

Direct Z-Scheme Heterostructures Based on MoSSe Quantum Dots for Visible-Light-Driven Photocatalytic Tetracycline Degradation

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Supporting Information (SI)

Experimental Section

Materials

The analytical grade sodium dihydromyldimolate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), Se powder, the L-cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$), hydrochloric acid (HCl), and tetracycline (TC) were purchased from Sigma-Aldrich. Deionized water was employed to produce solutions to be explored. All chemicals organized in this investigation were of rational class without further refining.

Synthesis of MoSSe quantum dots

The MoSSe QDs were synthesized by the hydrothermal method. In a typical run, 0.8 mmol Se powder was dispersed in a solution of 1.2 mmol of sodium dihydromyldimolate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in 20 ml distilled (DI) water with magnetic stirring for 20 min. Then, 2.4 mmol of L-cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$) was then added into 20 mL of DI water with magnetic stirring for 30 min. Afterward, 0.2 mL of HCl was associated dropwise. After 20 min of stirring, the obtained above solution mixtures were transferred into 50 mL Teflon-lined autoclave. After cooling down to room temperature, the product was collected by centrifugation at 12000 rpm for 10 min,

washed three times with DI water, NMP and absolute ethanol. Finally, dried overnight in a vacuum oven at 80 °C and further purpose. The photodegradation efficiency of photocatalysts were investigated by the photocatalytic of tetracycline (TC), Congo red (CR) and rhodamine B (RhB) under visible light at room temperature. A 300W tungsten halogen lamp, whose wavelength distribution is similar to that of sunlight, was chosen as the light source. Briefly, 10 mg of above fabricated photocatalysts was placed in a quartz cuvette containing 50 mL of 10.0 mg L⁻¹ TC aqueous solution under visible-light illumination. Prior to the irradiation, the aqueous solution was first magnetically stirred in a dark for 20 min to establish the adsorption/desorption equilibrium between QDs catalyst and TC. The concentration of pollutant solutions was measured with an ultraviolet-visible (UV-vis) spectrophotometer, high performance liquid chromatography (HPLC) and total organic carbon (TOC) after centrifugation before further characterization.

Characterizations

The obtained products were performed by X-ray Diffraction (XRD) (Bruker D8 Advance equipped with CuK α radiation ($\lambda = 0.1542 \text{ \AA}$)) to identify the configuration and crystal purity of the photocatalysts. X-ray photoelectron spectroscopy (XPS) was presented on an ESCALAB 250Xi mode using 300 W Al K α radiation (Thermo Fisher Scientific, USA). Morphological and microstructure examination was performed on a JEOL JEM-2000EX transmission electron microscope (TEM) and applied voltage of 160 kV, a JEOL-6330 field emission-scanning electron microscope (SEM) served with an energy dispersive X-ray spectrometer (EDS). The specific surface of the products was confirmed at -196 °C by a Brunauer–Emmett–Teller (BET) instrument (Micromeritics, Norcross, USA). The UV–Vis absorption spectra were recorded on a Hitachi U-3900H spectrometer (Hitachinaka-shi, Ibaraki, JAPAN). The photoluminescence (PL) spectra were reached on an F-7000 photoluminescence detector (Hitachi). Transient photocurrent response (TPR) and electrochemical impedance spectra (EIS) were obtained by applying a CH Instruments electrochemical analyzer. Finally, the concentration of TCs in above suspension was measured by an HPLC instrument (Hitachi HPLC system) with analytical column- ZORBAX-C18 (5 μm , 250mm \times 4.6 mm), and detection wavelength of 357 nm. The flow velocity of mobile phase, including 20 % v acetonitrile (solvent A) and 72 % water consists of 8 % methane acids (solvent B), flow rate of 1 mL min⁻¹, and injection volume of 2 μL .

TOC was measured through a LOTIX-US 16011003 Carbon Analyzer to perform the degradation rate of TC. Thermo-gravimetric (TGA) analyses was operated on a TA Instruments Q500 Thermogravimetric Analyzer in the ranging from 30 to 850 °C for a heating rate of 10 °C/ min under a nitrogen environment. The functional groups of resultant samples were observed by Nicolet iS10 FTIR spectrophotometer in the range (500–3500 cm⁻¹) by combining 0.01 g of the sample with 0.1 g of KBr. After, electron paramagnetic resonance (EPR) analysis was assisted on the Bruker ESR EMXplus-10/12/P/L SYSTEM spectrometer.

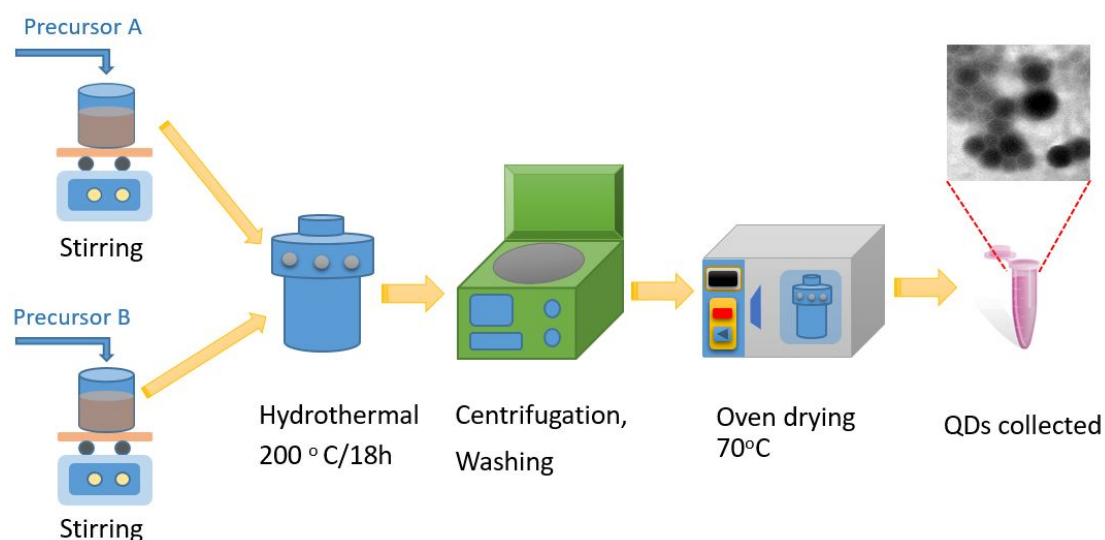
Photocatalytic activity tests

A 300 W tungsten light lamp was involved as the source. The photocatalytic tests were approved for the catalysts (10 mg) suspended in the 50 mL aqueous solution (pollutant concentration: TC: 10 mg/L) over consecutive stirring for 20 mins in the dark to accomplish adsorption-desorption equilibrium. At certified time (10 min) intervals under visible light irradiation, around 4 mL of the suspension was obtained to provide further analyze after the centrifugation. The concentration of TC remaining in the solution was examined utilizing a UV-vis spectrophotometer and UPLC with a wavelength of 352 nm. For revealing the active species developed in the photocatalytic pathway, 4-benzoquinone (BQ), isopropanol (IPA) and EDTA-2Na were used to superoxide radicals ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$) and capture holes (h^+), respectively. The work object was related to the former photocatalytic response studies, including trapping agent of TC (1 mmol). Furthermore, ESR analysis has also been utilized to arrange the attendance of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals under visible light. Sample organizing for appraising ESR is as following: 4.0 mg of product was dissolved in methanol or deionized water, and later 20 mM DMPO was combined by ultrasonic distribution for 10 min, respectively. We have included our photocatalytic studies in the mixture solution incorporate QDs was obtained via filtering the hydrothermal solution with a 0.22 μm syringe filter for each further cycling degradation tests.

Photocatalytic and photoelectrochemical tests

The photocatalytic tests of MoSSe QDs photocatalysts were determined by the photodegradation of TC with visible light activity (300 W electric power tungsten light lamp). In each step, 10 mg of photocatalysts was dissolved in DI water by ultrasound and associated with TC solution. The suspensions were formed to 30 mL (TC 10 mgL⁻¹)

and magnetically stirred in the dark for 20 mins due to procure a loaded TC absorption toward the QDs before irradiation. The total irradiation time was 60 mins with the test interval was 10 mins. The suspensions of 1 mL expanded would be filtered by a 0.22 μm filter toward eliminate photocatalysts. The concentrations of TC were detected applying an HPLC. The electrochemical properties were tested using 0.2M Na_2SO_4 as an aqueous solution on an electrochemical platform along a three-electrode unit type. Again, Ag/AgCl and platinum wire were used for the reference electrode and counter electrode, respectively. And the prepared MoSSe QDs film on fluorine-doped tin oxide (FTO, 1 cm \times 2 cm) glass was employed for the working electrodes. The associated visible light basis as photodegradation performance was promoted in this analysis. Photocurrent performing was studied with visible light activity (light on or off cycles of 50 s). The intermediates during the TC photodegradation by MoSSe QDs were determined by HPLC system. Subsequently, 2 μL of supernatant was included the HPLC with an associate with 20 vol% acetonitrile and 80 vol% water as the mobile phase under 1 ml/min rate.



Scheme S1. Schematic of the synthesis of MoSSe QDs.

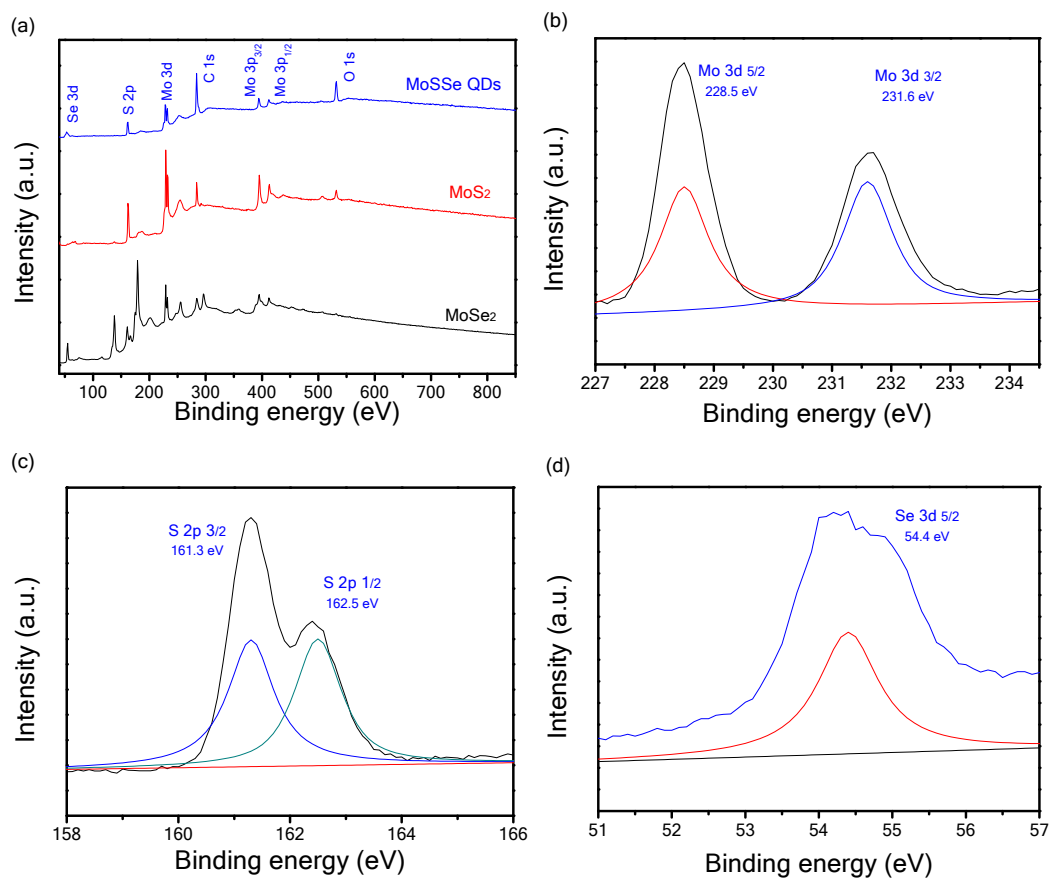


Figure S1. The XPS spectrum of MoS₂, MoSe₂, and MoSSe QDs. (a) Survey spectrum; (b) high resolution of Mo; (c) high resolution of S; (d) high resolution of Se.

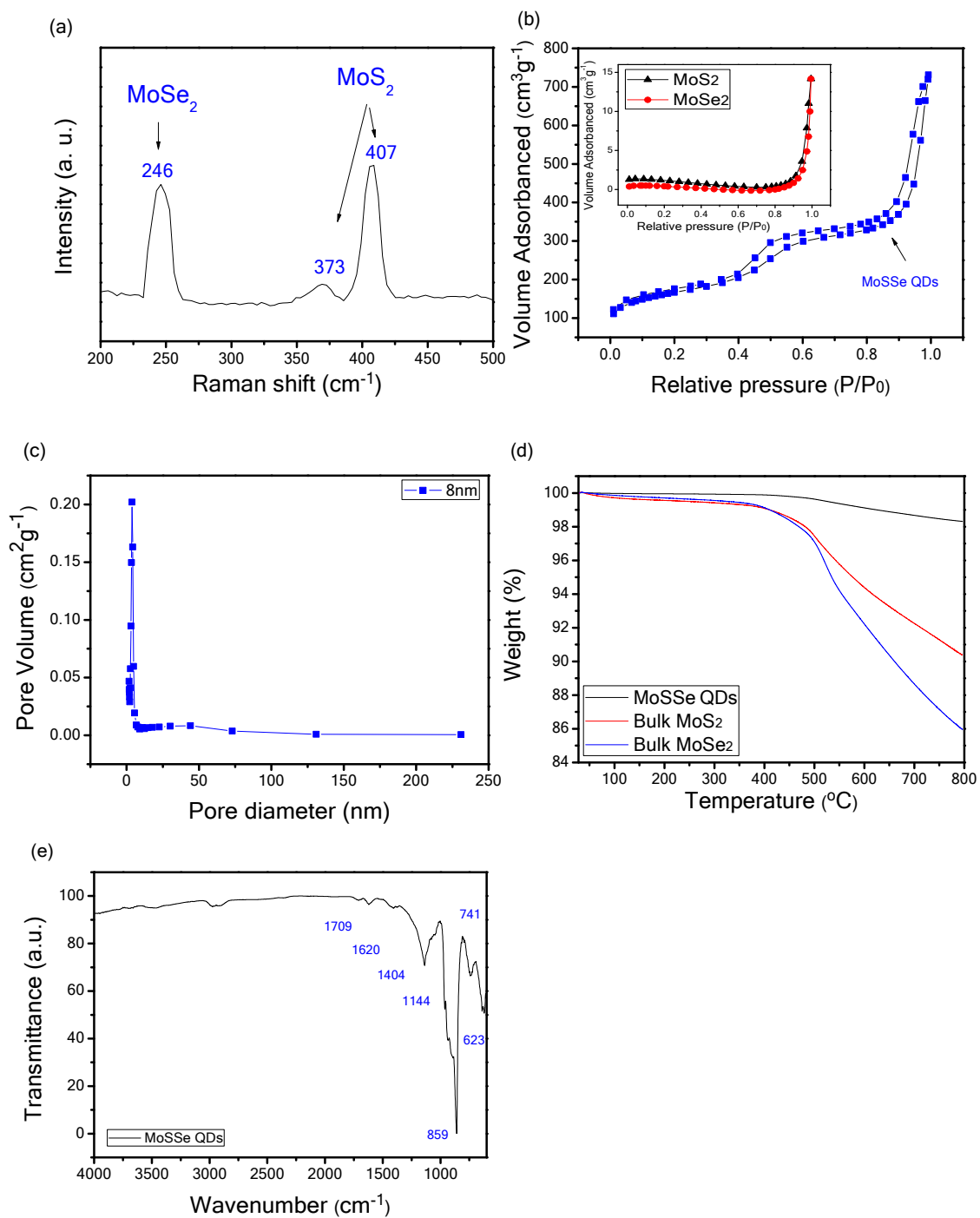


Figure S2. (a) Raman spectra of MoSSe QDs, N₂ adsorption–desorption isotherm of prepared samples. (b) BET-isotherm (c) pore size distribution, (d) TGA profiles of MoS₂, MoSe₂, and MoSSe QDs, and (e) FT-IR spectra of MoSSe QDs.

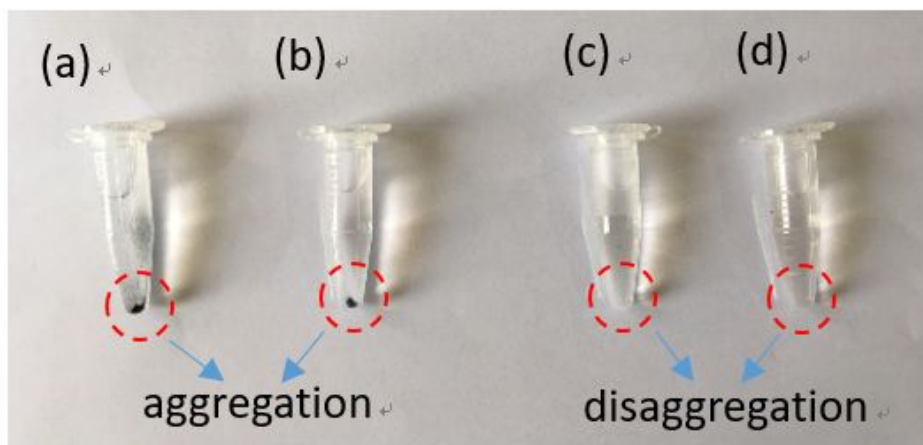


Figure S3. Photographs of bulk MoS₂ (a), MoSe₂ (b), MoSSe QDs before (c) and after (d) two months of storage. The experiment was performed in TC aqueous solution at room temperature.

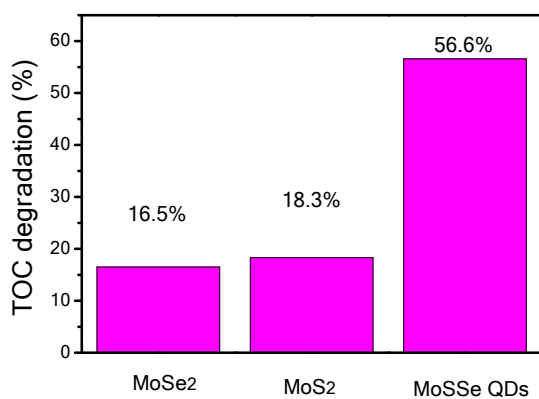


Figure S4. TOC removal rates of TC over different samples.

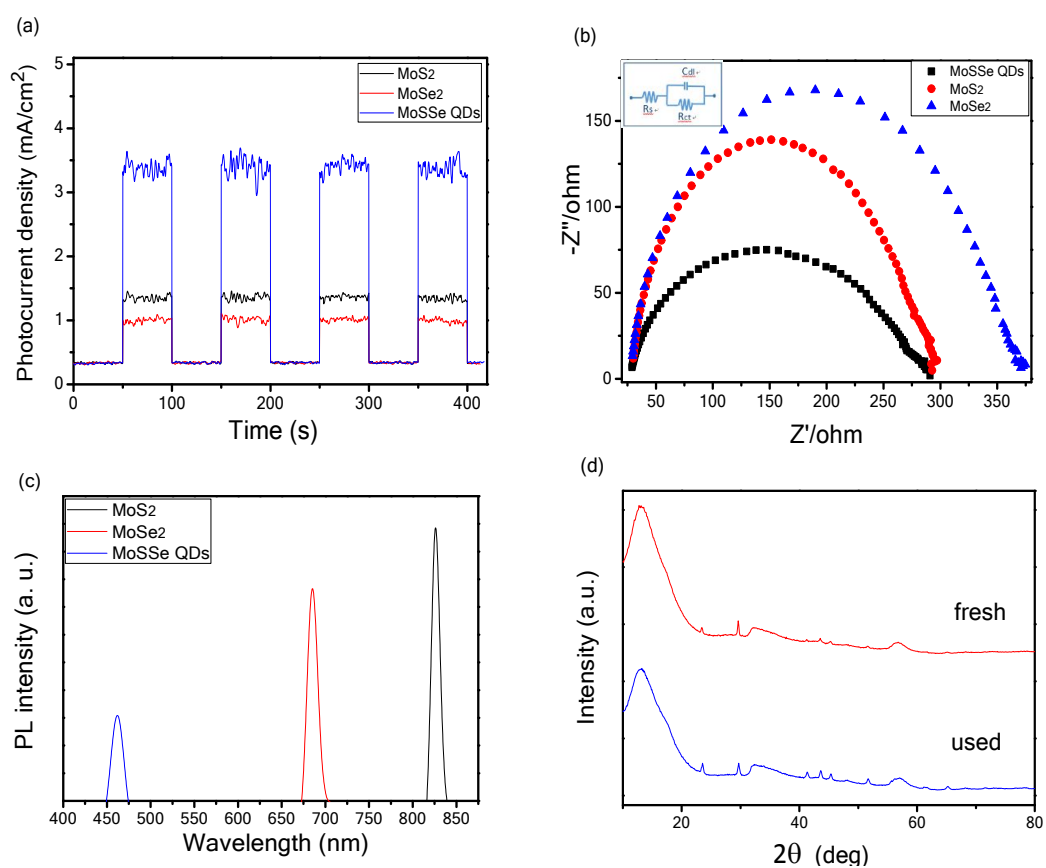


Figure S5. (a) Transient photocurrent responses of the samples, (b) EIS Nyquist impedance plots, (c) Photoluminescence spectra of prepared the bulk MoS₂, MoSe₂ and MoSSe QDs, (d) XRD patterns of MoSSe QDs before and after photocatalytic reaction.

Table S1 Comparison of photocatalytic efficiencies with respect to different MoS₂-based heterostructure photocatalysts for degradation TC in recent years.

Samples	C_{catalyst} gL⁻¹	C_{TC} mgL⁻¹	Reaction time	Degradation efficiency	Apparent kinetic constants K_{app}*10⁻³ (min⁻¹)/g	Reference
MoS ₂ /g-C ₃ N ₄	0.01	10 mg/L	240 min	96%	23	44
CDs/MoS ₂ @H-TiO ₂	0.05	10 mg/L	180 min	81.6%	5.2	45
N-doped ZnO-MoS ₂	0.5	10 mg/L	120 min	84%	0.8	46
MoS ₂ /Fe ₃ O ₄	0.5	10 mg/L	100 min	79.5%	0.9	47
ZnO-MoS ₂	0.5	10 mg/L	120 min	84%	0.8	48
CuBi ₂ O ₄ /MoS ₂	0.5	10 mg/L	120 min	76%	0.7	49
MoS ₂ -ZnSnO ₃	0.25	30 mg/L	60 min	80.2 %	9.3	50
S-CQDs/g-C ₃ N ₄	1	20 mg/L	60 min	82.6%	1.6	51
NCQs/g-C ₃ N ₄ /Bi ₂ WO ₆	0.2	10 mg/L	60 min	75.5%	3.6	52
CNQDs/BWO	1	20 mg/L	60 min	62.7%	1.2	53
MoSSe QDs	0.01	10 mg/L	60 min	92.8%	90	This work