Design and Development of Advanced $MoSe_2/MnO_2$ Nanocomposite for Direct yellow dye degradation for Enhanced photocatalytic Applications

Gokulnath Dhanasekaran [a], Nisha Parthiban [a], Nithya. N [b], D. Karthigaimuthu [a], G. Vijayakumar [b], Sangaraju Sambasivam [c], T. Elangovan[a, *]

[a] Smart Energy Materials Research Laboratory (SEMRL), Department of Energy Science and Technology, Periyar University, Salem, India-636011

[b] Department of Physics, PSG College of arts and Science, Coimbatore, India

[c] National Water and Energy Center, United Arab Emirates University, Al Ain, 15551, UAE

Abstract

$MoSe_2$, a significant component within the class of two-dimensional transition metal dichalcogenides, boasts a diverse set of photoelectrochemical characteristics. Herein, we propose a simple hydrothermal approach to synthesis $MoSe_2/MnO_2$ nanocomposites with controllable morphologies with enhanced photocatalytic activity. The obtained nanocomposite was confirmed by the analysed peaks of $MoSe_2/MnO_2$ observed in X-ray diffraction (13.6°, 18.1°, 37.5°), infrared spectra (495, 645, 1410 cm^{-1}), UV-Vis spectra (506, 640, 748 nm) and the band gap lowering (1.94 eV, 2.8 eV, and 4.57 eV). Due to the efficient separation of photogenerated electron-hole pairs facilitated by the rapid transfer of photogenerated electrons by the addition of MnO_2, the $MoSe_2/MnO_2$ composite demonstrates significantly enhanced solar-driven photocatalytic performance and excellent stability in degrading Direct Yellow (DY), a common pollutant found in industrial effluents. The $MoSe_2/MnO_2$ nanocomposite photocatalytic activity was found to be 1.2 to 1.6 times higher than that of its individual components of $MoSe_2$ and MnO_2, indicating synergistic effects leading to enhanced performance. This underscores its considerable potential for environmental remediation, offering a promising approach for the degradation of harmful industrial chemicals present in wastewater using sunlight.

Keywords: Molybdenum diselenide; Manganese dioxide; Nanocomposite; Photocatalysis; UV-Vis light

1. *Introduction*

The absorption of the semiconductor photocatalysts could be reducing the energy shortages while also removing pollutants from the environment [1], [2], [3]. For water pollutant treatment, it is very important to effectively convert solar light to active species. UV-Vis light photocatalysts are of great interests due to their extremely solar light utilizations. In recent years, transition metal dichalcogenides (TMDs) [4], [5], semiconductor – based photocatalysts viz, TiO_2 [6], ZnO [7], $BiVo_4$ [8], etc. have been studied as UV-Vis light photocatalytic material also among these materials, $MoSe_2$ is a promising candidate because it has a narrow bandgap for harvesting extremely sunlight [9]. It also possesses unique two- dimensional (2D) layered structure for surface reactions and it has good absorbance stability [10], [11]. However, the ease of charge recombination strongly decreases photocatalytic activity and limit its applications in water pollutant treatment. To satisfy these properties of $MoSe_2$ is an efficient strategy to separate the photo-generated charge carriers and reduce its internal recombination [12], [13], [14]. As a well-known oxide semiconductor, MnO_2 could generate superoxide radical and hydroxyl radical, respectively. These oxidizing radicals could effectively decompose various organic compounds [15], [16], [17], [18]. Among the different combination of forming $MoSe_2/MnO_2$ nanocomposite, it could be a good photocatalyst for pollutant treatment. However, it is still a challenge to controllable construct $MoSe_2/MnO_2$ nanocomposite with uniform interface and good dispersion.

So far combination of $MoSe_2/MnO_2$ nanocomposite were usually prepared by a different nano structure growth process. For example, some researchers analysed $MoSe_2$ nanosheets on MnO_2 nanorods [19], [20], [21], while the others grew oxides on $MoSe_2$ [22]. In comparison with these nanostructures which are easily agglomerate, the interface contact and uniformly could be more controllable when MnO_2 nanostructure were used as growing supports. And tuning network porosity and large amounts of active sites [23], [24], [25], [26]. These advantages are favourable for mass transport, surface nucleation and growth process, furthermore, their ultralong zero-dimensional structure might be also favour of transferring photo generated electrons to surface reactions sites [27], while their MnO_2 nanostructure network structure can also be easily separated by the reactions [15], [28], [29].

To overcome the uniform interface and good dispersion highlighted in previous reports, we developed a novel photocatalyst comprising a $MoSe_2/MnO_2$ nanocomposite. Utilizing the hydrothermal method, we ensured the $MoSe_2$ component exhibited excellent

dispersibility and controllable concentrations when integrated onto the MnO_2 nanostructure. Moreover, the Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and high-resolution transmission electron microscopy (HR-TEM) were used to characterise the chemical properties of the obtained $MoSe_2/MnO_2$ nanocomposites. The adsorption performance and wide spectrum photocatalytic activity of the as-fabricated composite were investigated using the target organic contaminants Direct Yellow (DY), and the degradation of DY in solution and adsorbed on catalyst surfaces was studied under Vis and UV light irradiation, respectively. $MoSe_2$ and MnO_2 as single components and $MoSe_2/MnO_2$ as a nanocomposite were used to compare the photocatalytic efficiency.

Experimental synthesis process

2.1 Chemicals

Sodium molybdate (Na_2MoO_4) power assay 98% is purchased from the Sisco Research Laboratories Pvt. Ltd. selenium powder block (Se) assay 99%, hydrazine hydrate ($N_2H_4.H_2O$) assay 99%, polyvinylpyrrolidone (PVP), Manganese sulphate ($MnSO_4.H_2O$) assay 99%, Potassium permanganate ($KmNo_4$) assay 99.99%, Direct yellow dye (DY) ($C_{26}H_{18}N_4Na_2O_8S_2$), were utilized for photocatalytic Process. All chemicals were analytical grade and were applied precisely as provided. Unless otherwise noted, the experiment used laboratory-made deionised (DI) water.

2.2 Synthesis of $MoSe_2$

$MoSe_2$ were synthesised by the hydrothermal approach. In solution A, 1.20 g of Na_2MoO_4 and 0.5 g polyvinylpyrrolidone were dissolved in 50 ml of distilled water and stirred for 1 hour. Following this, in solution B, 0.8 g of selenium (Se) was added with 30 ml of $N_2H_4.H_2O$ solution and stirred for half-an-hour separately. Subsequently, solution A is steadily added drop by drop to solution B until precipitation occurs. The resulting solution is then transferred to a 100 ml Teflon-lined autoclave and placed in an oven at 200°C for duration of 24 hours. Ultimately, the contents were subjected to centrifugation, with the resulting residue being washed using deionized water and ethanol. Following this, the residue was dried at 80°C for a period of 12 hours, yielding a pale block powder.

2.3 Synthesis of $MoSe_2$ /MnO_2 nanocomposite

Initially, a solution comprising 50 ml of deionized water was mixed with 1.20 grams of Na_2MoO_4 and 0.8 grams of selenium (Se). After that, 2.1 grams of $MnSO_4$ and 1.96 grams of $KMnO_4$ were individually mixed with 25 ml of deionized water and prepared. Next, both the solutions were added drop by drop while continuously stirring the mixture for 1 hour. To adjust the mixture, 75 ml of deionized water was added. Subsequently, the mixture was sonicated for 30 minutes and subjected to hydrothermal treatment at 180°C for duration of 24 hours. The heterogeneous material was allowed to cool for half an hour before undergoing centrifugation. The remaining residue underwent multiple washes using ethanol and deionized water. Following the cleansing process, it was subjected to drying in a hot air oven set at 80°C for duration of 12 hours, resulting in the acquisition of $MoSe_2/MnO_2$ powder. The manufactured sample is detailed and subsequently employed to evaluate its photocatalytic performance. Fig.1. illustrates a schematic representation of the chemical approach utilized to produce $MoSe_2/MnO_2$ nanocomposites, aiding in achieving uniformity.

2.4 Photocatalysis experiment

The photocatalytic activity of a $MoSe_2/MnO_2$ nanocomposite was studied under direct sunlight. To begin with, 0.5 g of $MoSe_2/MnO_2$ nanocomposites and 20 parts per million (PPM) of coloured (DY) dye were dissolved in 100 ml of deionized distilled water (DDW) and stirred for one hour at room temperature. Following the attainment of adsorption-desorption equilibrium, the mixture was stirred in darkness for 20 minutes. Afterward, the photocatalyst suspension was subjected to UV-visible light irradiation using a 500-watt Halogen lamp [30], positioned at a 15 cm distance from the surface of the DY photocatalyst mixed solution. To ensure a consistent temperature within the photoreactor, water from the water source was re-circulated. Using a UV-Vis spectrometer (model-JASCO V-670) that measures the 200-800 nm range, 5 ml of dye mixed solution was taken from the photoreactor at certain times (every 30 minutes) for up to 120 minutes of light irradiation. The concentrations of DY in samples were determined by measuring the absorbance at 395 nm. Using the experimental synthesis technique as well as Eq. (1), we were able to find the percentage of DY degradation.

$$\text{Degradation efficiency}(\%) = \frac{(CO - C)}{CO} X100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where C is the concentration of DY dye at the initial stage and CO is the concentration at the final stage respectively. We used XRD and SEM analysis to study the variations in crystal structure and morphology of the composite photocatalyst after four reuse experiments.

2.5. characterizations

The X-ray diffraction analysis (Rigaku D/max ultra III diffractometer) and Cu k± radiation (40 Kv, α =0.154 nm) were used to study the crystal structure of the $MoSe_2/MnO_2$ nanocomposite. The XRD pattern was obtained at room temperature among the 2 theta degrees of 10° and 80°. A (JASCO V-750) instrument from Japan was used to record the UV-vis spectrum, which has a wavelength range of 200 to 800 nm. A Bruker tensor 27 Fourier transform infrared (FTIR) spectrometer model was used to look at how the nanocomposites interacted with each other. To look at the shapes, a (JEOL JSM 7500F+) SEM scanning electron microscope with an EDS detector set to 2.0 kV was used to prepare the samples. For the study, a high-resolution transmission electron microscope (HR-TEM) (JEOL JEM -2100 +) working at 200 kV was used. The materials' shapes were studied based on their sizes.

3. Result and discussion

3.1. Characterization of X-Ray diffraction

Fig. 2. (a-c) shows the XRD patterns of $MoSe_2$, MnO_2, and $MoSe_2/MnO_2$, which were determined by XRD together with the samples crystallographic structures and phase compositions. For $MoSe_2$, there were found five strong characteristics of XRD diffraction peaks at 13.3°, 13.6°, 37.8°, 42.2° and 47.4°, which could be well assigned to (002), (100), (103), (104) and (105) diffraction planes $MoSe_2$ structure (JCPDS No: 01-077-1715) respectively [30]. These peaks were confirming the hexagonal structure of $MoSe_2$. As noted in the pattern, the $MoSe_2$ exhibits distinct and strong peaks, indicating a higher degree of crystallinity in the samples. In addition to these prominent peaks, supplementary low-intensity peaks within the 20° to 30° range, associated with the oxidized state of Mo, are also evident in the XRD spectra. The major diffraction peaks can be corresponding to the MnO_2 (JCPDS No: 00-044-0141), where 2θ at 6.91°, 18.1°, 28.8°, 37.5°, 41.9°, 49.8°, 60.2°, and 69.7 confirms the corresponding planes (110), (200), (310), (211), (301), (411), (521) and (541) for MnO_2 respectively [31]. The grain size (D) can be determined using the Debye–Scherrer formula, as shown in Eq. (2), which relies on the full width at half maximum (FWHM) of characteristic crystalline peaks.

$$A = \frac{K\lambda}{\beta cos\theta}$$

where, *D* is the size of the particle, *k* is the Scherrer constant (0.9), λ is the X-ray wavelength (1.5418 A), and β is the full width at half maximum of the particular diffraction angle (θ). The average grain sizes of the samples MnO_2, $MoSe_2$, and $MoSe_2/MnO_2$ were estimated to be 20.05 nm, 19.92 nm, and 12.46 nm respectively. The decline in the crystallite size analytically advocates that there could be the reduction in the grain roughening in the Nano composites. Moreover, the $MoSe_2$ lattice constant of a = b = 3.28 Å, c = 12.92 Å, MnO_2 lattice constant of a = b = 9.78 Å, c = 2.86 Å and $MoSe_2/MnO_2$ lattice constant of a = b = 4.9325 Å, c = 6.9205 Å respectively. In addition to these results, the lattice strain of the samples has been abbreviated to 0.0140, 0.0202, and 0.0070 respectively [32]. The XRD pattern of $MoSe_2/MnO_2$ clearly shows the crystalline peaks of $MoSe_2$ and MnO_2 which confirmed that both patterns of shows in figure.

3.2 FTIR Spectroscopy analysis

The Fourier-transform infrared (FTIR) spectra of $MoSe_2$ and MnO_2, recorded in the range of 400-4000 cm^{-1}, are depicted in Fig. 3. (a) and (b) respectively. The distinctive peaks detected at approximately 484 cm^{-1}, 556 cm^{-1}, 641 cm^{-1}, 781 cm^{-1}, 895 cm^{-1}, 1405 cm^{-1} and 1405 cm^{-1} correspond to the following chemical bonds: (Se-O-Se), (O-Mo-O), (M=O), (Se-O), (COOH), (Mo-OH), and (C-O) bonds, as well as C-H and O-H stretching vibrations, respectively [24]. $MoSe_2$, possessing functional groups like (-OH) and (-COOH), exhibits a negatively charged surface, rendering it highly effective for the degradation of organic dyes. The nanostructured MnO_2 displayed three vibration bands below 1000 cm^{-1}, specifically at 508 cm^{-1}, and 623 cm^{-1}. Each of these vibrational bands is characteristic of the metal-oxygen bond within the MnO6 octahedron, whether it involves the Mn-O or Mn-O-Mn bonding, and they exhibit good consistency with previously reported results. [33]. In Fig. 3. (c), the $MoSe_2/MnO_2$ nanocomposite exhibits shifted peaks corresponding to (Se-O-Se), (O-Mo-O), (M=O), (Se-O), (Mo-OH) and (Mn-O), (Mn-O-Mn) bonds, which are located at 453 cm^{-1}, 609 cm^{-1}, 736 cm^{-1}, 802 cm^{-1}, 1362 cm-1 and 514cm^{-1}, 611 cm^{-1} respectively. Both XRD and FTIR analysis results provide complementary information, confirming the structural and functional characteristics of the $MoSe_2/MnO_2$ nanocomposite simultaneously.

3.3 UV-Vis analysis

The UV-Vis spectra of the synthesized samples are depicted in Fig. 4. (a). The absorption peaks for $MoSe_2$ were observed at wavelengths of 220 nm, 662 nm, 571 nm and 759 nm respectively [34] Likewise, the absorption peaks for MnO_2 were observed at wavelengths of 214 nm, 371 nm, 447 nm and 527 nm respectively [35] whereas for the $MoSe_2/MnO_2$ composite, shifted peaks were observed at 218 nm, 356 nm, 436 nm, 505 nm, 647 nm, and 756 nm respectively. It is noteworthy to mention that the sample containing $MoSe_2/MnO_2$ exhibits the largest absorption peak, indicative of a synchronized effect between the two components. Thus, the band gap values may be inferred from the αhv_2 versus photon energy plot (tauc's plot) using the equation: $\alpha(hv)_2$ = const (hv-Eg) 1/2. The absorption coefficient, Planck's constant, the incident light frequency, and the band gap are represented by α, h, v, and Eg, respectively [36]. Fig. 4 (b) and (c) illustrates an estimated optical band gap by using Tauc's plot relations. The calculated bandgap for $MoSe_2$, MnO_2 and $MoSe_2/MnO_2$ nanocomposite were 1.94 eV, 2.8 eV, and 4.57 eV, respectively. The observed band narrowing in the $MoSe_2/MnO_2$ nanocomposite indicates that the combination can effectively capture a broader spectrum of visible light, including direct sunlight. The enhanced absorption of visible light contributes to the reduction in bandgap observed in the $MoSe_2/MnO_2$ nanocomposite. This is believed to enhance the photocatalytic efficiency of the material when exposed to UV-visible light.

3.4 Morphology analysis

The SEM images of $MoSe_2$ and $MoSe_2/MnO_2$ were shown in Fig. 5 The prepared samples display nanoparticles that are randomly oriented and interconnected, forming a 0D network, as illustrated in Fig. 5. (a-b). The surfaces generally appear smooth, and the diameters of the nanoparticles are similar. In Fig. 5 (c-d), it is evident that the highly localized $MoSe_2$ nanoparticles are uniformly distributed throughout the MnO_2 nanostructure. The $MoSe_2/MnO_2$ nanocomposite exhibits a sheet-like structure. The photocatalytic processes of these materials stand to benefit from their large surface area, high light-collecting capacity, and efficient charge mobility [37], [38]. Furthermore, it's crucial to highlight that the shape of $MoSe_2$ on the nanosheet-like structures can be effectively controlled by increasing the concentrations of reactants for $MoSe_2$ and $MoSe_2/MnO_2$ composite. Additionally, the

quantity of $MoSe_2$ on the sheet-like structure was also enhanced during the same periods, as confirmed by the energy dispersive X-ray (EDX) spectra in Fig. 6. (a-b) and the atomic ratios provided in the table. Additionally, both $MoSe_2$ (Table 1) and $MoSe_2/MnO_2$ (Table 2) composite nanosheets were synthesized using the same hydrothermal process.

The HR-TEM images of both $MoSe_2$ and $MoSe_2/MnO_2$ nanocomposite were depicted in Fig.7. (a-h). Notably, thin and small nanoparticle structures with $MoSe_2$ layers were visible in the prepared $MoSe_2$, as observed in the HR-TEM image captured from the sample edge. A substantial aggregation of $MoSe_2$, as depicted in the shaded area of the figure, suggests the successful synthesis of numerous thin $MoSe_2$ layers using a straightforward hydrothermal method. This observation aligns with the morphology reported in the existing literature [37]. Fig. 7. (e-h) display TEM images of $MoSe_2/MnO_2$ nanocomposites. As per the HR-TEM image, the prepared nanocomposite exhibited a distinct crystal structure. As anticipated, the measured d-spacing of 0.67 nm corresponds to the same value as the $MoSe_2$ (002) interplanar spacing [39]. Additionally, the observed d-spacing of 0.32 nm aligns with the (110) lattice of the MnO_2 nanostructure [39]. The successful formation of the $MoSe_2/MnO_2$ composite was confirmed by the close binding of their lattice fringes, indicating a strong interaction between the two materials. This interaction significantly enhances the electric structure at the interface, making it easier for charge carriers to separate [40]. Furthermore, the composite (002) lattice spacing of 0.70 nm for $MoSe_2$ was notably larger than the 0.67 nm corresponding to the (002) plane in standard $MoSe_2$. This discrepancy could be attributed to the replacement of Se at the Se site by O and the incorporation of O into the $MoSe_2$ structure.

To provide additional insight into the HR-TEM, the Energy Dispersive X-ray Spectroscopy (EDS) mapping of the composites was conducted and is depicted in Fig. 8. (a–f). The EDX spectrum reveals the presence of four elements in the composite: Mo, Se, Mn, and O. This indicates that $MoSe_2$ and MnO_2 in the composite were thoroughly mixed, and all four elements were uniformly distributed. The strong interaction between $MoSe_2$ and MnO_2 facilitated efficient movement of photocarriers, enhancing the effectiveness of the direct photocatalytic process.

3.5. X-ray photoelectron spectroscopy (XPS)

The elemental composition and binding energy of the $MoSe_2/MnO_2$ were analyzed using XPS, as illustrated in Fig. 9. In the XPS spectra of the $MoSe_2/MnO_2$ nanocomposite, peaks corresponding to the C, O, Mn, Mo, and Se elements were observed. The O 1S peak observed at 529.87 eV may be attributed to adventitious oxygen. Typically, the O 1S peak corresponds to the binding energy of oxygen atoms in a material and is often utilized as a standard for calibration purposes. The pattern of Mo 3d embedded in pure $MoSe_2$. It is possible to assign the peaks at 229.0 eV and 232.2 eV to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo^{4+}, then 233.0 eV and 230.3 eV to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo^{5+}, and 235.9 eV and 233.8 eV, to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo^{6+} respectively. The high-resolution Se 3d spectrum of $MoSe_2$, which has two peaks at 54.6 eV and 55.4 eV, respectively, correspond to both Se $3d_{5/2}$ and Se $3d_{3/2}$ of Se in $MoSe_2$, as previously reported [5]. To our obtained peaks of Mo 3d, Se 3d and Mn 2p core-level XPS spectra was shown in Fig. 9. (a-f) respectively. Fig. 9. (b-c) shows the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ peaks of $MoSe_2$ which were shifted at 232.1 eV and 235.1 eV, respectively. These match up nicely with the Mo (4+) chemical states in $MoSe_2$. The Se $3d_{5/2}$ and Se $3d_{3/2}$ shifted peaks of $MoSe_2$ at 49.8 eV and 48.2 eV showed that the Se atoms were in an oxidation chemical state-2 [41]. For MnO_2 nanostructure the Mn $2p_{3/2}$, Mn $2p_{1/2}$ and chemical state of atoms Mn^{4+} peaks also located at 640 eV, 652.5 eV and 642.2 eV, respectively. It also corresponds well with previously reported findings [42]. Fig. 9. (d) shows the high-resolution XPS Mn 2p spectrum of MnO_2. The shifted two peaks of Mn 2p3/2 (640.6 eV) and Mn $2p_{1/2}$ (652.5 eV), were shifted corresponding with the electronic state of Mn4+ [34]. It was confirmed by the MnO_2 presented in $MoSe_2$.

Notably, the peaks that correspond to Mo 3d and Se 3d, as well as the Mn 2p peaks in the composite, shifted towards lower binding energies. This shows that the $MoSe_2/MnO_2$ nanocomposites notably have a strong interaction [43]. Alternatively, three peaks may be seen in the O1 S spectrum. The peaks at 529.8 eV, 531.0 eV, and 532.4 eV in Fig. 9 (e) were identified as the lattice oxygen (Mn-O-Mn) surface absorption hydroxyl groups (Mn-OH) and the water that was absorbed on the surface of the material [44]. The Deconvoluting the C1 S signals into three Gaussian peaks allows for the detection of different chemical states of carbon atoms, as shown in Fig. 9 (f). The strong peak 2 at 284.4 eV is the binding energy of C atoms in the carbon structure with C-C. The small peaks at 285.9 eV and 288.5 eV are the binding energies of carbon from the C-O bond and the C=O-C bond, respectively [45]. In the combination, the hydroxyl group's peak moved slightly towards higher binding energy. In

this case, it suggests that the electron density of the surface hydroxyl groups decreased in the $MoSe_2/MnO_2$ nanocomposite. This phenomenon could be attributed to the strong interfacial interactions present in the $MoSe_2/MnO_2$ nanocomposite. It is also interesting that the greatly higher hydroxyl content on the composite's surface might not only enhance contaminant adsorption via hydrogen production, but also function as electron donors for photogeneration holes (h+). These holes might then be further oxidised to OH-, which allows improved separating of photogenerated carriers and enhancing photocatalytic process.

3.6. Light absorption and photocatalytic properties

To evaluate the photocatalytic performance of the photocatalyst, we employed an organic dye (Direct Yellow) as a model pollutant and the photodegradation occurred under UV-Vis light irradiation. Fig. 10. (a-f) shows the UV-Vis absorbance spectrum of DY dye degrading over (a) $MoSe_2$, (b) MnO_2, and (c) $MoSe_2/MnO_2$ at 120 minutes. The absorption of dye solution doesn't change the optimal conditions for absorption and release in large quantities Fig. 10 (d) displays the photo standard behaviour of the DY dye as analysed in a black test experiment with the photocatalyst adsorption. The $MoSe_2$, MnO_2 and $MoSe_2/MnO_2$ nanocomposite are added to the DY dye solution, and the solution is investigated for 120 min. In comparison to $MoSe_2$, the $MoSe_2/MnO_2$ nanocomposite demonstrates enhanced catalytic performance for the degradation of DY dye when exposed to under UV-Vis light.

The kinetics of the photocatalytic degradation of DY dye were assessed using Equation (2),

$$In\frac{C_t}{C_0} = -kt \quad \text{..... (2)}$$

Where, Co is the initial concentration of the DY dye and Ct is the final concentration at the time; k is the pseudo first-order rate constant (min^{-1}). The pseudo-first order kineties plot is shown in Fig. 10. (e) are shown in table 1: (1) The dye concentration in ppm, (2) degradation efficiency in percentage, (3) kinetic equation, (4) rate constant in k, (5) time in minutes, and (6) R2 values of $MoSe_2$, MnO_2, and $MoSe_2/MnO_2$ nanocomposite. From table. 3. The rate constant of $MoSe_2$ was 0.0290 min^{-1}, the highest among others 0.0136 min^{-1} for MnO_2 and 0.1294 min^{-1} for $MoSe_2/MnO_2$. The enhanced photocatalytic activity observed for $MoSe_2/MnO_2$ was attributed to its morphology. As photocatalysis is a surface phenomenon, therefore the activation of a large surface area is in proportion larger than the quantity of reactive oxygen species produced. The MnO_2 catalyst improves the interaction with DY molecules and dissolves in DI water. Consequently, $MoSe_2/MnO_2$ exhibited higher

photocatalytic efficiency compared to $MoSe_2$ alone. Therefore, the photocatalytic efficiency of $MoSe_2/MnO_2$ was superior to that of $MoSe_2$. Fig. 10 (f) shows the degradation efficiency of the produced photocatalysis under UV-Vis light irradiation. In the as-made materials, the photocatalytic degradation efficiency reached 96% for $MoSe_2/MnO_2$. Further investigation revealed that the $MoSe_2/MnO_2$ composite maintained excellent adsorption and photocatalytic activity. While the adsorption and photocatalytic synergistic reduction rate of Direct Yellow (DY) may have been somewhat lower, the $MoSe_2/MnO_2$ composite still exhibited enhanced adsorption and photocatalytic activity, along with improved durability.

Table 3

1) The Dye concertation in ppm, 2) Efficiency of degradation (%), (3) Kinetic equation, (4) Rate constant (k), (5) time (min) and (6) R^2 values are listed.

3.7. Photocatalytic mechanism of $MoSe_2/MnO_2$ Nanocomposite

Fig.11. illustrates a potential photocatalytic mechanism under irradiation. The observed changes in photocatalytic activity are attributed to variations in phase growth and morphological alterations associated with reduction and oxidation processes. The photocatalytic mechanism typically involves three main steps: (i) Absorption of photons with energy greater than the bandgap of the photocatalyst; (ii) separation, migration, or recombination of electron-hole pairs; and (iii) redox reactions occurring at the surface of the photocatalyst. In general, surface imperfections can serve as sites for the absorption of oxygen and water. Semiconductor photocatalysts, when exposed to air or oxygen, can effectively degrade numerous organic pollutants. When activated by UV-Vis light (hv), $MoSe_2/MnO_2$ generates electron-hole pairs, which act as strong antioxidants and reducing agents. The photocatalyst exhibits efficient performance because holes and photovoltaic electrons do not readily recombine on the surface of the semiconductor. The following expressions outline the photocatalytic mechanisms for the degradation of DY dyes (3)-(9). To enhance photocatalytic activity, the electrons that are produced by light engage in an oxidation-reduction process before recombination. The production of the electron-hole pairs in $MoSe_2/MnO_2$ nanocomposite in the absence of UV-Vis light is an accelerated oxidation process in which electors are activated from VB via substantial light absorption Eq (3). However, when oxygen molecules are absorbed by the excited electrons (ecb-), a number of

reactive substances are formed, including superoxide (•O_2-), hydroxyl (•OH) radicals, and hydrogen peroxide (H_2O_2) Eq. (4-6) [19]

The formation of highly oxidizable positively charged holes (hVB+) under visible light, on the other together, indicates that their source might instantly carry out the oxidative degradation of a yellow dye. In addition, another component of the holes known as hVB+ reacts with the absorbed H_2O and OH- in the DY solution to generate hydroxyl (•OH) radicals (Eq. 7 and 8) [19] as a result. A powerful oxidant, hydroxyl radicals (•OH) may be converted into water and carbon dioxide, two substances that are good for the environment. Eq. (9). $MoSe_2/MnO_2$ induces of •OH radicals and contributes to the development of the dye degradation process. The shortage of super oxide emit can also be seen in the measurements. So, this means that hydroxyl radicals make it possible for the dye degradation. Overall, it was determined that the synthetic $MoSe_2/MnO_2$ composite that has been created showed strong photocatalytic activity when it is exposed to UV light. As a result of influence of the synthesised sample size, quantum confinement, and the catalyst, the energy band gap as the thickness increases gradually towards it crosses the nanoscale. Additionally, the generated photocatalysts' performance in degrading organic pollutants was similar to that of the prior study and is shown in Table 4. In Fig. 11. the proposed photocatalytic mechanism of $MoSe_2/MnO_2$ for the degradation of DY dye is depicted schematically.

$$MoSe_2/MnO_2 + hv \rightarrow MoSe_2/MnO_2\,(h^+_{Vb} + e^-_{Cb}) \quad \ldots\ldots\ldots \quad (3)$$

$$e_{Cb}^- + O_2 \rightarrow O_2\bullet^- \quad \ldots\ldots\ldots \quad (4)$$

$$\bullet O_2^- + 2H^+ + e_{Cb}^- \rightarrow H_2O_2 \quad \ldots\ldots\ldots \quad (5)$$

$$H_2O_2 + e_{Cb}^- \rightarrow OH^- + \bullet OH \quad \ldots\ldots\ldots \quad (6)$$

$$h^+_{Vb} + H_2O \rightarrow H^+ + \bullet OH \quad \ldots\ldots\ldots \quad (7)$$

$$h^+_{Vb} + OH^- \rightarrow \bullet OH \quad \ldots\ldots\ldots \quad (8)$$

$$\bullet OH + dye \rightarrow Co_2 + H_2O \quad \ldots\ldots\ldots \quad (9)$$

Table 4

Comparison of our present work and earlier work.

4.Conclusion

We have successfully developed and synthesized a $MoSe_2/MnO_2$ nanocomposite with enhanced photocatalytic performance using a simple hydrothermal approach. The interface contact, surface morphology, and loading quantities of $MoSe_2$ can be precisely controlled by adjusting the reaction conditions. Under UV-Vis light irradiation, $MoSe_2$ exhibited a maximum absorption-photocatalytic removal rate of 55%, while MnO_2 demonstrated 47%. However, the $MoSe_2/MnO_2$ composite surpassed both individual components with a remarkable removal rate of 96% for Direct Yellow (DY) within 120 minutes. Moreover, the $MoSe_2/MnO_2$ nanocomposite exhibited excellent separation efficiency, retained stable shape, and maintained structural stability, all of which are advantageous for cyclic photocatalytic removal of water pollutants. Our study provides a fundamental understanding of the charge generation, separation, and transfer processes occurring in the $MoSe_2/MnO_2$ nanocomposite under UV-Vis light. The enhanced photocatalytic activity can be attributed to efficient wide-spectrum absorption, a large surface area, rapid electron transfer, and stable and uniform interface contacts. The concepts, techniques, and results obtained in this study could be valuable for the development of prospective photocatalysts with the capability for reducing H_2O and CO_2 under UV-Vis light. Our investigation thoroughly examined the photocatalytic performance of these nanostructures under both ultraviolet UV-Vis light. Our findings unequivocally demonstrate that the $MoSe_2/MnO_2$ nanocomposite exhibits exceptional responsiveness to UV-Vis light and delivers outstanding photocatalytic efficiency.

Data availability Data

Data will be made available on request.

References:

[1] Y. Qu und X. Duan, "Progress, challenge and perspective of heterogeneous photocatalysts", Chem Soc Rev, Bd. 42, Nr. 7, S. 2568–2580, März 2013, doi: 10.1039/c2cs35355e.

[2] P. Zhou, J. Yu, und M. Jaroniec, "All-solid-state Z-scheme photocatalytic systems", Advanced Materials, Bd. 26, Nr. 29. Wiley-VCH Verlag, S. 4920–4935, 6. August 2014. doi: 10.1002/adma.201400288.

[3] H. Wang u. a., "Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances", Chemical Society Reviews, Bd. 43, Nr. 15. Royal Society of Chemistry, S. 5234–5244, 7. August 2014. doi: 10.1039/c4cs00126e.

[4] Y. Li, Q. Wang, H. Wang, J. Tian, und H. Cui, "Novel Ag_2O nanoparticles modified MoS_2 nanoflowers for piezoelectric-assisted full solar spectrum photocatalysis", 2018.

[5] H. Chu u. a., "Hexagonal 2H-$MoSe_2$ broad spectrum active photocatalyst for Cr (VI) reduction", Sci Rep, Bd. 6, Okt. 2016, doi: 10.1038/srep35304.

[6] R. J. Tayade, P. K. Surolia, R. G. Kulkarni, und R. V. Jasra, "Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO_2", Sci Technol Adv Mater, Bd. 8, Nr. 6, S. 455–462, Sep. 2007, doi: 10.1016/j.stam.2007.05.006.

[7] S. Singh, R. Pendurthi, M. Khanuja, S. S. Islam, S. Rajput, und S. M. Shivaprasad, "Copper-doped modified ZnO nanorods to tailor its light assisted charge transfer reactions exploited for photo-electrochemical and photo-catalytic application in environmental remediation", Appl Phys A Mater Sci Process, Bd. 123, Nr. 3, März 2017, doi: 10.1007/s00339-017-0806-8.

[8] R. Sharma, Uma, S. Singh, A. Verma, und M. Khanuja, "Visible light induced bactericidal and photocatalytic activity of hydrothermally synthesized $BiVO_4$ nano-octahedrals", J Photochem Photobiol B, Bd. 162, S. 266–272, Sep. 2016, doi: 10.1016/j.jphotobiol.2016.06.035.

[9] S. Yang u. a., "Molybdenum diselenide nanosheet/carbon nanofiber heterojunctions: Controllable fabrication and enhanced photocatalytic properties with a broad-spectrum

response from visible to infrared light", J Colloid Interface Sci, Bd. 518, S. 1–10, Mai 2018, doi: 10.1016/j.jcis.2018.01.099.

[10] H. Jiang, "Electronic band structures of molybdenum and tungsten dichalcogenides by the GW approach", Journal of Physical Chemistry C, Bd. 116, Nr. 14, S. 7664–7671, Apr. 2012, doi: 10.1021/jp300079d.

[11] R. Coehoorn, C. Haas, J. Dijkstra, C. J. F. Flipse, R. A. De Groot, und A. Wold, "Electronic structure of $MoSe_2$, MoS_2, and WSe_2. I. Band-structure calculations and photoelectron spectroscopy".

[12] D. Zeng u. a., "Construction of network-like and flower-like 2H-$MoSe_2$ nanostructures coupled with porous g-C_3N_4 for noble-metal-free photocatalytic H_2 evolution under visible light", Appl Catalyst B, Bd. 233, S. 26–34, Okt. 2018, doi: 10.1016/j.apcatb.2018.03.102.

[13] Y. Wang u. a., "Construction of Z-scheme $MoSe_2$/CdSe hollow nanostructure with enhanced full spectrum photocatalytic activity", Appl Catal B, Bd. 244, S. 76–86, Mai 2019, doi: 10.1016/j.apcatb.2018.11.033.

[14] T. Xie, Y. Liu, H. Wang, und Z. Wu, "Layered $MoSe_2$ /Bi_2WO_6 composite with P-N heterojunctions as a promising visible-light induced photocatalyst", Appl Surf Sci, Bd. 444, S. 320–329, Juni 2018, doi: 10.1016/j.apsusc.2018.03.072.

[15] I. Khan, M. Sadiq, I. Khan, und K. Saeed, "Manganese dioxide nanoparticles/activated carbon composite as efficient UV and visible-light photocatalyst", Environmental Science and Pollution Research, Bd. 26, Nr. 5, S. 5140–5154, Feb. 2019, doi: 10.1007/s11356-018-4055-y.

[16] Y. Shi u. a., "2D/1D protonated g-C_3N_4/α-MnO_2 Z-scheme heterojunction with enhanced visible-light photocatalytic efficiency", Ceram Int, Bd. 46, Nr. 16, S. 25905–25914, Nov. 2020, doi: 10.1016/j.ceramint.2020.07.075.

[17] S. Panimalar u. a., "Studies of MnO_2/g-C_3N_4 heterostructure efficient of visible light photocatalyst for pollutants degradation by sol-gel technique", Surfaces and Interfaces, Bd. 20, Sep. 2020, doi: 10.1016/j.surfin.2020.100512.

[18] J. Zhao, J. Nan, Z. Zhao, N. Li, J. Liu, und F. Cui, "Energy-efficient fabrication of a novel multivalence Mn_3O_4-MnO_2 heterojunction for dye degradation under visible

light irradiation", Appl Catal B, Bd. 202, S. 509–517, März 2017, doi: 10.1016/j.apcatb.2016.09.065.

[19] H. Mittal und M. Khanuja, "Nanosheets-and nano-urchins-like nanostructures of $MoSe_2$ for photocatalytic water purification: kinetics and reusability study", doi: 10.1007/s11356-019-06275-8/Published.

[20] H. Xu, J. Zhang, Y. Chen, H. Lu, J. Zhuang, und J. Li, "Synthesis of polyaniline-modified MnO_2 composite nanorods and their photocatalytic application", Mater Lett, Bd. 117, S. 21–23, Feb. 2014, doi: 10.1016/j.matlet.2013.11.089.

[21] B. Yin, S. Zhang, Y. Jiao, Y. Liu, F. Qu, und X. Wu, "Crystl Eng Comm Facile synthesis of ultralong MnO_2 nanowires as high-performance supercapacitor electrodes and photocatalysts with enhanced photocatalytic activities". [Online]. Verfügbar unter: www.rsc.org/crystengcomm

[22] X. Zheng, L. Yang, Y. Li, L. Yang, und S. Luo, "Direct Z-scheme $MoSe_2$ decorating TiO_2 nanotube arrays photocatalyst for water decontamination", Electrochim Acta, Bd. 298, S. 663–669, März 2019, doi: 10.1016/j.electacta.2018.12.130.

[23] J. Zhang, X. Zan, X. Shen, und H. Zheng, "Preparation of direct Z-scheme hierarchical MoS_2/MnO_2 composite for efficient adsorption and wide spectrum photocatalytic degradation of organic pollutants in water". [Online]. Verfügbar unter: https://ssrn.com/abstract=4279267

[24] I. Siddiqui, H. Mittal, V. K. Kohli, P. Gautam, M. Ali, und M. Khanuja, "Hydrothermally synthesized micron sized, broom-shaped $MoSe_2$ nanostructures for superior photocatalytic water purification", Mater Res Express, Bd. 5, Nr. 12, Dez. 2018, doi: 10.1088/2053-1591/aae241.

[25] M. Xue u. a., "The direct synthesis of mesoporous structured MnO_2/TiO_2 nanocomposite: A novel visible-light active photocatalyst with large pore size", Nanotechnology, Bd. 19, Nr. 18, Mai 2008, doi: 10.1088/0957-4484/19/18/185604.

[26] X. Zheng, Z. Han, W. Yang, F. Qu, B. Liu, und X. Wu, "3D Co_3O_4@MnO_2 heterostructures grown on a flexible substrate and their applications in supercapacitor electrodes and photocatalysts", Dalton Transactions, Bd. 45, Nr. 42, S. 16850–16858, 2016, doi: 10.1039/c6dt03076a.

[27] J. Fei u. a., “Controlled preparation of MnO_2 hierarchical hollow nanostructures and their application in water treatment”, Advanced Materials, Bd. 20, Nr. 3, S. 452–456, Feb. 2008, doi: 10.1002/adma.200701231.

[28] M. F. Warsi, M. Bilal, S. Zulfiqar, M. U. Khalid, P. O. Agboola, und I. Shakir, “Enhanced visible light driven Photocatalytic activity of MnO_2 nanomaterials and their hybrid structure with carbon nanotubes”, Mater Res Express, Bd. 7, Nr. 10, Okt. 2020, doi: 10.1088/2053-1591/abbf8d.

[29] M. Sugantha, P. A. Ramakrishnan, A. M. Hermann, C. P. Warmsingh, und D. S. Ginley, “Nanostructured MnO_2 for Li batteries”, 2003. [Online]. Verfügbar unter: www.sciencedirect.comwww.elsevier.com/locate/ijhydene

[30] J. Sawadogo, M. Bougouma, J. Legma, und M. Ogletree, “Determination of stoichiometry from polycrystalline powders of transition metals lamellar dichalcogenides: $MoSe_2$, WSe_2, obtained by synthesis in laboratory”, Int J Biol Chem Sci, Bd. 9, Nr. 1, S. 454, Juni 2015, doi: 10.4314/ijbcs.v9i1.39.

[31] C. Shi u. a., “Synthesis of layered MnO_2 nanosheets for enhanced oxygen reduction reaction catalytic activity”, Electrochim Acta, Bd. 132, S. 239–243, Juni 2014, doi: 10.1016/j.electacta.2014.03.150.

[32] T. Elangovan, P. Kuppusami, R. Thirumurugesan, C. Sudha, E. Mohandas, und D. Mangalaraj, “A study on the influence of copper content in CrN/Cu nanocomposite thin films prepared by pulsed dc magnetron sputtering”, in Journal of Nanoscience and Nanotechnology, Sep. 2009, S. 5436–5440. doi: 10.1166/jnn.2009.1129.

[33] M. F. Warsi, M. Bilal, S. Zulfiqar, M. U. Khalid, P. O. Agboola, und I. Shakir, “Enhanced visible light driven Photocatalytic activity of MnO_2 nanomaterials and their hybrid structure with carbon nanotubes”, Mater Res Express, Bd. 7, Nr. 10, Okt. 2020, doi: 10.1088/2053-1591/abbf8d.

[34] H. Mittal, A. Ivaturi, und M. Khanuja, “$MoSe_2$-modified ZIF-8 novel nanocomposite for photocatalytic remediation of textile dye and antibiotic-contaminated wastewater”, Environmental Science and Pollution Research, Bd. 30, Nr. 2, S. 4151–4165, Jan. 2023, doi: 10.1007/s11356-022-22487-x.

[35] S. Vijayalakshmi und E. Kumar, “Synthesis and Investigations on structural, optical, thermal and electrical conductivity of α-MnO_2 nanoparticles”, 2019. [Online]. Verfügbar unter: https://www.researchgate.net/publication/335397323

[36] S. M. EL-Dafrawy, M. Tarek, S. Samra, und S. M. Hassan, “Synthesis, photocatalytic and antidiabetic properties of ZnO/PVA nanoparticles”, Sci Rep, Bd. 11, Nr. 1, Dez. 2021, doi: 10.1038/s41598-021-90846-8.

[37] Z. Lu u. a., “Enhanced interfacial electron transfer and boosted visible-light photocatalytic hydrogen evolution activity of g-C_3N_4 by noble-metal-free $MoSe_2$ nanoparticles”, J Mater Sci, Bd. 55, Nr. 27, S. 13114–13126, Sep. 2020, doi: 10.1007/s10853-020-04945-4.

[38] M. F. Warsi, M. Bilal, S. Zulfiqar, M. U. Khalid, P. O. Agboola, und I. Shakir, “Enhanced visible light driven Photocatalytic activity of MnO_2 nanomaterials and their hybrid structure with carbon nanotubes”, Mater Res Express, Bd. 7, Nr. 10, Okt. 2020, doi: 10.1088/2053-1591/abbf8d.

[39] S. Rong, T. He, und P. Zhang, “Self-assembly of MnO_2 nanostructures into high purity three-dimensional framework for high efficiency formaldehyde mineralization”, Appl Catal B, Bd. 267, Juni 2020, doi: 10.1016/j.apcatb.2019.118375.

[40] J. Zhang, Y. Hu, H. Zheng, und P. Zhang, “Hierarchical Z-scheme 1D/2D architecture with TiO_2 nanowires decorated by MnO_2 nanosheets for efficient adsorption and full spectrum photocatalytic degradation of organic pollutants”, Catal Sci Technol, Bd. 10, Nr. 11, S. 3603–3612, Juni 2020, doi: 10.1039/d0cy00419g.

[41] J. Lu u. a., “Identifying and Visualizing the Edge Terminations of Single-Layer $MoSe_2$ Island Epitaxially Grown on Au (111)”, ACS Nano, Bd. 11, Nr. 2, S. 1689–1695, Feb. 2017, doi: 10.1021/acsnano.6b07512.

[42] A. E. Reddy u. a., “Fabrication of a snail shell-like structured MnO_2@$CoNiO_2$ composite electrode for high performance supercapacitors”, RSC Adv, Bd. 7, Nr. 20, S. 12301–12308, 2017, doi: 10.1039/c7ra01126a.

[43] X. Li und K. Peng, “$MoSe_2$/montmorillonite composite nanosheets: Hydrothermal synthesis, structural characteristics, and enhanced photocatalytic activity”, Minerals, Bd. 8, Nr. 7, Juli 2018, doi: 10.3390/min8070268.

[44] Z. Li, W. Kang, Z. Han, J. Yan, B. Cheng, und Y. Liu, "Hierarchical MnOx@PVDF/MWCNTs tree-like nanofiber membrane with high catalytic oxidation activity", J Alloys Compd, Bd. 780, S. 805–815, Apr. 2019, doi: 10.1016/j.jallcom.2018.11.405.

[45] L. Huang, X. Luo, C. Chen, und Q. Jiang, "A high specific capacity aqueous zinc-manganese battery with a ε-MnO_2 cathode", Ionics (Kiel), Bd. 27, Nr. 9, S. 3933–3941, Sep. 2021, doi: 10.1007/s11581-021-04160-4.

[46] D. Monga und S. Basu, "Tuning the photocatalytic/electrocatalytic properties of MoS_2/$MoSe_2$ heterostructures by varying the weight ratios for enhanced wastewater treatment and hydrogen production", RSC Adv, Bd. 11, Nr. 37, S. 22585–22597, Juni 2021, doi: 10.1039/d1ra01760h.

[47] G. Khabiri u. a., "A novel α-Fe_2O_3@MoS_2QDs heterostructure for enhanced visible-light photocatalytic performance using ultrasonication approach", Ceram Int, Bd. 46, Nr. 11, S. 19600–19608, Aug. 2020, doi: 10.1016/j.ceramint.2020.05.021.

[48] J. Zhang, X. Zan, X. Shen, und H. Zheng, "Preparation of direct Z-scheme hierarchical MoS_2/MnO_2 composite for efficient adsorption and wide spectrum photocatalytic degradation of organic pollutants in water". [Online]. Verfügbar unter: https://ssrn.com/abstract=4279267

[49] I. Siddiqui, H. Mittal, V. K. Kohli, P. Gautam, M. Ali, und M. Khanuja, "Hydrothermally synthesized micron sized, broom-shaped $MoSe_2$ nanostructures for superior photocatalytic water purification", Mater Res Express, Bd. 5, Nr. 12, Dez. 2018, doi: 10.1088/2053-1591/aae241.

[50] J. Zhao, J. Nan, Z. Zhao, N. Li, J. Liu, und F. Cui, "Energy-efficient fabrication of a novel multivalence Mn_3O_4-MnO_2 heterojunction for dye degradation under visible light irradiation", Appl Catal B, Bd. 202, S. 509–517, März 2017, doi: 10.1016/j.apcatb.2016.09.065.

[51] X. Zheng, Z. Han, W. Yang, F. Qu, B. Liu, und X. Wu, "3D Co_3O_4@MnO_2 heterostructures grown on a flexible substrate and their applications in supercapacitor electrodes and photocatalysts", Dalton Transactions, Bd. 45, Nr. 42, S. 16850–16858, 2016, doi: 10.1039/c6dt03076a.