Applied Catalysis B: Environmental 209 (2017) 383–393

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Bi_2MoO_6 co-modified by reduced graphene oxide and palladium (Pd^{2+} and Pd^0) with enhanced photocatalytic decomposition of phenol

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ARTICLE INFO

Article history:
Received 10 September 2016
Received in revised form 7 January 2017
Accepted 12 January 2017
Available online 17 January 2017

Keywords:
Photocatalysis
Graphene
SPR
Bi_2MoO_6
Palladium

ABSTRACT

A ternary Bi_2MoO_6 photocatalyst composite was hybridized for the first time, with reduced graphene oxide (rGO) and palladium (Pd) nanoparticles decorated on the surface. As-prepared composites exhibited excellent photocatalytic activity in the degradation of organic pollutants (phenol) in wastewater under visible light irradiation. The enhanced photocatalytic performance when rGO and Pd nanoparticles combined with Bi_2MoO_6 may be attributed to the reduction of the recombination rate of photogenerated electrons/holes. Specifically, the rGO layer may serve as the electron accepter, which means photogenerated electrons can rapidly transfer to its surface instead of jumping back to the valence band and combining with positive holes. Additionally, the black-body property of graphite-like material contribute the increased harvesting capacity of visible-light photons. Furthermore, palladium nanoparticles distributed on the surface can also be stimulated by visible light photons due to the surface plasmon resonance effect, which further increased the utilization efficiency of visible light irradiation. This work opens a new possibility for efficient removal of phenolic compounds in wastewater via visible light-driven photocatalysis in the presence of a Pd-rGO- Bi_2MoO_6 ternary composite.

1. Introduction

Bismuth-based visible light-driven photocatalysts have attracted extensive interests of researchers, and have exhibited strong potential for industrialization from an economic stand-point compared to the most widely studied UV-driven photocatalysts, such as TiO_2 [1–4]. Two main application areas of photocatalysis can be summarized as water-splitting to generate H_2 and degradation of organic pollutants in wastewater [5,6]. When choosing a semiconductor for water splitting to generate both H_2 and O_2, two crucial factors must be considered: the availability of electrons on the conduction band for stronger capacity to reduce H^+ to H_2, and the maximum potential of a valence band being higher than the redox potential of O_2/H_2O. For bismuth-based photocatalyst semiconductors, the conduction bands are rarely suitable for the production of H_2 without modulation of the energy band as reported in [4]. Instead, photogenerated holes on the valence bands of bismuth-based semiconductors are usually oxidative enough to decompose most of the organic pollutants in wastewater.

Bi_2MoO_6, as a member of Aurivillius family, was originally considered because of their ferroelectric properties [7]. Recent results revealed that Bi_2MoO_6 may be a potential candidate as a visible light-driven photocatalyst applied in oxidizing organics in wastewater [8]. However, the relatively high recombination rate of photogenerated electrons/holes pairs for pure Bi_2MoO_6, when illuminated under visible light irradiation, hinders its widely application. Approaches such as doping [9,10] and heterojunction formation [11] have been adopted to suppress the recombination of photo-generated e^-/h^+ pairs. Among them, reduced graphene oxide (rGO) integrated Bi_2MoO_6 hybrid photocatalysts were reported with enhanced photocatalytic activity and opened new possibilities in environmental remediation using solar energy [12–15]. Graphene, which is a single layer of sp^2-bonded carbon atoms tightly packed into a two-dimensional honeycomb structure, has been extensively studied due to its excellent physiochemical properties [16]. It is proven to be an effective and inexpensive way to produce graphene nanosheets by reducing graphene oxide (GO). Graphene is regarded as an excellent electrons accepter. As a result, electrons photogenerated by Bi_2MoO_6 activated by light irradiation may be easily transferred to the wide graphene layer, so as to reduce their recombination rate and improve the photocatalytic activity. It was reported that silver nanoparticles decorated on the surface of Bi_2MoO_6 can greatly improve its performance in photocataly-

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http://dx.doi.org/10.1016/j.apcatb.2017.01.033
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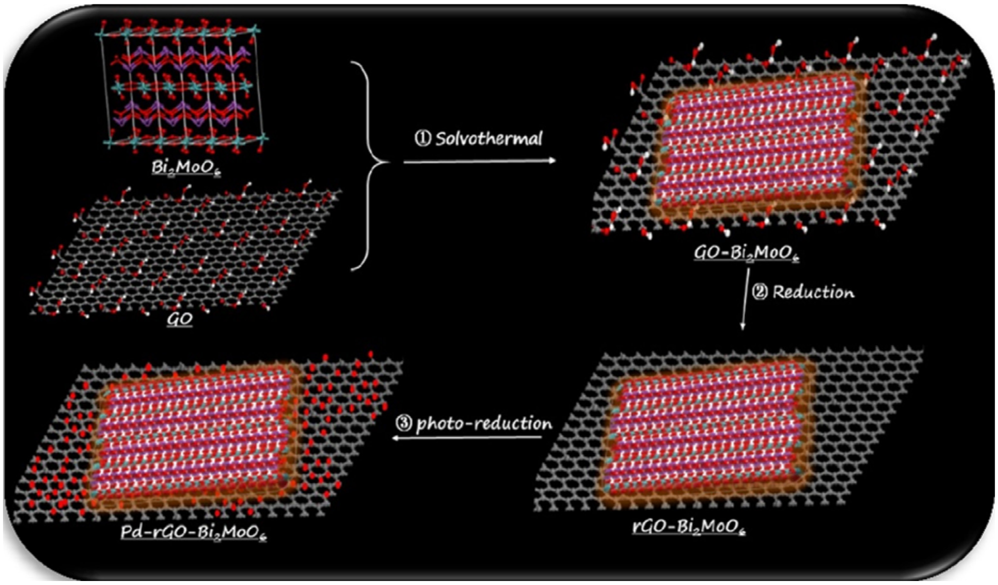

Fig. 1. Scheme of preparation processes of Pd-rGO-Bi_2MoO_6.

sis, which can also be activated by visible light photons via surface plasmon resonance (SPR) effect [10,17]. The SPR peaks of Palladium nanoparticles, as reported, can be tuned from 410 nm to 870 nm [18,19]. Also, 2D rGO sheets decorated with palladium nanoparticles were reported for efficient degradation of organic dyes [20,21]. We recently have prepared Pd nanoparticle decorated Bi_2MoO_6 hybrid photocatalysts, Pd-Bi_2MoO_6, and they exhibited enhanced visible-light-driven photocatalytic activity in the degradation of organic pollutants in wastewater [22]. Compared with the chemical deposition method to doping metal ions [23–25], the photoreduction approach to load metallic nanoparticles on the surface is more facile. Moreover, metallic nanoparticles promote the effective separation of the photogenerated charge carriers and also improve the visible light-responsivity because of the SPR effect. It is reported the metallic nanoparticles are more stable when they present in the forms of both metallic and ionic valence states [26], suggesting the structure of Pd^0/Pd^{2+} is supposed to be more stable compared to bare Pd^0. Recently, Bi et al. have reported on the preparation of ternary Au-rGO-Bi_2MoO_6 composites with enhanced photocatalytic activities under visible light irradiation [27]. Based on above reported work, a ternary (metallic nanoparticles)-rGO-Bi_2MoO_6 composite is supposed to be a promising photocatalyst and need to be further developed [28]. Palladium may be one of the promising candidates, owing for its electrophilicity for facilitating the uptake of photogenerated electrons [29].

This work reports the preparation of a ternary composite composed of Pd, rGO and Bi_2MoO_6. The visible light-driven photocatalytic activities of prepared samples were measured by degrading a colorless organic model, phenol which is widely found in wastewater from many industrial processes and generally difficult to decompose by traditional methods due to its high chemical stability [30,31]. This work has shed light on the possibility of using photocatalysis for treating phenolic compounds in wastewater under visible light irradiation.

2. Experimental

2.1. Preparation of rGO-Bi_2MoO_6

The GO-Bi_2MoO_6 composites were first prepared by the one-pot solvothermal method, as shown in Fig. 1. In a typical process, 264 μL of graphene oxide (GO, dissolved in H_2O with concentration of 4 mg/mL, Sigma-Aldrich Canada) were dissolved in 20 mL ethanol and the suspension was sonicated for 1 h. Next, 1.68 g of $Bi(NO_3)_3 \cdot 5H_2O$ (Fisher Scientific Canada, Certified ACS) was dissolved in 5 mL of ethylene glycol (EG, analytical purity, Fisher Scientific Canada) and 0.42 g of $Na_2MoO_4 \cdot 2H_2O$ (Fisher Scientific Canada, Certified ACS) was also dissolved in another 5 mL of EG. These three mixtures were then mixed together via magnetic stirring for 30 min. The mixture was then transferred to a 45-mL Teflon-lined stainless steel autoclave (Parr Instrument Company, USA) and heated at 160 °C for 20 h. The autoclave was then allowed to naturally cool down to room temperature. The precipitates were then filtered out and washed once with ethanol and twice with distilled deionized water (DD Water). The washed samples were then dried at 60 °C overnight before being collected. As-prepared GO-Bi_2MoO_6 composites were further reduced as reported in [32]. Typically, 0.50 g of GO-Bi_2MoO_6 composites were added in 50 mL EG and ultrasonicated for 30 min. The mixture was then heated and stirred at 140 °C for 2 h. The particle sample was then separated out, washed by ethanol and dried at 60 °C overnight before being collected. For comparison, pure Bi_2MoO_6 was also prepared using the solvothermal method without adding GO in the precursor solution.

2.2. Preparation of Pd-rGO-Bi_2MoO_6

Pd-rGO-Bi_2MoO_6 composite samples were synthesized by a photoreduction method, as shown in Fig. 1. In a typical procedure, 0.30 g of as-prepared rGO-Bi_2MoO_6 composites were suspended in 40 mL DD Water and sonicated for 30 min before adding a designated amount of $PdCl_2$ (Fisher Scientific Canada, ACS certified). The mixture was then magnetically stirred for 10 min, and illuminated under a 300-W halogen tungsten projector lamp (wavelength: 310–800 nm, Ushio, USA) for 1 h. After that, the resultant products were separated out via centrifugation, washed twice with DDW and dried at 60 °C overnight. Samples of 0.5, 1, 2 and 4 wt% Pd-rGO-Bi_2MoO_6 were prepared following the above procedures. For comparison, 2 wt% Pd-Bi_2MoO_6 were also prepared by changing the substrate to Bi_2MoO_6 instead of rGO-Bi_2MoO_6. Also, 2 wt% Pd-rGO composites were prepared by using $NaBH_4$ (Fisher Scientific Canada, 98%) as the reducing agent [20].