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Controllable synthesis of flower-like MoSe₂ 3D microspheres for highly efficient visible light photocatalyst degrading nitro-aromatic explosives

Jingwen Huang^a, Bo Jin^a*, Huiqiang Liu^b, Xiaojuan Li^a, Qingchun Zhang^a, Shijin Chu^a, Rufang Peng^a* and Sheng Chu^b*

a State Key Laboratory of Environmental Friendly Energy Materials & School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, Sichuan, P. R. China.

b State Key Laboratory of Optoelectronic Materials and Technology, Sun Yat-Sen University, Guangzhou 510275, Guangdong, P. R. China.

* Corresponding author. Tel: +86-0816-2419011

E-mail: jinbo0428@163.com; rfpeng2006@163.com and chusheng@mail.sysu.edu.cn

Abstract

Nitro-aromatic explosives are difficult to degrade, existing on the surface of the Earth, and greatly harm the ecological environment and human security. Herein, we successfully large-scale synthesized novel flower-like MoSe₂ 3D microspheres and nanospheres by using a simple hydrothermal method. The two MoSe₂ 3D spheres had a high crystal quality with abundant nanosheets and their diameters are approximately 1.5 μ m and 300-400 nm respectively. The Brunauer-Emmett-Teller (BET) and UV-vis diffuse reflectance spectra (UV-Vis DRS) tests revealed that the specific surface area and band gap of the MoSe₂ microspheres and nanospheres were 33.3 m²/g and 1.68 eV, and the nanostructure's were 13.6 m²/g and 1.52 eV. Moreover, the two different morphologies of MoSe₂ were used for degrading the nitrobenzene (NB), *p*-nitrophenol (PNP) and 2, 4-dinitrophenol (2, 4-DNP) through a photocatalytic process. The results demonstrated that the three nitro-aromatic explosives solution of NB, PNP and 2, 4-DNP (40 mg/L) could be completely degraded by MoSe₂ 3D microspheres under visible light irradiation for 3.5 h, 1.5 h and 2.5 h, and the degrading time for MoSe₂ nanospheres were 4.5 h, 2.5 h and 4 h, respectively. The

mechanism of the photocatalytic reaction was also investigated in detail, and the photocatalytic degradation process was found to follow the pseudo-first-order kinetics. Our study demonstrated the potential application of MoSe₂ microspheres as a photocatalyst for nitro-aromatic explosives and other organic contaminants.

Keywords: flower-like MoSe₂, 3D microspheres, hydrothermal method, Photocatalytic degradation, Nitro-aromatic explosives

1 Introduction

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Nitro-aromatic explosives are common pollutant compositions that are ground on the surface of the Earth. They are synthesized from intermediate products, such as chemical industry, dyestuff, and medicament products. Nitrophenols are regarded as undegradable organics because the nitro as a group for absorption electrons can greatly drop electron cloud density on the benzene ring and hinder the attack of oxydic electrons ¹⁻³. Thus, nitrophenols should be urgently degraded to protect the ecological environment and human security. In recent years, the continuous innovations for degradation of nitro-aromatic explosives have attracted increasing attention and investigation. TiO2, as a widely used catalyst, has been researched for the degradation of nitrophenols^{4, 5}. Owing to the intrinsic wide band gap, the photocatalytic activity can only be generated under UV light irradiation. The absorption of light quantum is limited, and the catalytic efficiency is poor ⁶. To overcome these issues, numerous composite materials have been designed, such as the Ag/ZnO⁷, Ag/C₃N₄⁸, and Fe₃O₄/TiO₂/Au⁹. The improvement in photocatalytic performance has complicated and introduced new contaminants to the preparation process of composite materials. Thus, finding a material with a novel-innovative, highly effective, low-cost and large-scale synthesis for the degradation of nitrophenols is urgent.

Transition metal dichalcogenides (TMDs) have attracted significant attention due to their similar structures with two-dimensional (2D) layered graphene and exhibited unique transformation from an indirect to a direct band gap semiconductor with a

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structure changed to nanoscale from bulk materials ¹⁰⁻¹². TMDs are characterized by a MX_2 formula, where M stands for a transition metal (M = Mo, W, and so on) and X stands for a chalcogen (X = S, Se, or Te) $^{13, 14}$. MoS₂ is the excellent representative one of the TMD group that has attracted extensive research attention as a device for optoelectronics application and for its potential value in energy sources ^{15, 16}. Apart from the layered structure of MoS₂, MoSe₂ also shows special properties in field-effect transistors ¹⁷, fast photodetection ¹⁸, electrocatalytic hydrogen evolution reaction ¹⁹, energy storage devices ²⁰, and the Terahertz photodetector ²¹. A series of synthesized methods has been carried out to prepare MoSe₂ nanosheets, such as the chemical vapor deposition (CVD)²², mechanical exfoliation²³, and hydrothermal methods ²⁴. The CVD method can grow the monolayer and few-layer MoSe₂ nanosheets, and mechanical exfoliation can easily acquire different thicknesses for the MoSe₂ nanosheets. However, both mainly obtain a 2D layered MoSe₂ material, which can result in a high tendency of restack and active sites ^{25, 26}. Interestingly, the hydrothermal method is a highly efficient and simple synthesis method that can form a 3D MoSe₂ structure of porous microspheres and nanospheres through process-oriented aggregation, self-assembly, and Ostwald ripening ^{27, 28}. Formed with 2D layered flakes, the 3D flower-like structure provides superior performance for photocatalysis and electrocatalysis owing to the plentiful active sites explored at the edge of MoSe₂ nanosheets ²⁹⁻³¹.

In this study, flower-like $MoSe_2$ 3D microspheres and nanospheres were synthesized successfully through a facile hydrothermal method. The BET test showed the $MoSe_2$ microspheres and nanospheres with a specific surface area of around 33.3 m^2/g and 13.6 m^2/g , respectively. The UV-vis DRS revealed a corresponding direct band gap of about 1.68 eV(microspheres) and 1.52 eV(nanoshperes). Considering that the high specific surface area can support abundant active sites and the narrow band gap is beneficial for absorbing the wavelength of visible light ^{32, 33}, we investigated the photocatalytic performance of the two different morphologies of $MoSe_2$ nanostructure with the degradation of NB, PNP and 2,4-DNP. The research results showed that all the three nitro-aromatic explosives could be degraded completely by MoSe₂ 3D microspheres under visible light irradiation. The photocatalytic degradation process followed the pseudo-first-order kinetics. Finally, the mechanism of the photocatalytic reaction was explored.

2 Experimental Section

2.1 Preparation of flower-like MoSe₂ 3D microspheres

Se powders (99.99%), sodium molybdate dehydrate (Na₂MoO₄·2H₂O, 99%), sodium borohydride (NaBH₄, 98%), potassium iodide (KI, 99.99%), and 4-benzoquinone (BQ, 99%) were purchased from Aladdin Chemistry Co., Ltd. Acetone, ethyl alcohol, and isopropyl alcohol (IPA) were analytical grade and obtained from Chengdu Kelong Chemical Reagents Co., Ltd. All the reagents were used as received without further purification.

In a typical reaction, 5 mmol Na₂MoO₄·2H₂O and 15 mmol Se powders were dissolved in 60 mL ethyl alcohol and distilled water mixture solvent (volume ratio of 1:1) under ultrasonic stirring (5 min) . Then, 5 mmol NaBH₄ was added into the mixture solution. After continuous stirring, the dark gray hybrid solution turned into reddish brown. The obtained resulted solution was transferred into a 100 mL Teflon lined stainless steel autoclave. The autoclave was heated at 200 °C and maintained for 48 h. After cooling to room temperature, the black sediment was acquired and washed with acetone, ethanol and distilled water for 3 times, respectively. Then, the final sediment was dried at 80 °C for 12 h in a vacuum drying and the collecting MoSe₂ powder was denoted as sample 1[#]. When the mixture solvent of ethylene glycol and distilled water (volume ratio of 1:1) was used instead of ethyl alcohol as a solvent, the final collected MoSe₂ powder was denoted as sample 2[#].

2.2 Characterization

Morphological and microstructural properties of the flower-like MoSe₂ 3D microspheres were characterized by Field emission scanning electron microscopy (FESEM, UItra 55, CARI ZEISS in Germany) equipped with energy dispersive X-ray

spectroscopy and X-Ray Diffraction (XRD, Philips X' Pert PRO, Netherlands) equipped with Cu Ka radiation (k=0.15418 nm). Composition analysis was characterized with XPS (Thermo VG 250, USA). Cross-sectional samples were prepared by TEM (Libra 200 PE, operated at 200 kV, Germany) to directly observe morphology. Ultraviolet photoemission spectroscopy the vertical (UPS) measurements were performed by the XPS (ESCALAB 250Xi, UK) equipped the He light source with the photon energy (21.22 eV). The room temperature Raman spectrum (model; InVia, UK) was recorded on a Raman microscope using a 514.5 nm He-Cd laser as the excitation source. The UV-vis diffused reflectance spectrum was detected by the UV-vis DRS (U-4100, Hitachi, Japan). UV-vis spectrophotometer (Thermo Scientific Evolution 201, USA) with a double beam light source from 190 to 1100 nm was used. BET surface area was measured by N2 adsorption-desorption isotherm (NOVA 3000, Quantachrome, USA).

2.3 Photocatalytic reactions

Photocatalytic activity of the flower-like 3D MoSe₂ microspheres was studied using NB, PNP, 2, 4-DNP as model pollutants under visible light irradiation. The photocatalytic reactor (Beijing NBT Technology Co., Ltd, China) composed of quartz glass tube with a system of circulating water jack, a light source (A 500 W xenon lamp) and magnetic stirring equipment. The experiments were performed by adding the photocatalysts (20 mg) into the glass tube fitted with a certain concentration aqueous solutions of NB, PNP and 2, 4-DNP (40 mg/L), respectively. Then these reaction mixtures were placed into the photocatalytic reactor and stirred in the dark reaction at room temperature for 15-30 min to ensure to reach the absorption/desorption equilibrium before starting irradiation. Thereafter, the Xenon lamp was switched on for photodegradation, and after each 15 min, 5 mL of reaction mixture was centrifuged and analyzed by recording changes of the maximum absorption spectra using UV-vis spectrometer. The total organic carbon (TOC) removal was detected by the TOC analyzer (HTY-CT1000M, Zhejiang Tailin BioEngineering Co., Ltd, China). The ions of NH₄⁺ and NO₃⁻ which generated from

the photocatalytic action were examined by the Ion Chromatograph (IC-881, Metrohm, Switzerland) behind filtration.

For the stability tests, 20 mg MoSe₂ $1^{\#}$ microspheres were added into 50 mL PNP (40 mg/L) solution and photocatalytic activity tested as described above for 90 min. After each test, the photocatalysts were collected carefully, washed several times and dried at 80 °C for 24 h. The obtained MoSe₂ microspheres were used for recycling test and characterization.

3 Results and discussion

3.1 Characterization of MoSe₂ photocatalyst

The representative SEM images of MoSe₂ nanostructure are shown in **Fig.1 Fig.1a-c** showed the SEM images of sample $1^{\#}$, and the surface of MoSe₂ was found to be hierarchical with a flower-like shape and a spherical diameter of approximately 1.5 µm. The uniform microspheres were composed of plentiful nanosheets and possessed a thickness of nearly 15-20 nm. Therefore, abundant active points might exist on the edge of these nanosheets by the dangling bonds. The active points might play an important role in electrocatalysis and photocatalysis. With the changed of reaction solutions, the corrugations and the size of the flower-like MoSe₂ microspheres begin to reduce. **Fig. 1d-f** showed the SEM images of the MoSe₂ sample $2^{\#}$. It can be seen that the morphology of sample $2^{\#}$ was flower-like shape and tended to be a nanosphere structure. Where the diameter of the spheres was approximately 300-400 nm, and the numbers of corrugations composed by single MoSe₂ nanosheet were slightly reduced compared to sample $1^{\#}$. The results demonstrated that different solvents have a great influence on the morphology and size of the product.



Fig. 1 Morphology characterization of $MoSe_2$ nanostructure: FETSEM images with different magnifications (a-c) sample $1^{\#}$ (d-f) sample $2^{\#}$

The XRD pattern was used to evaluate the crystal structure and the crystallization quality of the materials. The XRD pattern of the two different morphologies of MoSe₂ samples were shown in **Fig. 2a** with the main peaks at 13.3° (002), 27.1° (004), 31.5° (100), 37.5° (103), 55.9° (110), 65.4° (200), and 69.5° (203). These peaks corresponded to the hexagonal phase (P63/mmc space group) of MoSe₂. All data could be indexed from the standard card (JCPDS No.29-0914) ³⁴. Meanwhile, the EDS confirmed the stoichiometry of the flower-like MoSe₂ microspheres(sample 1[#]) and nanospheres(sample 2[#]). As shown in **Fig. 2b**, there only appeared elements Se and Mo The Mo and Se peaks of the two samples showed that the atom ratio of Mo to Se were approximately 1: 2.04 and 1: 2.01, which was near the stoichiometry (1:2) of MoSe₂³⁵.

Raman spectroscopy was performed on the surface area of the MoSe₂ microspheres (**Fig. 2c**). Both of the two different morphologies of MoSe₂ showed a strong and identifiable peak at 237.9 cm⁻¹, which was related to the out-of-plane A_{1g} mode. The A_{1g} mode showed a red shift compared with the MoSe₂ bulk materials (243.7 cm⁻¹). The relative weakness peak located at 283.4 cm⁻¹ was related to the in-plane E_{2g}^{1} mode. Furthermore, the Raman peak at around 347.5 cm⁻¹ belonged to the B_{2g}^{1} mode,

which was related to the interlayer interaction $^{17, 35}$. The presence of the B_{2g}^{1} mode suggested that both the flower-like MoSe₂ microspheres and nanospheres had a multilayer structure with numerous thin layers.

The UV-vis DRS of the two MoSe₂ samples were taken over the spectral range from 400 to 800 nm as shown in **Fig. 2d.** The two MoSe₂ samples displayed strong absorptions at 656.5 nm and 676.5 nm, respectively. **Fig. S1** showed the curve of $(Ah\nu)^2$ versus h ν , as an direct band gap of semiconductor, $(Ah\nu)^2 = A(h\nu-E_g)$, where the absorption coefficient A is a constant. The band gap of the MoSe₂ could be calculated by incising the curve and obtaining the intercept with X-axis. The calculated E_g values of flower-like MoSe₂ microspheres (sample 1[#]) and flower-like MoSe₂ nanospheres (sample 2[#]) were approximately 1.68 eV and 1.52 eV respectively, corresponding to the direct band gaps. Compared with that of the bulk MoSe₂ materials, the blue shift of the bands was from 1.1 eV (an indirect band gap), which indicated the good response of the MoSe₂ materials for the range of visible light photocatalytic degradation activity ³⁶.

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UPS experiments were carried out to determine the valence band (E_V) information of MoSe₂ samples. As shown in **Fig. 2d-e**, the valence band (E_{VB}) for flower-like MoSe₂ microspheres sample 1[#] and nanospheres sample 2[#] were located at 0.94 and 1.03 eV, respectively, below E_F by linearly extrapolating the leading edge of the spectrum to the baseline ³⁷. In addition, the conduction band (E_{CB}) minimum can be calculated using E_{CB} = E_{VB} - Eg ³⁸. According to UV-vis DRS, the band gap of MoSe₂ microsphere and nanosphere were 1.68 and 1.52 eV, respectively. Thus, the E_{CB} minimum should be present at about -0.74 and -0.49 eV by calculation.



Fig. 2 Structure characterization of MoSe₂ microspheres(sample $1^{\#}$) and nanospheres (sample $2^{\#}$) : (a) XRD pattern (b) EDS spectra (c) Raman spectra with the A_{1g} , E_{2g}^{-1} and B_{2g}^{-1} modes. (d) UV–Vis DRS of the as-obtained MoSe₂, the inset image is the curve of $(Ahv)^2$ - hv. The valence band maximum of the UPS spectra (d) MoSe₂ microsphere and (e) nanosphere

The ratio specific surface and porosity analyzer can obtain by testing the nitrogen adsorption and stripping of the spherical structure materials. The BET test of MoSe₂ microspheres and nanospheres were performed by using nitrogen adsorption-

desorption. Fig. 3a shows the pore size distribution curves. From desorption branch of the nitrogen isotherm by BJH method, the sharp peak at 34.9 nm was the maximum pore volume as a center from 25 to 50 nm. The narrow peak indicated that the major pores distributed on this area and pore diameter was uniform. Table S1 shows the multi BET surface areas transform data with a range of relative pressure, where the corresponding surface area transform curve was showed in Fig. 3a as an inset image. The intercept and slope of the curve were approximately 3.74 and 150.98, respectively. According to the BET equation ³⁹, the surface area of the MoSe₂ flowers was calculated to be 33.3 m^2/g . The isotherm curves (Fig. 3b) exhibited obvious hysteresis loops, revealing the mesoporous (2-50 nm) structure of MoSe₂. The adsorbing capacity was significant increased at the middle and low pressure area, and the adsorbing capacity curve began to separate and appeared a distinct hysteresis loop, revealing the type IV of isotherm curve ^{40, 41}. As shown in **Fig. S2a**, the surface area of MoSe₂ nanoshperes (sample $2^{\#}$) was calculated to be 13.6 m²/g, which was smaller than the MoSe₂ microspheres (sample $1^{\#}$). The nanosheets of composing to MoSe₂ nanoshperes structure were smaller than the microspheres, which might be the reason for their small surface area. The large surface area might provide a large number of active sites, which was beneficial for generating large amounts of photo-generated electrons and holes 42.

The XPS spectra for the as-synthesized flower-like MoSe₂ 3D microspheres by the simple hydrothermal method are shown in **Fig. 3(c, d)**. Information on stoichiometry and binding could be obtained from the 3d spectra of the Mo and Se elements. The binding energies of Mo at 228.8 and 231.9 eV belonged to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ spin orbit peaks of MoSe₂, which highlighted the existence of Mo⁴⁺. Whereas, the Mo⁶⁺ of the Na₂MoO₄·2H₂O which belonged to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ spin orbits located at 232.5 eV and 235.9 eV. These peaks of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ shifted, indicating the reduction with valence of Mo from Mo⁶⁺ to Mo⁴⁺. Furthermore, the Se $3d_{5/2}$ and Se $3d_{3/2}$ spin orbit peaks were located at 54.3 and 55.2 eV, respectively. This finding indicated the decline in the valence of the simple Se substance to Se²⁻. The

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XPS spectra of MoSe₂ nanospheres(sample $2^{\#}$) are shown in **Fig. S3**, which are similar to the results of sample $1^{\#}$. These results of XPS were consistent with previous works for MoSe₂ nanosheets ^{18, 24}.



Fig. 3 (a) Pore size distributions of MoSe₂ microspheres (inset) with corresponding surface area transform curve (b) Nitrogen adsorption–desorption isotherm for MoSe₂ 3D microspheres (c) XPS spectrum of Mo 3d and (d) XPS spectrum of Se 3d.

The crystal structure of the flower-like MoSe₂ 3D microspheres was examined by TEM. The results are shown in **Fig. 4**. **Fig. 4(a, b)** present different magnifications of the TEM images. The surface morphology displayed that the synthetic MoSe₂ microspheres were made up of abundant nanosheets and had a great crystal quality. The selected area electron diffraction (SAED) pattern (**Fig. 4c**) showed several cycle clear torus tori that demonstrated the obtained MoSe₂ microspheres with a polycrystalline structure. The radius of the first and second cycle torus in the Brillouin zone corresponded to the lattice distances of 0.28 and 0.165 nm, which were consistent with the (100) and (110) planes of the MoSe₂ hexagonal phase, respectively.

The high-resolution TEM as shown in **Fig. 4d**, further revealed the periodic arrays with a 0.28 nm distance assigned to the (100) lattice plane. In addition, an interlayer distance of nearly 0.7 nm was examined, which matched the thickness of the single layer of Se-Mo-Se unit and the corresponding (002) plane ²⁰. To observe the surface atomic distribution clearly, we conducted a simple filtering process on the dashed lines in **Fig. 4e**. The results are shown in **Fig. 4f**. The periodic arrays of the boundless honeycomb structure showed the MoSe₂ nanosheets with a graphene-like plane structure¹⁸.



Fig. 4 TEM characterization of the obtained $MoSe_2$ sample: (a, b) TEM image of a magnified view of the flower-like $MoSe_2$ 3D microspheres (c) The SAED pattern taken from the area marked with a black rectangle in (b). (d, e) The high resolution TEM image of the monolayer. (f) A simple filtering process to the dashed lines in (e)

3.2 Photocatalytic property of the MoSe₂ microspheres

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Fig. 5 Chemical structures of nitro-aromatic explosives NB, PNP and 2, 4-2DNP

Nitro-aromatic explosives (**Fig. 5**) are generally difficult to degrade owing to the existence nitro as a group for absorption electrons. Thus, significant works have been conducted to find a good material or composite materials with excellent photocatalytic activity. Nevertheless, few studies have focused on the TMD materials, especially their photocatalytic activity for degrading nitro-aromatic compounds. The 3D porous flower-like structures of MoSe₂ can provide abundant active sites and effective transport pathways. The narrow direct band gap of approximately 1.68 and 1.52eV may excite the photoresponse at the range of visible spectrum, thereby improving the quantum efficiency. In this work, as-synthesized flower-like MoSe₂ microspheres and nanospheres were used to degrade the NB, PNP and 2, 4-DNP under visible light irradiation.

The results of the photocatalytic activity of MoSe₂ microspheres (sample 1[#]) are shown in **Fig. 6.** It can be clearly discovered that the main UV-Vis absorption peak (NB: 268 nm, PNP: 318 nm and 2, 4-DNP: 356 nm) gradually decreased, and the target compound NB, PNP and 2, 4-DNP were completely degraded by the MoSe₂ microspheres (20 mg) after about 3.5 h, 1.5 h and 2.5 h, respectively. During the photocatalytic process, the main absorption peak position did not change, and no other absorption peak appeared; therefore, photocatalytic degradation mode was dominated and no other dye sensitization occurred ⁴³. In addition, the photocatalytic performance of MoSe₂ nanospheres (sample 2[#]) was also investigated under the same conditions. As shown in Fig. S4, NB, PNP and 2, 4-DNP were completely degraded by MoSe₂ nanospheres sample 2[#] (20 mg) after about 4.5 h, 2.5 h and 4.0 h, respectively, which may involve free radical degradation mechanisms. As a contrast, the removal rate of the same aqueous solution of NB, PNP and 2, 4-DNP were about 13.9%, 12.8% and 11.9%, respectively with the same visible light irradiation time in the absence of MoSe₂ (**Fig. S5**). The gradual color fading of the representative PNP reaction solution was recorded by camera as shown in **Fig. S6**, the color of the PNP solution changes from pale yellow to nearly colorless with the prolongation of photodegradation time.



Fig. 6 Photocatalytic property of MoSe₂ microspheres (sample 1#): The UV-vis absorption spectra of the 40 mg/L aqueous solution of NB (a), PNP (b) and 2, 4-DNP (c) under visible light irradiation.

The photocatalytic degradation of compounds NB, PNP and 2, 4- DNP follows the pseudo-first-order kinetics as seen from the linear fitting profiles shown in **Fig. 7**. The first-order rate constant (k) was calculated using **Equation 1**, as follows:

$$-\ln\left(C_t/C_0\right) = kt \tag{1}$$

where C_0 and C_t are the concentrations of nitro-aromatic compounds at the irradiation time of 0 and *t*, respectively ⁴⁴. As shown in **Table 1**, the calculated kinetic rate constant (*k*) were 0.009 min⁻¹ (NB), 0.027 min⁻¹ (PNP) and 0.019 min⁻¹ (2,4-DNP). The kinetic plot for all catalysts is approximately linear, corresponding to the correlation coefficient (r) of approximately 0.9930, 0.9757 and 0.9223, respectively.



Fig. 7 The kinetics of photocatalytic degradation of the nitro-aromatic compounds (a) NB, (b) PNP, (c) 2, 4- DNP.

Table 1. The linear fitting results of the reaction kinetics curve with NB, PNP and 2, 4- DNP.

	Kinetic rate constant (k)	Correlation coefficient (r)
NB	0.009 min^{-1}	0.9930
PNP	0.027 min^{-1}	0.9757
2,4-DNP	0.019 min ⁻¹	0.9223

To confirm that structure of the flower-like MoSe₂ microspheres were unchanged after the photocatalytic reaction process, more contrast experimental tests have being

carried out(**Fig. S7**) The SEM images (**Fig. S7 a, b**) were obtained after 4 cycle times under visible light irradiation. Comparison with **Fig. 1a-c**, the surfaces of the MoSe₂ microspheres were nearly unchanged, and the microspheres still composed tightly by plentiful nanosheets. XRD pattern (**Fig. S7 c**) also showed that the crystal structure of MoSe₂ microspheres before and after 4 cycle times photocatalytic action did not change significantly, which can be indexed the JCPDS card: No.29-0914 ³⁵. The bonding structure of the as-prepared product was confirmed by FT-IR measurements. **Fig. S7 d** shows the FT- IR spectra in the range of 4000-500 cm⁻¹ of the MoSe₂ before and after 4 cycle time photocatalytic action. It could clearly be observed that there were no peaks shifted and disappeared before and after photocatalytic action. The FT-IR spectra showed that the MoSe₂ displayed strong signals at 1096 cm⁻¹ and 621 cm⁻¹, which are attributed to the Mo-Se stretching and Se-Mo-Se stretching vibrations

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Fig. 8 Stability test for MoSe₂ microspheres for photocatalytic degradation of PNP under visible light irradiation.

Good stability is a crucial feature of a photocatalyst in a realistic application for cyclic utilization. The MoSe₂ powders were carefully collected after each common photocatalytic test and dried for the subsequent photocatalytic action to explore the stability in photocatalytic activity. **Fig. 8** and **Fig. S8** present the results of four cycle tests with PNP, NB and 2, 4-DNP. After four cycles of successive irradiation, the

removal rate (C_t/C_0) of PNP presented a slight reduce but still reached 90%, the NB was 83.7% and the 2,4-DNP was keep on 95%, respectively. The results showed that the flower-like MoSe₂ 3D microspheres had superior stability for cycle utilization. **Table 2.** The rates of photodegradation of nitro-aromatic explosives with different catalysts were

compared.

		-				
Catalyst	Substrate	$W_{cat}(g)/n_{sub}$	Reaction	Radiation	Dof	
Catalyst		(mmol)	time	source	Kel.	
$MoSe_2 1^{\#}$	NB	1.23	3.5 h	Visible light	This work	
$MoSe_2 2^{\#}$	NB	1.23	4.5 h	Visible light	This work	
$MoSe_2 1^{\#}$	PNP	1.39	1.5 h	Visible light	This work	
$MoSe_2 2^{\#}$	PNP	1.39	2.5 h	Visible light	This work	
$MoSe_2 1^{\#}$	2,4-DNP	1.87	2.5 h	Visible light	This work	
$MoSe_2 2^{\#}$	2,4-DNP	1.87	4 h	Visible light	This work	
[Au ₂ (dppatc) ₂]Cl ₂	NB	1.33	3.5 h	UV light	H X, Qi etl	
[Au ₂ (dppatc) ₂]Cl ₂	PNP	1.33	3.5 h	UV light	H X, Qi etl	
[Au ₂ (dppatc) ₂]Cl ₂	2,4-DNP	1.33	4 h	UV light	H X, Qi etl	
[Ag ₄ (NO ₃) ₄ (dpppda)] _n	NB	1.33	5 h	UV light	X Y, Wu etl	
[Ag ₄ (NO ₃) ₄ (dpppda)] _n	PNP	1.33	5 h	UV light	X Y, Wu etl	
[Ag ₄ (NO ₃) ₄ (dpppda)] _n	2,4-DNP	1.33	6 h	UV light	X Y, Wu etl	
TSA-MIP-TiO ₂	NB	2.0	1.5 h	UV light	X T, Shen etl	
Graphitic Carbon TiO	TO ND 0.40	0.40	4 h	UV light	Wan-Kuen	
Graphilic Carbon-110 ₂	IND	0.49			Jo etl	
MWCNTs/TiO ₂	2,4-DNP	38	2.5 h	solar light	H Wang etl	

Comparison on some experimental parameters of photodegradation catalyzed by $MoSe_2$ microspheres (sample 1[#]), $MoSe_2$ nanospheres (sample 2[#]) and some known catalysts in the oxidation photodegradation processes are listed in **Table 2.** The time of degrading NB catalyzed by TSA-MIP-TiO₂ (2.0 g/mmol (w_{cat}/n_{sub})) and graphitic carbon-TiO₂ (0.49 g/mmol (w_{cat}/n_{sub})) under the UV light were 1.5h ⁴⁶ and 4h ⁴⁷, respectively. When the amount of the catalyst was loaded at 1.33g/mmol (w_{cat}/n_{sub}), the time of degrading NB, PNP and 2,4-DNP catalyzed by [Ag₄(NO₃)₄(dpppda)]_n under the UV light irradiation were 5h, 5h and 6h, respectively ⁴⁸. Whereas, when [Au₂(dppatc)₂]Cl₂ was used as the catalyst ⁴⁹, the degrading time of NB, PNP and 2,4-DNP under the same condition with the former decreased to 3.5 h, 3.5 h and 4 h, respectively. Obviously, their degradation time on the same amount of the catalyst

were a bit more than our work by using MoSe₂ as catalyst, and the utilization of the visible sight can broaden the absorption region of the sunlight and increase the quantum efficiency. For MWCNTS/TiO₂ 50 , although the degradation time for 2,4-DNP (2.5 h) was the same, the amount of the catalyst (38 g/mmol) was much larger than the use of MoSe₂.

Table 3. Yields of NH_4^+ and NO_3^- existed in the NB, PNP and 2, 4-DNP solution after photocatalyzed degradation

Ion	NB	PNP	2,4-DNP
$\mathrm{NH_4}^+$	21.6%	20.5%	27.1%
NO ₃ -	33.8%	45.4%	38.1%

After photocatalyzed degradation, the yields of NH_4^+ and NO_3^- existed in the NB, PNP and 2, 4-DNP solution were also examined by Ion Chromatography (IC). As shown in **Table 3**, the yields of NH_4^+ in NB, PNP and 2, 4-DNP solution after photocatalyzed degradation were 21.6%, 20.5% and 27.1%, respectively. The yields of NO_3^- in NB, PNP and 2, 4-DNP solution after photocatalyzed degradation were 33.8%, 45.4% and 38.1%, respectively. The yield of NO_3^- was a little more than the yield of NH_4^+ . Whereas the remaining 34.1%-44.6% nitro group was probably released into air as the form of N₂ according to the previous reports ^{49, 51}.

For the purpose of further analysis the photocatalytic action products, the nitro-aromatic explosives solution before and after the visible light irradiation were filtrated and then analyzed by the TOC test showing in **Fig. 9a.** Compared with the undegraded solution, it has a great decline of the TOC content with each nitro-aromatic explosive, and the TOC removal rate of NB, PNP and 2, 4-DNP solution after photocatalyzed degradation were 62.7%, 65.2% and 61.5%, respectively. Obviously, the removal rate of TOC reduction is slower than that of the photocatalytic degradation, indicating that the nitro-aromatic explosives is partially decomposed into H_2O and $CO_2^{52,53}$.



Fig. 9 (a) The TOC test with the NB, PNP and 2, 4-DNP solution before and after the visible light irradiation. (b) Trapping tests of the active species $(h^+, \bullet OH, \bullet O_2^-)$ compared with the no quencher added to the 4-nirophonel under visible light irradiation.

To explore the mechanism of photocatalytic degradation, holes (h^+) , hydroxyl radicals (•*OH*), and superoxide radical (•*O*₂⁻) were detected by adding KI (a quencher of h^+), IPA (a quencher of •*OH*), and BQ (a quencher of •*O*₂⁻), respectively. The method showed no difference from the previous photocatalytic degradation test **Fig. 9b** indicates that the removal rate of the PNP decreased with the injection of KI, IPA, and BQ. The result showed that h^+ , •*OH* and •*O*₂⁻ existed during the photocatalytic activity. Obviously, the photocatalytic degradation rate of the 4-nitrophonel was strongly restrained by the trapping of h^+ (adding KI). Therefore, •*OH* could not be



generated successfully when h^+ was quenched by KI⁵⁴.

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Fig. 10 Photocatalytic degradation mechanism of flower-like MoSe₂ microspheres under visible light irradiation.

In accordance with the above-mentioned results and analysis, the potential photocatalytic degradation mechanism for the flower-like MoSe₂ 3D microspheres was proposed **Fig. 10.** The band gap of MoSe₂ was approximately 1.68 eV and could absorb the visible light. When visible light irradiated on the surface of MoSe₂ microspheres, photogenerated electron-hole pairs were produced (**Equation 2**). Then the photogenerated electrons (e_{cb}^{-}) were excited to the conduction band, while the photogenerated holes (h_{vb}^{+}) remained in the valence band. The MoSe₂ microspheres were composed of many ultrathin nanosheets, thereby enabling the photoholes to reach surface bound H₂O and generate $\cdot OH$ (**Equation 3**). By contrast, the photoelectrons combined molecular O₂ to $\cdot O_2^{-}$ on the microspheres surface (**Equation 4**). Nevertheless, the photocatalytic degradation of PNP was heterogeneous according to the previous reports by Paola et al ⁶. Initially, the nitro group at the para position was eliminated by the electrophilic substitution of the powerful oxidizing agent $\cdot OH$ with the generation of the intermediates as hydroquinone. Then, the

intermediates and •NO₂ continued to react with •*OH* and •*O*₂⁻ to produce CO₂, H₂O, N₂ and inorganic ions (**Equation 5**) $^{4, 55-57}$.

$$MoSe_2 + hv \rightarrow e_{cb}^- + h_{vb}^+ \tag{2}$$

$$h_{\nu h}^{+} + H_2 O \to \bullet OH + H^{+} \tag{3}$$

$$e_{cb}^- + O_2 \to \bullet O_2^- \tag{4}$$



4 Conclusions

Flower-like MoSe₂ 3D microspheres were synthesized by using a simple hydrothermal method. The as-obtained MoSe₂ samples had a specific surface area of nearly 33.3 m²/g and a direct band gap of around 1.68 eV. Considering that the flower-like structure MoSe₂ microspheres can absorb visible light and have abundant nanosheets, we have investigated its photocatalytic degradation activity with three nitro-aromatic explosives NB, PNP and 2, 4-DNP. The results showed that the NB, PNP and 2, 4-DNP could be degraded under visible light after 3.5 h, 1.5 h and 2.5 h, respectively, which showed a high efficient photocatalytic degrading performance than the flower-like structur MoSe₂ nanostructure. The photocatalytic activity process followed the pseudo-first-order kinetics. Trapping tests of active species (h^+ , $\cdot OH$, $\cdot O_2^-$) were added into the PNP to show that h^+ , $\cdot OH$, and $\cdot O_2^-$ were present during the photocatalytic activity and that h^+ was the most important influencing factor of the photocatalytic removal rate of PNP. Furthermore, the possible photocatalytic

mechanism was discussed, and we considered that the activity process of the photocatalytic degradation of PNP was heterogeneous. Photoelectron-holes were firstly generated and produced the active radical $\cdot OH$ and $\cdot O_2^-$ under visible light irradiation. Then, the nitro group was eliminated by the powerful oxidizing agent, $\cdot OH$, with the generation of intermediates. Finally, the intermediates and $\cdot NO_2$ continued to react with $\cdot OH$ and $\cdot O_2^-$ to produce CO₂, H₂O, N₂ and inorganic ions.

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