Communication

Synthesis, Characterization and Photocatalytic Activity of MoS₂/ZnSe Heterostructures for the Degradation of Levofloxacin

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Abstract: Antibiotics have been extensively used over the last few decades. Due to their extensive usage and persistence in the environment, they are considered as emergent pollutants. It is, therefore, important to synthesize new materials for efficient antibiotic degradation. Herein, we report the MoS₂/ZnSe heterostructures prepared by a simple ultrasonication method. Heterostructures were prepared with different ratios of MoS₂ and ZnSe, i.e., 1:3, 1:1 and 3:1. Characterization of the heterostructures was done by UV-vis diffused reflectance spectroscopy (UV-vis-DRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and photoluminescence (PL) techniques to understand the morphology and surface chemistry. The results show that an efficient interface was formed to harness the visible light and degrade levofloxacin, which was monitored by gradual decreases in the UV-vis absorbance signal of levofloxacin. Among the prepared heterostructures and their pure counter parts, MoS₂/ZnSe 3:1 (3:1 MZ) showed a better degradation activity of 73.2% as compared to pure MoS₂ (29%) and ZnSe (17.1%) in the presence of visible light in a time span of two hours. The reusability studies showed that the catalytic performance of 3:1 MZ did not decrease significantly after three cycles. Moreover, the morphology and the crystal structure also remained unchanged.

Keywords: photocatalysis; MoS₂; ZnSe; heterostructure; levofloxacin

1. Introduction

Antibiotics have become emerging pollutants due to their extensive usage and persistence in the environment [1]. These are used as therapeutic agents for humans and as veterinary medicine. The anthropogenic sources through which antibiotics enter the environment include household drainage systems, hospital waste, pharmaceutical industrial waste, agricultural runoff, the discarding of expired and unused medicines, and livestock [2]. The presence of antibiotics in water bodies is a matter of serious concern due to their potential for inducing resistance in the population and their biological activity. Antibiotics like levofloxacin belong to the fluoroquinolone class, with a broad-spectrum antibacterial activity against skin, respiratory tract, soft tissues and urinary tract infections [3]. Therefore, there is a high need to find a solution for their existence and persistence in the environment [4]. Photocatalysis is the emerging technology for the remediation of hazardous wastes from the environment [5]. It is being applied for degrading volatile organic compounds [6], degrading antibiotics [7], industrial dyes degradation [8] and photoelectrochemical water splitting [9].

Amongst the latest synthesized photocatalysts, molybdenum disulphide is gaining high consideration [10]. This is due to its layered structure, which is analogous to graphene and offers

efficient electron transport and absorbance of sunlight [11]. The two-dimensional layered (2D) structure comprises a total of three layers loaded together with the Mo layer in the middle and S atom layers on the top and bottom [12]. As the number of layers in the MoS₂ structure decreases, its band gap increases, showing the quantum confinement effect [13]. MoS₂ has a direct band gap of 1.8 eV, making it an active photocatalyst in visible light [14]. It has many qualities, such as high stiffness, reliability, strong oxidizing property [15], non-toxicity, a tunable band gap, and it is cost efficient [16]. All these properties make it a very promising photocatalyst. However, the rate of recombination of photoexcited holes and electrons is high and limits its performance. To overcome this shortcoming, semiconductors can be incorporated with MoS₂ to attain the required properties [17]. The morphology and the crystallinity of the photocatalysts are important parameters that affect the photocatalytic process. A recent study showed that increases in the crystallite size increase the decomposition of the substrate [18]. A more specific work on MoS₂ showed that surface area has no significant effect on the degradation of organic wastes, while surface morphology plays an important role in this process [19]. Lots of work is being done currently to find the best photocatalyst in the form of heterostructures; MoS₂/MoO₃/TiO₂ [20], MoS₂/ZnSnO₃ [21], MoS₂/g-C₃N₄/Bi₂₄O₃₁Cl₁₀ [22], CoO@ meso-CN@MoS₂ [23], and WO₃/MoS₂ [24] are a few among many heterostructures synthesized for photodegradation.

Semiconductors that belong to the II–VI groups have fascinated the researchers because of their promising applications. ZnSe is an important group member of this family, having a direct band gap of 2.8 eV [25]. It shows significant applicability in electronic and optoelectronic devices like transistors, non-linear optical devices, lasers and light emitting diodes [26]. The band gap of ZnSe makes it visible light-active, so it has also been studied as a photocatalyst, but it shows low efficiency in terms of degradation time, i.e., 96% in 10 h for methyl orange [27], 92.5% in 6 h for methylene blue [28], 95.1% in 10 h for methyl orange [29], and almost complete degradation in 9 h for methyl orange [30] and 10 h for methyl orange [31].

In this work, MoS₂ and ZnSe were synthesized by the using hydrothermal method and were used to prepare heterostructures via the ultrasonic method. Characterization of the heterostructure photocatalysts was performed to understand their morphological structures and properties. Compared to pure MoS₂ and ZnSe, their heterostructures showed significant enhancements in photocatalytic activity with reduced degradation time against levofloxacin. The photodegradation of levofloxacin was examined and a possible mechanism is proposed.

2. Results and Discussion

2.1. Phase and Microstructural Analysis

The phase purity and crystalline structure of the synthesized photocatalysts were determined by using XRD. Figure 1 shows the XRD patterns of pure MoS₂, 1:3 MoS₂/ZnSe (1:3 MZ), 1:1 MoS₂/ZnSe (1:1 MZ) and 3:1 MoS₂/ZnSe (3:1 MZ) heterostructures, and pure ZnSe. The diffraction peaks of MoS₂ agree with the hexagonal phase and match with the JCPDS card no. 37-1492. Diffraction peaks at 13.8°, 28.7°, 34.4°, 42.6° and 57.5° correspond to the (002), (103), (100), (105) and (110) planes of the hexagonal wurtzite structure of MoS₂ [32]. The diffraction peaks of ZnSe include peaks at 27.1°, 45.1°, 53.5° and 65.7°, as shown in Figure 1. These peaks correspond to the (111), (220), (311) and (400) planes of cubic ZnSe in accordance with the JCPDS card no. 37-1463 [33]. The sharpness of the peaks indicates the high crystallinity of ZnSe, and no extra peaks show that the prepared ZnSe is phase-pure. The steady increases in the peak intensities of MoS₂ in the heterostructures, with increases in wt. % ratio, indicate a brilliant coupling interaction owing to the better photocatalytic activity [34]. Slight shifts in the position of the peaks, i.e., for MoS₂ in the heterostructures it was 13.8° to 14°, and a shift of 0.2° was detected in the peak positions of ZnSe in the heterostructures, confirm the formation of the heterostructures.

Figure 1. X-ray diffraction spectra of MoS₂, ZnSe and their heterostructures.

X-ray photoelectron spectroscopy was employed to confirm the synthesis and oxidation states of the prepared materials. Figure 2a shows the XPS spectra of the Mo three-dimensional orbitals of MoS₂. The peaks of the binding energies of Mo3d_{5/2} and Mo 3d_{3/2} at 229.01 eV and 232.24 eV show the oxidation state of Mo⁺⁴. The peaks centered at 233.1 eV and 236.2 eV can be ascribed to the Mo⁺⁶ 3d_{3/2} and 3d_{1/2} oxidation states [35], which appear due to the slight oxidation of the edges during MoS₂ synthesis [36]. The peaks at 161.7 eV for S2p_{3/2} and at 163.48 eV for S2p_{1/2} (Figure 2b) also confirm the presence of sulphur [37]. The XPS spectra of ZnSe display the presence of two peaks, Zn 2p_{3/2} at 1022 eV and Zn 2p_{1/2} at 1046 eV, showing the successful synthesis of ZnSe. The Se three-dimensional spectrum shows a peak at 54.4 eV, which is exactly on point for 3d_{5/2}, and 55.13 eV for the 3d_{3/2} orbital of selenium [38]. These results indicate that catalysts are clearly formed with no impurities.

Figure 3 displays the SEM images (scale 1 µm) of pure MoS₂, ZnSe and the 3:1 MZ composite, from which we can determine the morphology of the synthesized materials. Figure 3a shows clearly that large microspheres of flower-like MoS₂ nanosheets are formed [39]. The sheets have a thickness range of 32–43 nm. The SEM image of sheet thickness is shown in Figure S7 (Supplementary Information), and Figure 3b shows the flower-like microspheres of cubic ZnSe [30]. The petals of the flower have a diameter range of 54–180 nm. The flower-like ZnSe is distinctly decorated on the nanosheets of MoS₂ microspheres, as is clearly seen in Figure 3c. The SEM images of 1:3 MZ and 1:1 MZ are shown in Figure S1 (Supplementary Information), and also show a clear ornamentation of ZnSe microspheres on the MoS₂ microspheres.

Energy dispersive X-ray spectroscopy helps to determine the elemental composition and hence the purity of the synthesized materials. The EDS spectra in Figure S2a–e (Supplementary Information) show that there are no impurities present in MoS₂, ZnSe, or their composites.

Figure 2. XPS spectra of (a) Mo 3d, (b) S 2p, (c) Zn 2p and (d) Se 3d orbitals.

Figure 3. SEM images of (a) MoS₂, (b) ZnSe and (c) 3:1 MZ at 1 μm scale.

2.2. Alignment of Energy Level

Band gap energy and the position of the valence bands against standard hydrogen electrode (SHE) are the two important key factors used to understand the mechanism of the photocatalytic degradation, and help to draw the alignment of the energy levels [40]. UV-vis-DRS was employed to determine the band gap of the prepared material. The band gaps of both MoS₂ and ZnSe were calculated by using the Kubelka Munk equation and by the Tauc plots [41], as shown in Figure 4a. Molybdenum sulfide showed a narrow band gap of 1.73 eV, and the band gap of ZnSe was calculated to be 2.70 eV, as shown in Figure 4b. UV-vis-DRS spectra of all the composites are shown in Figure S3 (Supplementary Information). The XPS spectra of these compounds show a valence band position of 1.07 eV for MoS₂ in Figure 4c and 1.02 eV for ZnSe, as shown in Figure 4d. Based on this information (Figure 4), the energy levels are drawn and aligned.

2.3. Photocatalytic Degradation of Levofloxacin

The photocatalytic activity of the prepared samples was measured as a function of the degradation of the antibiotic levofloxacin. All measurements were performed under the same conditions. Detailed absorption spectra of the degradation process are shown in Figure S2 (Supplementary Information).

The heterostructures showed efficient degradation as compared to the pure semiconductors. The rate of degradation, i.e., C/C_0 , is plotted against time, as shown in Figure 5a. The heterostructure of 3:1 MZ showed the best result, with a 73.2% degradation of levofloxacin in 2 h. On the other hand, MoS₂, ZnSe, 1:1 MZ and 1:3 MZ showed 29%, 17.1%, 53% and 52% degradations, respectively. The degradation rates are shown in Figure 5b,c. These show that the composite 3:1 MZ caused the highest degradation rate, i.e., 0.00878 k/min. The absorption spectra of the 3:1 MZ heterostructure for the degradation of levofloxacin are shown in Figure 5d. This also implies that a good interface has been developed between MoS₂ and ZnSe in the heterostructures.

The photocatalytic activity is examined by the electron transfer through the heterojunction [42]. So, the PL studies were performed. The PL spectra in Figure 6 show the emission intensity of the different photocatalysts. A high-intensity peak in the PL spectrum shows rapid recombination, and vice versa [43]. The results show that the 1:3 MZ composite manifested a 28.6% decrease in the PL intensity, and 1:1 MZ an 85.7% decrease in the PL intensity. The 3:1 MZ composite manifested a 96.2% decrease in the PL intensity as compared to the pure counterpart. It can be inferred from the results that the increase in the concentration of MoS₂ in the photocatalyst decreases the electron/hole recombination.

The results of the reusability studies of the 3:1 MZ photocatalyst for the degradation of levofloxacin, over three cycles, are shown in Figure 7. The concentration of the antibiotic was adjusted to the initial value after the degradation studies. The photocatalyst 3:1 MZ was studied for three cycles under visible light irradiation. The degradation values after the first, second and third run were found to be 73.2%, 72.3% and 71.9%, respectively, indicating that the performance efficiency of the photocatalyst was not reduced significantly. The photocatalyst was centrifuged and collected from the reaction mixture. The recovered photocatalyst was analyzed with XRD, SEM and EDS, and no change in the crystal phase or morphology, and no impurities, were observed, as shown in Figures S5 and S6 (Supplementary Information).

Figure 4. UV-visible DRS spectra of (a) MoS₂ and (b) ZnSe with insets showing the respective Tauc plots and band gap of MoS₂ and ZnSe. XPS spectra of (c) MoS₂ and (d) ZnSe with their respective insets showing valence band positions.

Figure 5. (a) Photodegradation rate of MoS₂, ZnSe and composites, (b) kinetic plots of the photocatalytic degradation, (c) rate of degradation as a function of time and (d) absorption spectra of photodegradation of levofloxacin by 3:1 MZ.

Figure 6. PL spectra of the photocatalysts.

Figure 7. Reusability of 3:1 MZ under visible light illumination.

The degradation mechanism is proposed based on the results obtained and schematically drawn in Figure 8. When the photocatalyst is exposed to light, electrons in the valence band get excited and move to the conduction band of ZnSe, and holes are produced [44]. These photoexcited electrons are transferred to the conduction band of MoS₂, which acts as electron receiver [45]. This transfer decreases the electron–hole recombination, as shown in the PL spectra [46]. The transferred electrons on the conduction band of MoS₂ react with the adsorbed oxygen, and convert it to superoxide radical (O₂^{•−}), which can instantly decompose the antibiotic [47]. The holes in the valence band are transferred from low-energy MoS₂ to high-energy ZnSe. These holes react with water and produce HO [34]. These hydroxyl and superoxide radicals degrade the antibiotic [48]. So MoS₂ provides a platform for the separation and effective transport of the photogenerated electrons and holes [49,50]. Therefore, this binary system provides active sites that show the ability to harvest large amounts of light, hence their better degradation efficiency. Many heterostructure systems have been reported before now; for example, rGO-Bi₂WO₆ degraded 74.3% levofloxacin in 120 min [51], Ag/AgBr/BiOBr degraded 74% levofloxacin in 150 min [52], and CeV-BiV degraded 95.7% levofloxacin in 5 h [53]. Regarding the present study, the 3:1 MZ heterostructure shows a comparable activity of 73.2% in 120 min. However, this was an entirely new study for the ZnSe and MoS₂ heterostructures, performed to understand their behavior and photocatalytic activity.

Figure 8. Schematic illustration of alignment of the energy level of 3:1 MoS₂/ZnSe nanocomposite.

3. Materials and Methods

All the chemicals, viz. sodium molybdate, thiourea, zinc acetate, Se powder, hydrazine hydrate and ethanol, were purchased from Sigma Aldrich (St. Louis, MO, USA). All chemicals were of analytical grade and were used without purification.

3.1. Synthesis of MoS₂

Analytical-grade chemicals were used in this study without further purification. MoS₂ was synthesized using the hydrothermal method. Totals of 1.451 g sodium molybdate and 2.283 g thiourea were dissolved in 32 mL of water and placed in a 40 mL Teflon-lined stainless steel autoclave. The autoclave was heated in an oven at a temperature of 200 °C for 24 h. The obtained black powder was washed 3 times with water and one time with ethanol and dried in a vacuum oven at 80 °C for 24 h.

3.2. Synthesis of ZnSe

The synthesis of ZnSe was also carried out by the hydrothermal method. Totals of 0.175 g of zinc acetate and 0.016 g of selenium powder were dissolved in 8 mL of 6 M KOH solution and 2 mL of hydrazine hydrate was added in it. The mixture was then stirred for 1 h and transferred into a 40 mL Teflon-lined stainless steel autoclave and heated in an oven at 200 °C for 3 h. The resultant product was washed three times with water and one time with ethanol and vacuum dried at 70 °C for 10 h.

3.3. Synthesis of MoS₂/ZnSe Heterostructures

MoS₂/ZnSe heterostructures were prepared by the ultrasonic method. The heterostructures were prepared with 1:3, 1:1 and 3:1 wt.% of MoS₂ and ZnSe, respectively. Totals of 25 mg of MoS₂ and 75 mg of ZnSe were mixed in 25 mL of ethanol under ultrasonic shaking for 3 h. They were then dried at 80 °C for 10 h. These heterostructures were used for photocatalytic degradation.

3.4. Photodegradation of Levofloxacin

The photodegradation was measured by irradiating 11 ppm solution of levofloxacin under visible light using a 500 W Xe lamp with a light intensity of 100 mW/cm² of AM 1.5 G and a cut-off filter $\lambda > 420$ nm. The reaction mixture was placed 10 cm below the lamp. A total of 30 mg of the photocatalyst was added into 100 mL of the antibiotic solution and stirred for 30 min in the dark to achieve the adsorption–desorption equilibrium. The mixture was then irradiated with visible light for two hours, then 3 mL samples were collected at a time interval of 30 min, which were centrifuged, and its concentration in terms of absorbance was measured using a UV-vis spectrophotometer.

3.5. Characterization

XRD analysis was carried out on an X-ray powder diffractometer (STOE Darmstadt, Germany) by using Cu K α at $\lambda = 1.54$ Å. UV-vis and DRS analyses were performed on a Perkin Elmer Lambda 365 spectrometer. A VEGA3 TESCAN scanning electron microscope in combination with an energy dispersive X-ray spectroscope was used to obtain images and elemental compositions of the photocatalysts at an acceleration voltage of 20 KV. Photoluminescence spectra were obtained by using a Perkin Elmer FL 6500/8500 spectrometer. The X-ray photoelectron spectroscopic analyses were recorded on an ESCALAB 250 Xi X-ray photoelectron spectrophotometer.

4. Conclusions

In summary, MoS₂/ZnSe heterostructures were successfully prepared for the first time, to the best of our knowledge, with different ratios through a facile sonochemical method. The as-prepared flower-like heterostructures showed excellent photocatalytic activity, as compared to the pure MoS₂ and ZnSe counterparts. Levofloxacin was successfully degraded using these photocatalysts. The heterostructure 3:1 MZ showed the best catalytic activity of 73.2% in two hours. The prepared photocatalysts showed no significant change in morphology, crystal structure or photocatalytic activity after three cycles of use. This study shows that the formation of heterostructures led to the efficient light absorption and degradation of the antibiotic.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/12/1380/s1>. Figure S1: SEM images of 1:3 MZ (a) at 5 μ m and (b) 500 nm and 1:1 MZ at (c) 5 μ m and (d) at 500 nm, Figure S2: EDS spectra of, (a) MoS₂, (b) ZnSe, (c) 1:3 MoS₂/ZnSe, (d) 1:1 MoS₂/ZnSe, and (e) 3:1 MoS₂/ ZnSe photocatalysts, Figure S3: DRS spectra of pure MoS₂, ZnSe and their composites, Figure S4: Photocatalytic study for all the photocatalyst, shows the detailed absorption spectra for degradation of Levofloxacin, Figure S5: XRD of 3:1 MZ heterostructure before and after degradation, Figure S6: SEM of 3:1 MZ heterostructure, (a) before and (b) after degradation, and EDS spectra (c) before and (d) after degradation, Figure S7: SEM image of MoS₂ nanosheets.

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