

*Synthesis and Characterization of BiOI/TiO₂ Photocatalysts for
Waste Water Treatment*

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The Asian Conference on Sustainability, Energy & the Environment 2016
Official Conference Proceedings

Abstract

The main cause of water pollution was generally due to human acts. Activities such as transporting the already used industrial or generated waste water and garbages from the community and put them into the water resources. As a result of the pollution occurring, organic matters were degraded and natural forms were eventually changed into other organic compounds that were not suitable in human lives and aquatic life. This research aimed to synthesize the series of BiOI doped titanium dioxide (TiO₂) photocatalysts by wetness impregnation method to test the decomposition of organic matter (Methyl orange, MO) under UV-Visible light irradiation. The study focused on the effects of BiOI doped at 2% and 4% by weight on the performance of photocatalytic process. These photocatalysts were characterized by BET technique. With that, we found out when BiOI were doped, the specific surface area and pore size was decreased in comparison with TiO₂ substance. From FT-IR the spectrum showed that the presence of adsorption peak of Ti-O-Ti stretching at 400-800 cm⁻¹. And the UV-DRS technique also reflected that the BiOI/TiO₂ was a stronger absorption, ranging from 190-300 nm. Moreover, the photocatalysts were thoroughly investigated via the photocatalytic degradation process of MO at a room temperature with a time period of 48 hrs. The degradations of MO were further analyzed by UV-Visible spectroscopy at 464 nm. This analysis clearly shown that 4%BiOI/TiO₂ was the best photocatalysts. The outcome reflected that 97.26% degradation of MO at time range of 16 hrs as compared to other series of synthesized photocatalysts for the same period of time.

Keywords: BiOX/TiO₂ Photocatalysts, Photodegradation, Waste water treatment

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1. Introduction

Water is one of the essential requirements for all living things including human lives and has a very great effect on aquatic life. Due to the rapid increase in human population worldwide and the rapid growth of industrial development, the demand for water resources also increases respectively. This includes the vital role of new technology played in human life where the important reasons that causes the expansion of the water pollution. [1]

Domestic households, industrial and agricultural practices produce wastewater that can cause water pollution. The wastewater contained high concentration of organic compound such as polychlorinated biphenyl (PCBs), phenols, polycyclic aromatic hydrocarbons (PAHs), aliphatic and heterocyclic compounds. These waste organic compounds cause damages to the aquatic lives. For example the scenery degeneration of polluted water contained diseases that have an adverse impact on aquatic living.

Various methods are currently used for treatment of industrial contaminated wastewater such as precipitation, neutralization, adsorption and ion-exchange. In addition to these methods mentioned, the photocatalytic method is an alternative for the removal of organic compound in water resource using heterogeneous catalysts such as cadmium sulfide (CdS), zinc oxide (ZnO) and titanium dioxide (TiO₂). [2-4]

TiO₂ having a crystal form of anatase is known to be one of the most effective photocatalysts for the removal organic compound due to strong oxidation, high photocatalytic degradation ability, chemical and biological stability, low cost and abundance. Mechanism of the photocatalytic degradation of organic compounds is under uv-visible light irradiation, the electrons from valence band (VB) are first excited to conduction band (CB) of TiO₂. This method results in more effective separation of photogenerated electron-hole pair. The excited electrons can be trapped by surface absorbed molecular oxygen (O₂) to form super oxide anion radicals ($\bullet\text{O}_2^-$). Meanwhile, the photogenerated holes in the VB can be trapped by OH⁻ or H₂O species absorbed on the surface to generated hydroxyl radicals ($\bullet\text{OH}$). These two radicals are powerful oxidizing agents capable of degrading organic compound form to carbon dioxide (CO₂) and H₂O.

However, the large band gap of TiO₂ (3.2 eV) and high recombination rate of the electron-hole pairs causes photocatalytic activity of TiO₂ in visible light is very low. To solve these problems, we have attempted to improve activity of TiO₂ by modifying surface or bulk properties such as doping, surface chelating and impregnation of two semiconductor.

Bismuth oxyhalides (BiOI) semiconductors have demonstrated excellent photocatalytic activities. [5] During this process, we synthesized BiOI/TiO₂ photocatalysts varied the amount of BIOI by wetness impregnation. Methyl orange (MO) is chosen as model pollutants to evaluate the photocatalytic performance of the series of BiOI/TiO₂ under uv-visible light irradiation.

2. Experiment

2.1 Synthesis of photocatalysts.

The BiOI doped TiO₂ photocatalysts (ABiOIT where A is 2% and 4%) were synthesized by wetness impregnation method at room temperature. In a typical synthetic route, Bi(NO₃)₃•5H₂O was dissolved in 30 mL glycerol and 20 mL distilled water with stirring (Solution A). Meanwhile KI was dissolved in 30 mL distilled water with stirring then added TiO₂ 20 g (Solution B). The Solution A was added dropwise to solution B under vigorous stirring. The mixture was stirred overnight. Then the mixture was clean by acetone and poured through a filter paper (125mm) in a Buchner funnel. The resulted was dried at 120 °C for 4 hrs. and calcined at 550 °C for 3hrs. Then the particle size was sieved between 250-75 μm.

2.2 Characterization of photocatalysts.

The surface area and pore size of the BiOI doped TiO₂ were characterized by the Brunauer-Emmett-Teller (BET) surface area and porosity analyzer (BEL Japan Model BELSORP-mini) at liquid nitrogen temperature (77K). The UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS, UV-Visible Spectrometer; Analytic-Jena AG; SPECORD 210) equipped with an integrating sphere attachment. The function group of photocatalysts has been studied by Fourier Transform Infrared Spectroscopy (FT-IR, Perkin-Elmer, Spectrum one)

2.3 Photocatalytic activity test.

The photocatalytic activity test was carried out by decomposing of methyl orange (MO) under uv-visible light irradiation at room temperature. The uv-visible light source was a 30 W (uv-c range 100-280 nm). In a typical experiment, 0.036 g BiOI doped TiO₂ photocataysts were add into 250 ml of a 15 ppm MO solution. Before irradiation, the mixture was stirred in the dark for 45 min to ensure the equilibrium adsorption-desorption. Then the mixture was stirring for 48 hrs and collected MO solution at 15, 30 min 1, 2, 4, 8, 12, 16, 32 and 48 hrs.

The MO solution was analyzed by UV-Visible spectroscopy (UV-Vis DRS, UV-Visible Spectrometer; Analytic-Jena AG; SPECORD 210) at 464 nm. The degradation of MO (%D) was calculated by the following equation.

$$\%D = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

(1)

where, C₀ was initial concentration of MO solution (15 ppm) and C_t was final concentration of MO solution after irradiation.

3. Results and discussion

3.1 BET analysis.

The surface area and pore size of BiOI doped TiO₂ photocatalysts were investigated by using nitrogen adsorption and desorption isotherm. **Table 1** clearly shown that the series of BiOI doped TiO₂. As a result, all photocatalysts included mean pore diameters in range of 2-50 nm indicated the presence of mesoporous. The adsorption and desorption isotherm in **Figure 1** indicated that the adsorption and desorption isotherm of 4%BiOI doped TiO₂ summarized type IV due to in the first period, it showed the less amount of p/p₀. However, the amount of adsorption was increased rapidly when there was a lot of p/p₀ (S shape) because of the condensation in the capillary pore. It caused hysteresis effect which also caused from the instability of adsorption and desorption in the graph since the adsorption happened more difficultly because it needed to conquer the capillary force and the adsorption and desorption isotherm were happened at high p/p₀, Thus, that isotherm included characterized pore were funnel shape. Moreover, surface area was increased when increased the amount of BiOI.

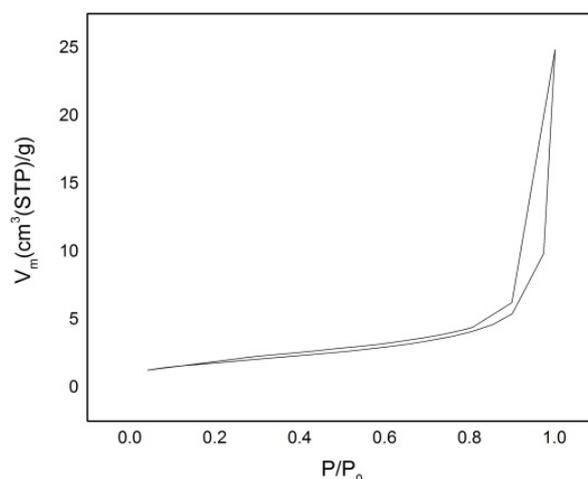


Figure 1 The adsorption and desorption isotherm of 4%BiOI doped TiO₂

Table 1 Properties of photocatalysts.

Photocatalysts	S _{BET} (m ² /g)	M _d (nm)	V _m (cm ³ (STP)/g)	W (nm)	E _g (eV)
T	5.64	25.19	1.29	400	3.10
2BiOIT	5.99	13.28	1.37	405	3.06
4BiOIT	6.25	18.87	1.43	410	3.03

3.2 FT-IR Spectroscopy analysis.

The BiOI doped TiO₂ photocatalysts were observed by FT-IR spectroscopy that resulted shown in **Figure 2** the presence broad peak at 3200-3800 cm⁻¹ and 400-800 cm⁻¹ were indicated that -OH stretching and Ti-O-Ti stretching respectively.

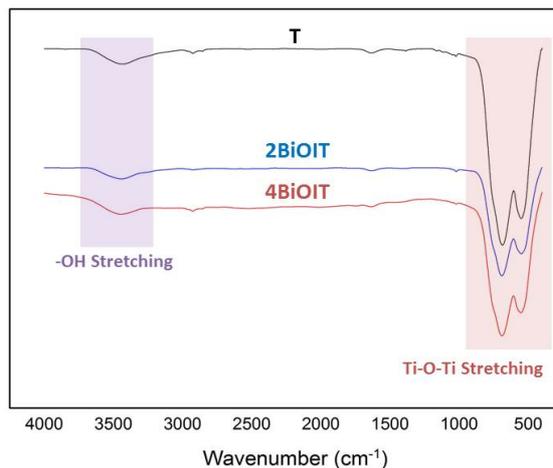


Figure 2 FT-IR spectra for 2%, 4% BiOI doped TiO_2 and pure TiO_2

3.3 UV-Vis DRS Spectroscopy analysis

The UV-Vis diffuse reflectance spectrum of the BiOI doped TiO_2 series photocatalysts shown in **Figure 3** the results shown that pure TiO_2 , 2BiOIT and 4BiOIT were absorbed at 400, 405 and 410 nm respectively. As a result, from **Table 1** the band gap energy of the photocatalysts were decreased when increased the amount of BiOI. Thus the photocatalysts were added BiOI can absorbed light at increased wavelength (visible light).

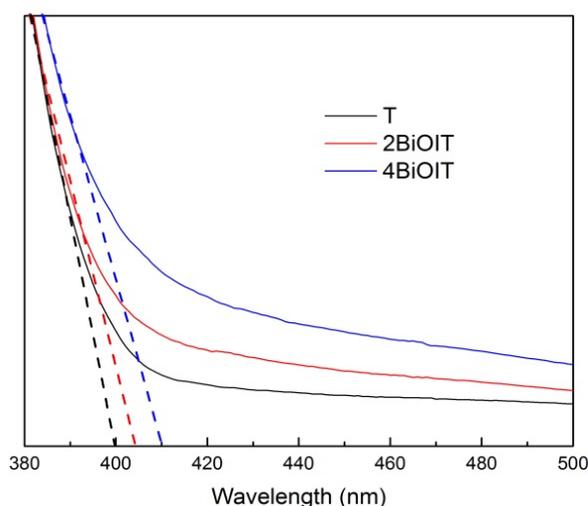


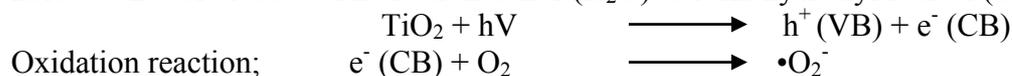
Figure 3 The UV-Vis DRS for 2%, 4% BiOI doped TiO_2 and pure TiO_2

3.4 Photocatalytic activity test.

The photocatalytic activity test carried out by decomposing of MO under uv-visible light irradiation at room temperature for 48 hrs, then used pure TiO_2 , 2BiOIT and 4BiOIT. The result shown in **Figure 4** the 4BiOIT photocatalyst was the best performance for degraded MO at 16 hrs, about 97.26% caused when added BiOI on TiO_2 . As a result, the band gap energy of BiOI and TiO_2 were overlapped caused decreased electron-hole combination. Thus the BiOI doped TiO_2 photocatalysts can be generated scavenger radicals form redox reaction for degraded MO better than pure TiO_2 . This is the one reason corresponding with surface area of photocatalysts.

3.5 Mechanism of photocatalytic process.

The photocatalytic degradation mechanism of MO by 2BiOI, 4BiOI and pure TiO₂ following the process of equation when photocatalysts absorbed high energy from uv-visible source or sunlight, it produced excited electron transferred through band gap to the electron to the conduction band (CB) and hole at valence band (VB). The electron at CB were reacts with electron acceptor (O₂) to form superoxide anion (O₂^{•-}) and the hole at VB were reacts with electron donor (H₂O) to form hydroxyl radical (OH•)



The hydroxyl radical and super oxide anion that the best oxidize reagent for degraded organic compounds to form H₂O and CO₂.

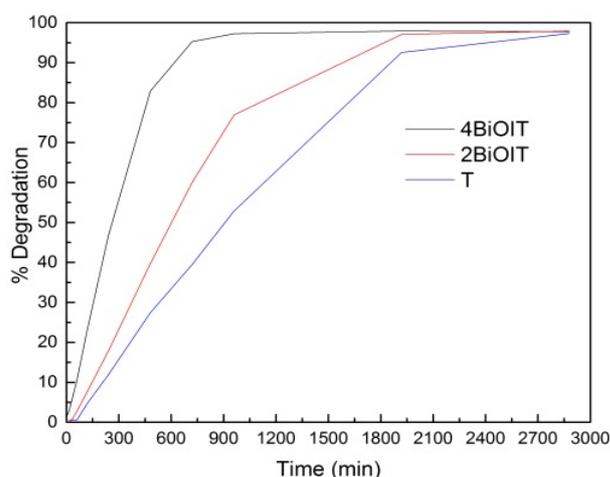


Figure 4 %Degradation for 2%, 4%BiOI doped TiO₂ and pure TiO₂

4. Conclusions

In summary, we synthesized BiOI/TiO₂ photocatalysts varied the amount of BiOI by wetness impregnation. Methyl orange (MO) is chosen as model pollutants to evaluate the photocatalytic performance of the series of BiOI/TiO₂ under uv-visible light irradiation. This analysis clearly shown that 4%BiOI/TiO₂ was the best photocatalysts. The outcome reflected that 97.26% degradation of MO at time range of 16 hrs as compared to other series of synthesized photocatalysts for the same period of time. The enhanced photocatalytic activity test was attributed to low band gap for decreased electron-hole recombination energy and high surface area.

5. References

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