Synthesis and Characterization of MoS₂/TiO₂ Nanocomposites for Enhanced Photocatalytic Degradation of Methylene Blue under Sunlight Irradiation

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Abstract. 2D nanosheets/ nanoparticles based MoS₂/TiO₂ nanocomposites were prepared in different weight compositions which were further employed to investigate photocatalytic degradation of methylene blue. Anatase TiO₂ powder was prepared via sol-gel reflux method using titanium tetraisopropoxide as Ti precursor. MoS₂/TiO₂ nanocomposites were prepared by in situ addition of exfoliated MoS₂ (2D-nanosheets) in different weight ratios of 0.1%, 0.5%, 1%, 2% and 5% in TiO₂ sol. Surface morphology, phase analysis, optical properties were studied using SEM, XRD, UV-Vis spectroscopy respectively. SEM results showed that TiO₂ nanoparticles were completely adsorbed over the surface of MoS₂ sheets as reflux synthesis was employed. Efficient charge carrier separation was achieved which reduced recombination, and hence, enhanced photodegradation of methylene blue was observed. The hetero-structures showed less operation time in sunlight for photodegradation of methylene blue and a highest rate constant was observed by 2 wt.% loading of MoS₂ on TiO₂. These composites can also be used commercially as they show promising results.

Introduction

Organic pollutants in groundwater have become a persistent problem, as they affect human beings and other creatures. These organic pollutants can cause eutrophication [1] as they compete for dissolved oxygen present in water. Moreover, the effluents from textile and paper industries which include organic dyes pollute and destroy marine life. In the recent years, many compounds have been synthesized and applied for the degradation of various organic dyes. Many wide-band-gap semiconductors like ZnO[2,3], TiO₂[4,5], N-doped TiO₂[6] and ferrites[7] have been exploited to degrade these organic compounds for water purification and remediation[8]. Among these semiconductors, anatase TiO₂ has been widely utilized as it is anti-corrosive, environmentally friendly, cost-effective and widely available. Rutile TiO₂ has a direct band gap of 3.0 eV while anatase TiO₂ has an indirect band gap of 3.26 eV[9]. As less e⁻/h⁺ pair recombination occurs in anatase TiO₂, therefore it is the most widely used form. In the presence of UV light electron-hole pair[10] is generated as:

Due to the large band gap of TiO₂, its many heterostructures have been prepared via doping[11,12] and composites formation [13,14]. These structures have been prepared to enhance its photo-generation of electrons and creating a red shift in absorption spectrum[14]. Transition metal dichalcogenides (TMDs) have also been exploited in recent years[15] because of their novel properties. Among TMDs, MoS₂[16] has been exploited recently as it has a graphene-like 2D structure, is chemically stable, and shows excellent photocatalytic properties. It also shows flexible properties for various optoelectronic devices, and it is anti-corrosive so it can be used in aqueous media as well. Bulk MoS₂ shows absorption spectrum in the near infra-red region at 1040nm, and

when it is exfoliated down to monolayer its band gap (E_g) increases from 1.2 eV to 1.9 eV[17]. The thickness reduction from bulk to nanoscale increases the redox potential of MoS_2 , and the effective electron transfer takes place from the conduction band of MoS_2 to TiO_2 [16,18].

In this study, MoS_2 2D nanosheets/ anatase TiO_2 nanoparticles based nanocomposites[8] were prepared for efficient photocatalytic degradation of organic pollutant. The goal was to prepare nano-sized MoS_2 sheets with increased band gap so that they can act as a photosensitizer to TiO_2 for improved photocatalytic degradation activities[13,19]. The nanocomposites were prepared with different weight ratios of MoS_2 sheets, i.e. 0.1 wt.%, 0.5 wt.%, 1 wt.%, 2 wt.% and 5 wt.% respectively.

Experimental

Titanium Tetraisopropoxide (TTIP, Sigma Aldrich) was used as a precursor material to form TiO_2 . 11.6 g of TTIP was mixed with 2.4 g of glacial acetic acid (CH_3COOH , Merck) for initiating the reaction. CH_3COOH was added as a proton (H^+) donor and as a chelating agent. The chemicals were mixed for 15 minutes for the complete reaction. After that, 74 ml of water was added to the reaction mixture for hydrolysis of TTIP, and it was stirred for 60 minutes. 0.8 ml of HNO_3 was added in the reaction mixture for peptization to prepare TiO_2 sol[20]. The reaction mixture was subjected to reflux condensation for 24 hours and was dried at 80 °C to prepare pure TiO_2 powder. 2.3 grams of powder was obtained as result of this synthesis.

For the synthesis of MoS_2 nanosheets, 20mg/ml of molybdenum (IV) sulphide powder (Sigma Aldrich) was taken in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich). The mixture was sonicated at 1000 rpm for 64 h that resulted in the exfoliation of bulk MoS_2 to 2D nanosheets. These sheets were added in ratios of 0.1, 0.5, 1, 2 and 5 wt.% respectively in TiO_2 sol before reflux, respectively. Then the reaction mixture was subjected to reflux condensation for 24 hours. The product obtained was dried at 80 °C to obtain a greyish powder of the composites and was further annealed in a tube furnace at 450 °C in inert argon gas atmosphere. Fig. 1(a) shows complete schematics for preparation of nanocomposites.

Fig. 1: (a) Schematics of synthesis of 2D MoS_2 nanosheets/ TiO_2 NPs composites (b) Illustration of apparatus used for reflux condensation

Material Characterization

Scanning electron microscope (SEM) of samples was carried out by (JOEL JSM-6490A) to analyze structure and morphology of prepared composites. The MoS_2 sheets were characterized by Atomic Force Microscope (AFM) using (JEOL-SPM 5200) to determine dimensional aspects. Raman spectroscopy was done by (μ Ramboss DONGWOO OPRTON) and for XRD studies, an X-ray diffractometer (STOE Stadi MP) was employed at operating voltage and current of 40 kV and 20 mA, respectively. Cu- α radiation was used as source. UV-Vis was observed by (Jenway 7315 UV-Vis spectrometer) to observe optical properties and photodegradation of samples.

Results and Discussion

Scanning Electron Microscope (SEM) was used to determine the morphology and lateral dimensions of the MoS₂ nanosheets. MoS₂/TiO₂ nanocomposites were also analyzed via SEM. Fig. 2(a) shows pure anatase TiO₂ NPs produced as a product of sol-gel reflux synthesis within 24 hours. It can be seen that all the particles have a spherical morphology and particles range from 20 nm to 35 nm. Fig. 2(b) shows MoS₂ nanosheets obtained at 1000 rpm centrifugation speed. Fig. 2(c,d) shows the morphology of the composites. In high resolution images, it can be seen that TiO₂ nanoparticles are completely adsorbed over the surface of the MoS₂ nanosheets as also shown in Fig. 2(e,f). Therefore, it can be concluded that there is good interfacial bonding between MoS₂/TiO₂ which will further aid photodegradation.

Fig. 2: SEM images of (a) Anatase TiO₂ nanoparticles (b) MoS₂ flakes centrifuged at 1000 rpm (c,d) MoS₂/TiO₂ nanocomposites prepared via sol-gel reflux synthesis (e,f) High resolution images of composite prepared

Atomic Force Microscope (AFM) was used to determine the thickness of MoS₂ sheets. 2 mg of exfoliated MoS₂ sheets centrifuged at 1000 rpm were dispersed in 10 ml of NMP. It was drop cast over glass slide to analyze the sample. As shown in Fig. 3, it was observed that the sheets were around 0.54 nm to 2.69 nm thick which approximately equals to 1-4 layers of MoS₂, as its monolayer thickness is 0.65 nm[17]. Therefore, by exfoliation at 1000 rpm the thickness of MoS₂ sheets decreased and hence, its band gap increased.

Powdered X-ray Diffraction (PXRD) was done to evaluate the phase of composites. The peaks were observed at 25.06°, 37.9°, 47.8°, 53.77°, 54.77°, 62.6° and 76° which corresponds to tetragonal anatase TiO₂ (JCPDS 21-1272). This confirms that only anatase TiO₂ is formed as shown in Fig. 3(b) as a result of this synthesis with no extra peak corresponding to rutile or brookite phase. No peak of MoS₂ were present due to its relatively very thin layers. UV-Visible spectrum of pure anatase TiO₂ and nanocomposites with MoS₂ are shown in Fig. 4(a). Samples were prepared by dispersing 2 mg of samples in 10 ml of distilled water. With MoS₂ loading, the absorption bands are showing a red shift as shown in zoomed part of Fig. 4(a). This can be attributed to nano-sized MoS₂ sheets which provide more active sites and intermediate energy levels for faster chemical activities [21]. And hence, the photocatalytic degradation in the presence of sunlight should be enhanced.

Raman spectroscopy of MoS₂/TiO₂ composites was done to determine the coordination of O-Ti-O. Fig. 4(b) shows the Raman spectra for the composite. TiO₂ was also analyzed to ensure the formation of pure anatase phase. All Raman active modes expected by group theory were observed at 120 cm⁻¹ (E_g), 197 cm⁻¹ (E_g), 395 cm⁻¹ (B_{1g}), 515 cm⁻¹ (A_{1g}) and 635 cm⁻¹ (E_g) respectively.

Fig. 3: Thickness profile of MoS₂ sheets obtained at 1000 rpm centrifuge speed after exfoliation (b) PXRD spectra of composites prepared with different weight ratios of MoS₂

Due to external vibration of anatase structure, E_g mode at 140 cm^{-1} is well resolved. Weak E_g mode at 197 cm^{-1} is also well distinct due to the weak repulsion of oxygen atoms bonded with titanium with the large bond length of $3.04\text{ \AA}$. Anatase characteristic peaks were also observed at 395 cm^{-1} (B_{1g}), and 515 cm^{-1} (A_{1g}) are due to stretching modes of O-Ti-O and Ti-O bonds [22] respectively. It was seen that pure anatase TiO₂ is obtained as result of sol-gel synthesis. Due to the low amount of MoS₂ in the samples, no MoS₂ peak was observed.

Fig. 4: (a) UV-Vis absorption spectrum of pure anatase TiO₂ and prepared photocatalysts (b) Raman Spectrum of pure anatase TiO₂ NPs

The photocatalytic degradation of methylene blue (MB) dye was evaluated under sunlight irradiation. MB dye was used as it is a hazardous organic water pollutant. Also, it is used in dyes, cosmetics, paper industries and given off in water which affects marine life [23,24]. 10mg of MB dye was added in 1L of distilled water. 50ml of this solution was used in each beaker and 5mg of photocatalyst was added to it. Before irradiation, the samples were added to MB dye solution and sonicated for 30 minutes in the dark for uniform dispersion of photocatalysts. Fig. 5(a) shows that when samples were irradiated in the presence of sunlight, MB dye started to degrade. This happened due to efficient interfacial bonding between nanosheets and nanoparticles. The degradation was highest for 2 wt.% MoS₂/TiO₂ nanocomposites, and complete degradation was achieved in just 5 hours. The reaction rate constant of the composites increased up to 2 wt.% of MoS₂ addition and then decreased, as MoS₂ sheets start to agglomerate causing the recombination rate of the photo-generated electrons and holes to increase. The degradation rate and irradiation time follow the first-order reaction kinetics[13,25]. This can be expressed as $\ln(C/C_0) = -kt$, where k is rate constant and C and C_0 are the initial and final concentration of methylene blue respectively, and ' k ' is the apparent reaction rate constant. This is elaborated graphically in figure 5(b). Fig. 5(c) shows the rate constants which various photocatalysts depicted. Table 1 shows that reaction rate constant reached an optimum value of $0.559\text{ (hr}^{-1}\text{)}$ by 2 wt.% addition and then decreased by further addition of MoS₂ sheets.

Fig. 5: (a) C/C_0 curve concerning time for the dye degradation via different nanocomposite catalysts (b) $\ln(C/C_0)$ curve to elucidate rate constants of reaction (c) Rate constants observed via prepared nanocomposites (d) Degradation of MB dye by 2 wt.% $\text{MoS}_2/\text{TiO}_2$ nanocomposites

Fig. 6 shows photocatalytic degradation mechanism of nanocomposites prepared. In case of pure anatase TiO_2 , degradation occurs solely due to electrons and holes production in its valence band. In case of nanocomposites, when sunlight is irradiated on photocatalyst e^-/h^+ production takes place in MoS_2 as exfoliated MoS_2 has high redox potential level [25].

Fig. 6: Photodegradation mechanism as shown by the photocatalysts

Electrons move from its valence to conduction band and are further transferred to the conduction band of TiO_2 . These holes react with OH^- ions to form peroxide ($\text{OH}\cdot$) radicals. Also, electrons react with oxygen (O_2) to form superoxide ($\cdot\text{O}_2^-$) radicals [26,27]. These species formed then degrade organic pollutants like methylene blue.

Table 1: Rate constants ' k_{app} ' and band gaps for various photocatalysts prepared are shown

Samples	Rate constant ' k ' (hr ⁻¹)	Band Gap (eV)
Pure TiO ₂ as-prepared NPs	0.07	3.35
0.1wt. % MoS ₂ /TiO ₂	0.174	3.08
0.5wt. % MoS ₂ /TiO ₂	0.316	3.06
1wt. % MoS ₂ /TiO ₂	0.351	3.02
2wt. % MoS ₂ /TiO ₂	0.559	2.95
5wt. % MoS ₂ /TiO ₂	0.139	2.76

Conclusions

TiO₂ was synthesized via facile sol-gel reflux method, and nanocomposites with MoS₂ were prepared by in-situ addition of exfoliated MoS₂ nanosheets in different weight ratios. XRD and Raman spectrum confirmed the formation of a pure anatase phase of TiO₂. SEM images revealed that the TiO₂ nanoparticles were completely adsorbed over MoS₂ ts. AFM analysis showed that the exfoliated MoS₂ were only 1-4 layers thick. The prepared nanocomposites showed increased photo-generated electron-hole pair production and improved charge transfer as more active edges were present in MoS₂ due to exfoliation, so an enhanced photocatalytic activity was observed. UV-Vis results showed that loading of exfoliated MoS₂ leads to an increase in the photodegradation activity due to increase the charge carrier separation in the visible light. The reaction rate constant gradually increased and reached to 0.559 h⁻¹ which was optimum at 2 wt.% addition of MoS₂ and then decreased due to agglomeration of the sheets and fast recombination rate of the charge carriers.

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