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Photocatalytic degradation of thiobencarb by a visible light-driven MoS_2 photocatalyst

Shiyun Huang[a], Chiingchang Chen[b], Hweiyan Tsai[a], Janah Shaya[c], Chungshin Lu[d,*]

[a] School of Medical Applied Chemistry, Chung Shan Medical University, Taichung 402, Taiwan, ROC
[b] Department of Science Application and Dissemination, National Taichung University of Education, Taichung 403, Taiwan, ROC
[c] Institut de Physique et Chimie des Matériaux (IPCMS), UMR 7504, CNRS-Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg Cedex 2, France
[d] Department of General Education, National Taichung University of Science and Technology, Taichung 403, Taiwan, ROC

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ABSTRACT

In this study, molybdenum disulfide (MoS_2) microsphere was prepared and employed as a visible-light catalyst for the photocatalytic degradation of thiobencarb (TBC), a carbamate pesticide. The as-prepared MoS_2 photocatalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). TBC elimination using MoS_2 proved to be efficient and practical in both deionized and environmental water samples. This photocatalytic method presented a set of advantages over other TBC removal processes such as using visible light source without the need of costly additives (e.g.·H_2O_2). Optimization studies of this process showed that the degradation efficiency could reach 95% in 12 h at a pH range of 6–9. Further, the effect of anions (Cl^- and NO_3^-) was minor on the photocatalytic activity of MoS_2. Experiments using radical scavengers indicated that hydroxyl radicals and holes are the prevailing reactive species involved in this process. Three possible photodegradation pathways were proposed based on the major intermediates as verified by gas chromatography/mass spectrometry technique. The practicality of this MoS_2 photocatalyst was validated by its use in the removal of TBC from real water samples and by its stability and reusability in three successive runs, evidencing its prospective applications in the treatment of environmental water and contaminated wastewater samples.

1. Introduction

Carbamates are used as one of the main classes of the widely consumed pesticides in the world [1]. Indeed, this family is well known for the diversity of its biological activity so that it is utilized as insecticides, fungicides, nematocides, miticides, and molluscicides [2]. Carbamates are recognized with their toxicological effects to environment and specifically to human beings by their neurological effects as acetylcholinesterase inhibitors [3]. The United States Environmental Protection Agency (EPA) included carbamates on the priority list of pollutants [4]. The major problem with usage of carbamates is their persistence in the environment that might last for many years for certain compounds. Owing to their high solubility in water, their residues can circulate in aqueous mediums by leaching and runoff from soil into ground and surface water [5]. Furthermore, their broad applications in agriculture result in raising their residues in environmental matrices.

In particular, thiobencarb (TBC, S-4-chlorobenzyl diethylthiocarbamate) represents a carbamate pesticide frequently used in rice fields. The chemical structure of TBC is displayed in Fig. 1. The worldwide rate of TBC consumption is around 18,000 tons per year (40 countries) [6]. TBC has been detected in river waters constituting a threat to the aquatic ecosystem due to its resistance to degradation by hydrolysis and its moderate toxicity in acute toxicity tests [7,8]. In Japan for instance, the Ministry of Health and Welfare specified the TBC level to be lower than 20 μg/L in tap water [9]. The search to find a simple and efficient method to remove TBC from water is still ongoing and will definitely help in reducing the environmental problems that result from its current applications.

Recent years have witnessed the development of innovative technologies for water treatment technologies and removal of organic residues such as the advanced oxidation processes (AOPs) [10]. In essence, photocatalytic processes [11,12] using semiconductors that can generate reactive hydroxyl radicals upon exposition to UV–vis radiation have been thoroughly investigated. Titanium dioxide (TiO_2), as one of the most applied photocatalysts, has been successfully implemented to degrade thiobencarb [13,14]. However, the major drawback of this catalyst is its absorption of ultraviolet light only at wavelengths below 387.5 nm, which accounts for about 4% of sunlight. Thus, the

* Corresponding author.
E-mail address: cslu6@nutc.edu.tw (C. Lu).

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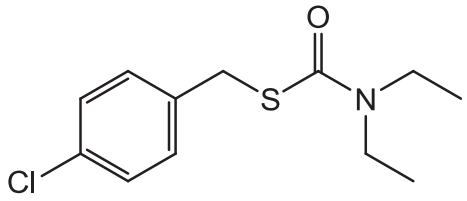

Fig. 1. Chemical structure of thiobencarb.

photocatalytic activity of TiO_2 is low under visible light limiting its utility in the removal of organic molecules that requires high energy especially at a large scale [15,16].

In our previous studies, we have demonstrated the efficient degradation of thiobencarb using a visible light-driven monoclinic $BiVO_4$ catalyst [17]. $BiVO_4$ is found to be stable during 3 successive runs achieving a TBC removal level of 97% within 5 h. Nonetheless, the addition of hydrogen peroxide is indispensable to establish a prominent photocatalytic activity of $BiVO_4$. Hydroxyl radicals are only generated in considerable amount on $BiVO_4$ if H_2O_2 is added; else it is below the blank level [18]. There exist many studies that evaluate the economical and technical feasibility of treatment processes from all perspectives including the usage of additives. Therefore, the costly H_2O_2 is a major drawback that restricts the employment of $BiVO_4$ in large-scale treatments of water-soluble pesticides. In addition, the presence of anions has a dramatic effect on the catalytic activity of $BiVO_4$. In this study, we setup to find a suitable photocatalyst that operates effectively in the photodegradation of thiobencarb using only visible light irradiation without the need of any additives such as H_2O_2.

Molybdenum disulfide (MoS_2) has captivated large attention since it possesses exceptional features like large surface area and catalytically active sites [19,20]. MoS_2 has found important applications in different domains including hydrogen evolution reaction, hydrodesulfurization, and photocatalytic degradation of organic pollutants [21]. MoS_2 is characterized by a narrow band gap that allows the absorption of visible light and generation of electron–hole pairs upon excitation [22,23]. This attribute has made MoS_2 a potential candidate for photocatalytic applications under visible light. The photooxidation activity of MoS_2 nanoclusters and their catalytic role in the photolysis of organic molecules using visible light were first reported by Thurston et al. [24]. The higher utilization of solar radiation for nano MoS_2 announces it as an attractive alternative to TiO_2. James et al. [25] realized MoS_2 nanoparticles *via* thermal decomposition method and tested them in photocatalytic degradation of methylene blue bringing about an efficiency of 30%. Hu et al. [26] investigated the activity of nano-slice,

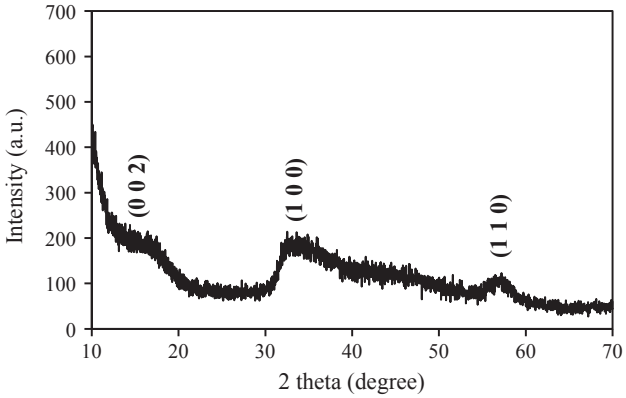

Fig. 2. XRD pattern of the as-prepared MoS_2 photocatalyst.

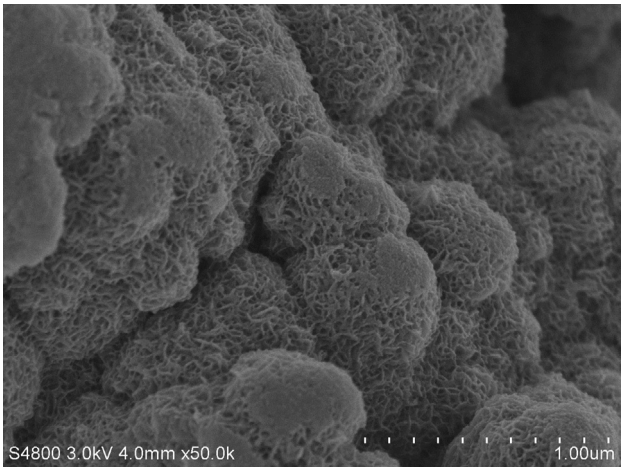

Fig. 3. SEM image of the as-prepared MoS_2 photocatalyst.

Table 1
Summary of recent related papers collected for MoS_2.

	Sodium molybdate	Sulfur source[a]	pH	Reaction temperature	Reaction time	Use	Reference
This study	5 mmol	CYS 40 mmol	7	180 °C	24 h	Photocatalyst	
Chen et al.	1.5 mmol	CYS 4.5 mmol	< 1	240 °C	24 h	–	[29]
Park et al.	6 mmol	CYS 25 mmol	1	220 °C	36 h	Li-ion storage	[30]
Huang et al.	1 mmol	CYS 3 mmol	6.5	180 °C	48 h	Supercapacitor electrode	[31]
Wang et al.	1.25 mmol	CYS 10 mmol	–	220 °C	24 h	Supercapacitor electrode	[32]
Zhou et al.	2 mmol	TAA 10 mmol	–	240 °C	24 h	Photocatalyst MB	[21]
Guo et al.	1 mmol	TAA 8 mmol	0.5 mmol oxalic acid	200 °C	24 h	Hydrogen evolution	[33]
Patel et al.	0.124 mmol	TAA 0.80 mmol	–	200 °C	24 h	Energy storage	[34]
Feng et al.	4 mmol	TU 15 mmol	3 mmol oxalic acid	200 °C	24 h	–	[35]
Kim et al.	2.77 mmol	TU 11.1 mmol	–	210 °C	24 h	–	[36]
Sun et al.	7 mmol	TU 35 mmol	< 1	200 °C	24 h	N_2 reduction	[37]

[a] Sulfur source: L-cysteine (CYS); thiourea (TU); thioacetamide (TAA).