Nanodot MoS_2@3DOM TiO_2 composites for their photocatalytic application

Krobkrong, Navapat
The Department of Chemistry, Faculty of Science, Kasetsart University | The Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Thaweechai, Thammanoon
The Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

Sirisaksoontorn, Weekit
The Department of Chemistry, Faculty of Science, Kasetsart University | The Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University

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_2@3DOM TiO_2 composites for their photocatalytic application

Navapat Krobkrong[1,2], Thammanoon Thaweechai[2], Weekit Sirisaksoontorn[1,2,*]
[1]The Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand.
[2]The Centre of Excellence for Innovation in Chemistry, Faculty of Science, Kasetsart University, 50 Ngam Wong Wan Road, Lat Yao, Chatuchak, Bangkok 10900, Thailand.
fsciwks@ku.ac.th

Abstract: *Nanodot MoS_2@3-dimentional ordered macroporous (3DOM) TiO_2 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_2, 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_2. Finally, nanodot MoS_2 and 3DOM TiO_2 were combined via an impregnation method. Interestingly, nanodot MoS_2@3DOM TiO_2 exhibited the higher performance in degradation than unmodified 3DOM TiO_2. It strongly emphasizes that nanodot MoS_2 provides the quantum confinement effect and prohibits the electron-hole recombination on TiO_2. Furthermore, 3DOM structure of TiO_2 can improve the diffusion rate of involved compounds during the photocatalytic reaction.*

Keywords: Nanodot MoS_2; 3DOM TiO_2; Photocatalyst; Degradation

1. INTRODUCTION

The transition-metal dichalcogenides (TMDs) are semiconductors of the MX_2–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_2) has been attractive by enormous scientists because of the unique properties. The transformation of MoS_2 from bulk to 2D structure can transform its semiconductor property from indirect band gap (E_g ~1.2 eV) to direct band gap (E_g ~1.9 eV). Interestingly, 0D MoS_2 with diameter less than 10 nm, also known as MoS_2 nanodots, shows higher photocatalytic efficiencies than large-plane bulk MoS_2 due to the larger band gap (E_g ~3.96 eV) and higher exposition of edge sites or active sites [1,2]. Thus, in this project, MoS_2 nanodots are utilized as a co-catalyst to improve photocatalyst properties of titanium dioxide (TiO_2) by charge separation and increase of active sites.

TiO_2 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_2 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_2 performance.

Currently, there are many methods for improving TiO_2 efficiency such as modification with other components, like MoS_2. Moreover, the increase of surface area of TiO_2 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_2 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_2 composites to improve photocatalytic activities. Nevertheless, the method for depositing MoS_2 nanodots on 3DOM TiO_2 is still very challenging and has not been reported yet. Herein, fabrication of MoS_2 nanodots and 3DOM TiO_2 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 MoS_2 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

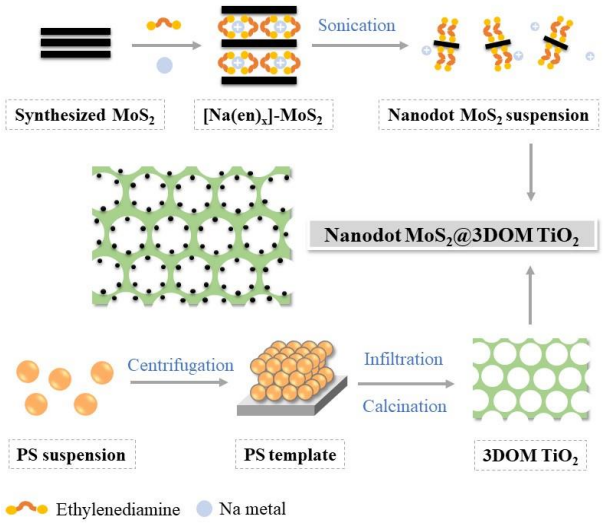
ethylenediamine under N_2 atmosphere. After that, the sample was centrifuged and dried for 3 h under vacuum to collect the MoS_2-intercated compound. Next, the intercalated MoS_2 was readily exfoliated in 45% ethanol under bath sonication [4]. The MoS_2 suspension was centrifuged and purified by 0.22 µm filters to remove unexfoliated compounds. Finally, the nanodot-MoS_2 suspension was obtained.

2.1.2 Preparation of 3DOM TiO_2

3DOM TiO_2 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 5½ h under N_2-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_2 was successfully synthesized and denoted as 3DOM TiO_2.

2.1.3 Preparation of MoS_2@3DOM TiO_2

The MoS_2 nanodot was deposited on 3DOM TiO_2 via the impregnation method [5]. Firstly, The MoS_2 suspension was mixed with 3DOM TiO_2 with different %wt of MoS_2 (based on an ICP-OES result of MoS_2 suspension). The solution was then sonicated for 10 min and dried at 60°C. Finally, the nanodot MoS_2@3DOM TiO_2 composites were formed and denoted as x% MoS_2@3DOM (x%= %wt of MoS_2; 1%, 3%, 5%, 10% and 20% respectively).



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_2 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.

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

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].

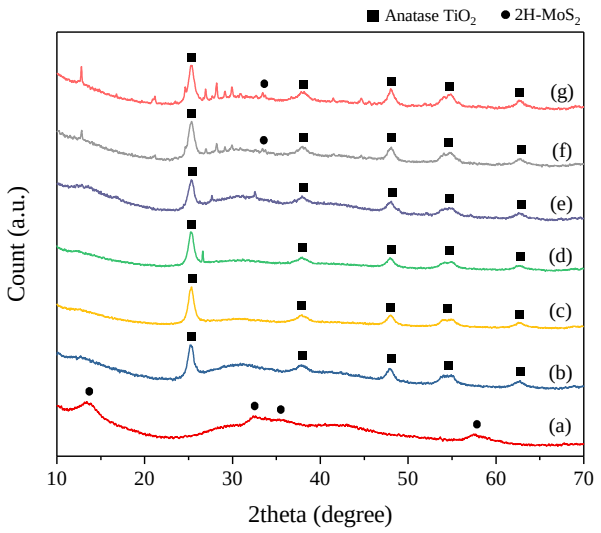


Fig. 1. XRD patterns of (a) as-synthesized MoS_2 (b) 3DOM TiO_2 (c-g) 1%, 3%, 5%, 10% and 20% MoS_2@3DOM TiO_2, respectively.

In case of 3DOM TiO_2 support, the PS template of 3DOM TiO_2 shows spherical shape and homogenous size of 380 nm as shown in Fig. 2b. Moreover, 3DOM TiO_2 exhibits anatase phase of TiO_2 (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_2 dramatically decreases about 37% compared to the spherical size of PS template. It is because of the shell thickness of 3DOM TiO_2 and the shrinkage of the structure after eliminating PS beads [10].

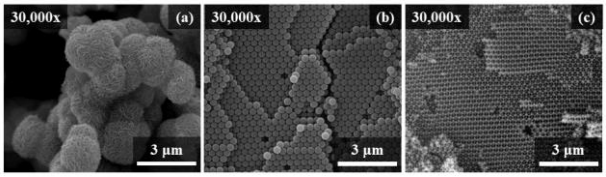


Fig. 2. SEM images of (a) synthesized MoS_2, (b) PS opal template and (c) 3DOM TiO_2.

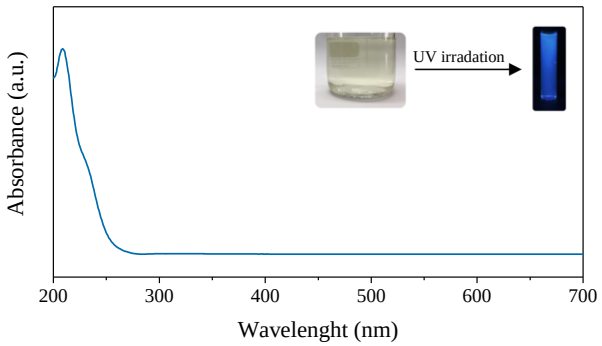


Fig. 3. UV-vis spectrum and fluorescence characteristic of nanodot MoS_2 suspension under UV irradiation.

After depositing nanodot MoS_2 on 3DOM TiO_2, 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_2@3DOM show diffraction peaks of anatase TiO_2 like 3DOM TiO_2. Besides, the (100) peak of internal plane of MoS_2 is only observed in 10% and 20% MoS_2@3DOM due to increase of MoS_2 loading and low crystallinity of MoS_2 suspension before deposited on 3DOM TiO_2. However, the unknown peaks are clearly observed when increase of MoS_2 loading. It corresponds to the molybdenum-oxide (MoO_x) impurities which were formed during the impregnation. Morphologies of nanodot MoS_2@3DOM TiO_2 composites were investigated as shown in Fig. 4. Some MoS_2 aggregates or MoO_x components are slightly appeared in the honey-comb structure and strongly found in high percentage of MoS_2 loading. However, it does not thoroughly block the catalyst pores, so the diffusion rate of involved compounds in the reaction is not interfered.

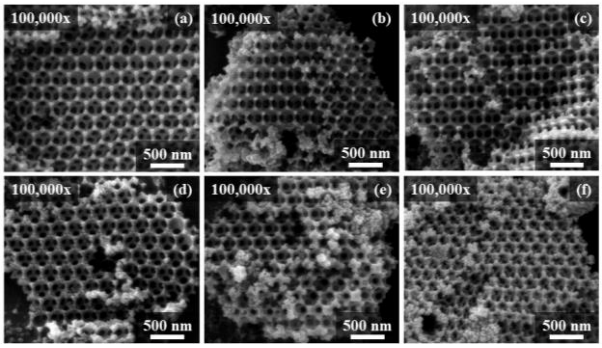


Fig. 4. SEM images of (a) 3DOM TiO_2, (b-f) 1%, 3%, 5%, 10% and 20% MoS_2@3DOM, respectively.

3.2 Photocatalytic activities

The photocatalytic activities of nanodot MoS_2@3DOM TiO_2 composites were evaluated via the degradation of MB as shown in Fig. 5. Obviously, 3DOM TiO_2 can degrade MB only 40% for 4 h, but nanodot MoS_2 on TiO_2 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_2 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_2 [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

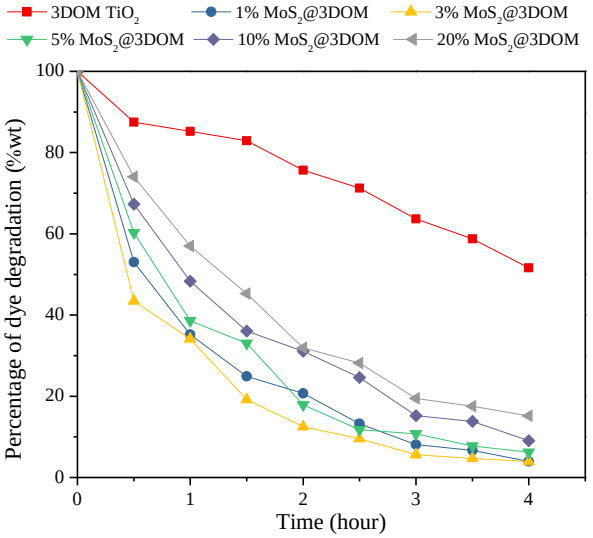


Fig. 5. The percentage of degradation of MB (%wt) as a function of time (hour).

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_2 and 1%, 3%, 5%, 10% and 20% MoS_2@3DOM, respectively. The linear correlation between ln(C/C_0) and irradiation time of all reaction is found with correlation coefficient (R^2) more than 0.94. It clearly demonstrates that the addition of MoS_2 on 3DOM TiO_2 provides the enhanced photocatalytic activity compared to unmodified 3DOM TiO_2 catalyst. Especially, 3% MoS_2@3DOM exhibits the highest degradation with a rate constant of 0.9073 h^{-1} which is 6 times higher than that of 3DOM TiO_2. However, when MoS_2 loading contents increase to 20%, the rate constant of the composite slightly decreases to 0.5076 h^{-1}. It is because the increase in MoS_2 contents can gradually reduce the light absorption ability of the composite due to the high reflection index of MoS_2 [11]. Moreover, high MoS_2 loading also causes particle aggregates as well as the phase transformation of MoS_2 to MoO_x. The aggregation of nanodot MoS_2 can reduce edge sites or active sites of MoS_2 and suppress quantum confinement effect of nanodot MoS_2. Furthermore, the photocatalytic activity of MoS_2 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

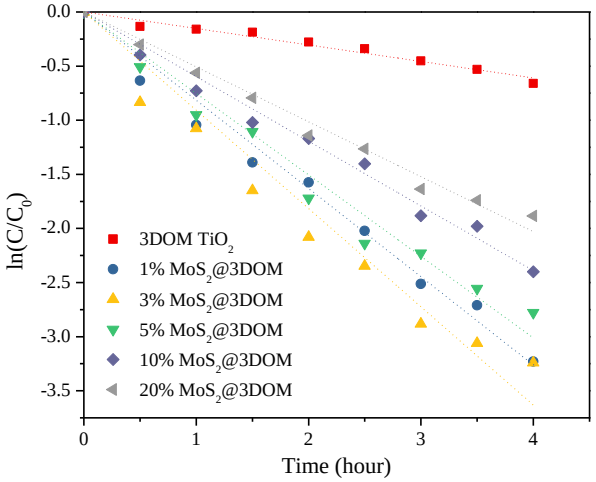
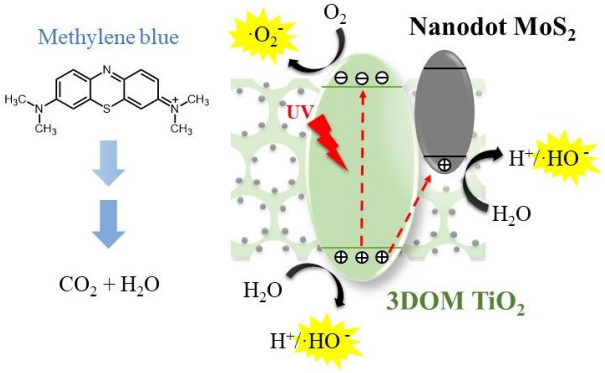


Fig. 6. The pseudo-first ordered kinetic plots of ln(C/C_0) as a function of time (hour) for degradation of MB.

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

Sample	Rate constant (h^{-1})	R^2	Maximum degradation (%)
3DOM TiO_2	0.1524	0.9717	51.64
1%MoS_2@3DOM	0.8164	0.9816	3.95
3%MoS_2@3DOM	0.9073	0.9460	3.91
5%MoS_2@3DOM	0.7529	0.9687	6.21
10%MoS_2@3DOM	0.5977	0.9854	9.06
20%MoS_2@3DOM	0.5076	0.9839	15.18

shown in Scheme 2. Under the irradiation of UV light, TiO_2 absorbs photons and generates excited electrons and holes. In general, CB of MoS_2 is lower than that of TiO_2, but when MoS_2 domain is reduced less than 10 nm, the band gap of MoS_2 is wider due to the quantum confinement effect. As a result, the CB of MoS_2 locates at a higher energy than that of TiO_2 and the VB of MoS_2 still remains in the middle of the TiO_2 band gap [14,15]. The hole of excited TiO_2 can migrate to VB of MoS_2 and, hence, the recombination of electron-hole pairs in TiO_2 can be suppressed. However, amount of MoS_2 loading should be concerned to avoid the light reflection, particle aggregation and phase transformation of MoS_2. Although, some limitations in nanodot MoS_2@3DOM TiO_2 catalysts need to be considered, the outstanding photocatalytic abilities of MoS_2@TiO_2 composites over 6 times compared to unmodified TiO_2 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_2 was completely synthesized with different %loading; 1%, 3%, 5%, 10% and 20%, respectively. Nanodot MoS_2@3DOM TiO_2 composites exhibit the higher performance in degradation of MB than unmodified 3DOM TiO_2. It strongly emphasizes that nanodot MoS_2 provides the appropriate overlapping band gap with TiO_2, resulting in the suppression of the electron-hole recombination on TiO_2 surface. Furthermore, the 3DOM structure of TiO_2 can also improve the scattering of incident light. Thus, nanodot MoS_2@3DOM TiO_2 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.

6. REFERENCES

[1] Y. Jiang, et al., Designing MoS_2 nanocatalysts with increased exposure of active edge sites for anthracene hydrogenation reaction, Catal. Sci. Technol. 7 (2017) 2998-3007.

[2] S. Pal, et al., Temperature assisted shear exfoliation of layered crystals for the large-scale synthesis of catalytically active luminescent quantum dots, Mater. Chem. Front. 1 (2017) 319-325.

[3] A. U. Liyanage, M. M. Lerner, Use of amine electride chemistry to prepare molybdenum disulfide intercalation compounds, RSC Adv. 4 (2014) 47121-47128.

[4] A. A. Jeffery, C. Nethravathi, M. Rajamathi, Scalable large nanosheets of transition metal disulphides through exfoliation of amine intercalated MS_2 [M = Mo, W] in organic solvents, RSC Adv. 5 (2015) 51176-51182.

[5] D. Wang, et al., Enhanced photocatalytic activity of TiO_2 under sunlight by MoS_2 nanodots modification, Appl. Surf. Sci. 377 (2016) 221-227.

[6] X. Zhang, et al., Hydrothermal synthesis and characterization of 3D flower-like MoS_2 microspheres, Mater. Lett. 148 (2015) 67-70.

[7] J. Theerthagiri, et al., Recent advances in MoS_2 nanostructured materials for energy and environmental applications – A Review, J. Solid State Chem. 252 (2017) 43-71.

[8] W. Qiao, et al., Luminescent monolayer MoS_2 quantum dots produced by multi-exfoliation based on lithium intercalation, Appl. Surf. Sci. 359 (2015) 130-136.

[9] W. Gu, et al., One-step synthesis of water-soluble MoS_2 quantum dots via a hydrothermal method as a fluorescent probe for hyaluronidase detection, ACS Appl. Mater. Interfaces 8 (2016) 11272-11279.

[10] M. Wu, et al., High photocatalytic activity enhancement of titania inverse opal films by slow photon effect induced strong light absorption, J. Mater. Chem. A 1 (2013) 15491-15500.

[11] D. Wang, et al., Enhanced photocatalytic activity of TiO_2 under sunlight by MoS_2 nanodots modification, Appl. Surf. Sci. 377 (2016) 221-227.

[12] G. Zhou, et al., Vertically aligned MoS_2/MoO_x heterojunction nanosheets for enhanced visible-light photocatalytic activity and photostability, CrystEngComm 16 (2014) 9025-9032.

[13] M. J. Hwang, et al., Preparation of MoO_3/MoS_2/TiO_2 composites for catalytic degradation of methylene blue, J. Nanosci. Nanotechnol. 12 (2012) 5884-5891.

[14] H. Liu, et al., Efficient synthesis of MoS_2 nanoparticles modified TiO_2 nanobelts with enhanced visible-light-driven photocatalytic activity, J. Mol. Catal. A: Chem. 396 (2015) 136-142.

[15] J. Low, et al., Two-dimensional layered composite photocatalysts, Chem. Commun. 50 (2014) 10768-10777.