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Effects of metal oxide semiconductors on the photocatalytic degradation of 4-nitrophenol

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ABSTRACT

Multifarious catalysts including bismuth oxide (Bi_2O_3), titanium oxide (TiO_2), zinc oxide (ZnO) and zirconium oxide (ZrO_2) were used to investigate the impact on photocatalytic degradation of 4-nitrophenol (4-NP) under halogen lamp. The results of photocatalytic reactions were measured by UV–visible spectrophotometer and high-performance liquid chromatography (HPLC). The catalysts were analysed by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), Photoluminescence measurement (PL), scanning and transmission electron microscopy, (SEM-TEM) and Brunauer–Emmett–Teller (BET) techniques. Further along, the study has been carried on with the most efficient catalysts bismuth oxide, along with its binary oxide which were prepared by solid-state dispersion method, to the removal of 4-nitrophenol from waste water.

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1. Introduction

Since Global warming has become a serious topic of our life, protecting existing water resources as well as recycling of wastewater is one of the most important things to do. Being wildly use in pharmaceuticals, petrochemical manufacturing, fungicides, rubber, wood preservation operations, dyes, and Leather industry etc. [1–3] the amount of *p*-nitrophenol (PNP) and its derivatives directly discharge to the environment has come to a level that makes one concern, because of not biodegradable and its high toxicity. Exposure to PNP can cause injury to blood cells, damage to the nervous central system and mutagenic effects to the organisms, also its cancer-causing chemical that threatening all human and aquatic life [4–6]. as a result, PNP which is soluble and stable in water has become an important organic compound that has to be removed from the industrial wastewater. Therefore, lots of studies have been done for removal of nitrophenols. Such as adsorption using active carbon treatment [7,8], ozonation [9], denitrification process [10], electro-Fenton degradation [11] electrochemical sensor [12].

In this study, we choose Heterogeneous photocatalytic degradation which has aroused considerable interest as a potentially efficient method for degrading recalcitrant environmental

contaminants to remove PNP. In the previous study, photocatalytic degradation of PNP had focused on TiO_2 and complete under UV light [13–17]. Regarding this study, we achieve up to 100% degradation of PNP using various semiconductors and cheaper lighting system.

Photocatalytic degradation has several advantages over conventional oxidation processes such as the complete mineralization of pollutant, the utilization of near-UV light and no addition of chemicals [18]. These photocatalytic reactions are initiated by the excitation of a semiconductor catalyst with energy greater than its band gap, resulting in the promotion of an electron from the valence band to the conduction band, thus producing an electron/hole pair [19,20].

Photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself. In addition, the photocatalyst which has a filled valence band and an empty conduction band is the substance which can modify the rate of chemical reaction using light irradiation.

A wide range of nanomaterials can be prepared, ZrO_2 , ZnO , TiO_2 and Bi_2O_3 . Pure ZrO_2 was prepared by calcinating zirconium hydroxide at 650 °C for 5 h [21]. In addition, Cho et al. various basic ZnO structures, including nanorods, nanocandles, nanoneedles, nanodisks, nanonuts, microstars, micro UFOs, and microballs simply synthesized at a low temperature (90 °C) with low power microwave-assisted heating (about 50 W) and a subsequent aging process [22]. TiO_2 nano-powders were prepared via a sol–gel method using tetra-*n*-butyl-titanate and deionized water as the

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starting materials [23]. Moreover, H–TiO₂NPs were synthesized by hydrothermal reaction [24]. Bi₂O₃ has an added advantage as a photocatalytic material because of its ease of synthetic methods, availability of precursors, non toxic nature and suitable band gap [25].

Regarding the results, it was achieved up to 100% degradation of PNP using various semiconductors and cheaper lighting system. We used ZrO₂, ZnO, TiO₂ and Bi₂O₃ as our semiconductors that have respectively large surface area and require lower energy to promote an electron from valence band to conduction band and most importantly well response to the halogen light to indicate how these are going to affect the photocatalytic degradation of 4-nitrophenol. We selected PNP as a model pollutant in our study because of the wastewater contains a various number of toxic chemicals.

2. Experimental

2.1. Materials

The precursors used in this study were commercially on hand and used without further purification treatment as follows; bismuth (III) nitrate pentahydrate (Alfa Aesar Company, 98%), zinc nitrate hexahydrate (ACROS Organics, 98%), zircon (IV) oxynitrate hydrate (ACROS Organics, ≥99%), titanium tetrachloride (Merck Company, 99%) and 4-nitrophenol (Sigma Aldrich, 99%) The other chemicals including nitric acid (65%), ethanol (absolute), methanol (for HPLC, ≥99%), ammonia solution (25% in water) and sodium hydroxide (97%) were all purchased from Merck company.

2.2. Synthesis methods of catalysts

Bi₂O₃ catalyst was synthesized by using a facile co-precipitation method. 0.94 g Bi(NO₃)₃·5H₂O and 0.8 g NaOH were separately dissolved in 10 mL 1.12 M nitric acid (65%) solution and deionized water, respectively. The resulting solutions were stirred magnetically for 15 min at room temperature. Hereafter, 0.2 M sodium hydroxide solution were added dropwise into the bismuth (III) nitrate solution (until pH value reached at 11) and stirred for 2 h at 75 °C to obtain a uniform yellowish mixture. The precipitate was filtered, washed with distilled water and absolute ethanol several times, and then dried in a furnace at 80 °C for 2 h, and calcined in an air oven at 450 °C for 2 h.

ZnO and ZrO₂ nanopowders were also prepared by microwave assisted co-precipitation method. An appropriate amount of zinc nitrate hexahydrate and zirconium (IV) oxide nitrate hydrate was dissolved in deionized hot water and the resulting solutions were heated up to 65 °C, separately. These mixtures were precipitated by adding dropwise ammonia solution (25 wt %) until pH values reached at 10. The resultant solutions were stirred magnetically for 2 h at 65 °C. After that, the solutions were irradiated under 500 W microwave for 3 min. The precipitate was then filtered, washed with deionized water and dried at 100 °C for 20 h and then calcined at 500 °C for 5 h.

TiO₂ powders were easily prepared by using a sol-gel method. 1.5 mL titanium tetrachloride was slowly added dropwise into absolute ethanol (15 mL) at room temperature. HCl gas was largely exhausted during the mixing process to form the sol solution. The obtained transparent-yellow solution was gelatinized for several days to form a sol-gel. The resulting gel was dried in an oven at 105 °C for 1 day, ground to obtain a fine powder, and calcined at 600 °C for 4 h.

2.3. Characterization of catalyst

Powder XRD patterns of the prepared samples were obtained

using a Rigaku D/Max-2200 diffractometer with CuK α ($\lambda = 1.540 \text{ \AA}$) radiation. Samples were scanned from 10° to 80° (2 θ) at a rate of 2°/min. The sizes of the crystalline domains were calculated using the Scherrer equation, $t = C\lambda/\beta\cos\theta$, where λ is the X-ray wavelength (\AA), β is the full width at half maximum, θ is the Bragg angle, C is a factor that depends on the crystallite shape (taken to be 0.94), and t is the crystallite size (\AA).

The morphologies and size distributions of the photocatalysts were determined using scanning electron microscopy (SEM) model JEOL/JSM-6335F and transmission electron microscopy (HRTEM) model JEOL HRTEM 2100 at 200 kV. For the TEM image, the sample was prepared by depositing a methanol suspension of the composite on a carbon coated copper grid.

The BET surface areas of the samples were determined by nitrogen adsorption–desorption isotherm measurement at 77 K (Quantachrome Inst.). The samples were degassed at 200 °C for 4 h prior to the actual measurements.

UV–visible (UV–vis) DRS was performed using a UV–vis spectrophotometer (Shimadzu UV3600), with BaSO₄ as the reference.

Photoluminescence measurement (PL) was carried out on a fluorescence spectrophotometer (Agilent Technologies-Cary Eclipse) using a Xenon lamp as the excitation source at room temperature. The sample was dispersed in ethanol using ultrasonic bath and the excitation wavelength used in PL measurement was 350 nm.

2.4. Photocatalytic measurement

The photocatalytic activities of the as-prepared samples were evaluated by the decomposition of 4-nitrophenol (4-NP) under visible light irradiation at the natural pH value and room temperature. In every photocatalytic experiment, 100 mg of catalyst was typically dispersed in 50 mL 4-NP solution of initial concentration of 25 mg L⁻¹ under magnetic stirring.

4-NP photodegradation runs were executed with a three-necked quartz batch flask of cylindrical shape. The lighting system were well rounded in order to enhance lighting performance also it contains a heat-extraction system prevent reactor from overheating. Halogen lamp photoreactor was used in all experiments. The light sources used were T3 120 v 150 W 118 mm halogen lamp. The spectral irradiance of the halogen lamp is from 303 to 518 nm and the illumination distance is 18 cm from the target. Before the irradiation experiments, the solution was stirred for 60 min in dark to ensure good adsorption equilibrium between the catalyst and the solution. During the irradiation for 45 min, the 4-NP solution was taken at certain intervals and filtered by means of a PTFE filter (pore size 0.45 μm). The concentration of 4-NP and products were analysed by HPLC equipped with C-18 column. The mobile phase used in HPLC consisted of a mixture of acetonitrile/water (60/40, v/v) and was fed into the column at a flow rate of 1 mL min⁻¹.

To handle the reusability issue of the catalyst, after separating it via centrifugation, the recovered catalyst was used with fresh dye solutions. All the experimental parameters were kept constant and the experiments were repeated for 5 sets of fresh dye solutions.

3. Results and discussion

3.1. Catalyst characterization results

The specific BET surface areas of the samples calcined at 450 °C are shown in Table 1 with a range between 2 and 96 m² g⁻¹. BET surface areas of metal oxide catalysts were found to be as follows: ZrO₂ (96 m² g⁻¹) > TiO₂ (40 m² g⁻¹) > ZnO (28 m² g⁻¹) > α -Bi₂O₃ (2 m² g⁻¹). Regarding the BET surface area, Bi₂O₃ present low

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