Research Article

Synthesis and Structural Characterization of Al_2O_3 -Coated MoS_2 Spheres for Photocatalysis Applications

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This paper reports the synthesis of novel monodisperse Al_2O_3 -coated molybdenum disulfide nanospheres (i.e., core-shell structures) using a one-step facile hydrothermal method. XPS analysis confirmed the purity and stable structure of the Al_2O_3 -coated MoS_2 nanospheres. A possible growth mechanism of the core-shell structure is also reported, along with their influence on the photodegradation process of rhodamine B (RhB). The Al_2O_3 -coated MoS_2 nanospheres demonstrate good photocatalytic activity and chemical stability compared to MoS_2 spheres. TG-DTA analysis provided insight into the decomposition process of the precursor solution and the stability of the nanoparticles. The enhanced photocatalytic activity makes the Al_2O_3 -coated MoS_2 nanospheres a promising candidate as a photocatalyst that could be used in place of traditional $\text{Al}_2\text{O}_3/\text{MoS}_2$ photocatalyst for the removal of pollutants from waste water.

1. Introduction

Molybdenum disulfide (MoS_2) is one of the important transition metal dichalcogenides (TMDs) with indirect band gap (1.23 eV) semiconductor characteristics [1]. Because of their outstanding properties like mechanical-to-electrochemical capabilities, MoS_2 is used in wide spectrum of applications in catalytic support materials [2, 3], solar cells [4], batteries [5], solid lubricants [6], and gas sensors [7]. These unique properties have attracted many researchers to design new synthesis approaches for uniform and well-controlled MoS_2 nanostructures. Synthesis methods include chemical vapor deposition [8], wetness impregnation method [9], hydrothermal methods [10], and solid state reaction [11]. These techniques have been used to prepare various morphologies of MoS_2 , like fullerene-like (IF) structures, nanoflowers, nanorods, nanosheets, nanoplates, and nanospheres.

In a recent report, Wang et al. demonstrated that carbon-decorated MoS_2 nanospheres have better cycling performance with good capacity as a Na-iron battery anode [12]. MoS_2 is clearly one of the most significantly and broadly used TMDs for transistors due to its favorable band gap

compared to graphene. In addition, MoS_2 is also a suitable candidate for photocatalytic materials. MoS_2 is an indirect narrow-band-gap semiconductor with good stability against photocorrosion in solution [13]. General issues with semiconductor catalysts in the conversion of solar energy to hydrogen are poor charge transport ability, slow kinetics for evolution reactions, poor stability, and the hydrophobic nature of the catalyst [14, 15]. On the other hand, individual MoS_2 catalyst has lower charge separation due to its poor crystallinity.

Despite previous efforts, there has been no material system that can simultaneously satisfy all the criteria for cost-effective photoelectrochemical hydrogen production, and new materials with new properties are needed. To overcome these problems, core-shell structures of MoS_2 coupled with another material with different activity are promising. Such structures could enable charge separation by gathering electrons and holes. The major parameters for the selection of shell materials are band alignment and small lattice mismatch between the core and shell materials [16]. There are very few studies that have focused on preparing MoS_2 nanosphere structures. Wu et al. [17] synthesized MoS_2 microspheres (with diameter up to $2\mu\text{m}$) using a solvothermal method

FIGURE 1: Schematic illustration of the methodology for the formation of Al₂O₃-coated MoS₂ nanospheres.

with the addition of SUDEI. Wu et al. [18] prepared MoS₂ nanospheres (with average diameter of 100 nm) using HCl as a surfactant. Park et al. [19] synthesized MoS₂ nanospheres with high capacity and cycle stability for lithium ion batteries using L-cysteine in a surfactant-assisted solvothermal route.

Common ways to synthesize core-shell structures are decorating the core particles with a surface coating [5] or shell formation using surface modification processes [20]. In this study, we report the influence of Al₂O₃ as a shell material on the photocatalytic activity of MoS₂ nanosphere core-shell structures under UV light irradiation. We studied the variations of the activity and selectivity in the degradation of rhodamine B (RhB) using Al₂O₃-coated MoS₂ nanospheres as a catalyst.

2. Experimental Procedure

A schematic illustration of the methodology for the formation of Al₂O₃-coated MoS₂ nanospheres is shown in Figure 1. For the synthesis, 0.3 g of ammonium heptamolybdate tetrahydrate and 0.17 g of L-cysteine were dissolved in 30 mL of deionized water. This solution was stirred vigorously for 1 h at 80°C. The suspension was continuously stirred and refluxed near pH 1. Then, 1.2 mmol of Al(NO₃)₃ · 9H₂O and 0.3 mmol of trisodium citrate dehydrate (TSC) were added to the stirred solution and again stirred for 30 min at 80°C. Then, the solution was transferred to a Teflon-lined autoclave and heated at 230°C for 24 h. Finally, the resulting precipitates were collected by centrifugation and then the precipitates were washed three times with acetone and water. The obtained precipitates were dried at 250°C for 6 h and sintering at 450°C for 2 h.

The structural properties of the obtained precipitates were characterized by powder X-ray diffraction (XRD) with a Shimadzu Labx XRD 6100 using Cu-Kα radiation ($\lambda = 0.14056$ nm). The scan range was 10–80°, and the scan speed was 3 deg/min. The nanoparticles were analyzed with a transmission electron microscope (TEM, Hitachi H-7000) at 100 kV and a high-resolution TEM (HRTEM, Tecnai G² F 20

FIGURE 2: XRD pattern of MoS₂ nanospheres (curve (a)) and Al₂O₃-coated MoS₂ nanospheres (curve (b)).

S-Twin TEM) at an accelerating voltage of 210 kV. The optical properties of the nanoparticles were studied using UV-visible spectroscopy (Cary 5000 UV-Vis spectrophotometry). Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on a SDT Q600 thermogravimetric analyzer under N₂ flow at a rate of 30 cm³/min. The furnace temperature was increased from room temperature to 900°C at a heating rate of 10°C per minute. The purity of the final product was examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha surface analysis instrument).

The photocatalytic experiments were carried out at the natural pH of the RhB organic pollutant solution. The photoreactor has a 150-W mercury lamp with a main emission wavelength of 254 nm as an internal light source, which is surrounded by a quartz vessel. The suspension includes

FIGURE 3: TEM images of ((a), (b)) MoS₂ nanospheres, ((c), (d)) Al₂O₃-coated MoS₂ nanospheres.

the Al₂O₃-decorated MoS₂ nanosphere catalyst and aqueous RhB (100 mL, 10 mg/L), which completely surrounds the light source. Before irradiation, the suspension was stirred in the dark for 30 min to obtain a good dispersion and to ensure adsorption-desorption equilibrium between the organic pollutant molecules and the catalyst. During light irradiation, the samples of the reaction solution were collected at given intervals and examined using an optical spectrophotometer.

3. Results and Discussions

The XRD patterns of MoS₂ nanospheres and Al₂O₃-coated MoS₂ nanospheres were shown in Figure 2. In case of MoS₂ sphere sample exhibits three well-resolved peaks which can be indexed as the 002, 103, and 110 reflections of the 2D hexagonal structure, which is matched with JCPDS number 77-1716. On the other hand, XRD pattern of Al₂O₃-coated MoS₂ sample exhibits hexagonal structure, whereas Al₂O₃ layer is been crystallized, which is corresponding to JCPDS number 78-2426. The coexisting peaks of Al₂O₃-coated MoS₂ nanospheres corresponding to the 012, 110, 006, 024, and 018

crystal plane are ascribed to γ -Al₂O₃ phase for the sintered samples at 450°C [21, 22]. The diffraction lines characteristics of MoS₂ and Al₂O₃ and no other elemental peaks were detected.

The morphology of the MoS₂ nanospheres and Al₂O₃-coated MoS₂ nanospheres was examined using TEM, as shown in Figure 3. MoS₂ nanospheres were coated with Al₂O₃ using Al(NO₃)₃·9H₂O as a precursor via a hydrothermal method. For better understanding of the morphology of the composite, we initially tested the MoS₂ nanospheres without using Al precursors. The morphology of the MoS₂ nanospheres is shown in Figures 3(a) and 3(b). The MoS₂ materials reveal typical sphere-like morphology with several nanometers in diameter. On the other hand, the MoS₂ spheres obtained using Al precursors retained their spherical morphology with the formation of a uniform layer, forming a core-shell structure (Figures 3(c) and 3(d)). The average thickness of the Al₂O₃ layer around the periphery of the MoS₂ is about 15 nm.

Further understanding of the structural and compositional characterizations of Al₂O₃-coated MoS₂ nanospheres was obtained using HRTEM. The HRTEM image of an edge

FIGURE 4: HR-TEM images ((a)–(e)) of Al_2O_3 -coated MoS_2 nanospheres, ((f)–(i)) HR-TEM elemental mapping images of Al_2O_3 -coated MoS_2 nanospheres.

portion of a core-shell sphere is shown in Figures 4(a)–4(d). The HRTEM image (Figure 4(a)) confirms that the Al_2O_3 colloids are aggregated on the MoS_2 nanospheres. The lattice fringes of the core-shell structure with lattice spacings of about 0.213 and 0.316 nm could be attributed to the (103) and (110) planes of 2H- MoS_2 , respectively. Figures 4(e)–4(i) show typical energy dispersive X-ray spectrometer (EDX) elemental mappings of the core-shell spheres of various elements in the core-shell structure, along with its TEM image. The Mo, S, Al, or O signals are predominantly distributed in the core and shell regions within the selected area, respectively. Figure 5 shows the EDX mapping of Al_2O_3 -coated MoS_2 nanospheres. There are no other traces observed.

FIGURE 5: HR-TEM EDX data of Al_2O_3 -coated MoS_2 nanospheres.

FIGURE 6: TG-DTA analysis of Al_2O_3 -coated MoS_2 nanospheres.

Thermogravimetric and differential thermal analysis (TG-DTA) was conducted to quantitatively determine the Al_2O_3 content present in the Al_2O_3 -coated MoS_2 nanospheres, as shown in Figure 6. The initial weight loss below 220°C is ascribed to the evaporation of physically absorbed water from the product, whereas the weight loss between 550 and 680°C that occurred with an exothermic peak at 650°C could essentially be attributed to the decomposition and separation of the Al_2O_3 layer. The Al_2O_3 content was estimated to be approximately 47.25% by weight.

The electronic states of the metals and sulfur in the Al_2O_3 -coated MoS_2 nanospheres were tested using XPS, as shown in Figures 7(a)–7(e). The XPS survey spectra of the Al_2O_3 -coated MoS_2 nanospheres are shown in Figure 7(a). The $\text{Al}2\text{p}$ XPS spectra were estimated for the Al_2O_3 -coated MoS_2 nanospheres to examine the chemical state of Al. The $\text{Mo}3\text{d}$, $\text{S}2\text{p}$, $\text{Al}2\text{p}$, and $\text{O}1\text{s}$ peaks from the Al_2O_3 -coated MoS_2 sphere sample (Figures 7(b)–7(e)) show no presence of addition chemical states. The binding energy difference ΔE between the $\text{Al}2\text{p}$ and 2s levels is 53.34 eV for the Al_2O_3 -coated MoS_2 nanospheres. The XPS results strongly indicate that Al species interacted with the MoS_2 nanospheres and are preferentially formed in the Al_2O_3 - MoS_2 composite using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a precursor. The $\text{Al}2\text{p}$ and $\text{O}1\text{s}$ peaks were centered at 74.45 eV and 532.36 eV , as described elsewhere [23].

The $\text{S}2\text{p}$ spectrum shows a supplementary peak at 164.58 eV coexisting with an $\text{O}1\text{s}$ peak, which is ascribed to the oxidation of sulfur. The formation of covalent S-O bonding without breakage of the Mo-S bond is likely due to the oxidation state of sulfur. No S-O bond is observed in the $\text{S}2\text{s}$ spectrum, which suggests that only the top surface of sulfur atoms of MoS_2 are oxygen functionalized. This is good evidence that the Al_2O_3 formed a bond with MoS_2 nanospheres, resulting in the formation of the core-shell structure. The XPS binding energies $\Delta E1$ ($\text{Mo } 2\text{p}_{3/2} - \text{S } 2\text{p}_{3/2}$) and $\Delta E2$ ($\text{Mo } 3\text{d}_{5/2} - \text{S } 2\text{p}_{3/2}$) of the Al_2O_3 -coated MoS_2 nanospheres are 70.3 and 67.09 eV , respectively.

The UV-Vis spectrum of the synthesized Al_2O_3 -coated MoS_2 nanospheres is shown in Figure 8(a). The absorption edge at 275 nm could be attributed to the absorption of Al_2O_3 - MoS_2 in the UV region. The absorption spectrum

shows two absorption edges at 603 and 660 nm . These are attributed to excitonic transitions of the Brillouin region at the K point, which is consistent with an earlier report [24]. The energy separation between the two absorption peaks (at 603 and 660 nm) is 0.15 eV due to the spin-orbit splitting at the K point at the surface of the valence band [24]. Moreover, there is weak absorbance in the visible region at a wavelength of 425 nm . The UV-absorption behavior of MoS_2 strongly depends on its size due to quantum effects [25]. For example, the absorption edges of MoS_2 nanoparticles with average diameters of about 4.5 and 9 nm have edges at 470 and 700 nm , respectively, in the visible light region [26]. In contrast, bulk MoS_2 (with a band gap of 1.23 eV) has an absorption peak at around 1040 nm [25]. MoS_2 -based composites have diverse absorption edges with respect to their dimensional parameters [26].

The indirect band gap is estimated using the Tauc equation with optical absorption data for near the band edge [24]: $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$. The band gaps (E_g) are determined from extrapolation of a linear fit onto the x -axis. A plot of $(\alpha h\nu)^{1/2}$ versus the photon energy ($h\nu$) and the intercept of the tangent to the x -axis gives the band gap of the Al_2O_3 -coated MoS_2 nanospheres, as shown in Figure 8(b). The band gap energy of Al_2O_3 -coated MoS_2 nanospheres was found to be 2.42 eV .

Figure 9 shows the progressive changes of the UV-Vis absorption spectra of RhB solution in the presence of Al_2O_3 -coated MoS_2 nanosphere catalyst under UV light as a function of time. The strong absorption peak of the RhB solution at 564 nm gradually decreases from dark conditions to 60 min , and the color of the solution turns from pink to colorless at the end of the photodegradation process. Figure 10 shows the photodegradation efficiency of MoS_2 nanospheres and Al_2O_3 -coated MoS_2 nanosphere catalysts under UV light in RhB solution. The results are shown as the relative concentration (C/C_0) as a function of irradiation time, where C_0 and C (mg/L) are the initial and final concentrations of the pollutant solution.

A blank experiment was carried out in the absence of photocatalyst for comparison, which showed no obvious change in the RhB concentration within 60 min . The introduction of MoS_2 nanospheres and Al_2O_3 -coated MoS_2 nanosphere catalysts can greatly enhance the photocatalytic activity under UV light. Interestingly, the Al_2O_3 -coated MoS_2 nanosphere photocatalysts displayed much higher photodegradation performance than the MoS_2 nanospheres, and more than 97% of the RhB was degraded within 60 min . The presence of Al_2O_3 -coated MoS_2 nanospheres plays a key role in the photocatalytic degradation process. The significant enhancement in photoactivity can be ascribed to the favorable van der Waals surfaces of the Al_2O_3 -coated MoS_2 nanospheres.

Figure 11 shows a kinetic plot of the photocatalytic degradation of RhB over time under UV light irradiation as $\ln(C/C_0)$. The removal efficiency of the Al_2O_3 -coated MoS_2 nanospheres was much faster than that of the MoS_2 nanosphere catalyst. To understand the photostability and reusability of the photocatalyst, four successive recycling tests of the photocatalysts were done for the degradation of RhB under UV light, as shown in Figure 12. There were no

FIGURE 7: XPS data of Al_2O_3 -coated MoS_2 nanospheres: (a) survey spectrum, (b) Mo 3d, (c) S2p, (d) Al2p, and (e) O1s.

significant changes in photocatalytic activity, which shows the steadiness of the degradation efficiency of RhB solution. This result implies that the Al_2O_3 -coated MoS_2 nanosphere photocatalysts have high stability during the photocatalytic oxidation of the pollutant molecules and are reusable.

The catalytic activity increased with the Al_2O_3 -coated MoS_2 nanospheres. Figure 13 shows the RhB removal efficiency of the Al_2O_3 -coated MoS_2 photocatalytic nanospheres with 5 mg of catalyst and 50 mL of 10 mgL^{-1} RhB solution. The pollutant removal efficiency and the adsorption amount

FIGURE 8: (a) UV-Vis light spectra of the Al₂O₃-coated MoS₂ nanospheres, (b) Tauc plots of Al₂O₃-coated MoS₂ nanospheres.

FIGURE 9: Time-dependent UV-Vis absorbance spectra of Al₂O₃-coated MoS₂ nanospheres of the rhodamine B solution samples at different times.

FIGURE 10: Photodegradation rate of the rhodamine B under UV light and light irradiation time for without catalyst, MoS₂ nanospheres, and Al₂O₃-coated MoS₂ nanospheres.

at equilibrium (q_e) were calculated using the following equation:

$$\text{Pollutant removal efficiency (PR\%)} = \frac{100(C_0 - C)}{C_0}, \quad (1)$$

where C_0 and C (mg/L) are the initial and final concentrations of the pollutant, respectively, V is the volume of the pollutant solution, and m (g) is the mass of the catalyst. The Al₂O₃-coated MoS₂ nanospheres exhibit high RhB removal efficiency (95%), in contrast to the (69%) MoS₂ nanosphere sample. It is well known that catalytic ability increases with

increasing content of the catalyst with respect to processing time and other environmental conditions like temperature and pH. In this work, the degradation rate of the RhB solution also increased with increasing catalyst content due to the small particle size and good dispersibility of the Al₂O₃-coated MoS₂ nanoparticles, which facilitate electron migration between the catalyst and pollutant. The Al₂O₃-coated MoS₂ nanospheres exhibit high catalytic activity due to the high dispersibility of the Al₂O₃ coating around the MoS₂ nanospheres, which secured more efficient charge transfer between the MoS₂ and Al₂O₃.

The MoS₂ behaves as the photoactive center, which is generating excited photoelectron pairs under UV irradiation,

FIGURE 11: The kinetic plot of Al₂O₃-coated MoS₂ nanospheres photocatalytic degradation of rhodamine B under UV light irradiation.

FIGURE 12: Recycling photocatalytic degradation of rhodamine B in the presence of Al₂O₃-coated MoS₂ nanospheres photocatalytic under UV light irradiation.

while the Al₂O₃ provides better adsorption sites in the vicinity of the MoS₂. The presence of insulating layers of Al₂O₃ on the surface of MoS₂ nanospheres suppresses the unwanted charge recombination, thus enhancing the photocatalytic activity. The greater photocatalytic activity of Al₂O₃-coated MoS₂ nanospheres can be explained as follows. The HRTEM mapping results indicated that the periphery of the MoS₂ was covered with Al₂O₃. Under UV light irradiation, both MoS₂ and Al₂O₃ are photoexcited, and holes and electrons form in the valance band and conduction band. The photogenerated holes and electrons are transferred within the valance and conduction bands of both the MoS₂ and Al₂O₃ materials. This tendency helps to extend the charge carriers. The excited electrons and holes react with dissolved oxygen in the water or directly oxidize the pollutant molecules to form oxide

FIGURE 13: RhB removal efficiency of Al₂O₃-coated MoS₂ nanospheres photocatalytic, adsorption conditions: 5 mg catalyst, 50 mL 10 mgL⁻¹ RhB solution (conditions: 5 mg of catalyst and 50 mL of 10 mgL⁻¹ RhB solution).

radicals (O₂^{•-}) and hydroxyl radicals (•OH), which are responsible for the degradation of RhB.

A possible mechanism for formation of MoS₂@Al₂O₃ core-shell structure is suggested involving MoS₂ spheres acting as a template for the formation of the coated nanospheres. Due to hydrothermal reactions between the metal-oxoanions and surfactant, cations form a composite phase at the surfactant/inorganic interfaces. Thus, nucleation domains were formed during the hydrothermal reaction between MoO₄²⁻ and S²⁻ and formed MoS₂ spheres. In this manner, the diameter of the nanospheres is no longer limited by the micelle dimensions. A spherical phase of MoS₂ is formed during hydrothermal treatment under the synthetic conditions, in which L-cysteine acts as a sulfur source to stabilize the spherical organization of Mo and S species. The Al species of the precursor solution can absorb to the surface of MoS₂ spheres, and layer upon layer is formed by the electrostatic interaction. The TSC could be considered a crucial component for the growth mechanism of Al₂O₃ coating because it acts as a capping agent for the formation of the coating surface on the MoS₂ nanospheres. The complete synthetic mechanism is expressed in Figure 1.

4. Conclusions

Al₂O₃-coated MoS₂ nanospheres were successfully synthesized using a simple hydrothermal method. The Al₂O₃ shell materials serve as additional electron sources that can significantly recover the electron conduction in MoS₂, which favors the photodegradation of the pollutant. We revealed the appropriate selection of surfactants that could facilitate the adherence of Al species to the surfaces of the cores. Hydrothermally synthesized Al₂O₃-coated MoS₂ nanosphere catalysts show photocatalytic activity higher than that of the

MoS₂ nanosphere catalyst due to the enhanced crystallites with high metal content, which minimize the poisoning effect of sulfur by the chemisorption process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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