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Honey Mittal, Manika Khanuja

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Journal Pre-proof



### Optimization of MoSe<sub>2</sub> nanostructure by surface modification using conducting polymer for degradation of cationic and anionic dye: photocatalysis mechanism, reaction kinetics and intermediate product study

Honey Mittal and Manika Khanuja\*

Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi, India manikakhanuja@gmail.com

#### Abstract

In the present work, optimum nanocomposites of MoSe<sub>2</sub>-PANI (polyaniline) were successfully synthesized by modifying the surface of MoSe<sub>2</sub> with PANI to enhance the photocatalytic efficiency. A series of MoSe<sub>2</sub>-PANI nanocomposites with different MoSe<sub>2</sub> to PANI weight percent ratios (1:1, 1:2, 1:3 and 2:1) were prepared by in-situ polymerization method to study the effect of variation of surface charge on photocatalytic efficiency. Samples were characterized using X-Ray Diffractometer (XRD), Field-Emission Scanning Electron Microscopy (FESEM), Fourier-transform infrared (FTIR) spectroscopy, Diffuse Reflectance spectroscopy (DRS), zeta potential measurements, Photoluminescence (PL) spectroscopy and time-correlated single photon counting (TCSPC). Comparative photocatalytic degradation of cationic dye (Rhodamine B) and anionic dye (Congo red) were performed. The mechanism of degradation was explained using active species trapping experiments. Intermediate products formed during the degradation process were determined using Liquid chromatography-mass spectroscopy (LC-MS). Reaction kinetics for the adsorption of dyes were also studied. MoSe<sub>2</sub>-PANI nanocomposite having MoSe<sub>2</sub>:PANI in 2:1 ratio showed the most significant charge separation and optimized surface charge for photocatalytic degradation of cationic dye.

#### Keywords

MoSe<sub>2</sub>-PANI; photocatalysis; zeta potential; TCSPC; LC-MS

#### Introduction

Carcinogenic wastes and toxic pollutants viz. Rhodamine B (RhB) and Congo Red (CR) in water are causing serious environmental problems not only because of their color which results in health problems but also because their degradation products are toxic to various forms of

human and marine life [1-3]. Photocatalysis is an encouraging method for wastewater treatment as it converts toxic organic pollutants into less toxic products [4-8]. MoSe<sub>2</sub> is a promising candidate for multiple applications including catalysis, energy storage, lubricants and electrodes in high energy density batteries due to its narrow band gap, large surface area and high chemical stability [9]. MoSe<sub>2</sub> can be obtained by numerous physical and chemical methods including mechanical exfoliation, chemical vapor deposition, liquid-phase exfoliation, hydrothermal, solvothermal and colloidal route [9-11]. In this study, MoSe<sub>2</sub> nanostructures were synthesized by a facile hydrothermal method. This method is better than other conventional methods due to its low cost, control over growth, large scale production and simplicity as no catalyst, seed, and harmful surfactants are used [12-14]. In hydrothermal process, sample can be obtained directly from the solution, resulting in uniformity of nucleation and size of the nanoparticles. MoSe<sub>2</sub> has some shortcomings as a photocatalyst, including lack of porosity, slow rate of charge transfer, low conductivity and high recombination probability of photogenerated electron-hole pairs [15]. Interacting MoSe<sub>2</sub> with conductive material, such as carbon nanotubes, graphene, conducting polymers could possibly decrease their resistance [15,16]. Porous materials, such as polyaniline (PANI) can enhance photocatalytic efficiency because of its large specific surface area and high absorption capabilities [17,18]. Nanocomposites of inorganic materials and conductive polymers have been widely studied in the field of photocatalysis as heterojunction improves the separation probability of electron and hole by providing an internal electric field [19-23]. In photocatalysis, movement of charge carriers and redox reactions take place at the surface of the photocatalyst [24, 25]. In this way, surface modification is an effective method of enhancing photocatalytic activity.

Main focuses of current study were to (i) synthesize nanocomposites of MoSe<sub>2</sub>-PANI in different weight percent ratios by in-situ oxidative polymerization method, (ii) investigate the effect of weight ratio of MoSe<sub>2</sub> to PANI on the photocatalytic activity for degradation of cationic (RhB) and anionic (CR) dyes and (iii) study of interaction between dye and photocatalyst surface as a function of surface charge. This study highlighted the effect of modified surface on photocatalytic degradation efficiency.

#### Materials

Sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>, 99.99%) and hydrochloric acid (HCl.H<sub>2</sub>O, 99.96%) were purchased from Thermo fisher scientific India Pvt. Ltd. Selenium (Se, 99.99%), Hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O 98%), tert-butyl alcohol ((CH<sub>3</sub>)<sub>3</sub>COH), Congo Red (C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub>) and aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, 99.98%) were purchased from Central Drug House Pvt. Ltd. Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with max impurity limit of 0.005 % were purchased from Sisco research laboratories Pvt. Ltd. p-benzoquinone (C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>) was supplied by Molychem Pvt. Ltd. Potassium iodide (KI) was supplied by Pallav chemicals and solvents Pvt. Ltd. Rhodamine B (C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>) was supplied by RHB Loba Chemie Pvt. Ltd.

#### **Synthesis Process**

#### Synthesis of MoSe<sub>2</sub>

Sodium molybdate (0.02 moles) was dissolved in 50 mL of milli-Q water under constant stirring at room temperature until a transparent solution is obtained. In a separate beaker, selenium powder (0.04 moles) is dispersed in 10 mL of hydrazine hydrate under constant stirring for 15 minutes to get a black suspension. Selenium solution was dropwise added to sodium molybdate solution and stirred for 20 minutes. Finally, the dark brown color solution was collected and transferred to the hydrothermal bomb and put in the furnace for 24 hours at 200°C. The hydrothermal bomb is then allowed to cool down at room temperature. The obtained dark black color solution is sequentially washed with milli-Q water and ethanol followed by drying at 50°C for 4 hours [14].

#### Synthesis of PANI

1mL of aniline, 3mL of HCl and 16mL of milli-Q water were mixed using magnetic stirrer and the obtained solution was put in the refrigerator for 3 hours. 0.1M in 50 mL of APS was added to the refrigerated solution in an ice bath under constant stirring for 3 hours. Finally, the collected dark green color solution was sequentially washed with milli-Q water and ethanol, followed by drying at 50 °C for 4 hours.

#### Synthesis of MoSe<sub>2</sub>-PANI composite

The schematic of MoSe<sub>2</sub>-PANI synthesis is as shown in figure 1. Synthesized MoSe<sub>2</sub> powder was ultrasonicated in 30mL of milli-Q water for 20 min and mixed with a refrigerated solution of HCl, aniline and milli-Q water in an ice water bath under constant stirring. After 10 minutes, 0.1M in 50 ml of APS was added to the above solution and stirred for 3 hours. Finally, the dark

green color solution was collected and washed with milli-Q water and ethanol. The sample was dried at 50 °C for 4 hours [15]. Similarly, MoSe<sub>2</sub>-PANI nanocomposites with varying weight ratios of MoSe<sub>2</sub> to PANI {(1:1(0.1g MoSe<sub>2</sub>), 1:2 (0.05g MoSe<sub>2</sub>), 1:3 (0.025g MoSe<sub>2</sub>) and 2:1(0.20g MoSe<sub>2</sub>)} were prepared by the in-situ oxidative polymerization method and labelled as MP11, MP12, MP13 and MP 21, respectively.



Figure 1: Schematic of MoSe<sub>2</sub>-PANI nanocomposite synthesis

The morphologies of the as-prepared nanocomposites were observed using a Field Emission Scanning Electron Microscopy (FESEM) (Quanta 3D FEG, (FEI's)). The crystalline structures of MoSe<sub>2</sub>-PANI nanocomposites were characterized by X-ray diffractometer (XRD) (Rigaku Smart Lab) with 40kV tube voltage and 30mA current. Samples were scanned in the range of 2θ from 5° to 90° with a step size of 0.02°. Band gap of the materials was determined using UV-Vis diffuse reflectance spectroscopy (Agilent technologies, Cary 100 series). Functional groups on the surface of nanocomposites were analyzed by Fourier transform infra-red (FTIR) spectroscopy (Bruker Tensor 37 FTIR spectrometer) in the range of 500-2000 cm<sup>-1</sup>. Photoluminescence (PL) spectroscopy was performed at room temperature on Cary Eclipse (MY15120007) instrument using 350 nm emissions source with a scan rate of 600nm/min. Time correlated-single photon counting (TCSPC) was performed using Horiba (DeltaFlex01-DD) spectrometer. The signals were collected at the excitonic emission of 284nm wavelength. The emission decay data were analyzed and fitted with triexponential kinetics model which generates

lifetime values and the corresponding amplitudes. Surface charge of the nanocomposites was determined using Zeta potential measurements (Zetasizer Ver. 7.12, MAL1192921 from Malvern instrument Ltd.) at room temperature using milli-Q water as dispersant.

The concentration of dyes was taken from absorbance wavelength using UV-Vis spectroscopy (Agilent technologies, Cary 100 series). 1 mL of sample was taken after fixed interval of time for 150 minutes and analyzed using UV-Vis spectrophotometer. The intermediates after degradation of dye were detected by Liquid Chromatography-Mass Spectroscopy (LC-MS) (Agilent Technologies, 6540 UHD Accurate-Mass Q-TOF LC-MS). The samples were separated chromatographically using Agilent extend C18 (1.8 micrometer 2.1\*50 mm) column at a flow rate of 0.3 mL/min using nitrogen gas.

#### **Result and Discussion**

Figure 2 (a-f) showed the SEM images of pure MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples, respectively. Figure 2 (a) showed SEM image of ultrathin uniform MoSe<sub>2</sub> nanostructure. Figure 2 (b) showed the flake-like morphology of PANI, indicating the formation of a cross-linked polymeric network with a high degree of porosity. It is observed in figure 2 (c-f) that MoSe<sub>2</sub> nanostructures and PANI are highly interconnected. The effect of change in weight ratio of MoSe<sub>2</sub> to PANI on morphology is clearly evident through FESEM images.



#### Figure 2: FESEM images of (a) pure MoSe<sub>2</sub>, (b) pure PANI, (c) MP11, (d) MP12, (e) MP13 and (f) MP21 samples

Figure 3 (i, a-f) showed XRD diffractograms of MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples, respectively. Symbols \* and # were assigned for MoSe<sub>2</sub> and PANI peaks, respectively. For MoSe<sub>2</sub>, peaks observed at 2 $\theta$  (hkl): 13.7° (002), 23.4° (004), 29.5° (100), 41.3° (006), 47.5° (105), 56.1° (110) and 65.3° (200) (JCPDS No. 29-0914) [26,27]. PANI peaks observed at 2 $\theta$  (hkl): 8.9° (001), 14.7° (010), 20.6° (011), 25.8° (020) and 27.4° (200) (JCPDS No. 53-1891) [28]. In sample MP11, peaks corresponding to both MoSe<sub>2</sub> and PANI peaks were present as shown by \* and # symbols, respectively. As evident, in samples MP12 and MP13 peaks corresponding to PANI were dominant whereas in sample MP21, peaks corresponding to MoSe<sub>2</sub> were dominant. Thus, the XRD peaks intensity in XRD diffractograms are in accordance with the weight ratio of MoSe<sub>2</sub> to PANI in different MoSe<sub>2</sub>-PANI nanocomposites.

In order to confirm the functional groups present in nanocomposites, FTIR spectra of MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples were recorded, as shown in figure 3 (ii, a-f). Symbols \* and # are assigned to MoSe<sub>2</sub> and PANI peaks. The characteristics peaks of PANI were observed at 795 cm<sup>-1</sup>, 1255 cm<sup>-1</sup>, 1297 cm<sup>-1</sup> and 1420 cm<sup>-1</sup>, corresponding to aromatic C-H out of plane deformation vibration, C-N<sup>+</sup> stretching, C-N stretching and benzenoid ring stretching of secondary aromatic amine, respectively [29]. Peaks of MoSe<sub>2</sub> were observed at 675 cm<sup>-1</sup>, 1040 cm<sup>-1</sup> and 1694 cm<sup>-1</sup> corresponded to deformation of the benzene ring, Se-O bond and C=O, COO<sup>-</sup> stretching bonds, respectively [30,31]. In samples MP11 and MP21, peaks corresponding to MoSe<sub>2</sub> were dominant whereas in samples MP12 and MP13, peaks corresponding to PANI were dominant. Adsorption of CR and RhB dyes onto the surface of MoSe<sub>2</sub>-PANI nanocomposite depends on the functional groups. Nitrogen and oxygen containing functional groups (SO<sup>3-</sup>) of dye and positive groups (NH<sup>+</sup>) present on photocatalyst react via electrostatic interaction.



Figure 3 (i) XRD diffractograms and (ii) FTIR spectra of (a) MoSe<sub>2</sub>, (b) PANI, (c) MP11, (d) MP12, (e) MP13 and (f) MP21 samples

The optical absorbance ability of MoSe<sub>2</sub>-PANI nanocomposites and pure samples were examined by UV-Vis diffuse reflectance spectroscopy (DRS) as shown in figure 4(a). As observed from DRS spectra, MoSe<sub>2</sub>-PANI nanocomposites exhibited absorption ability in the visible region and can be excited efficiently by the solar light. The corresponding band gap energy value can be calculated by using a Kubelka-Munk (KM) equation (i).

$$F(R) = \frac{(1-R)^2}{2R}$$
 (i)

where F(R) is the Kubelka-Munk function and R is the reflectance of material. The band gap of the material was determined by the x-axis intercept of  $[hv(F(R)]^n$  vs hv plot, value of n is determined by the nature of the semiconductor: n=2 for direct and n=1/2 for indirect band transition[32]. Band gap of pure MoSe<sub>2</sub> and PANI was observed to be 1.82eV and 3.46eV, considering indirect and direct optical transition respectively [17,33]. Figure 4 (b) showed KM plot assuming direct absorption behavior of MP11, MP12, MP13, PANI samples and figure 4(c) showed the KM plot assuming indirect absorption behavior of MoSe<sub>2</sub> and MP21 samples. In samples MP12 and MP13, direct optical transitions were assumed due to higher concentration of PANI in MoSe<sub>2</sub>-PANI (1:2 and 1:3) nanocomposites. However, in order to study the effect of gradual variation of PANI concentration on energy band gap, direct optical transition is assumed in MP11 (MoSe2: PANI = 1:1) nanocomposite. The direct band gap of MP11, MP12, and MP13 were found to be 2.0eV, 3.0eV and 3.1eV respectively. However, in sample MP21, indirect optical transitions were taken into account due to the higher concentration of MoSe<sub>2</sub> in MoSe<sub>2</sub>-PANI (2:1) nanocomposite. The indirect band gap of MP21 was found to be 2.15eV. The values obtained for energy band gap are in good agreement with the concentration of MoSe<sub>2</sub>:PANI in MoSe<sub>2</sub>-PANI nanocomposite.



Figure 4: (a) The UV-Vis diffuse reflectance spectra (DRS) and KM plots assuming (b) direct absorption behavior of MP11, MP12, MP13, PANI samples and (c) indirect absorption behavior of MoSe<sub>2</sub> and MP21 samples

Photoluminescence spectroscopy (PL) is an ideal characterization technique for the determination of the defects in materials [34]. Figure 5 (a) showed the PL spectra of the MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples. The PL spectra of all the samples were taken

with an excitation wavelength of 350 nm. PL emission peaks were observed at 404 nm and 430 nm corresponding to  $\pi^*$ - $\pi$  transition and polaronic band of PANI, respectively and a shoulder peak around 453 nm is also observed [35]. In sample MP21, PL intensity is significantly lower as compared to other MoSe<sub>2</sub>-PANI (MP11, MP12 and MP13) nanocomposite. The decreased PL intensity corresponds to increase in defects which help in improvement of photocatalytic degradation efficiency [36]. The lower recombination rate is helpful for creating more photoactive species such as  $O_2^-$  and OH radical, which are responsible for higher photocatalytic efficiency [37-39].

Time-correlated single photon counting (TCSPC) was used to determine the recombination time. In TCSPC, the time between sample excitation by a pulsed laser and the arrival of the emitted photon at the detector is measured [40-42]. The signals collected after excitation were detected and then correlated using a single photon counting card. Upon laser excitation (280nm), the photoexcited electrons of PANI were moved to MoSe<sub>2</sub> due to the higher CB of PANI (-1.9 eV) than that of MoSe<sub>2</sub> (-0.8 eV). The electrons transferred from PANI to MoSe<sub>2</sub> were determined by comparing the emission decay kinetics between PANI and MoSe<sub>2</sub>-PANI nanocomposites.

The fitting of data and calculation were done using triexponential function with an equation as shown in eq. (ii).

$$y = A_1 + B_1 e^{\left(-\frac{i}{T_1}\right)} + B_2 e^{\left(-\frac{i}{T_2}\right)} + B_3 e^{\left(-\frac{i}{T_3}\right)}$$
(ii)

where  $B_1$ ,  $B_2$  and  $B_3$  are amplitude of components 1, 2 and 3, respectively;  $T_1$ ,  $T_2$  and  $T_3$  corresponded to the life-time of component 1, 2 and 3, respectively.

Value of electron-transfer rate constant (ket) was calculated using equation (iii):

$$k_{et} (MoSe_2 - PANI) = \frac{1}{\langle T_{(PANI)} \rangle} - \frac{1}{\langle T_{(MoSe_2 - PANI)} \rangle}$$
 (iii)

The emission decay data were analyzed and fitted with an appropriate kinetics. Figure 5 (b) showed the decay-associated spectra of the  $MoSe_2$ -PANI nanocomposites upon excitation with 284 nm laser source. These spectra were fitted with triexponential function and yields slow (T<sub>2</sub>) and fast (T<sub>3</sub>) decay components, corresponded to radiative and nonradiative relaxation pathway, respectively [24]. All the fitting results were summarized in Table 1. The average life-time (T) of samples MP11, MP12, MP13 and MP21 were observed to be 3.10 ns, 6.56 ns, 5.78 ns and 16.71 ns, respectively. For pristine PANI and MoSe<sub>2</sub> samples, average life-time was 1.41 ns and 17.95 ns, respectively. With reference to pristine PANI, in MP21 nanocomposite the contribution of

slow decay time  $(T_2)$  increases 11 times from 31.91 ns to 336.25 ns with corresponding increase in contribution  $(f_2)$  from 22.44% to 93.83%. However, the decrease in average life-time (T) in sample MP13 as compared to sample MP12 is attributed to dominance of charge recombination instead of electron scavenging at MoSe<sub>2</sub>/PANI interface. This observation is in agreement with the earlier reports on CdS-CdSnO<sub>3</sub> composite [24]. The enhanced life-time in MP21 sample implies significant charge separation property leading to enhanced photocatalytic degradation efficiency. Calculated ket values of MP11, MP12, MP13 and MP21 samples with reference to pristine PANI were 0.300 ns<sup>-1</sup>, 0.557 ns<sup>-1</sup>, 0.537 ns<sup>-1</sup> and 0.650 ns<sup>-1</sup>. MP21 has maximum ket value, verifying the relatively significant electronic interaction of MoSe<sub>2</sub> and PANI. It was signified from the results that MoSe<sub>2</sub>-PANI nanocomposite with MoSe<sub>2</sub>:PANI in 2:1 ratio (MP21 sample) influenced the charge carrier kinetics of MoSe<sub>2</sub> more considerably by attracting more photogenerated electrons from PANI which results in lower recombination rate in MoSe<sub>2</sub>-PANI nanocomposite. The significant charge separation property (life-time (T) = 16.71 ns and electron transfer rate constant ( $k_{et}$ ) = 0.650 ns<sup>-1</sup>) of MP21 is due to dominated electron scavenging over interfacial charge recombination, thus, providing abundant charge carriers for photocatalytic degradation utilization [21,42].



Figure 5: (a) PL spectra and (b) TCSPC of MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples

Sample	Lifetime (ns)		Relative Intensity			Average	$\chi^2$	$\mathbf{K}_{et}$ (ns <sup>-1</sup> )	
				(%)			lifetime		
	<b>T</b> <sub>1</sub>	<b>T</b> <sub>2</sub>	<b>T</b> <sub>3</sub>	f <sub>1</sub>	<b>f</b> <sub>2</sub>	f <sub>3</sub>	T(ns)		
MP11	4.79	146.86	0.62	13.44	68.53	18.03	3.10	1.97	0.396
MP12	5 17	254.62	0.73	6.07	83.83	10.10	6.56	1 45	0 557
	5.17	231.02	0.75	0.07	05.05	10.10	0.50	1.15	0.557
MP13	5.55	229.69	0.76	7.10	80.9	-12.0	5.78	1.52	0.537
MP21	5.25	336.25	0.73	2.32	93.83	3.84	16.71	1.94	0.650
PANI	4.93	31.91	0.63	37	22.44	39.72	1.41	1.32	-
MoSe <sub>2</sub>	3.73	257.06	0.51	1.87	95.75	2.38	17.95	3.23	-

Table 1: l	Kinetic analysis	of emission decay	v for MoSe <sub>2</sub> ,	PANI, MP11	l, MP12, N	/IP13 and
MP21 sar	nples					

#### **Photocatalytic experiment**

The photocatalytic degradation efficiency of the prepared nanocomposites was determined by the degradation of CR and RhB dye under irradiation from a xenon lamp. For this experiment, 100 ml of each dye solution (5 mg/L) and 20 mg of prepared photocatalyst (MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21) were used. The solutions were stirred for 150 minutes under the xenon arc lamp. The concentration of dye was determined using UV-Vis spectroscopy after fixed interval of time. As shown in figure 6 (a & c), degradation efficiency (η) of MoSe<sub>2</sub>, PANI, MP11, MP11, MP12, MP13 and MP21 for CR dye was 8.4%, 23.4%, 83.3%, 99.8%, 99.06% and 88.6%, respectively. Thus, all nanocomposites of MoSe<sub>2</sub>-PANI were very efficient for degradation of CR dye as compared to pure MoSe<sub>2</sub> and PANI samples. On the contrary, as

observed from figure 6 (b & d), degradation efficiency (η) of MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 for RhB dye was 3%, 17.2%, 34%, 23%, 22% and 83.17%, respectively. Thus, the optimized nanocomposite for photocatalytic degradation of RhB and CR dye was MP21 as it showed high photocatalytic degradation efficiency for both cationic and anionic dyes. MP21 has high photocatalytic degradation efficiency due to its optimized surface charge as observed from zeta potential and lower recombination rate of electron and hole as observed from PL and TCSPC. Some of the previously reported results of photocatalytic degradation of dyes and organic compounds using MoSe<sub>2</sub>, PANI and their composites were summarized in Table 2. As evident from the summarized reports that present MoSe<sub>2</sub>-PANI (MP21) nanocomposite showed superior photocatalytic efficiency for both cationic as well as anionic dyes.



## Figure 6: $C/C_0$ vs time plot for degradation of (a) CR and (b) RhB dye; degradation efficiency ( $\eta$ ) vs time plot for degradation of (c) CR and (d) RhB dye

#### Table 2: State of art of photocatalytic degradation efficiency of MoSe<sub>2</sub> and its composites

Photocatalyst	Pollutant	Degradation	Reaction	References
		efficiency	rate constant	
MoSe <sub>2</sub> -Bi <sub>2</sub> WO <sub>6</sub>	Toluene	80%	$0.44 \text{ h}^{-1}$	[43]
Flower shaped MoSe <sub>2</sub>	Nitrobenzene	62.7%	0.009 min <sup>-1</sup>	[44]
	p-nitrophenol	65.2%	0.027 min <sup>-1</sup>	
	2,4 dinitrophenol	61.5%	0.019 min <sup>-1</sup>	
C fibre @ MoSe <sub>2</sub>	4Chlorophenol	3.02%	$0.0028~\mathrm{min}^{-1}$	[10]
	Potassium dichromate	34.7%	$0.0034 \text{ min}^{-1}$	
Carbon quantum dot	Chromium(VI)	99%	0.026 min <sup>-1</sup>	[45]
decorated MoSe <sub>2</sub>				
Hexagonal MoSe <sub>2</sub>	Chromium (VI)	100%	$0.0267 \text{ min}^{-1}$	[46]
MoSe <sub>2</sub> /MMT	Rhodamine B	98%		[47]
MoSe <sub>2</sub> /CdSe <sub>2</sub>	Chromium (VI)	100%	0.0441 min <sup>-1</sup>	[48]
Broom shaped MoSe <sub>2</sub>	Methylene blue	90%	$0.365 \text{ min}^{-1}$	[17]
MoSe <sub>2</sub> -PANI	Methylene blue	65%	$-0.036 \text{ min}^{-1}$	[15]
	Methyl orange	94%	$-0.020 \text{ min}^{-1}$	
MoSe <sub>2</sub> /TiO <sub>2</sub>	Methylene blue	7.8%	0.0235 min <sup>-1</sup>	[49]
MoSe <sub>2</sub> -PANI	Congo Red	88.6%	1.483 min <sup>-1</sup>	Present
(MP21)	Rhodamine B	83.3%	1.3205min <sup>-1</sup>	work

Surface charge is an important factor for the adsorption and degradation of the charged pollutants. Surface charge of the photocatalyst was optimized by varying weight ratio of MoSe<sub>2</sub> and PANI. Zeta potential (ZP) of MoSe<sub>2</sub>-PANI nanocomposites were as shown in figure 7 (a-f).

ZP measurements showed that the surface of MoSe<sub>2</sub> is negatively charged with ZP of -23.01mV whereas the surface of PANI is positively charged with ZP of 9.51 mV (Figure 7(a)) [50]. In sample MP11, a single peak at 5.75 mV is observed whereas in samples MP12 and MP13, two peaks: dominant peak at 8.5 mV and 10.5 mV and weak shoulder peak at 21.6 mV and 30.3 mV; were observed, respectively. The appearance of shoulder peak at 21.6 mV and 30.3 mV is due to the enhancement in PANI proposition in MP12 and MP13 samples. The net surface charge on sample M12 and MP13 is 8.30 and 11.7mV, respectively. In sample MP21, two strong peaks were observed at -14.5mV and 11.8mV and a minor peak at 35.4mV. The net surface charge on MP21 sample is -5.7mV. (Figure 7(e)) From Figure 7(f), it can be seen that the ZP of MoSe<sub>2</sub>-PANI nanocomposite gradually shifted from negative to positive with increasing PANI ratio. Thus, with varying MoSe<sub>2</sub> to PANI weight ratio, surface charge of nanocomposite can be tuned. As a result, cationic dye (RhB) molecules would preferably adsorb on the MoSe<sub>2</sub> surface (negative zeta potential) while that of anionic dye (CR) molecules adsorb on the PANI surface (positive zeta potential) in MoSe<sub>2</sub>-PANI nanocomposites. Enhanced photocatalytic degradation of MP21 sample for both cationic and anionic dyes is attributed to the presence of both types of charges on the surface of MP21 sample as evident through zeta potential measurements.



# Figure 7: Zeta potential of (a) MoSe<sub>2</sub> and PANI, (b) MP11, (c) MP12, (d) MP13, (e) MP21 samples and (f) Net surface charge of samples

Pollutants first get adsorbed on the surface of photocatalyst and then radical species degrade them into CO<sub>2</sub>, H<sub>2</sub>O and other less toxic substances. There are four kinds of interactions between dye and photocatalyst viz. (i) hydrogen bonding, (ii)  $\pi$ – $\pi$  interaction, (iii) van der Waals forces and (iv) electrostatic interaction as shown in figure 8 [51]. The amine and hydroxyl groups of the photocatalyst form a hydrogen bond with the azo, hydroxyl and amine groups of dye molecules. Sulfonic groups of the dye and positively charged amine and hydroxyl groups of the photocatalyst surface interact via electrostatic interaction [52]. The increase in photocatalytic degradation efficiency of MP12 and MP13 samples as compared to MP11 sample is due to the higher adsorption (via electrostatic interaction) of negatively charged CR molecule on protonated MoSe<sub>2</sub>-PANI nanocomposite. Thus, all nanocomposites of MoSe<sub>2</sub>-PANI were able to degrade CR effectively.



Figure 8: Mechanism for adsorption of dyes on the surface of MoSe<sub>2</sub>-PANI nanocomposite

Mechanism for photocatalytic degradation of dyes in the presence of MoSe<sub>2</sub>-PANI nanocomposite is as shown in Figure 9. First, generation of electrons and holes in the conduction

band (CB) and valence band (VB) of MoSe<sub>2</sub>-PANI nanocomposite took place upon irradiation with NIR-visible-light. The holes in the VB of PANI were transferred to MoSe<sub>2</sub> as VB potential (0.8eV) of PANI is more positive than VB of MoSe<sub>2</sub> (0.6eV). Electrons and holes transferred to the surface of the photocatalyst, thereby, they react with atmospheric oxygen and water to produce superoxide radicals ( $O_2^-$ ) and hydroxyl radicals (OH), respectively.  $O_2^-$  and OH are mainly responsible for the degradation of RhB and CR that are adsorbed on the surface of photocatalyst.



Figure 9: Mechanism for photocatalytic degradation of dyes in the presence of MoSe<sub>2</sub>-PANI nanocomposite

#### **Adsorption Kinetics**

First, dyes get adsorbed on the surface of photocatalyst then active radical species degrade them into less toxic substances. Parameters such as time, photocatalyst concentration and initial pollutant concentration highly affect the photocatalysis process. Figure 10 (a and d) showed the adsorption of CR and RhB on MoSe<sub>2</sub>-PANI nanocomposites as a function of time, respectively. Since the photocatalytic degradation is considered as heterogeneous reaction, which includes solid, liquid and gas phases, two kinetic models (pseudo first order and pseudo second order) were used to simulate the adsorption of CR and RhB onto MP11, MP12, MP13 and MP21 with time t, which are given as follows:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \tag{iv}$$

equation (iv) is called the pseudo first order kinetic equation.

Where  $Q_t (mg/g)$  is the amount of dye adsorbed at any time t (min),  $Q_e (mg/g)$  is the amount of dye adsorbed at equilibrium and calculated by eq. (v)

$$Q_e = (C_0 - C_e) * \nu/w \tag{v}$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of dye, v (l) is the volume of solution and w (g) is the amount of photocatalyst used for photocatalysis.  $k_1$  (min<sup>-1</sup>) is the kinetic constant of pseudo first order adsorption.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{vi}$$

equation (vi) is called pseudo second order kinetic equation, whereas  $k_2$  {g/(mg min)}is the pseudo second order rate constant. Figure 10 (b & e) showed linear plot of log (Q<sub>e</sub>-Q<sub>t</sub>) vs time for CR and RhB and its slope determined the first-order rate constant (k<sub>1</sub>). Figure 10 (c & f) showed linear plot of t/Q<sub>t</sub> vs time and its slope determined the pseudo second order rate constant (k<sub>2</sub>) (Eq. (vi)) for CR and RhB, respectively. The kinetics data for adsorption of CR and RhB onto MP11, MP12, MP13 and MP21 were fitted better by pseudo second order model than first order model with their high correlation coefficient (R<sup>2</sup>). The R<sup>2</sup> values for degradation of RhB are 0.783, 0.922, 0.905 and 0.899 for MP11, MP12, MP13 and MP21, respectively. The R<sup>2</sup> values for degradation of CR are 0.995, 0.9971, 0.9972 and 0.993 for MP11, MP12, MP13 and MP21, respectively. It suggested that the overall adsorption process is dominated by the chemisorption process and there are significant valence forces due to sharing or exchange of electrons between photocatalyst and dyes.



Figure 10: Plot of (a,d) Q<sub>t</sub> vs time , (b,e) pseudo first order adsorption model and (c,f) pseudo second order model for CR and RhB dye

Role of active species (OH, holes and  $O_2^-$ ) in photocatalytic degradation of CR using MP13 were explained by performing trapping experiments using different scavengers such as parabenzoquinone (BQ), tert-butyl alcohol (TBA), also called tert-butanol or t-butanol (t-BuOH) and potassium iodide (KI) in the concentration of 1mM in 100ml as shown in figure 11. BQ was used to trap  $O_2^-$ , t-BuOH to trap OH radicals and KI to trap OH and photogenerated holes  $h^+$  [53]. Degradation efficiency was reduced from 90% to 81% using BQ, 37% using t-BuOH and 24% using KI, implying strong effect of holes and hydroxyl radicals on photocatalytic degradation.



#### Figure 11: Trapping experiment to determine active species in presence of BQ, t-BuOH and KI

In photocatalytic degradation of RhB dye, hydroxyl radicals and holes could attack the central carbon of RhB to degrade the dye and further degraded it into harmless products. Intermediate products after photocatalytic degradation of RhB dye using MoSe<sub>2</sub>-PANI nanocomposite were analyzed using liquid chromatography-mass spectroscopy (LC-MS). The intermediates formed during RhB decomposition were observed at 150min of degradation period and compared with 0 min (before treatment) as shown in Figure 12 (a and b). From the ESI spectra (figure 12(a)), the main peak at m/z-443.25 corresponds to RhB. The relative abundance of the RhB peak present at m/z-443.25 decreases from  $8.13 \times 10^4$  to  $2.06 \times 10^4$  after 150 minutes of degradation in the presence of MP21 [54]. RhB dye degraded into possible intermediate at m/z ratios of 116 and 122 corresponded to 4-oxapentanoic acid and benzonic acid, respectively [55]. Figure 12 (b) showed relative abundance vs acquisition time (min) for RhB at 0 min (before treatment) and 150 min of degradation period. A prominent peak of RhB dye was identified at retention time of 7.5 min before treatment. After 150 min of degradation period, the intensity of peak present at 7.5 min decreases and new peaks at retention time of 6.7 and 7.1 min were identified corresponding to oxalic acid and malonic acid, respectively [56]. These formed intermediate were further mineralized into simple compounds such as CO<sub>2</sub> and H<sub>2</sub>O.



Figure 12: ESI mass spectra for degradation of RhB dye in presence of MP21 sample (a) relative abundance vs m/z and (b) relative abundance vs time detected by LC-MS

#### Conclusion

An inorganic-organic nanocomposite, MoSe<sub>2</sub>-PANI, was synthesized and used as a photocatalyst for the removal of CR and RhB dye. The adsorption and degradation of CR and RhB were found to be dependent on the surface charge of a photocatalyst. The adsorption kinetics and isotherms for adsorption of CR and RhB dyes were well-fitted to the pseudo second order kinetics. The optimized ratio of MoSe<sub>2</sub> to PANI is found to be 2:1 as it degrades both RhB and CR dyes with high photocatalytic degradation efficiency. The high photocatalytic degradation efficiency of MP21 is explained on the basis of surface charge and lower recombination rate as observed from zeta potential measurements TCSPC studies, respectively.

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#### **Figure captions:**

Figure 1: Schematic of MoSe<sub>2</sub>-PANI nanocomposite synthesis

**Figure 2:** FESEM images of (a) pure MoSe<sub>2</sub>, (b) pure PANI, (c) MP11, (d) MP12, (e) MP13 and (f) MP21 samples

Figure 3 (i): XRD diffractograms and (ii) FTIR spectra of (a) MoSe<sub>2</sub>, (b) PANI, (c) MP11, (d)

MP12, (e) MP13 and (f) MP21 samples

**Figure 4:** (a) The UV-Vis diffuse reflectance spectra (DRS) and KM plots assuming (b) direct absorption behavior of MP11, MP12, MP13, PANI samples and (c) indirect absorption behavior of MoSe<sub>2</sub> and MP21 samples

Figure 5: (a) PL spectra and (b) TCSPC of MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples

**Figure 6:**  $C/C_0$  vs time plot for degradation of (a) CR and (b) RhB dye; degradation efficiency ( $\eta$ ) vs time plot for degradation of (c) CR and (d) RhB dye

**Figure 7:** Zeta potential of (a) MoSe<sub>2</sub> and PANI, (b) MP11, (c) MP12, (d) MP13 (e) MP21 samples and (f) Net surface charge of samples

Figure 8: Mechanism for adsorption of dyes on the surface of MoSe<sub>2</sub>-PANI nanocomposite

**Figure 9:** Mechanism for photocatalytic degradation of dyes in the presence of MoSe<sub>2</sub>-PANI nanocomposite

**Figure 10:** Plot of (a,d) Q<sub>t</sub> vs time , (b,e) pseudo first order adsorption model and (c,f) pseudo second order model for CR and RhB dye

Figure 11: Trapping experiment to determine active species in presence of BQ, t-BuOH and KI

**Figure 12:** ESI mass spectra for degradation of RhB dye in presence of MP21 sample (a) relative abundance vs m/z and (b) relative abundance vs time detected by LC-MS

#### **Table caption:**

**Table 1:** Kinetic analysis of emission decay for MoSe<sub>2</sub>, PANI, MP11, MP12, MP13 and MP21 samples

Table 2: State of art of photocatalytic degradation efficiency of MoSe<sub>2</sub> and its composites

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## **Highlights**

- 1. Synthesis of MoSe<sub>2</sub>:PANI nanocomposite at different weight percent ratio of MoSe<sub>2</sub> to PANI.
- 2. Characterization using XRD, FESEM, FTIR, DRS, Zeta potential, TCSPC and PL.
- 3. Photocatalytic degradation of cationic dye (Rhodamine B) and anionic dye (Congo Red) with ultra-high degradation efficiency.
- 4. Study of intermediate products using LC-MS.
- 5. Study of photocatalysis mechanism with trapping experiment and reaction kinetics.

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#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Dr. Manika Khanuja: deduced and designed the experiment and ensured that the descriptions are accurate and agreed by all authors; Honey Mittal: synthesized the material, performed photocatalytic experiments and analyzed the data; Dr. Manika Khanuja and Honey Mittal: proofread the final draft; All authors approved the final manuscript.