



Recent development on MoS₂-based photocatalysis: A review

Zizhen Li^{a,b}, Xiangchao Meng^{a,b}, Zisheng Zhang^{a,b,*}

^a Department of Chemical & Biological Engineering, University of Ottawa, Ottawa, Canada

^b Center for Catalysis Research and Innovation, University of Ottawa, Ottawa, Canada



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ABSTRACT

MoS₂-based photocatalysts attract wide attention as they possess a suitable band gap for visible-light harvesting, making it a promising earth-abundant photocatalyst for hydrogen production, environmental remediation, and photosynthesis. However, the rapid recombination of photogenerated electron-hole pairs, limited quantity of active edge sites, and difficult photocatalyst separation and recycling hinder the practical application of this material. In this review, recent development of MoS₂-based photocatalysts in various photocatalytic applications is summarized. In addition, possible approaches to enhance photocatalytic activity and separate photocatalysts from reaction media are discussed to provide a future direction in highly efficient photocatalyst design.

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* Corresponding author at: Department of Chemical & Biological Engineering, University of Ottawa, Ottawa, Canada.

E-mail addresses: zli125@uottawa.ca (Z. Li), xmeng086@uottawa.ca (X. Meng), zzhang@uottawa.ca (Z. Zhang).

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Zizhen Li received her Bachelor's degree from Ocean University of China in Tsingtao in 2013 and Master of Applied Science degree in Chemical Engineering at the University of Ottawa in 2016, and upon graduation started her graduate study for a Ph.D. degree in the Department of Chemical and Biological Engineering at the University of Ottawa under the supervision of Dr. Zisheng (Jason) Zhang. Her research is focused on 1) preparation, characterization and testing of two-dimensional materials, and 2) implementation of 2D materials in photo(electro)-catalytic detoxification and disinfection.



Xiangchao Meng got his Bachelor's degree from Ocean University of China in Tsingtao in 2013, and Master of Applied Science degree in Chemical Engineering at the University of Ottawa in 2015. He started his graduate study for a Ph.D. degree in the same department at the University of Ottawa under the supervision of Dr. Zisheng (Jason) Zhang. His recent research focuses on preparation and development of photoactive materials, novel photo(electro)catalytic reactor design, photo(electro)catalytic oxidation, CO₂ reduction and N₂ fixation for energy conversion and storage via experimental and DFT studies.



Zisheng (Jason) Zhang is professor in the Department of Chemical and Biological Engineering and the Vice-Dean (International Affairs) at the Faculty of Engineering, University of Ottawa, Canada. He obtained his Bachelor's degree from Hebei University of Technology in Tianjin, Master's degree from Tianjin University, and his Ph.D. degree from the University of Waterloo. After over 30 years of practice as a professional engineer, he has gained rich R & D and consulting experience in chemical, biochemical, as well as environmental engineering, co-authored over 200 publications, and has trained more than 60 graduate students and post-doctoral fellows. Currently his research is focused on 1) catalyst, equipment and process development for renewable energies, photo(electro)catalytic environmental control and solar energy conversion and 2) bioreactor and process development for efficient mass production using microbial and microalgal cells.

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1. Introduction

Photocatalysis, as one of the advanced oxidation processes (AOPs), has been extensively studied since 1972 [1]. Applications of this advanced technique were developed from hydrogen evolution to environmental application as well as photosynthesis. Various semiconductors were also explored as a photocatalytic material. It is well known that even though TiO₂ is the original material for photocatalysis and is mostly applicable in commercial processes [2,3], hindrances are still apparent. One of the intrinsic hindrances is the band gap of TiO₂ (~3.2 eV for anatase and brookite, ~3.0 eV for rutile), which determines that the excitation wavelength is in the UV region. It means only 5% of solar flux incident in the spectral regime can be utilized by TiO₂-mediate photocatalytic system. To overcome this problem, one of the approaches is to tune the band gap of TiO₂ via surface modification, doping *etc.* [4,5]. Another effective method is to prepare novel visible light-responsive photocatalysts with suitable band gaps.

Among recently developed photocatalytic materials, noble-metal-free MoS₂ has attracted attention and various results were reported, due to its high mobility of charge carriers and excellent

optical absorption property [6–8]. Bulk MoS₂ is an excellent catalyst for hydrodesulfurization, but not for photocatalysis due to its edge activity. That is because the S-Mo-S coordination in the crystal lattice generates unsaturated Mo and S atoms at the edge, leading to the activity sites existing at the edges [7]. To overcome this problem to improve the photocatalytic activity of MoS₂, several studies were reported and implemented in various applications.

In this review, MoS₂-based photocatalysis applied in various fields would be comprehensively summarized. Moreover, the emerged problems as well as possible approaches would be mentioned and suggested. Future development of MoS₂-based photocatalysis would be proposed.

2. Properties and structures

Bulk MoS₂ has a layered structure stacked by weak van der Waals forces as shown in Fig. 1 [9]. Each layer consists of a plane of Mo atoms sandwiched between two planes of S atoms [10]. According to the stacking sequence of MoS₂-layers and atomic coordination between a central Mo atom and surrounding S atoms, the MoS₂ crystal structure can be classified into 4 types: 1H, 1T, 2H and 3R (Fig. 1) [11]. The 1H polytype is the most stable phase with hexagonally packed Mo atom coordinated by six S atoms. The tetragonal polytype layered crystals (1T) has Mo atoms coordinated by six S atoms in an octahedral arrangement. The hexagonal polytype layered crystals (2H) is the most common phase and can be transformed from semiconductor into the metallic 1T phase by phase engineering [12]. Rhombohedral polytype layered crystals (3R) has three layers per unit cell and each Mo atom is surrounded by six S atoms in a trigonal prismatic arrangement. Among them, the 1T and 3R structures are metastable [13]. The electronic and optical properties of MoS₂ can be varied by band gap adjustment due to the quantum confinement effect [7]. The bulk MoS₂ has a small indirect bandgap (1.3 eV), which is not sufficient to induce photocatalytic reactions and not beneficial for the separation of charge carriers. However when the size of MoS₂ is reduced to the 2-dimensional scale (e.g. MoS₂ nanosheets), the indirect bandgap transfers to a direct bandgap of 1.9 eV [7]. Thus, the low-dimensional MoS₂ is considered as a promising visible light-responsive photocatalyst. The fabrication methods of two-dimensional (2D) MoS₂ can be classified into mechanical exfoliation, chemical exfoliation and bottom-up approaches, such as chemical vapor deposition (CVD), physical vapor transport and wet chemical approaches. [11,15]. The first emergence of monolayer MoS₂ is reported in 2005 using the mechanical cleavage strategy [16]. Various synthesis methods have their own advantages and intrinsic limitation. Among them, chemical exfoliation is capable of producing large quantities of mono- or few-layered MoS₂ nanosheets with relatively high carrier mobility compared with mechanically exfoliated method. As a result, it may be potentially applied to a scaled-up fabrication of two-dimensional (2D) MoS₂ [17,18]. It is reported that the quality and quantity of prepared MoS₂ nanosheets via chemical exfoliation is highly dependent on the solvent surface tension [18,19]. When the surface tension (γ) of solvent is about 40 mJ/m², the required exfoliation energy was

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