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https://doi.org/10.15017/1961300

出版情報: Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 4, pp.112-115, 2018-10-18. 九州大学大学院総合理工学府 バージョン: 権利関係:

# Nanodot MoS<sub>2</sub>@3DOM TiO<sub>2</sub> composites for their photocatalytic application

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**Abstract:** Nanodot  $MoS_2@3$ -dimentional ordered macroporous (3DOM) TiO<sub>2</sub> was represented to be a photocatalyst in the degradation of methylene blue. Nanodot  $MoS_2$  suspension was synthesized by intercalation and exfoliation processes. To give the high yield,  $MoS_2$  prepared by a hydrothermal method was selected as a nanodot  $MoS_2$  source instead of large-plane commercial  $MoS_2$ . In case of 3DOM TiO<sub>2</sub>, polystyrene opal prepared by a self-assembly method was used as the 3DOM template. Then, the hydrolysis and calcination of titanium alkoxide filled in template void were further employed to obtain the 3DOM TiO<sub>2</sub>. Finally, nanodot  $MoS_2$  and 3DOM TiO<sub>2</sub> were combined via an impregnation method. Interestingly, nanodot  $MoS_2@3DOM$  TiO<sub>2</sub> exhibited the higher performance in degradation than unmodified 3DOM TiO<sub>2</sub>. It strongly emphasizes that nanodot  $MoS_2$  provides the quantum confinement effect and prohibits the electron-hole recombination on TiO<sub>2</sub>. Furthermore, 3DOM structure of TiO<sub>2</sub> can improve the diffusion rate of involved compounds during the photocatalytic reaction.

Keywords: Nanodot MoS<sub>2</sub>; 3DOM TiO<sub>2</sub>; Photocatalyst; Degradation

# 1. INTRODUCTION

The transition-metal dichalcogenides (TMDs) are semiconductors of the MX2-type compounds of which M is a transition metal (Mo, W, or Nb), and X is a chalcogen (S, Se or Te). Among all types of TMDs, molybdenum disulfide (MoS<sub>2</sub>) has been attractive by enormous scientists because of the unique properties. The transformation of MoS<sub>2</sub> from bulk to 2D structure can transform its semiconductor property from indirect band gap ( $E_g \sim 1.2 \text{ eV}$ ) to direct band gap ( $E_g \sim 1.9 \text{ eV}$ ). Interestingly, 0D MoS<sub>2</sub> with diameter less than 10 nm, also known as MoS<sub>2</sub> nanodots, shows higher photocatalytic efficiencies than large-plane bulk MoS<sub>2</sub> due to the larger band gap ( $E_g \sim 3.96 \text{ eV}$ ) and higher exposition of edge sites or active sites [1,2]. Thus, in this project, MoS<sub>2</sub> nanodots are utilized as a co-catalyst to improve photocatalyst properties of titanium dioxide (TiO<sub>2</sub>) by charge separation and increase of active sites.

TiO<sub>2</sub> is one such compound that is notable for being used as a photocatalyst because of inertness and suitable energy level of conduction band (CB) and valence band (VB). However, the wide band gap of TiO<sub>2</sub> has limited the absorption under the ultraviolet spectrum ( $\lambda < 387$  nm). Additionally, it also hinders photocatalytic activities by electron-hole recombination. Thus, the strategies for reducing their band gap and inhibiting charge carrier recombination are the key objectives to improve TiO<sub>2</sub> performance.

Currently, there are many methods for improving  $TiO_2$  efficiency such as modification with other components, like MoS<sub>2</sub>. Moreover, the increase of surface area of TiO<sub>2</sub> also enhances photocatalytic activities due to the short diffusion length of electron and hole, leading to the inhibition of electron-hole recombination. Thus, nanostructures of TiO<sub>2</sub> have been extensively fabricated in order to shorten the travel length of charge carriers. Remarkably, the 3-dimentional ordered macroporous

(3DOM)  $TiO_2$  such as an inverse opal structure provides a new opportunity to improve photocatalytic activities. This structure not only improves the diffusion rate of involved compounds during reaction, but it is also capable of manipulating the incident light based on photonic crystal properties. Thus, this structure enables the enhancement of solar light harvesting.

Therefore, we aim to study the synthesis of nanodot  $MoS_2@3DOM$  TiO<sub>2</sub> composites to improve photocatalytic activities. Nevertheless, the method for depositing MoS<sub>2</sub> nanodots on 3DOM TiO<sub>2</sub> is still very challenging and has not been reported yet. Herein, fabrication of MoS<sub>2</sub> nanodots and 3DOM TiO<sub>2</sub> is deeply investigated. Their activities on photocatalytic reaction are also tested by degradation of methylene blue (MB) and compared their efficiencies with unmodified catalyst.

# 2. EXPERIMENTAL PROCEDURE

# 2.1 Catalyst preparation

# 2.1.1 Preparation of MoS2 nanodots

 $MoS_2$  nanodots were prepared by intercalation and exfoliation methods (Scheme 1). To increase the number of nanodots, the few-layer  $MoS_2$  was used as a  $MoS_2$  precursor for an intercalation process. Initially, 0.5 mmol of ammonium molybdate and 15 mmol of thiourea were dissolved in deionized water. Then, the solution was transferred into Teflon-line stainless-steel autoclave (50% by vol) and kept in an oven at 200°C for 24 h. The obtained sediment was thoroughly washed by water and ethanol several times and dried under vacuum for 2 h. Finally, few-layer  $MoS_2$  was obtained.

Based on  $MoS_2$  intercalation from the previous work [3], Na metal (50 mg) and as-synthesized few-layer  $MoS_2$ (100 mg) were vigorously stirred for 24 h in ethylenediamine under N<sub>2</sub> atmosphere. After that, the sample was centrifuged and dried for 3 h under vacuum to collect the MoS<sub>2</sub>-intercated compound. Next, the intercalated MoS<sub>2</sub> was readily exfoliated in 45% ethanol under bath sonication [4]. The MoS<sub>2</sub> suspension was centrifuged and purified by 0.22  $\mu$ m filters to remove unexfoliated compounds. Finally, the nanodot-MoS<sub>2</sub> suspension was obtained.

### 2.1.2 Preparation of 3DOM TiO<sub>2</sub>

3DOM TiO<sub>2</sub> was synthesized by an infiltration and calcination (Scheme 1) by using polystyrene (PS) opal prepared by a self-assembly method as a template. Firstly, 6% w/v of styrene reacted with 3% w/v of potassium persulfate (KPS) as an initiator. Then, the solution was vigorously stirred at 80°C for 51/2 h under N<sub>2</sub>-flowing to form PS suspension with 300-400 nm in diameter. After that, PS suspension was centrifuged at 10,000 rpm for 20 min to form a PS template with the face-centered cubic structure. After taking the supernatant out, the sample was kept for a couple of days and dried at 60°C under vacuum for 6 h. Next, the PS template was immersed in titanium isopropoxide for about 12 h and washed by ethanol to eliminate the excess titanium isopropoxide. After hydrolyzed under the air overnight, the sample was calcined at 500°C for 5 h. Finally, 3DOM TiO<sub>2</sub> was successfully synthesized and denoted as 3DOM TiO<sub>2</sub>.

## 2.1.3 Preparation of MoS<sub>2</sub>@3DOM TiO<sub>2</sub>

The MoS<sub>2</sub> nanodot was deposited on 3DOM TiO<sub>2</sub> via the impregnation method [5]. Firstly, The MoS<sub>2</sub> suspension was mixed with 3DOM TiO<sub>2</sub> with different % wt of MoS<sub>2</sub> (based on an ICP-OES result of MoS<sub>2</sub> suspension). The solution was then sonicated for 10 min and dried at 60°C. Finally, the nanodot MoS<sub>2</sub>@3DOM TiO<sub>2</sub> composites were formed and denoted as x% MoS<sub>2</sub>@3DOM (x%= % wt of MoS<sub>2</sub>; 1%, 3%, 5%, 10% and 20% respectively).



🛹 Ethylenediamine 🔵 Na metal

Scheme 1. The synthesis diagram of nanodot  $MoS_2@3DOM TiO_2$  composite.

### 2.2 Degradation of methylene blue

The photocatalytic activities of nanodot  $MoS_2@3DOM$  TiO<sub>2</sub> composites were evaluated by examining the degradation of MB at room temperature under a UV lamp at ~254 nm. In typical reactions, 10 mg of each catalyst was added to the MB solution (10 ppm, 50 mL) and the mixture was sonicated for 10 min in dark.

Before irradiation, the mixture was stirred for 1 h to reach an adsorption-desorption equilibrium. During the reaction, the mixture was extracted and centrifuged at 3,000 rpm for 10 min to remove the catalyst. Finally, the UV-Vis spectrometer was utilized to observe the concentration of MB (at 664 nm) for determining the degradation efficiency.

Precentage of degradation =  $\frac{[MB]_{solution}}{[MB]_{initial solution}} \times 100\%$ 

# 3. RESULTS AND DISCUSSION

### 3.1 Characterization

The  $MoS_2$  synthesized by a hydrothermal method was characterized by XRD and SEM techniques. The XRD pattern of synthesized  $MoS_2$  is comparable with 2H- $MoS_2$  standard (PDF 00-037-1492) as shown in Fig. 1a. Moreover, its morphology gives a layered-type compound with a flower-like structure (Fig. 2a) that also corresponds to the  $MoS_2$  structure from the previous reports [6,7]. After intercalation and exfoliation,  $MoS_2$  nanodots in suspension exhibit a small domain less than 10 nm as confirmed by the characteristics of nanodot behaviors; fluorescence property under UV light and absorption peak at about 209 nm as shown in Fig. 3 [8,9].



**Fig. 1.** XRD patterns of (a) as-synthesized  $MoS_2$  (b) 3DOM TiO<sub>2</sub> (c-g) 1%, 3%, 5%, 10% and 20%  $MoS_2@3DOM TiO_2$ , respectively.

In case of 3DOM TiO<sub>2</sub> support, the PS template of 3DOM TiO<sub>2</sub> shows spherical shape and homogenous size of 380 nm as shown in Fig. 2b. Moreover, 3DOM TiO<sub>2</sub> exhibits anatase phase of TiO<sub>2</sub> (PDF 03-065-5714, Fig. 1b) with the homogenous pore size of 220 nm (Fig. 2c). It is noticed that the pore size of 3DOM TiO<sub>2</sub> dramatically decreases about 37% compared to the spherical size of PS template. It is because of the shell thickness of 3DOM TiO<sub>2</sub> and the shrinkage of the structure after eliminating PS beads [10].



Fig. 2. SEM images of (a) synthesized  $MoS_2$ , (b) PS opal template and (c) 3DOM TiO<sub>2</sub>.



**Fig. 3.** UV-vis spectrum and fluorescence characteristic of nanodot MoS<sub>2</sub> suspension under UV irradiation.

After depositing nanodot  $MoS_2$  on 3DOM TiO<sub>2</sub>, the crystal structure was studied by the XRD technique as shown in Fig. 1c-g. The XRD results indicate that 1%,

3%, 5%, 10% and 20% MoS<sub>2</sub>@3DOM show diffraction peaks of anatase TiO<sub>2</sub> like 3DOM TiO<sub>2</sub>. Besides, the (100) peak of internal plane of MoS<sub>2</sub> is only observed in 10% and 20% MoS<sub>2</sub>@3DOM due to increase of MoS<sub>2</sub> loading and low crystallinity of MoS2 suspension before deposited on 3DOM TiO<sub>2</sub>. However, the unknown peaks are clearly observed when increase of MoS<sub>2</sub> loading. It corresponds to the molybdenum-oxide (MoO<sub>x</sub>) impurities which were formed during the impregnation. Morphologies of nanodot MoS<sub>2</sub>@3DOM TiO<sub>2</sub> composites were investigated as shown in Fig. 4. Some MoS<sub>2</sub> aggregates or MoO<sub>x</sub> components are slightly appeared in the honey-comb structure and strongly found in high percentage of MoS<sub>2</sub> loading. However, it does not thoroughly block the catalyst pores, so the diffusion rate of involved compounds in the reaction is not interfered.



**Fig. 4.** SEM images of (a) 3DOM TiO<sub>2</sub>, (b-f) 1%, 3%, 5%, 10% and 20% MoS<sub>2</sub>@3DOM, respectively.

### 3.2 Photocatalytic activities

The photocatalytic activities of nanodot  $MoS_2@3DOM$  TiO<sub>2</sub> composites were evaluated via the degradation of MB as shown in Fig. 5. Obviously, 3DOM TiO<sub>2</sub> can degrade MB only 40% for 4 h, but nanodot  $MoS_2$  on TiO<sub>2</sub> composites can degrade MB more than 80% for the same reaction time. It is strongly confirmed that the nanodot  $MoS_2$  deposited on 3DOM TiO<sub>2</sub> can enhance photocatalytic activities of MB degradation due to the quantum confinement effect of  $MoS_2$  nanodots, which enable the suppression of charge recombination in 3DOM TiO<sub>2</sub> [5].

To further investigation, the kinetic studies were expressed as the pseudo-first order reaction with an equation,  $\ln (C/C_0) = -kt$ , where k is a current rate constant,  $C_0$  and C are the initial concentration of MB



**Fig. 5.** The percentage of degradation of MB (% wt) as a function of time (hour).

and the concentration of MB at time, t, respectively (Fig. 6 and Table 1). Obviously, the apparent rate constants are 0.1524, 0.8164, 0.9073, 0.7529, 0.5977, 0.5076 for 3DOM TiO<sub>2</sub> and 1%, 3%, 5%, 10% and 20% MoS<sub>2</sub>@3DOM, respectively. The linear correlation between  $ln(C/C_0)$  and irradiation time of all reaction is found with correlation coefficient  $(\mathbf{R}^2)$  more than 0.94. It clearly demonstrates that the addition of MoS<sub>2</sub> on 3DOM TiO<sub>2</sub> provides the enhanced photocatalytic activity compared to unmodified 3DOM TiO<sub>2</sub> catalyst. Especially, 3% MoS<sub>2</sub>@3DOM exhibits the highest degradation with a rate constant of 0.9073 h<sup>-1</sup> which is 6 times higher than that of 3DOM TiO<sub>2</sub>. However, when MoS<sub>2</sub> loading contents increase to 20%, the rate constant of the composite slightly decreases to 0.5076 h<sup>-1</sup>. It is because the increase in MoS<sub>2</sub> contents can gradually reduce the light absorption ability of the composite due to the high reflection index of  $MoS_2[11]$ . Moreover, high MoS<sub>2</sub> loading also causes particle aggregates as well as the phase transformation of MoS<sub>2</sub> to MoO<sub>x</sub>. The aggregation of nanodot MoS<sub>2</sub> can reduce edge sites or active sites of MoS<sub>2</sub> and suppress quantum confinement effect of nanodot MoS<sub>2</sub>. Furthermore, the photocatalytic activity of MoS2 was also decreased when contaminated by  $MoO_x$  [12,13].

Based on the above experimental results, the possible mechanism of degradation of MB can be proposed as



**Fig. 6.** The pseudo-first ordered kinetic plots of  $ln(C/C_0)$  as a function of time (hour) for degradation of MB.

**Table 1.** The pseudo-first ordered rate constant ( $h^{-1}$ ),  $R^2$  values, maximum degradation (%) of samples.

Sample	Rate constant (h <sup>-1</sup> )	R <sup>2</sup>	Maximum degradation (%)
3DOM TiO <sub>2</sub>	0.1524	0.9717	51.64
$1\%MoS_2@3DOM$	0.8164	0.9816	3.95
3%MoS <sub>2</sub> @3DOM	0.9073	0.9460	3.91
5%MoS <sub>2</sub> @3DOM	0.7529	0.9687	6.21
10% MoS <sub>2</sub> @3DOM	0.5977	0.9854	9.06
20%MoS <sub>2</sub> @3DOM	0.5076	0.9839	15.18

shown in Scheme 2. Under the irradiation of UV light, TiO<sub>2</sub> absorbs photons and generates excited electrons and holes. In general, CB of MoS<sub>2</sub> is lower than that of TiO<sub>2</sub>, but when MoS<sub>2</sub> domain is reduced less than 10 nm, the band gap of MoS<sub>2</sub> is wider due to the quantum confinement effect. As a result, the CB of MoS<sub>2</sub>locates at a higher energy than that of TiO<sub>2</sub> and the VB of MoS<sub>2</sub> still remains in the middle of the  $TiO_2$  band gap [14,15]. The hole of excited TiO<sub>2</sub> can migrate to VB of MoS<sub>2</sub> and, hence, the recombination of electron-hole pairs in TiO<sub>2</sub> can be suppressed. However, amount of MoS<sub>2</sub> loading should be concerned to avoid the light reflection, particle aggregation and phase transformation of MoS<sub>2</sub>. Although, some limitations in nanodot MoS<sub>2</sub>@3DOM TiO<sub>2</sub> catalysts need to be considered, the outstanding photocatalytic abilities of MoS<sub>2</sub>@TiO<sub>2</sub> composites over 6 times compared to unmodified TiO<sub>2</sub> still challenge us to further develop the synthesis method that can provide the photocatalyst with optimal structural design and strong synergistic effect.



Scheme 2. Proposed mechanism of MB degradation using a nanodot  $MoS_2@3DOM TiO_2$  composite.

# 4. CONCLUSION

In summary, nanodot  $MoS_2$  deposited on 3DOM TiO<sub>2</sub> was completely synthesized with different %loading; 1%, 3%, 5%, 10% and 20%, respectively. Nanodot  $MoS_2@3DOM$  TiO<sub>2</sub> composites exhibit the higher performance in degradation of MB than unmodified 3DOM TiO<sub>2</sub>. It strongly emphasizes that nanodot  $MoS_2$  provides the appropriate overlapping band gap with TiO<sub>2</sub>, resulting in the suppression of the electron-hole recombination on TiO<sub>2</sub> surface. Furthermore, the 3DOM structure of TiO<sub>2</sub> can also improve the scattering of incident light. Thus, nanodot  $MoS_2@3DOM$  TiO<sub>2</sub> composites are underlined to be of interest in the competent photocatalyst.

# 5. ACKNOWLENGTMENTS

This work was financially supported by the Graduate School, Department of Chemistry, Faculty of Science, Kasetsart University, and the Centre of Excellence for Innovation in Chemistry (PERCH-CIC). We would like to acknowledge the Kasetsart University Research and Development Institute (KURDI) for partially financial support.

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