Article ID: 1000-324X(2019)11-1205-05 **DOI:** 10.15541/jim20190010

MoS_2 Quantum Dots Decorated NH_2-MIL-125 Heterojunction: Preparation and Visible Light Photocatalytic Performance

HAN Li, ZHANG Xiao-Min, WU De-Yong

(Hubei Key Laboratory of Biological Resources Protection and Utilization, School of Chemical and Environmental Engineering, Hubei Minzu University, Enshi 445000, China)

Abstract: MoS_2 quantum dots (QDs) decorated NH_2-MIL-125 (MoS_2 QDs/NH_2-MIL-125) heterostructures were successfully fabricated by a facile method. XRD results exhibit that NH_2-MIL-125 and MoS_2 form crystals in the synthesis process of MoS_2 QDs/NH_2-MIL-125 heterojunctions. TEM results demonstrated clearly that the MoS_2 Quantum dots with size of about 4 nm successfully disperse on the surface of NH_2-MIL-125 plate. Compared with bulk MoS_2 and NH_2-MIL-125, the MoS_2 QDs/NH_2-MIL-125 heterostructures exhibit enhanced photocatalytic performance in degradation of methyl orange under visible light irradiation, about 5.8 and 7.4 times higher that of pure bulk MoS_2 and NH_2-MIL-125, respectively. Meanwhile, MoS_2 QDs/NH_2-MIL-125 composites exhibit good stability and reusability during cycle experiment. The excellent photocatalytic activity of MoS_2 QDs/NH_2-MIL-125 heterostructures is attributed to the formation of heterojunctions between MoS_2 QDs and NH_2-MIL-125, Tacilitating separation of the photogenerated charge carries. PL results prove that MoS_2 QDs/NH_2-MIL-125 composites own lower recombination of photogenerated electrons and holes, resulting in superior photocatalytic ability.

Key words: MoS_2 quantum dots(QDs); metal-organic frameworks; heterojunction; photocatalysis

Due to the permanent porosity, high surface area, and diverse structures, metal-organic frameworks (MOFs) have gathered increasing attention in the field of sensing[1], absorption[2] and catalysis[3-5]. NH_2-MIL-125(Ti) with visible light absorption ability has been applied in the degradation of organic pollutants[6]. Moreover, constructing heterojunction between semiconductor and NH_2-MIL-125 is an effective strategy to further improve the photocatalytic activity of NH_2-MIL-125. Because the heterojunction can improve the separation of photogenerated charge carries, resulting in the superior photocatalytic activity[7-8]. For example, as compared with pure Ag_3PO_4, NH_2-MIL-125 and P25, Ag_3PO_4@NH_2-MIL-125 photocatalyst exhibited enhanced visible-light-induced activity toward MB and RhB[9]. Bi_2S_3@NH_2-MIL-125(Ti) composites showed higher activity toward Cr(VI) reduction and RhB degradation than pure NH_2-MIL-125(Ti) and Bi_2S_3[10]. BiOBr/NH_2-MIL-125 composites also exhibited enhanced photocatalytic performance for RhB degradation under visible light irradiation[11].

Herein, we prepared a new hybrid photocatalyst by coupling MoS_2 QDs and NH_2-MIL-125(Ti). Due to the unique advantages of small sizes and short charge-transfer lengths, semiconductive QDs have attracted more and more interest[7,12]. However, pure QDs are easy to self-aggregate and have rapid recombination of the photogenerated charge carriers[13]. To solve these problems, loading QDs onto other materials has been proved as an effective strategy[14]. MoS_2 QDs can trap the photo-induced electrons and efficiently improve the photogenerated charge carriers separation efficiency, consequentially increase the photocatalytic performance[13,15]. For example, MoS_2 QDs can improve the photocatalytic detoxification and disinfection of Bi_2WO_6 in the wastewater[15], and also enhance the photocatalytic activity of g-C_3N_4 toward the degradation of MO and phenol under visible light irradiation[13]. In this report, MoS_2 QDs decorated NH_2-MIL-125 heterostructures were synthesized by a two-step method, and the synthesized MoS_2 QDs/NH_2-MIL-125 composites exhibited significantly enhanced photocatalytic performance for the degradation of MO under visible light irradiation.

Received date: 2019-01-04; **Modified date:** 2019-04-12
Foundation item: National Natural Science Foundation of China (21767009); China Scholarship Council (201808420149); Hubei Key Laboratory of Biological Resources Protection and Utilization (PKLHB1908); Lindergraduate Innoration Progran (201910517006)
First author: HAN Li (1996–), female, undergraduate. E-mail: 2213651218@qq.com
Corresponding author: WU De-Yong, associate professor. E-mail: wdy001815@126.com

1 Experimental

1.1 Preparation of MoS_2 QDs/NH_2-MIL-125

Metal-organic frameworks NH_2-MIL-125 were prepared according to the reference [16], and the MoS_2 QDs solution was synthesized through one-step solvothermal route reported in reference [17]. MoS_2 QDs/NH_2-MIL-125 composites were constructed as follows: NH_2-MIL-125 powders (0.50 g) were ultrasonically dispersed in ethanol (40 mL), and as-prepared MoS_2 QDs solution (0.514 mL) was added dropwise under ultrasonication into the NH_2-MIL-125 suspension. The mixed suspension was magnetically stirred at room temperature until the solvent was naturally evaporated, and finally dried at 80 ℃ for 12 h to get MoS_2 QDs/NH_2-MIL-125 composites.

1.2 Characterization

The morphology of the catalyst was observed by scanning electron microscope (SEM, JEOL JSM-7001F, Japan) and transmission electron microscope (TEM, JEOL-100CX, Japan). The crystallinity of powder was characterized by powder X-ray diffraction (XRD, D/max-2200/PC, Rigaku Corporation, Japan) with Cu K α radiation. A diffuse reflectance UV-Vis spectrophotometer (DRS, TU-1901) was used to obtain the absorption spectra of samples. The photoluminescence (PL) spectra of the samples were obtained by using a Varian Cary Eclipse spectrometer with an excitation wavelength of 325 nm. The visible light photocatalytic activity of catalyst was evaluated according to the reference [18].

2 Results and discussion

Fig. 1 shows the TEM images of MoS_2 QDs/NH_2-MIL-125 composites. The size of NH_2-MIL-125 is about 1.5–3 μm (Fig. 1(a)), and MoS_2 QDs are dispersed uniformly on the surface of NH_2-MIL-125 plate (Fig. 1(b)). Observed from the high-magnification TEM images (Fig. 1(c-d)), the size of MoS_2 QDs is about 4 nm, an interplanar spacing of 0.23 nm is corresponded to the (103) planes of the MoS_2 QDs[13]. And the elemental mapping analysis (Fig. 1(e-f)) suggest the presence and uniform distribution of Mo and S in the MoS_2 QDs/NH_2-MIL-125 composites.

XRD patterns of the bulk MoS_2, NH_2-MIL-125 and MoS_2 QDs/NH_2-MIL-125 are shown in Fig. 2. The peaks at 2θ=14.43°, 32.75°, 39.58°, 44.18° and 49.86° are attributed to the (002), (100), (103), (006) and (105) planes of bulk MoS_2, which match the standard pattern of MoS_2 (JCPDF 37-1492)[13,17]. The XRD pattern of NH_2-MIL-125(Ti) was in accordance with simulated XRD patterns[6,19], indicating the formation of NH_2-MIL-125(Ti)

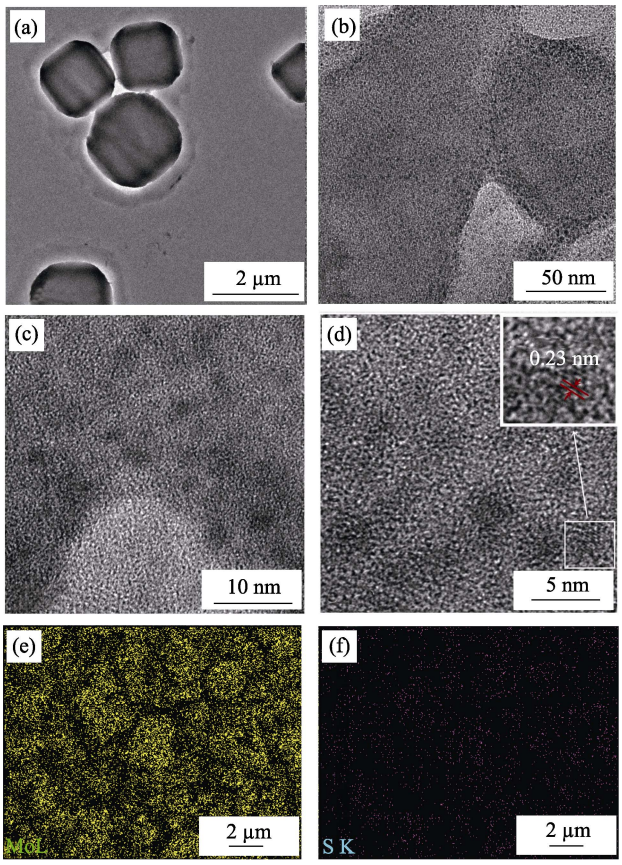

Fig. 1 TEM images (a, b), HRTEM images (c, d) and the partial element mappings (e, f) of MoS_2 QDs/NH_2-MIL-125 composites

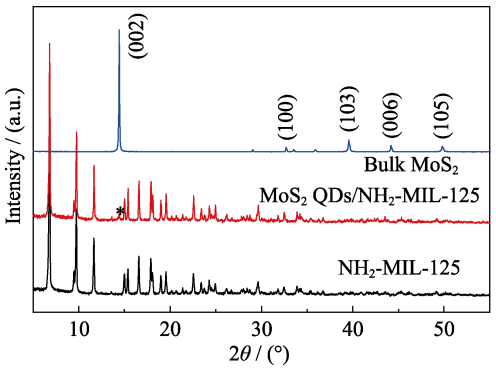

Fig. 2 XRD patterns of bulk MoS_2, NH_2-MIL-125 and MoS_2 QDs/NH_2-MIL-125 composites

crystal. From the XRD pattern of MoS_2 QDs/NH_2-MIL-125, the peak at 2θ= 14.43° of MoS_2 can be observed, but other peaks of MoS_2 don't emerge.

The photocatalytic activities of the bulk MoS_2, NH_2-MIL-125 and MoS_2 QDs/NH_2-MIL-125 were investigated through photodegradation of MO under visible light irradiation (λ>420 nm). As shown in Fig. 3(a), bulk MoS_2 and NH_2-MIL-125 removed about 21% and 16% of MO, respectively. Satisfactorily, QDs/NH_2-MIL-125 composites exhibited enhanced photocatalytic performance, and degraded 81% MO over 120 min. Generally,

the photocatalytic degradation of pollutants follows pseudo-first-order reaction[10]. The degradation rate constant (k) can be calculated by the equation: $\ln(C/C_0) = -kt$, where C_0 and C are the initial concentration of MO and the concentration of MO at a reaction time of t, respectively. Fig. 3(b) shows the kinetic fitting curves for the MO degradation with different samples. The photocatalytic degradation rates are 0.00198, 0.00157 and 0.01157 min^{-1} for bulk MoS_2, NH_2-MIL-125 and MoS_2 QDs/NH_2-MIL-125, respectively. The rate of MoS_2 QDs/NH_2-MIL-125 is 5.8 and 7.4 times of pure bulk MoS_2 and NH_2-MIL-125, respectively.

The enhanced photocatalytic activity of MoS_2 QDs/NH_2-MIL-125 should be attributed to the formation of heterojunctions between MoS_2 QDs and NH_2-MIL-125, not to the light absorption of MoS_2 QDs. In Fig. 4(a), it was clearly observed that MoS_2 QDs have little effect on the light absorption ability of NH_2-MIL-125. However, the heterojunctions between MoS_2 QDs and NH_2-MIL-125 are of great benefit to the photo-generated charge carries separation[20]. The PL spectra always be utilized to analyze the photogenerated electron-hole recombination efficiency. Fig. 4(b) shows the PL spectra of pure NH_2-MIL-125 and the MoS_2 QDs/NH_2-MIL-125 composites. NH_2-MIL-125 has stronger PL peak, and MoS_2 QDs/NH_2-MIL-125 shows lower PL peak. This results indicate that MoS_2 QDs/NH_2-MIL-125 composites own lower recombination of the photo-generated electrons and holes[21-22]. As a result, MoS_2 QDs/NH_2-MIL-125 composite exhibits a better visible-light-induced photocatalytic activity. Meanwhile, the stability of MoS_2 QDs/NH_2-MIL-125 composites was investigated by repeating the photocatalytic degradation of MO for five cycles under the same conditions. As shown in Fig. 5, there is no obvious inactivation in the photocatalytic activity after five recycles, indicating the composites have good stability and reusability.

3 Conclusions

In summary, MoS_2 QDs/NH_2-MIL-125 composites were successfully prepared by a facile method. MoS_2 QDs with size of about 4 nm dispersed uniformly on the surface of NH_2-MIL-125 plate. Compared with pure bulk MoS_2 and NH_2-MIL-125, MoS_2 QDs/NH_2-MIL-125 photocatalysts display greatly improved photocatalytic activity over methyl orange under visible light irradiation. The photocatalytic degradation rate of MoS_2 QDs/NH_2-MIL-125 is 5.8 and 7.4 times of pure bulk MoS_2 and NH_2-MIL-125, respectively. This excellent property should be attributed to the formation of heterojunction between MoS_2 QDs and NH_2-MIL-125, which can lower the recombination of the photo-generated electrons and holes. This work could provide a novel strategy for designing semiconductor/MOF heterostructured photocatalysts.

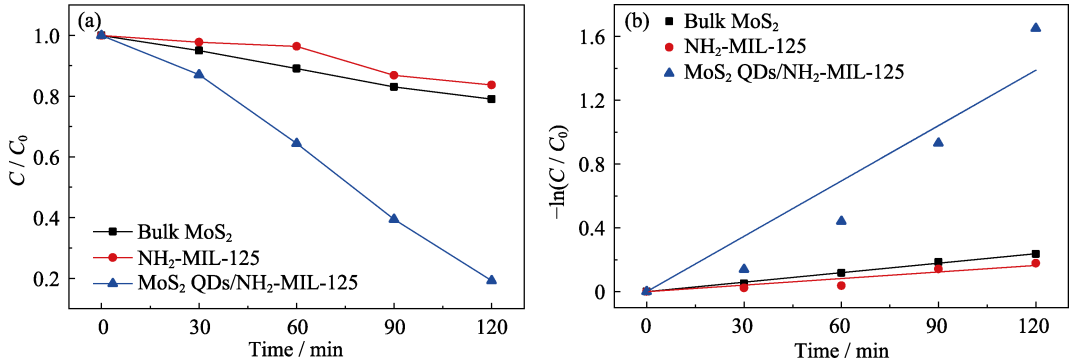

Fig. 3　(a) Photocatalytic activity and (b) plot of $-\ln(C/C_0)$ of bulk MoS_2, NH_2-MIL-125 and MoS_2 QDs/NH_2-MIL-125 composites over MO as a function of irradiation time

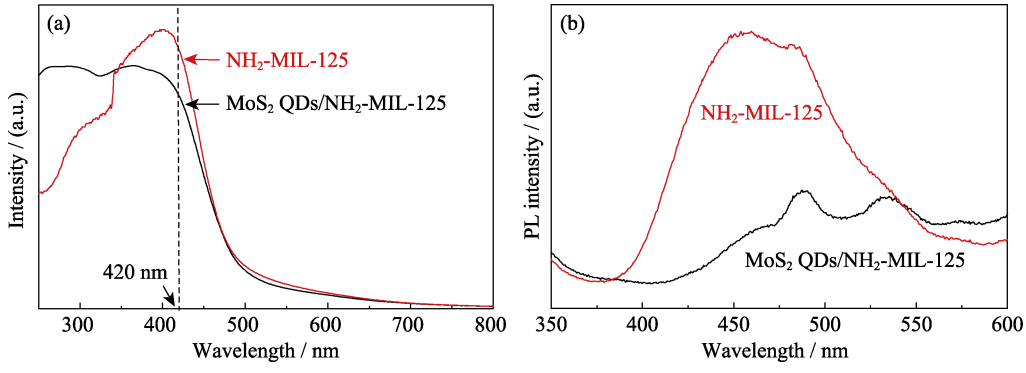

Fig. 4　UV-Vis diffuse reflectance spectra (a) and PL spectra (b) of NH_2-MIL-125 and MoS_2 QDs/NH_2-MIL-125 composites

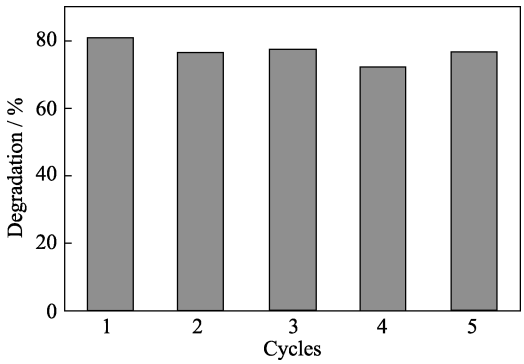

Fig. 5 Stability test of MoS_2 QDs/NH_2-MIL-125 composites for MO degradation under visible light irradiation

References:

[1] GOGOI C, YOUSUFUDDIN M, BISWAS S. A new 3D luminescent Zn(II)-organic framework containing a quinoline-2,6-dicarboxylate linker for the highly selective sensing of Fe(III) ions. *Dalton Trans*., 2019, **48(5):** 1766–1773.

[2] LIU D X, GU J J, LIU Q L, *et al.* Metal-organic frameworks reactivate deceased diatoms to be efficient CO_2 absorbents. *Adv. Mater.*, 2014, **26(8):** 1229–1234.

[3] JIANG D, XU P, WANG H, *et al.* Strategies to improve metal organic frameworks photocatalyst's performance for degradation of organic pollutants. *Coord. Chem. Rev.*, 2018, **376:** 449–466.

[4] YANG Y F, WANG W J, LI H, *et al.* NH_2-MIL-53(Al) nanocrystals anchored on the surface of RGO hollow spheres and its visible light degradation of methylene blue. *Mater. Lett.*, 2017, **197:** 17–20.

[5] KHANDAN F M, AFZALI D, SARGAZI G, *et al.* Novel uranyl-curcumin-MOF photocatalysts with highly performance photocatalytic activity toward the degradation of phenol red from aqueous solution: effective synthesis route, design and a controllable systematic study. *J. Mater. Sci: Mater. El.*, 2018, **29(21):** 18600–18613.

[6] HU S, LIU M, LI K Y, *et al.* Surfactant-assisted synthesis of hierarchical NH_2-MIL-125 for the removal of organic dyes. *RSC Adv.*, 2017, **7(1):** 581–587.

[7] ZHANG Z J, XU J Y, ZENG H B, *et al.* Carbon quantum dots/$BiPO_4$ nanocomposites with enhanced visible-light absorption and charge separation. *J. Inorg. Mater.*, 2018, **33(5):** 582–586.

[8] CORRIEA F C, CALHEIROS M, MARQUES J, *et al.* Synthesis of Bi_2O_3/TiO_2 nanostructured films for photocatalytic applications. *Ceram. Int.*, 2018, **44(18):** 22638–22644.

[9] ABDLHAMEED R M, TOBALDI D M, KARMAOUI M. 2018. Engineering highly effective and stable nanocomposite photocatalyst based on NH_2-MIL-125 encirclement with Ag_3PO_4 nanoparticles. *J. Photoch. Photobio.* a-*Chem.*, 2018, **351:** 50–58.

[10] WANG M, YANG L, YUAN J, *et al.* Heterostructured Bi_2S_3@NH_2-MIL-125(Ti) nanocomposite as a bifunctional photocatalyst for Cr(VI) reduction and rhodamine B degradation under visible light. *RSC Adv.*, 2018, **8(22):** 12459–12470.

[11] ZHU S R, LIU P F, W M K, *et al.* Enhanced photocatalytic performance of BiOBr/NH_2-MIL-125(Ti) composite for dye degradation under visible light. *Dalton Trans*., 2016, **45(43):**17521–17529.

[12] CHEN W, GU J, LIU Q, *et al.* Quantum dots of 1T phase transitional metal dichalcogenides generated *via* electrochemical Li intercalation. *ACS Nano*, 2018, **12(1):** 308–316.

[13] SHI L, HE Z, LIU S Q. MoS_2 quantum dots embedded in g-C_3N_4 frameworks: a hybrid 0D-2D heterojunction as an efficient visible-light driven photocatalyst. *Appl. Surf. Sci.*, 2018, **457:** 30–40.

[14] ZHAO F F, RONG Y F, WAN J M, *et al.* MoS_2 quantum dots@TiO_2 nanotube composites with enhanced photoexcited charge separation and high-efficiency visible-light driven photocatalysis. *Nanotechnology*, 2018, **29(10):** 105403.

[15] MENG X C, LI Z Z, ZENG H M, *et al.* MoS_2 quantum dots-interspersed Bi_2WO_6 heterostructures for visible light-induced detoxification and disinfection. *Appl. Catal. B-Environ*., 2017, **210:** 160–172.

[16] ZHANG B X, ZHANG J L, TAN X N, *et al.* MIL-125-NH_2@TiO_2 core-shell particles produced by a post-solvothermal route for high-performance photocatalytic H_2 production. *ACS Appl. Mat. Interfaces*, 2018, **10(19):** 16418–16423.

[17] GU W, YAN Y, CAO X, *et al.* A facile and one-step ethanol- thermal synthesis of MoS_2 quantum dots for two-photon fluorescence imaging. *J. Mater. Chem. B*, 2016, **4(1):** 27–31.

[18] WU D, WU C, TAN H. Facile synthesis of novel I-doped $Bi_4O_5Br_2$ nanosheets with enhanced visible light photocatalytic activity. *J. Mater. Sci: Mater. El.*, 2018, **29(13):** 11090–11095.

[19] WU Z Y, HUANG X B, ZHENG H Y, *et al.* Aromatic heterocycle-grafted NH_2-MIL-125(Ti) *via* conjugated linker with enhanced photocatalytic activity for selective oxidation of alcohols under visible light. *Appl. Catal. B-Environ.*, 2018, **224:** 479–487.

[20] CARVALHO K T G, NOGUEIRA A E, LOPES O F, *et al.* Synthesis of g-C_3N_4/Nb_2O_5 heterostructures and their application in the removal of organic pollutants under visible and ultraviolet irradiation. *Ceram. Int.*, 2017, **43(4):** 3521–3530.

[21] YE F, LI H F, YU H T, *et al.* Hydrothermal fabrication of few-layer MoS_2 nanosheets within nanopores on TiO_2 derived from MIL-125(Ti) for efficient photocatalytic H_2 evolution. *Appl. Surf. Sci*., 2017, **426:** 177–184.

[22] WANG F Z, LI W J, GU S N, *et al.* Facile fabrication of direct Z-scheme MoS_2/Bi_2WO_6 heterojunction photocatalyst with superior photocatalytic performance under visible light irradiation. *J. Photoch. Photobio. A-Chem.*, 2017, **335:** 140–148.

具有可见光催化活性的 MoS_2 量子点/NH_2-MIL-125 复合材料的制备及性能表征

韩　丽，张晓敏，吴德勇

(湖北民族大学 化学与环境工程学院，湖北省生物资源保护与利用重点实验室，恩施 445000)

摘　要: 采用水热法合成金属–有机骨架材料 NH_2-MIL-125，并修饰硫化钼量子点，从而构筑具有增强电荷分离的二硫化钼量子点/NH_2-MIL-125 复合光催化材料(MoS_2 QDs/NH_2-MIL-125)。利用 XRD、HRTEM、DRS、PL 对材料性能进行分析，通过降解甲基橙 MO 染料测试 MoS_2 QDs/NH_2-MIL-125 复合材料的光催化性能。结果表明：尺寸约 4 nm 的 MoS_2 QDs 均匀分散在 NH_2-MIL-125 上，在可见光照射下，MoS_2 QDs/NH_2-MIL-125 复合材料的光催化性能极大优于单一的 Bulk MoS_2 和 NH_2-MIL-125，降解常数分别是它们的 5.8 和 7.4 倍。循环光催化实验结果表明，MoS_2 QDs/NH_2-MIL-125 复合材料的光催化能力具有良好的稳定性。DRS 和 PL 的测试结果表明，MoS_2 QDs/NH_2-MIL-125 复合材料优异的可见光催化性能主要归因于异质结构的形成，抑制了光生电子–空穴的复合，进而提高了光催化性能。

关　键　词: 二硫化钼量子点；金属–有机骨架材料；异质结构；光催化

中图分类号: TB34　　**文献标识码:** A