrochlore-type structure, Photocatalysis, Marine plankton removal, Sol-gel photocatalyst,Bi_2InTaO_7.

Introduction

Red and green tides are caused by the rapid population growth of microscopic plankton. The toxins released by these microorganisms have severe effects on marine life and humans [1], causing acute gastroenteritis with neurologic symptoms after ingestion of contaminated shellfish. Another health problem is the apparent reversible upper respiratory syndrome after the inhalation of the aerosols of the dinoflagellate and their toxins (i.e. aerosolized red tide toxins respiratory irritation) [2]. These cellular microorganisms could have a short time life due to natural degradation, and insufficient nutrients. However, the visual effects on coastal water along with the release of the toxins are causing serious ecological damage, and the economic impact of all the harmful algae blooms is difficult to quantify [3].

In order to reduce the ecological damage from these natural phenomena, suitable countermeasures should be taken [4]. It is well known that heterogeneous photocatalysis is an ideal and powerful technology to eliminate pollutants in air and water [5], where TiO_2 based-semiconductor materials are used as photocatalysts [6-7]. According to this context, several research studies on modified TiO_2 have been developed to eliminate different microorganisms, such as bacteria, viruses, fungi and alga [8-11]. Recently, it was reported that the inactivation of bacteria [12] and marine plankton such as red (*Amphidium carterae*) and green (*Tetraselmis suecica*) tide algae [13] was achieved by using different photocatalyst materials of TiO_2, which had higher photocatalytic activity. These results made a big role of the development of new photocatalyst materials with bactericidal capability preferably those that could be activated under UV and visible light [12, 13].

According to the aforementioned, Wang *et al*., reported a new series of ceramic compounds: Bi_2MTaO_7 (M = Fe, Ga or In). These materials are synthesized by a solid state reaction, which was crystallized in the pyrochlore-type structure, $A_2^{+3}B_4^{+2}O_7$, and present high photocatalytic activity in the water conversion reaction [14-17].

Among these ceramic compounds, Bi_2InTaO_7 compound shows the best performance as photocatalyst, which is mainly due to its distorted structure. This characteristic causes an increase in the concentration of holes (carriers), which has a dramatic effect on the charge mobility, improving the photocatalytic properties of the semiconductor [14-17]. In this way, this compound could be an active material in the photocatalytic process for removal of plankton in seawater.

In the present study, Bi_2InTaO_7 compounds were prepared in order to evaluate their photocatalytic capability for the removal of marine plankton, red (*Amphidium carterae*), and green (*Tetraselmis suecica*) algae. In addition, some properties of the material such as specific surface area (S_{BET}), energy band gap value (*Eg*) and morphology were investigated. The parameters strongly influence the photocatalytic reactions. which have been improved by employing a sol-gel synthesis method.

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Experimental

Synthesis of Bi_2InTaO_7 by sol-gel method

The synthesis of Bi_2InTaO_7 was carried out by a sol-gel method using bismuth acetate III (99.99%, Aldrich), tantalum ethoxide (99.98%, Aldrich), and indium acetate III (99.99%, Aldrich) as precursors. Absolute ethanol (DEQ) and anhydrous ethylene glycol (99.8%, Aldrich) were used as solvents. Nitric acid, glacial acetic acid (DEQ) as well as ammonium hydroxide (DEQ) were used as hydrolysis and condensation catalysts, respectively. A stoichiometric amount of indium acetate was dissolved in 50 ml of 3 : 2 ratio of EtOH/H_2O solution. Concentrated nitric acid was added to adjust the pH to 3. The reaction mixture was magnetic stirred for 3 h and refluxed at 70 ºC. A stoichiometric amount of bismuth acetate was dissolved in 20 ml of ethylene glycol anhydrous and heated at 90 ºC, keeping magnetic stirring and reflux for 1 h. Glacial acetic acid was added to obtain a colorless bismuth solution. At the same time, a stoichometric amount of tantalum ethoxide was mixed with 50 ml of absolute ethanol, obtaining a solution with slightly agglomerated particles. In order to break the agglomerates formed, this solution was ultrasonically treated for 0.5 h.

Both the bismuth and tantalum solutions were slowly added to the indium sol. The pH of the new reaction mixture was adjusted to 3 with concentrated nitric acid. It was refluxed and heated at 70 ºC, keeping magnetic stirring for 72 h. After this time, the pH of the sol was changed to 10 with NH_4OH in order to promote the condensation in the sol. This sol was kept under the same conditions for other 72 h. The final product was aged at 70 ºC for 24 h and dried at 90-120 ºC to obtain the fresh sample. Portions of this material were calcined at 400, 600 and 800 ºC for 6 h, using a heating rate of 1 K·minute^{-1}.

Synthesis of Bi_2InTaO_7 by solid state reaction

In order to prepare the Bi_2InTaO_7 compound by the solid state reaction, Bi_2O_3 (99.9%, Aldrich), Ta_2O_5 (99.99%, Aldrich) and In_2O_3 (99.99%, Aldrich) were used as starting materials. Stoichiometric amounts of these oxides were weighed and intimately mixed in an Agatha mortar after drying at 150 ºC for 3 h. The mixture was placed in a platinum crucible and reacted under atmospheric air at several temperatures and time steps. Finally, the mixture was heated at 950 ºC for 12 h, using a heating rate of 1 K·minute^{-1}.

Characterization

Identification of the crystalline compounds was determined by means of the X-ray diffraction (XRD) technique using a Bruker D8 Advance difractometer with CuKα radiation (λ = 1.5418 Å). The morphology of the compounds was analyzed with a JEOL JSM-6490-LV scanning electron microscope (SEM). The specific surface area (S_{BET}) values were determined by nitrogen adsorption at 77 K, using a Quantachrome NOVA 2000e analyzer. The band gap (*Eg*) values were determined from the UV-Vis spectra obtained with a Perkin-Elmer Lambda 35 UV-Vis spectrometer.

Marine plankton removal: Photocatalytic evaluation

Photocatalytic tests were carried out using 100 mg of Bi_2InTaO_7 as the photocatalyst, which was added to 200 mL of *Amphidium carterae* aqueous solution (Natural Live Plankton Co., Ltd., 99.9%) whose initial concentration was 115-190 × 10^3 cells·m^{-1} and *Tetraselmis suecica* aqueous solution (Natural Live Plankton Co., Ltd., 99.9%) with 200-290 × 10^3 cells·m^{-1}, at room temperature and constant stirring (180 rpm). Then this solution was irradiated under UV-light type A (315-400 nm) using two lamps of 30 W (Black light lamp-BL, Sankyo Denky, Japan). In order to perform the algae countdown, samples of 0.1 m were taken at every 10 minutes and analyzed by optical microscopy in a Motic-BA200 microscope at 40X. The counting was carried out three times for each sample. For comparative purposes, photo-inactivation experiments were also performed using commercial TiO_2 P-25.

Results and Discussion

Structural characterization of Bi_2InTaO_7

Fig. 1 shows the XRD patterns of the Bi_2InTaO_7 compound prepared by both, the sol-gel method (heated at 600 and 800 ºC) and the solid state reaction (950 ºC). These patterns were compared with previous data reported by Wang *et al*. [15]. According to these results, all the samples show the pyrochlore-tsype structure. In the XRD patterns it seems that there is also a small amount of the In_2O_3 phase, but peaks showed very low intensity. Sol-gel syntheses commonly have impurities because of the soft chemical conditions. In the case of the solid state reaction the synthesis temperature of this material is 50 ºC lower than that reported by Wang *et al*. [15]. According to the XRD results, the Bi_2InTaO_7 compound with the pyrochlore type-structure was obtained by both, the sol-gel method and the solid state reaction.

Micrographs of the sol-gel and solid state Bi_2InTaO_7 pyrochlores are presented in Fig. 2. The samples obtained

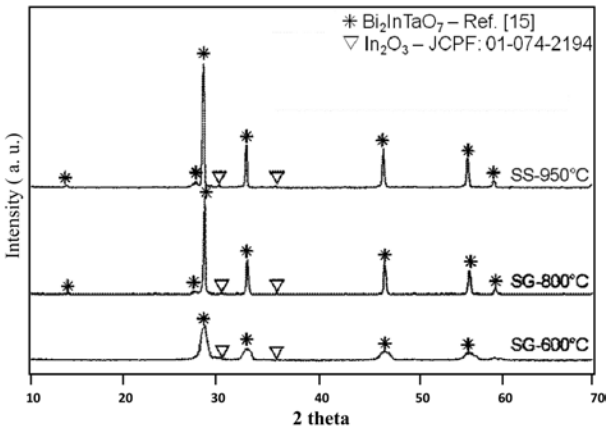

Fig. 1. XRD patterns of Bi_2InTaO_7 photocatalysts prepared by the sol-gel (SG) and solid state (SS) methods.

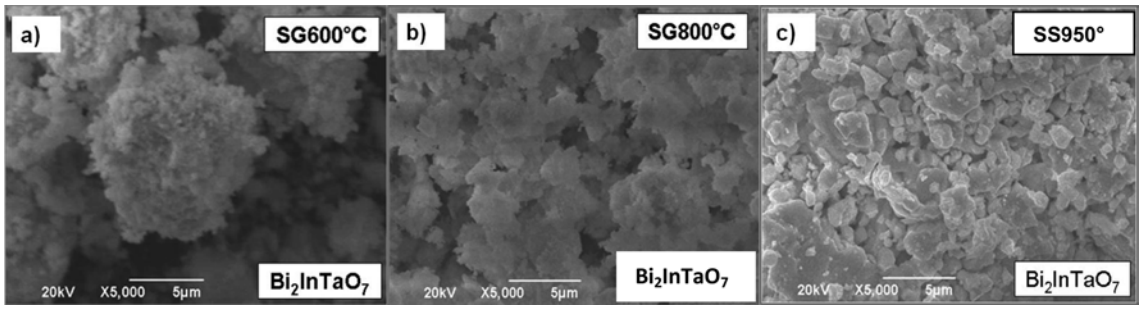

Fig. 2. Micrographs of Bi_2InTaO_7 photocatalysts obtained by the sol-gel and solid state methods. (a) SG-600 ºC, (b) SG-800 ºC and (c) SS-950 ºC.

by the sol-gel method (a-b) exhibit a heterogeneous morphology. Porous spherical grains are observed, which were formed with particles having a size lower than 1 μm. On the other hand, the solid state material (c) shows a homogeneous morphology with particle sizes around 5 μm because of the well-sintered particles.

Specific surface area (S_{BET}) and Energy band gap (Eg) of $Bi_2In\ TaO_7$

The textural properties of Bi_2InTaO_7 compounds were determined from their nitrogen adsorption isotherms. The sol-gel samples show S_{BET} values that are higher than those of the solid state samples, see Table 1. The *Eg* values calculated for the sol-gel Bi_2InTaO_7 photocatalysts are also included in this table. These values were calculated from the UV-Vis spectra shown in Fig. 3 by extrapolating the absorption curve to the x axis for the y axis equal to zero. The *Eg* values were between 2.1-2.7 eV, corresponding the highest value to the SS preparation.

Table 1. S_{BET} and *Eg* values of Bi_2InTaO_7 photocatalysts

Compound	$S_{BET}(m^2g^{-1})$	*EG* (ev)
Bi_2lnTaO_7, SG-600 ºC	17	2.2
Bi_2lnTaO_7, SG-800 ºC	9	2.1
Bi_2lnTaO_7, SS-950 ºC	< 5	2.7
Commercial TiO_2 P25	55	3.2

Marine plankton removal by Bi_2InTaO_7 under UV-irradiation

The Bi_2InTaO_7 photocatalytic results concerning the marine plankton removal are shown in Fig. 4. Since commercial cellular microorganisms present a short life time (~72 h), the initial concentration of the model pollutants slightly varied in all the experiments. Apparently, red (*Amphidium carterae*) is easier to eliminate than green (*Tetraselmis suecica*) tide algae, as can be observed in the photolysis behavior. However, under UV-irradiation in

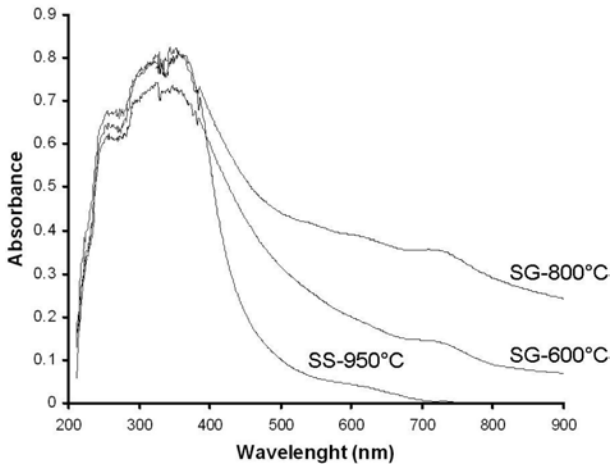

Fig. 3. UV-Vis spectra of Bi_2InTaO_7 photocatalysts prepared by the sol-gel and solid state methods.

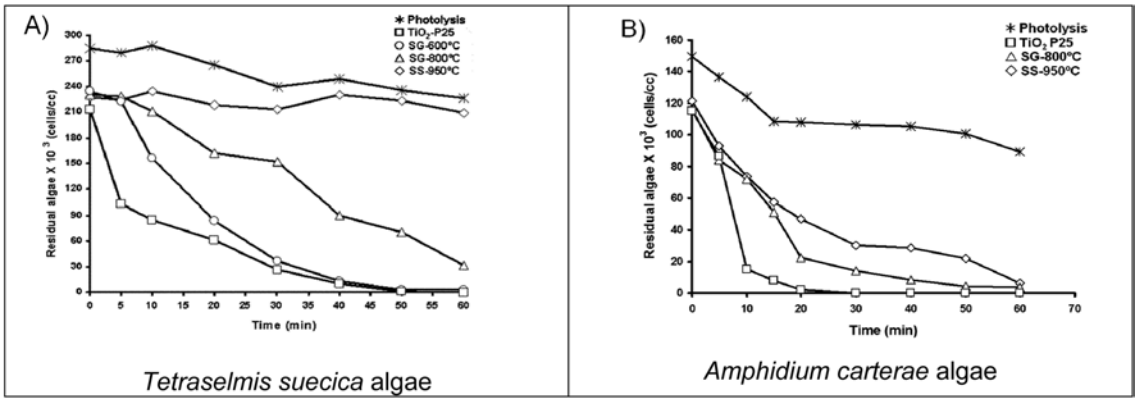

Fig. 4. Photocatalytic tests of marine plankton removal using Bi_2InTaO_7 as photocatalyst under UV-Irradiation. (A) *Tetraselmis suecica* algae (Green tide) and (B) *Amphidium carterae* algae (Red tide)

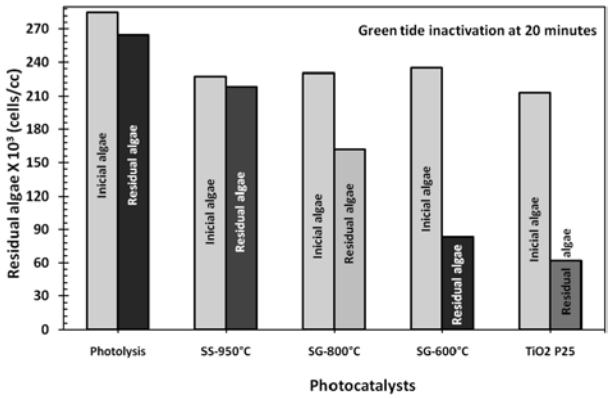

Fig. 5. Residual algae measurements after the photocatalytic test after 20 minutes of UV-Irradiation in combination with photocatalysts.

combination with the photocatalyst, *Tetraselmis suecica* algae can be totally eliminated after 50 minutes using the Bi_2InTaO_7 photocatalyst (SG-600 ºC), whereas *Amphidium carterae* algae was eliminated after 50 minutes using the Bi_2InTaO_7 photocatalyst (SG-800 ºC). When the Bi_2InTaO_7 photocatalyst (SS-950 ºC) was used, it required more than 1 h to eliminate the marine plankton, *Tetraselmis suecica* and *Amphidium carterae* algae. *Tetraselmis suecica* showed a higher resistance to the photocatalysis reaction when TiO_2 was used as the photocatalyst. In Fig. 5 the residual algae of the *Tetraselmis suecica*, after 20 minutes of UV-irradiation in combination with the photocatalysts, are shown. It was clearly observed that the number of cells decreased considerably when TiO_2 P-25 and Bi_2InTaO_7 (SG-600 ºC) were used as photocatalysts. It is well known that the high activity of TiO_2 P-25 is because of its high S_{BET} value (55 m^2g^{-1}). Nevertheless, Bi_2InTaO_7 compounds prepared in this study showed lower S_{BET} values than TiO_2 P-25, their photocatalytic activity for the totally marine plankton removal after 50 minutes under UV-irradiation was very similar to that shown by TiO_2. In that sense, it is possible to assume that the Bi_2InTaO_7 photocatalyst compounds can be considered as promising semiconductor materials to be used as photocatalysts for the removal of marine plankton. Their photocatalytic activities could also be improved if these compounds were prepared by other soft chemistry methods in order to increase their S_{BET} values.

Conclusions

Pyrochlore-type compounds, Bi_2InTaO_7, semiconductor materials were synthesized by both the sol-gel and solid state methods. It is concluded that the Bi_2InTaO_7 semiconductor prepared by the sol-gel method had better textural (S_{BET}), photophysical *(Eg)* and morphological properties than those obtained with the solid state material. The pyrochlore-type, Bi_2InTaO_7, photocatalysts prepared by the sol-gel method were able to eliminate *Tetraselmis suecica* and *Amphidium carterae* algae totally after 50 minutes of UV-irradiation showing similar photocatalytic activity to that observed for the commercial TiO_2 P-25. The synthesis by the sol-gel method improved considerably the photocatalytic activity of Bi_2InTaO_7 for the elimination of the marine plankton. It is evident that pyrochlore-type compounds such as Bi_2InTaO_7 are promising semiconductor materials for marine plankton removal, in particular for *Amphidium carterae* and *Tetraselmis suecica* algae removal.

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