Single-Step Production of a TiO$_2$@MoS$_2$ Heterostructure and Its Applications as a Supercapacitor Electrode and Photocatalyst for Reduction of Cr(VI) to Cr(III)

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ABSTRACT: In this study, we have reported a one-step synthesis of a TiO$_2$@MoS$_2$ heterostructure. TiO$_2$@MoS$_2$ was synthesized using a facile and cost-effective method. The as-synthesized TiO$_2$@MoS$_2$ heterostructure was characterized by suitable spectroscopic techniques. The obtained TiO$_2$@MoS$_2$ was utilized as a supercapacitor electrode material. Electrochemical studies show that the TiO$_2$@MoS$_2$ heterostructure possesses a specific capacitance of 337 F/g at a current density of 1 A/g in an aqueous solution. Furthermore, an application as a photocatalyst for the photoreduction of toxic hexavalent chromium was reported for the first time. This heterostructure showed the photoreduction of Cr$^{VI}$ to Cr$^{III}$ in 120 min with formic acid as a scavenger under direct sunlight. A plausible mechanism of photoreduction of Cr$^{VI}$ to Cr$^{III}$ under natural sunlight irradiation using TiO$_2$@MoS$_2$ is proposed.

1. INTRODUCTION

In the last few decades, two-dimensional materials such as graphene and molybdenum disulfide have become more popular because of their engineered energy applications, extraordinary electronic properties, large surface areas, and high electrical and thermal conductivity.$^{1−4}$ The exfoliated transition metal dichalcogenide such as MoS$_2$ was utilized in energy applications such as supercapacitor devices.$^4$ A layered dichalcogenide with photoactive material such as TiO$_2$ has been proven to have application in the supercapacitor and photocatalytic performance.$^5$ TiO$_2$ demonstrates to be highly active, and a stable photocatalyst that is nontoxic has long durability, is abundantly available in nature, and is inexpensive.$^6$ For the first time in 1972, Fujishima and Honda used TiO$_2$ as a photocatalyst for water photolysis. TiO$_2$ acts as a photocatalyst, but it only absorbs UV radiations as it has a bandgap energy of 3.2 eV. Hence, after adding a selective cocatalyst such as molybdenum disulfide, the photocatalytic property can be improved. MoS$_2$ is a suitable candidate as a cocatalyst because it is abundant in nature, has a highly active layered structure, and is stable. The layered dichalcogenide with titanium dioxide was known as a sunlight receiver and can delay the electron−hole recombination process.$^7$ It was studied that MoS$_2$@TiO$_2$ showed improved properties.$^8,9$ In the literature, the researchers reported the synthesis of MoS$_2$@TiO$_2$ and TiO$_2$@MoS$_2$ heterostructures using various methods. The TiO$_2$@MoS$_2$ synthesis was carried out by chemical vapor deposition, hydrothermal, micromechanical peeling, and solvothermal methods.$^{10,11}$ The solvothermal method is the best method to obtain multilayered structures or small-sized heteronanostructures when used with a specific solvent. Zhu et al. fabricated 3D MoS$_2$ decorated with TiO$_2$ nanoparticles via a two-step hydrothermal method that exhibits good electrochemical performance compared to MoS$_2$. Thus, this may be due to the increased stability of MoS$_2$, as it forms composites with TiO$_2$, which reduces ion movement and enhances the rate of charge transfer capability across the surface.$^{12}$ Pang et al. synthesized the graphene encapsulated MoS$_2$−TiO$_2$ microspheres via a multistep procedure. The microspheres exhibited enhanced properties such as electronic conductivity, long cycle stability, and large specific capacity.$^{13}$ Cravanzola et al. prepared a hybrid MoS$_2$−TiO$_2$ and S-doped TiO$_2$, out of which, MoS$_2$−TiO$_2$ showed enhanced photocatalytic activity toward the degradation of carbamazepine (CBZ) even better than TiO$_2$ that prevented acridine derivative formation; thus, it is a better-managed treatment toward CBZ.$^{14}$ Bing et al. synthesized the flowerlike MoS$_2$@TiO$_2$ using the metal−organic framework as a precursor; furthermore, the material was utilized for the hydrogen evolution reaction.$^{15}$ Recently, the reduction of N$_2$ to NH$_3$ achieved using MoS$_2$−TiO$_2$.$^{16}$ Tahira et al. observed improved photoluminescence using monolayer MoS$_2$ on TiO$_2$nanorods, grown by chemical vapor deposition.$^{17}$ Fu et al. synthesized
MoS2@TiO2 and TiO2@MoS2 nanoheterojunctions via additive-free hydrothermal processes. Due to the generation of heterojunctions, the reintegration of electron–hole pairs decreases. Thus, the MoS2@TiO2 had a better field emission due to the dense distribution of sharp-edged TiO2 nanoparticles, while TiO2@MoS2 has better means for the absorption capability in the UV–visible region. Thus, an enhanced photocatalytic degradation of methylene blue is observed due to the highly reactive (001) site of TiO2 nanorods.18

Recently, the nanoheterostructure of TiO2@MoS2 is explored for various applications, such as enhanced solar-driven hydrogen generation,19 sodium-ion storage,20 bioapplications (110), can be seen in the diad planes, that is, (002), (100), (102), (103), (104), (106), and (220), and (215) planes of TiO2 have been observed. They are also well decorated onto the good quality few-layered MoS2 sheets. TiO2@MoS2 composites for sensing purposes and other applications have been proven. For example, the use of TiO2@MoS2/CoFe2O4 composites for sensing of L-cysteine24 applications exclusively. Figure 1 shows the X-ray diad pattern of the TiO2@MoS2 heterostructure. The main objective of this work is to synthesize a TiO2@MoS2 nanoheterostructure using a top-down process and to study its applications exclusively. Figure 1 shows the X-ray diffraction pattern of the TiO2@MoS2 heterostructure. The XRD pattern of the TiO2@MoS2 heterostructure obtained via the solvothermal route in the ethylene glycol solvent.

2. RESULTS AND DISCUSSION

The main objective of this work is to synthesize a TiO2@MoS2 nanoheterostructure using a solvothermal method. During synthesis, bulk TiO2 and MoS2 were used to get the desired nanorod-shaped TiO2 on few-layered MoS2 sheets. The TiO2 nanoparticles are well decorated onto the good quality few-layered MoS2 sheets. The heterostructure morphology opens up active sites that are few-layered MoS2 nanosheets, thereby increasing catalytic activity sites.29

Figure 2a displays the SEM image of TiO2@MoS2 nanoheterostructures wherein the TiO2 particles distributed and embedded in the MoS2 nanosheets; thus, a rough surface structure was obtained as compared to sheets of MoS2, and this may improve the number of active sites for the photocatalytic reaction and increase the electrochemical performance. Figure 2b shows the EDAX of TiO2@MoS2, which shows the presence of titanium, oxygen, molybdenum, and sulfur in the material.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the materials are shown in Figure 3. The distinct thin-layered structures of MoS2 are seen with a d-spacing of 0.26 nm. This value is attributed to the (100) plane of MoS2.28 The lattice fringes of the anatase TiO2 with a d-spacing of 0.35 nm correspond to the (101) plane; the TiO2 nanoparticles are distributed uniformly on MoS2 sheets, and the presence of the (200) crystal plane indicates that there is an interaction existing at the TiO2@MoS2 junctions.26,29 These observations suggest that there is a formation of good quality crystalline TiO2@MoS2 hetero-junctions.29

Figure 4 shows the Raman spectrum of the TiO2@MoS2 nanoheterostructure. The peaks observed at 156, 513.56 and 639 cm−1 attributed to E1g, A1g + B1g, and E2g modes of anatase TiO2 respectively.30,31 A peak at 396 cm−1 is due to the B1g vibrational mode of anatase TiO2. The peak observed at 407 cm−1 corresponds to A1g mode (out-of-plane optical vibration of S atoms), and a peak at 384 cm−1 corresponds to in-plane E2g mode (in-plane optical vibration of the Mo=S bond) of MoS2.32,33

2.1. Electrochemical Performance. The electrochemical performance of the TiO2@MoS2 nanoheterostructure was measured with a three-electrode system in a 3 M KOH electrolyte. The cyclic voltammetry (CV) curve of TiO2@MoS2 at different scan rates of 10, 20, 50, and 100 mV s−1 with a potential window of 0.0−0.55 V is shown in Figure 5a. Figure 5a shows that the CV curves have redox peaks, that is, anodic and cathodic peaks, which are shifted to a positive potential and negative potential with the increasing scan rate, confirming the pseudocapacitive behavior of the TiO2@MoS2, which is providing a reversible faradic reaction. The results observed that the TiO2@MoS2 electrode possesses high charge transfer stability. Figure 5b shows the charge–discharge curve of the as-prepared material TiO2@MoS2 at different current densities. The galvanostatic charge/discharge (GCD) curve shows that for each pair of the charge and discharge curve, at low current density, the discharge time increases, and at high current density, the discharge time decreases. The specific capacitances were calculated from the charge–discharge curve using the following equation.24

\[ C = \frac{I \times \Delta t}{m \times \Delta V} \]

where \( C \) (F g⁻¹) is the specific capacitance of the electrode based on the loading of active mass materials, \( I \) (A) is the discharge current, \( \Delta t \) is the discharge time (s), \( \Delta V \) is the potential window (\( \Delta V = 0.4 \) V), and \( m \) (g) is the mass of the
active materials. The specific capacitance values calculated were found to be 337, 324, 294, 276, 273, and 188 F g$^{-1}$ at the current densities of 1, 2, 3, 4, 5, and 10 A g$^{-1}$, respectively. Also, a graph of specific capacitance vs current density is plotted (Figure 5c). Figure 5d presents the Nyquist plot. It shows a negligible semicircle at the higher frequency region and a straight line at the lower frequency region, indicating that the electrode has a better capacitive behavior. The comparative study of the electrochemical performance of the TiO$_2$ was carried out, and the specific capacitances were calculated to be 62.3 F g$^{-1}$ at a current density of 1 A g$^{-1}$ (Figures S1 and S2).

2.2. Photocatalytic Reduction of Cr(VI) to Cr(III). The objective of our study was to study the photocatalyst for the reduction of Cr$^{6+}$. The photoreduction was studied with and without the TiO$_2$@MoS$_2$ nanocomposite to obtain relative data. The absorption spectrum in Figure 6a was recorded with a UV–visible spectrophotometer for TiO$_2$/MoS$_2$ in the range of 300–700 nm. A significant extent of absorbance in the visible region can be attributed to bandgap energy absorption by MoS$_2$. Due to the large spectrum absorbance by tandem in the UV and visible region, it can be capitalized for photocatalytic activity. The absorption spectrum and Tauc’s relation$^{35–37}$ were used for determining the bandgap of the tandem. The observed bandgap values using Tauc’s plot for MoS$_2$ and TiO$_2$ are 2.597 and 3.237 eV, respectively, (Figure 6b). Our bandgap for MoS$_2$ agrees well with the 2.5 eV reported elsewhere.$^{38,39}$
Using bandgap values (Figure 6b), the valence band (VB) and conduction band (CB) potentials can be located. The closeness of the CB to that of the Cr(VI) ions results in the fast utilization of photo-induced electrons. The VB and CB potentials (eqs 1 and 2) can be calculated using Mulliken electronegativity (eqs 3 and 4) of the individual elements involved.\(^{40}\)

\[
E_{\text{CB}} = \chi - E_e - 0.5E_g \\
E_{\text{VB}} = E_{\text{CB}} + E_g \\
\chi = \left( \chi_A^a \chi_B^b \chi_{\ldots} \right)^{1/(a+b+\ldots)} \\
\chi = 0.5(E_{A\text{A}} + E_{E\text{A}})
\]

In the above equations, \(E_e = 4.5\) eV (free-electron energy on the hydrogen scale); \(E_g\) is the bandgap obtained from Tauc’s plot for TiO\(_2\)/MoS\(_2\), and \(\chi\) represents the electronegativity of the Mo, Ti, S, and O elements. The number of atoms represented by \(a, b, \ldots\) while \(A, B, \ldots\) are the ions present in the system.

Figure 7 shows the complete reduction of Cr(VI) to Cr(III) in 120 min. Potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)) was used as a source of Cr(VI). Cr(VI) gives an intense absorption peak at 349.6 nm. As the conversion of Cr(VI) to Cr(III) takes place, the intensity of this peak decreases. After reduction, a colorless solution of Cr(III) is obtained [Figure 7, inset (a) and (b)].

Figure 7. UV–vis absorption spectra for catalytic reduction of Cr(VI) to Cr(III) using TiO\(_2\)/MoS\(_2\) under solar light irradiation at a different time interval and the inset image showing (a) Cr(VI) and (b) Cr(III) solution.

Figure 8 shows a plausible mechanism with calculated E vs NHE values shown for TiO\(_2\) and MoS\(_2\) with VB values of +2.929 and +2.130 eV and CB values of −0.308 and −0.467 eV, respectively, obtained using eqs 2 and 3. In the case of TiO\(_2\)/MoS\(_2\), the photo-induced electrons–holes (eq 5) are generated under sunlight. The intersystem transfer of these charges is possible due to the proximity of band positions. The capture of holes by formic acid (hole scavenger) results in CO\(_2\)·\(^-\) species (eq 6),\(^{42}\) which then combines with HCrO\(_4\)\(^-\) ions (eq 7).\(^{42}\) The photo-excited electrons in the CB of MoS\(_2\) shift to the CB of TiO\(_2\) for further reactions. The reduction of Cr(VI) to Cr(III) can be completed either by accepting electrons from the CB of TiO\(_2\) or by its reaction with CO\(_2\)·\(^-\), thus releasing CO\(_2\) (eqs 7–9).\(^{13}\) The electron–hole recombination is hindered as the electrons were utilized via the TiO\(_2\) surface and holes from the VB of MoS\(_2\).

\[
\text{Nanocomposite} + h\nu \rightarrow \text{Nanocomposite}(e_{\text{CB}}^- + h_{\text{VB}}^+) \\
2\text{HCOO}^- + h^+ \rightarrow \text{CO}_2^- + \text{CO}_2 + \text{H}_2 \\
\text{HCrO}_4^- + 3\text{CO}_2^- + 7H^+ \rightarrow \text{Cr}^{3+} + \text{CO}_2 + 4\text{H}_2\text{O} \\
\text{Cr}_2\text{O}_7^{2-} + 6e^- + 14H^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

Figure 8. Plausible mechanism of photoreduction of Cr\(^{6+}\) to Cr\(^{3+}\) by natural sunlight irradiation with TiO\(_2\)/MoS\(_2\).

Figure 6. (a) UV–visible spectrum and (b) Tauc’s plot for TiO\(_2\)/MoS\(_2\).
The TiO2@MoS2 nanoheterostructure was prepared by adding a saturated solution of sodium hydroxide in the colorless solution. A green-colored Cr(OH)3 solution is obtained [Figure 9a (inset image)]. To investigate the reaction kinetics, relative concentration versus irradiation time was plotted. A straight line was obtained, as shown in Figure 9a. A plot of ln(Ct/C0) versus time is shown in Figure 9b. These plots indicate that the reaction proceeds through first-order kinetics. The rate constant of the reaction is found to be 0.0183 min−1, which is calculated using the formula k = ln(C0/ Ct) and the regression coefficient is 0.97.

3. CONCLUSIONS

The present finding briefs about the simple, bulk synthesis of the TiO2@MoS2 nanoheterostructure with well-decorated TiO2 nanoparticles on the MoS2 nanosheets. The TiO2@MoS2 nanoheterostructure exhibited low charge transfer resistance and a high specific capacitance of 337 F g−1. This enhancement of the specific capacitance and photocatalytic property of the nanoheterostructure is attributed to the presence of the heterostructure between TiO2 nanoparticles and MoS2 sheets. The TiO2@MoS2 nanoheterostructure was used as a photocatalyst for the photo reduction of the toxic Cr(VI) to a nontoxic Cr(III) under natural sunlight. Under the optimal operational condition (4 mL of formic acid; 20 mg of TiO2@MoS2) within 120 min sunlight irradiation, Cr(VI) could be reduced completely on the TiO2@MoS2 nanoheterostructure. The use of a noble metal-free TiO2@MoS2 nanoheterostructure is most captivating due to its minimal cost, environmental benignity, and greater chemical stability.

4. EXPERIMENTAL DETAILS

4.1. Materials. Molybdenum disulfide (MoS2), titanium-(IV) dioxide (TiO2), K2Cr2O7, carbon black, and polyvinylidene difluoride (PVDF) were purchased from Sigma-Aldrich, and ethylene glycol (C2H6O2), potassium hydroxide (KOH), N-methyl pyrrolidone (NMP), and methanol were purchased from S.D. Fine Chem. Ltd. All the chemicals used in the synthesis of the nanocomposite were analytical grade and used without further purification.

4.2. Synthesis of TiO2@MoS2. In a typical synthesis, molybdenum disulfide (0.700 g, 4.3731 mmol) and titanium dioxide (0.700 g, 8.765 mmol) were taken in two separate 100 mL beakers. To each of the containers, add 25 mL of ethylene glycol, and then, the contents were sonicated for 30 min. Then, the MoS2 solution in ethylene glycol was transferred to a two-necked round-bottom flask, and it was refluxed at 198 °C for 30 min under an inert atmosphere. To this refluxing solution, dispersed TiO2 solution was added carefully with the help of a syringe at a rate of 5 mL per minute with continuous stirring. The reaction mixture was further refluxed for 2 h and cooled down. The grayish black product obtained was centrifuged and washed with methanol and dried under a vacuum.

4.3. Electrochemical Study. All the performed electrochemical measurements used a three-electrode system in 3 M KOH aqueous electrolyte at room temperature. The AUTO87573 equipped with a USB electrochemical interface Nova 2.1.3 electrochemical workstation carried out the CV and GCD measurements. The electrochemical impedance (EIS) study was in a frequency range of 0.01 Hz to 100 kHz, at an amplitude of 10 mV. The working electrode was prepared by mixing TiO2@MoS2, acetylene black, and PVDF in a weight ratio of 80:10:10 with N-methyl-2-pyrrolidinone (NMP) as a solvent. The resulting slurry was pasted onto a clean nickel foam (1 cm × 1 cm) substrate. The mass loading of the electrode material was around ~2 mg. The electrode was dried at 80 °C for 10 h in a vacuum oven. A platinum wire is used as the counter electrode and a silver chloride electrode (Ag/AgCl) as the reference electrode.

4.4. Photocatalytic Reduction of Toxic Cr(VI) to Cr(III). The conversion of Cr(VI) to Cr(III) occurred in the presence of TiO2@MoS2 nanoheterostructures under natural sunlight. K2Cr2O7 was used for the preparation of 100 ppm solution using double-distilled water. In a 250 mL beaker, 40 mL of the 100 ppm solution of K2Cr2O7 and 20 mg of TiO2@MoS2 were added and sonicated for 15 min, and then, 4 mL of formic acid was added to the mixture. The suspension was exposed to sunlight for successive time intervals, to determine the reaction kinetics. UV–visible spectra were recorded after a time interval of 15 min, by placing 3 mL aliquots in the UV–visible spectrophotometer.

4.5. Materials Characterization. The powder x-ray diffraction data of the as-prepared nanocomposite were obtained using an Xpert PRO PANalytical x-ray diffractometer (Philips) in the 2θ range of 10–80° (λ = 1.5415A) using Cu Kα radiation. The morphologies, textures, and elemental composition of the materials were studied using a scanning electron microscope (Model: JEOL JSM-840) with an operating voltage of 20 kV. Morphologies and structural information were studied using HRTEM and selected area electron diffraction patterns with an accelerating potential of 200 kV and resolution point of 0.19 to 0.1 nm (JEOL, model...
no-JEM2100F). Raman Spectra was recorded on a Thermo-
fischerAlmega XR spectrophotometer using a 532 nm Ar laser
(green). The instrument is standardized with quartz that gave
Raman shift at 466.86 cm$^{-1}$. The absorption spectra were
recorded with a UV-1800 PC Shimadzu UV–vis spectropho-
tometer in the range of 200–800 nm. An AUTO87573
electrochemical workstation carried out CV, GCD, and EIS
measurements.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
https://pubs.acs.org/doi/10.1021/acsomega.1c00121.

(Figure S1) (a) Cyclic voltammogram and (b) galvanostatic charge/discharge curve for TiO$_2$ NPs and
(Figure S2) Nyquist plot of TiO$_2$ NPs (PDF)

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Notes

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