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Er^{3+}/Yb^{3+} co-doped bismuth molybdate nanosheets upconversion photocatalyst with enhanced photocatalytic activity

Rajesh Adhikari [a], Gobinda Gyawali [a], Sung Hun Cho [a], R. Narro-García [b], Tohru Sekino [c], Soo Wohn Lee [a,*]

[a] Research Center for Eco-Multifunctional Nanomaterials, Sun Moon University, Republic of Korea
[b] Centro de Investigaciones en Óptica, A. P.1-948, León, Gto. 37150, México
[c] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan

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ABSTRACT

In this paper, we report the microwave hydrothermal synthesis of Er^{3+}/Yb^{3+} co-doped Bi_2MoO_6 upconversion photocatalyst. Crystal structure, morphology, elemental composition, optical properties and BET surface area were analyzed in detail. Infrared to visible upconversion luminescence at 532 nm and 546 nm of the co-doped samples was investigated under excitation at 980 nm. The results revealed that the co-doping of Er^{3+}/Yb^{3+} into Bi_2MoO_6 exhibited enhanced photocatalytic activity for the decomposition of rhodamine B under simulated solar light irradiation. Enhanced photocatalytic activity can be attributed to the energy transfer between Er^{3+}/Yb^{3+} and Bi_2MoO_6 via infrared to visible upconversion from Er^{3+}/Yb^{3+} ion and higher surface area of the Bi_2MoO_6 nanosheets. Therefore, this synthetic approach may exhibit a better alternative to fabricate upconversion photocatalyst for integral solar light absorption.

1. Introduction

After the discovery of TiO_2 photoelectrode by Honda and Fujishima [1], heterogeneous photocatalysis on semiconductor surface has attracted much attention due to its potential applications such as hydrogen evolution and removal of the organic pollutants in the environment [2]. TiO_2 has been the most widely studied and used in many applications because of its strong oxidizing abilities, super hydrophilicity, chemical stability, long durability, nontoxicity and low cost [3]. However, the photocatalytic activity of TiO_2 is limited only to the UV region due to its large band gap energy thereby utilizing only 3–5% solar energy of the total solar spectrum [4]. Various approaches have been developed to extend the response of photocatalysts from ultraviolet light into the visible-light region, such as optimizing the low band gap binary semiconductors like CdS, WO_3, In_2O_3 [5–7], incorporation of metallic elements Pt, Au and Ag on semiconductor surface [8–10] and doping of nonmetallic (N, S and F) elements in conventional photocatalysts [11–13] to decrease the band gap in order to utilize the larger fraction of energy available in the solar spectrum. However, the efficient utilization of solar energy is not adequate to address the current energy and environmental issues.

Recently, besides UV and visible light, various approaches have been employed to harvest near infrared light. Out of several approaches, doping of semiconductor lattice by the rare earth metal ions is the most effective method to utilize near infrared light due to sufficient energy levels present in the rare earth elements. Doping of rare earth elements on the semiconductor can effectively transform near infrared light to the visible and UV light by means of a process called the upconversion (UC) luminescence. After the discovery of Upconversion process by Auzel, Ovsyankin and Feofilov in 1960 [14], upconversion luminescence has been the focus of research topic. Upconversion (UC) process is a non-linear optical effect that can be used to convert low energy incident radiation (infrared light) into higher energy emitted radiation (visible light) via multiple absorption or energy transfer [15,16]. Upconverting materials could be used in many applications, including bio-imaging, lasers, novel display technologies, and solar cells. Besides these applications, upconversion process has also been utilized for the effective photocatalysis in recent years. Various literatures have reported that the rate of photocatalysis has been increased by using upconversion agent on the conventional photocatalysts. Table 1 shows some of the upconversion photocatalysts reported by different authors with their results. Hence, above literatures reveal that the upconversion photocatalysts doped with rare earth ions can utilize the broad absorption of the solar spectrum.

Bi_2MoO_6 is an active member of the Aurivillius oxide family that has attracted considerable attention because of its dielectric,

* Corresponding author. Tel.: +82 41 530 2882; fax: +82 41 530 2840.
E-mail address: swlee@sunmoon.ac.kr (S.W. Lee).

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Table 1
Review of some recent research work in upconversion photocatalysis.

Materials	Synthesis methods	Probe molecule	Results	Ref.
Er^{3+}: $Y_3Al_5O_{12}$ coated TiO_2 particles	Sol–gel	Congo red	High activity under visible and sunlike type irradiation	[17]
TiO_2 doped with $40CdF_2 \cdot 60BaF_2 \cdot 0.8Er_2O_3$	Ultrasound assisted precipitation	Acid red B	Photocatalytic activity was found to be increased under phosphor lamp irradiation	[18]
$NaYF_4$:Yb,Tm/CdS composite	Hydrothermal	Rhodamine B, Methylene Blue	Investigation of Photocatalytic activity under NIR irradiation	[19]
Er^{3+}:$Y_3Al_5O_{12}/Bi_2WO_6$	Sol–gel	Phenol	Photocatalytic activity enhanced beyond the absorption edge of Bi_2WO_6	[20]
Er^{3+}-doped Bi_2WO_6	Hydrothermal	Rhodamine B, Phenol	Photocatalytic activity enhanced under LED irradiation	[21]
SAC supported Er^{3+}:$YAlO_3/TiO_2$	Sol–gel	Methylene Orange	Higher photocatalytic activity under visible and LED irradiation in presence of upconversion agent.	[22]
Er^{3+} loaded $BaMoO_4$	Hydrothermal	Methylene Blue	Photocatalytic activity increased in presence Er^{3+} loaded samples under simulated solar light irradiation	[23]
Er^{3+} doped Bi_2MoO_6	Hydrothermal	Rhodamine B, Phenol	Photocatalytic activity enhanced significantly due to specific facet and effective transformation of NIR light by Er^{3+} ion	[24]
Er^{3+}:$YAlO_3/TiO_2$–SnO_2	Sol–gel/ultra sound	Acid Red B	Er^{3+}:$YAlO_3/TiO_2$–SnO_2 could act as broad-spectrum sonocatalyst feasible to treat dyes and wastewater.	[25]
Er^{3+}–TiO_2 suspension	Sol–gel	Orange I	The transitions of 4f electrons of Er^{3+} and the red shift of the optical absorption edge of TiO_2 by Er^{3+} doping were useful to enhance photocatalytic activity under visible light.	[26]

ion-conductive, luminescent and catalytic properties [24]. Recent research revealed that Bi_2MoO_6 could perform as an excellent photocatalyst for water splitting and degradation of organic compounds. Moreover, two dimensional (2D) structural semiconductor materials like nanosheet, plate, disk or film attract increasing interests due to their high percentage of selectively exposed reactive facets and fast separation of electron and hole [27]. Therefore, in this paper, we report the enhanced photocatalytic activity of Er^{3+}/Yb^{3+} co-doped Bi_2MoO_6 nanosheets upconversion photocatalyst synthesized by microwave hydrothermal method for the first time. Mechanism of the enhanced photocatalytic activity is discussed based on the upconversion effect caused by the Er^{3+}/Yb^{3+} ion.

2. Experimental

2.1. Materials and methods

All the chemicals used were of analytical grade and used without further purification. Bi $(NO_3)_3 \cdot 5H_2O$ (99.99%), H_2MoO_4 (99.9%), Er $(NO_3)_3 \cdot 5H_2O$ (99.999%), Yb$(NO_3)_3 \cdot 5H_2O$ (99.9%) were purchased from Sigma Aldrich. Ethylene glycol was received from Alfa Aesar Ltd. Aqueous ammonia solution (30%) was used to maintain pH of the solutions. Deionized water was used throughout during washing process. Rare-earth (Er^{3+} and Yb^{3+}) nitrate solutions were prepared by dissolving the corresponding metal nitrate in double distilled water at room temperature.

2.2. Preparation of photocatalyst

Er^{3+}/Yb^{3+} co-doped Bismuth molybdate nanopowders were synthesized by microwave assisted hydrothermal process. In a typical experiment, 3.24 g of Bi_2 $(NO_3)_3 \cdot 5H_2O$ and 1.62 g of H_2MoO_4 were dissolved in 20 mL ethylene glycol in separate beakers (a) and (b). Similarly, 2 mol% of erbium nitrate was dissolved in 10 ml double distilled water in another beaker (c). In this research work, concentration of Er^{3+} ion was fixed to be 2 mol% for all samples and concentration of Yb^{3+} was varied from 0 to 20 mol% with steps of 5 mol%. Aqueous solution of ytterbium nitrate (0 mol%, 5 mol%, 10 mol%, 15 mol% and 20 mol%) was prepared in a separate beaker (d). After making all the precursor solutions, solution (a) was mixed to the solution (b) dropwise with continuous stirring and the solution (c) and (d) were added to the suspension formed from (a) and (b). The pH of the whole suspension formed after mixing all the precursor solutions was adjusted to 9 by using ammonia solution. The whole mixture was then transferred to the Teflon lined autoclave for microwave hydrothermal treatment (Eyela MWO-1000 Wave Magic). The mixture was heated at 150 °C for 1 h under microwave irradiation by using 200 W powers. After the completion of the process, the samples were washed with deionized water several times by centrifuging, dried in air at 70 °C overnight and finally annealed in air at 450 °C for 4 h. For reference, undoped Bismuth molybdate was also prepared by similar procedure. For convenience, samples are identified hereafter as BIM-00, BIM-20, BIM-25, BIM-210, BIM-215 and BIM-220, respectively. The formation mechanism of Bi_2MoO_6 under hydrothermal condition follows the following reaction pathways [28].

$$Bi(NO_3)_3 + H_2O \leftrightarrow BiO(NO_3) + 2H^+ + 2NO_3^- \quad (1)$$

$$2BiO(NO_3) + H_2O \leftrightarrow Bi_2O_2(OH)(NO_3) + H^+ + NO_3^- \quad (2)$$

$$Bi_2O_2(OH)(NO_3) + H_2MoO_4 \leftrightarrow Bi_2MoO_6 + H^+ + NO_3^- + H_2O \quad (3)$$

2.3. Photocatalytic experiment

In the photocatalytic experiment, 0.1 g of the catalyst powder was placed in a Pyrex glass cell. 50 ml of aqueous dye (10 mg/L) was slowly poured in the cell and then dispersed well by using magnetic stirrer. The solution with dispersed catalyst particles was then put in dark to achieve adsorption–desorption equilibrium for 30 min. The suspension was then irradiated with continuous stirring under simulated solar light by using solar simulator (PEC-L01, pecell, Am 1.5G). The distance between the lamp and pyrex glass cell containing dye suspensions was 5 cm and the overall light intensity illuminated on the reactor was 11.9 W/cm^2 and the light intensity per unit area at the sample distance was 0.476 W/cm^2. The temperature of the photocatalytic system was maintained at 25 °C by using cooling fan assembled with reactor. The concentrations of dye solution during the reaction period were determined by using spectrophotometer measuring the absorbance at 554 nm using a spectrophotometer (MECASYS Optizen 2120). Each aliquot was withdrawn at every 30 min, centrifuged to remove the nanoparticles and the absorbance was measured by UV–vis spectrophotometer (MECASYS Optizen 2120).