Research Article

MWCNT-Based Ag₂S-TiO₂ Nanocomposites Photocatalyst: Ultrasound-Assisted Synthesis, Characterization, and Enhanced Catalytic Efficiency

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Multiwalled carbon nanotube based nanoscale Ag₂S and TiO₂ composites have successfully synthesized via a facile ultrasound-assisted method. The nanocomposites were characterized by Fourier transform infrared (FT-IR) spectroscopy, UV-vis absorption spectra, BET surface area measurements, X-ray diffraction (XRD), and transmission electron microscopy (TEM). The Ag₂S-TiO₂/CNT nanocomposites exhibited much higher photocatalytic activity than pure TiO₂ for the degradation of Rhodamine B (Rh.B) under UV and visible light. The improved photocatalytic activities may be attributed to increased adsorbability of Rh.B molecules and increased charge transfer rate in the presence of a one-dimensional MWCNT network.

1. Introduction

Industrial dyestuffs including textile dyes are recognized as being a major environmental threat. Physical, chemical, and biological methods are available for the treatment of such waste. However, they are not sufficient and have some disadvantages. Therefore, advanced oxidation processes (AOPs), including peroxone, nonthermal plasma, photo-Fenton, UV/O₃, UV/H₂O₂, and semiconductor photocatalysis processes, have been developed by many researchers as processes for the degradation of organic compounds that are suitable for achieving the complete elimination and mineralization of various pollutants [1–4].

The present work focuses on coupled nanoscale semiconductors. It has been reported that the development of coupled semiconductors with nanometer sizes is an effective approach to prepare photocatalytic materials that can utilize sunlight effectively [5]. In addition, these coupled semiconductors, including MS/TiO₂ (where M = Pb, Zn, Cd), also exhibit fine optical properties (absorption and photoluminescence) compared with those of their corresponding bulk materials due to quantum confinement effects [6]. However, it has been revealed that MS/TiO₂ photocatalysts have some

disadvantages, such as difficult recovery, easy cohesion, and low utilization rate in practical applications, due to the weak surface forces, when the particle size is small, thus it can easily agglomerate. So by the accumulation of carriers the adsorption mass transfer rate and efficiency of photocatalytic degradation are reduced to a certain extent [7, 8]. Therefore, in order to solve this problem, an alternative method was employed in this study, which involved immobilizing nanoparticles onto an inert and porous supporting matrix.

Multiwalled carbon nanotubes (MWCNTs) have been widely applied as a promising raw material in many areas of science and technology due to their outstanding physical and electrical properties, such as high tensile strength and elastic modulus and excellent thermal and electrical conductivity [9, 10]. So far, MWCNTs have been used to synthesize not only various composite materials, including polymer/MWCNTs [11] and metal/MWCNTs [12] composites, but also various MWCNTs/metal sulphide nanoparticle hybrid catalysts, where the MWCNTs can function as supporting materials [13–16].

Among the metal sulphide materials, Ag₂S is an important semiconductor that has been used in photovoltaic cells, electrochemical storage cells, IR detectors, photoconductors,

and so on [17, 18]. Its conduction band (-0.3 eV) is less anodic than the corresponding TiO_2 band (-0.1 eV), and its valence band ($+0.7$ eV) is more cathodic than the TiO_2 valence band ($+3.1$ eV) [19, 20]. Nanocrystalline Ag_2S will be a good candidate for the photosensitization of TiO_2 catalysts.

In this work, we focused on the fabrication and characterization of the nanoscale $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composite photocatalyst. The microstructure, surface state, and elemental compositions of the prepared $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composites were investigated. The new products were characterized by the Fourier transform infrared (FT-IR) spectroscopy, energy dispersive X-ray (EDX) analysis, nitrogen adsorption Brunauer-Emmett-Teller (BET) specific surface area analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and UV-vis diffuse reflectance spectra (DRS). The photocatalytic activity of the $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ nanocomposites was assessed by examining the degradation of Rh.B in model aqueous solutions as a probe reaction under UV-vis light irradiation. The kinetics and mechanism of the photocatalysis were also studied.

2. Experimental

2.1. Materials and Reagents. MWCNT (95.5%) powder, containing nanotubes with diameters of 20 nm and lengths up to $5\text{ }\mu\text{m}$, was purchased from Carbon Nano-material Technology Co., Ltd., Korea. To oxidize the surface of the MWCNTs, we used *m*-chloroperbenzoic acid (MCPBA) purchased from Acros Organics, New Jersey, USA as an oxidized reagent. Ethyl alcohol was purchased from Duksan Pure Chemical Co. (Korea) and used as received. Titanium (IV) *n*-butoxide (TNB, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) was used as a titanium source. Silver nitrate (AgNO_3) and sodium sulfide $\cdot 5$ -hydrate ($\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$) were used for the preparation of Ag_2S and were supplied by Duksan Pure Chemical Co., Ltd, Korea, and Yakuri Pure Chemicals Co., Ltd., Japan, respectively. Analytical-grade Rhodamine B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$) was purchased from Samchun Pure Chemical Co., Ltd., Korea. All chemicals were used without further purification, and all experiments were carried out using distilled water.

2.2. Preparation of $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ Composite Photocatalysts. Although MWCNT present remarkable intrinsic properties, it is necessary to functionalize their surfaces to obtain higher performances and to produce well-dispersed supported catalysts [21]. The purposes of these oxidative treatments are (i) to improve the interaction of MWCNTs with solvents and their dispersion; (ii) to allow the grafting of nanoparticles; (iii) to modify the adsorption properties of MWCNTs; (iv) to perform chemical treatments on MWCNTs. Here, the original MWCNTs were treated with a particular acid (MCPBA) and not the nitric-sulfuric acid ($\text{HNO}_3\text{-H}_2\text{SO}_4$, volumetric ratio: $v/v = 1/3$) used elsewhere in the literature [22].

A total of 2.0 g of MCPBA was dissolved in 60 mL of benzene to obtain the oxidizing agent. Then 0.6 g of MWCNTs was put into the oxidizing agent, refluxed for 6 h, filtered, and dried. The 0.03 g of oxidized MWCNTs

TABLE 1: Nomenclature of the samples prepared with the as-prepared composite.

Preparation method	Nomenclatures
MCPBA + benzene + MWCNT	Oxidized MWCNT
Oxidized MWCNT + AgNO_3 + $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$	$\text{Ag}_2\text{S-CNT}$
$\text{Ag}_2\text{S-CNT}$ + ethyl alcohol + H_2O + TNB + ultrasound	$\text{Ag}_2\text{S-TiO}_2/\text{CNT}$
AgNO_3 + $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ + benzene + TNB	$\text{Ag}_2\text{S/TiO}_2$
MCPBA + benzene + MWCNT + TNB	CNT-TiO_2

and 10 mL of absolute alcohol was put into a glass beaker and ultrasonically dispersed until the alcohol was completely volatile, and then 50 mL of AgNO_3 solution was added under stirring for 1 h. A stoichiometric amount of 30 mL of 0.003 mol $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ solution was prepared separately and added dropwise to the solution with continuous stirring for 3 h at 343 K. After that, the obtained suspension was heated and refluxed for another 4 h under stirring. The final products were filtered and washed repeatedly with distilled water and ethanol and then vacuum dried at 373 K.

The Ag_2S -treated CNT composites were placed into a mixed solution with the molar ratios of ethanol : H_2O : TNB = 35 : 15 : 4, and finally the suspension was sonicated at room temperature for 3 h using a Controllable Serial-Ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea). The final products were filtered and washed repeatedly with distilled water and ethanol and then vacuum dried at 373 K, then the dried catalyst was ground in a ball mill (FRITSCH Pulverisette 6, Daemyung Scientific. Co. Ltd.) and calcined at 773 K for 3 h to get a $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composite.

Meanwhile, for comparison, another three photocatalysts, marked as TiO_2 , CNT/TiO_2 , and $\text{Ag}_2\text{S/TiO}_2$, were prepared using similar procedures. The preparation conditions of the samples are listed in Table 1.

2.3. Characterization of Photocatalysts. FT-IR spectroscopy (FTS 3000MX, Biorad Co., Korea) was used to characterize the functional groups of $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composites. EDX spectra were also used for elemental analysis of the samples. The BET surface areas of the photocatalysts were determined by measuring nitrogen adsorption at 77 K using a BET analyzer (Monosorb, USA). All the samples were degassed at 623 K before the measurement. The morphologies of the photocatalysts were analyzed by SEM (JSM-5200 JOEL, Japan) at 3.0 keV, which was equipped with an energy dispersive X-ray analysis system (EDX). Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) with an accelerating voltage of 200 kV was used to examine the size and size distribution of the photocatalyst particles. The crystallographic structures of the composite photocatalysts were observed by using XRD (Shimatz XD-D1, Japan) at room temperature with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm) and a graphite monochromator, operated at 40 kV and 30 mA. To analyze the light absorption of the photocatalysts, UV-vis absorption spectra was obtained by using a scan UV-vis spectrophotometer (Neosys-2000) equipped with

an integrating sphere assembly. The UV-vis spectra for Rh.B solutions degraded by TiO_2 , Ag_2S -CNT, CNT/ TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$ and $\text{Ag}_2\text{S}-\text{TiO}_2/\text{CNT}$ composite photocatalysts under UV-vis light irradiation were recorded using a UV-Vis (Optizen Pop Mecasys Co., Ltd., Korea) spectrometer.

2.4. Measurement of Photocatalytic Activities. The photocatalytic experiments were performed at ambient temperature to test the ability of the as-prepared composites (TiO_2 , Ag_2S -CNT, CNTs/ TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$ and $\text{Ag}_2\text{S}-\text{TiO}_2/\text{CNT}$) to catalyze the degradation of Rhodamine B. The photocatalytic activities of the samples were evaluated in terms of the degradation of Rhodamine B under UV-vis light illumination. The UV (8 W, $\lambda = 365$ nm, B. P. 66, Vilber Lourmat) and visible light sources (8 W, $\lambda > 420$ nm, KLD-08L/P/N, Fawoo Technology) were used at a distance of 100 mm from the solution in a darkness box. The initial concentration of Rh.B (c_0) was 3.0×10^{-5} mol/L. The photocatalyst powder (0.03 g) was dispersed in a 100 mL glass photoreactor containing 100 mL of dye solution. The mixture was sonicated for 10 min and stirred for 30 min in the dark in order to reach adsorption—desorption equilibrium. At the given time intervals a sample of 3.5 mL was taken from the mixture and immediately centrifuged to remove the dispersed photocatalysts. The concentration of the clean transparent solution was analyzed by checking the absorbance at 554 nm for Rh.B with the UV-vis spectrophotometer. The reproducibility was checked by repeating the measurements at least three times and was found to be within the acceptable limit ($\pm 5\%$).

3. Results and Discussion

3.1. Physicochemical Properties. The FT-IR spectrum of the MWCNTs was rather simple and suggested extensive oxidation (Figure 1). The spectra of the crystalline material showed well-distinguished and sharp bands, whereas the amorphous spectra were less resolved. Figures 1(a) and 1(b) show the FT-IR spectra of oxidized MWCNTs and Ag_2S -CNT, respectively.

After oxidation by a strong oxidant (MCPBA), the MWCNTs have various kinds of functional groups (Figure 1(a)). The bands at 2910 and 2847 cm^{-1} were assigned to the C–H stretching vibration. The bands at 891, 1210, and 1726 cm^{-1} were assigned to the C–H, C–O, and C=O stretching vibrations, respectively [23]. The above observations suggest that oxidation was promoted in all treatments and caused the formation of functional groups which can increase the number of active sites on the surface of MWCNTs [24, 25].

From Figure 1(b), the weak peak at 1220 cm^{-1} and the strong peak at 1170 cm^{-1} were assigned to the C–O bond and the weak peak at 1687 cm^{-1} and the strong peak at 1726 cm^{-1} were assigned to the characteristic C=O bond in carbonyl groups. Peaks corresponding to C–H functional groups were observed at approximately 2921 cm^{-1} . From this, it was found that the functional group density on oxidized MWCNTs was decreased, which could be attributed to some of the functional groups which had combined with Ag_2S particles.

FIGURE 1: FT-IR spectra: (a) MCPBA-oxidized MWCNTs and (b) Ag_2S -CNT.

The EDX spectra of CNTs/ TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, and $\text{Ag}_2\text{S}-\text{TiO}_2/\text{CNT}$ composites are shown in Figure 2, and elemental microanalyses (wt%) of the samples are listed in Table 2. EDX indicated C, O, Ti, and Ag, S as the major elements in the composites. In the comparison of the spectra between the $\text{Ag}_2\text{S}/\text{TiO}_2$ and $\text{Ag}_2\text{S}-\text{TiO}_2/\text{CNT}$ composites, the latter have not only the peaks of S, Ag, Ti, and O, but also of C. For the $\text{Ag}_2\text{S}/\text{TiO}_2$ sample, some impure elements including Cu existed which may have been introduced by the $\text{Ag}_2\text{S}/\text{TiO}_2$ preparation process. In CNT/ TiO_2 and $\text{Ag}_2\text{S}-\text{TiO}_2/\text{CNT}$ samples, the spectra show the presence of C, O, and Ti, as major elements, and the strong peaks of Ag and S elements were also observed.

The specific surface areas (BET) of the as-prepared composites were also listed in Table 2. In comparison to MWCNTs, The BET value was decreased from $211.43\text{ m}^2/\text{g}$ of MWCNTs to $101.27\text{ m}^2/\text{g}$ of CNT/ TiO_2 . The BET surface area was decreased to $87.89\text{ m}^2/\text{g}$ when the Ag_2S particles were obtained in $\text{Ag}_2\text{S}-\text{TiO}_2/\text{CNT}$ composites. This suggests that the TiO_2 and Ag_2S nanoparticles were introduced

TABLE 2: EDX elemental microanalysis, BET surface areas, and adsorption efficiency of the composites.

Sample name	C (%)	O (%)	Ti (%)	Ag (%)	S (%)	Impurity (%)	BET (m ² /g)	Adsorption efficiency (%)
MWCNTs	99.99	—	—	—	—	0.01	211.43	—
TiO ₂	—	—	99.99	—	—	0.01	11.54	3.84
Ag ₂ S/TiO ₂	—	35.42	50.89	8.85	4.43	0.41	41.67	12.86
CNT-TiO ₂	20.84	44.11	35.05	—	—	—	101.27	37.02
Ag ₂ S-TiO ₂ /CNT	20.99	30.74	38.23	6.43	3.61	—	87.89	22.96

FIGURE 2: EDX elemental microanalysis: (a) CNT-TiO₂, (b) Ag₂S/TiO₂, (c) Ag₂S-TiO₂/CNT catalysts.

into the pores of the MWCNTs, which decreased the BET surface area. The Ag₂S/TiO₂ sample has a slight tendency to agglomerate, and thus it has a smaller BET surface area of 41.67 m²/g.

The typical microsurface structures and morphologies of the as-prepared composites were characterized by SEM and TEM in Figure 3. Figure 3(a) is a typical SEM image of the prepared microrod-shaped Ag₂S nanoparticles, from which it is clear that large-scale uniform microrods with an average diameter of ca. 1.5 μ m have been prepared. Figure 4(b) shows that the Ag₂S-CNT composite has a favorable morphology. Most of the Ag₂S particles were uniformly enclosed or overlapped by the functionalized MWCNTs, which thus set the stage well for the coating of the TiO₂ particles onto the surface of the Ag₂S-CNT composite

as it allowed for excellent dispersity. From Figure 3(c), it is clear that the prepared Ag₂S/TiO₂ composite has a little tendency to agglomerate. The agglomeration may occur because when the crystal particle size is very small, they can easily agglomerate due to weak surface forces. From Figure 3(d), the as-prepared Ag₂S-TiO₂/CNT composites exhibit fine surface nanostructures. The surface of MWCNTs was coated with uniformly dispersed Ag₂S and TiO₂ particles. The surface nanostructures and particle sizes of Ag₂S-TiO₂/CNT composites were further confirmed by TEM analysis. Figures 3(e) and 3(f) show high-magnification TEM images of TiO₂ and Ag₂S-TiO₂/CNT composites. Pure TiO₂ displayed well-dispersed nanoparticles with an average size of around 10 to 15 nm. A few black dots can be observed in these images, which correspond to the deposition of Ag₂S nanoparticles with an average size of 10–15 nm. This indicates that the presence of the MWCNTs can efficiently inhibit the agglomeration of Ag₂S/TiO₂ and improve the dispersion of nanoparticles.

The crystal phase structures of as-prepared TiO₂, Ag₂S, and Ag₂S-TiO₂/CNT samples were characterized by X-ray diffraction measurements in Figure 4. It can be confirmed that the TiO₂ in the as-prepared photocatalysts is anatase-phase, while the Ag₂S appears as the predominant crystalline phase of acanthite. For these three samples, (101), (004), (200), (105), (211), and (204) crystal planes originated from the anatase TiO₂ phase while (111), (112), (121), (103), (031), (200), (213), and (134) crystal planes originated from the acanthite Ag₂S phase [26]. After refinement, the cell constants are calculated to be $a = 4.2261$ Å, $b = 6.9238$ Å, and $c = 7.8547$ Å (JCPDS card no. 14-0072). No impurity phase is detected. The broadening of these diffraction peaks indicates that the sample is nanosized. The crystalline size of the sample is estimated to be 15 nm from the Scherrer equation. However, the strong (002) diffractions of the hexagonal graphite at a 2θ of about 25.88° are very difficult to discover in all of the composites due to strong overlapping by the TiO₂ diffraction peak. Therefore, it can be suggested that the as-prepared samples have a single and clear crystal structure, of anatase type.

The UV-vis absorption spectra of the different samples are presented in Figure 5. As expected, we find that TiO₂, Ag₂S/TiO₂, CNT/TiO₂, and Ag₂S-TiO₂/CNT composites have great absorption in the ultraviolet region. After the introduction of MWCNTs or Ag₂S nanoparticles, the absorption edges of Ag₂S/TiO₂, CNT/TiO₂, and Ag₂S-TiO₂/CNT were shifted toward the visible region, which means that

FIGURE 3: SEM images of as-prepared composites: (a) Ag₂S, (b) Ag₂S-CNT, (c) Ag₂S/TiO₂, (d) Ag₂S-TiO₂/CNT, and TEM images of samples: (e) TiO₂, (f) Ag₂S-TiO₂/CNT.

these composites have photocatalytic activity under visible light irradiation [27, 28]. Combining with MWCNTs and Ag₂S nanoparticles, the Ag₂S-TiO₂/CNT composites show an intense absorption whose onset is red shifted compared to that of pure TiO₂. The absorbance spectra increase in intensity in the order of Ag₂S/TiO₂, CNT/TiO₂, and Ag₂S-TiO₂/CNT, which indicates that the Ag₂S-TiO₂/CNT composites at high wavelength could present excellent photocatalytic activities under visible light irradiation. This phenomenon results not only from the excellent conductivity of MWCNTs that can facilitate the separation of photogenerated charges [29], but also from the introduction of the semiconductor quantum dot Ag₂S by which the conduction and valence bands of TiO₂ are bent downward [19, 20]. The

diffuse reflectance spectra of Ag₂S/TiO₂ was transformed by performing the Kubelka-Munk transformation of the measured reflectance according to the following equation:

$$K = \frac{(1 - R)^2}{2R} = F(R). \quad (1)$$

K is reflectance transformed according to Kubelka-Munk, R is reflectance (%), and $F(R)$ is the so-called remission or the Kubelka-Munk function. It is well known that the bandgap E_g and the absorption coefficient α are related as in following equation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (2)$$

FIGURE 4: XRD patterns of as-prepared samples: (a) TiO_2 , (b) Ag_2S , (c) $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$.

where α , ν , E_g , and A are the absorption coefficient, light frequency, bandgap, and a constant, respectively. If the compound scatters in a perfectly diffuse manner, K becomes equal to 2α . In this case, we can use the following expression:

$$[F(R)h\nu]^2 = A(h\nu - E_g). \quad (3)$$

The estimated E_g value was 1.95 eV for the $\text{Ag}_2\text{S}/\text{TiO}_2$ sample. This value is red shifted from the typical E_g of the TiO_2 used (3.2 eV) in Figure 5(b).

3.2. Degradation Performances. The photocatalytic activities for pure TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, CNT/TiO_2 , and $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ nanocomposites were measured by the degradation of Rh.B under UV-vis light irradiation, as shown in Figures 6(a) and 6(b). The order of the photodegradation efficiency of Rh.B under UV light is as follows: $\text{Ag}_2\text{S-TiO}_2/\text{CNT} > \text{CNT}/\text{TiO}_2 > \text{Ag}_2\text{S}/\text{TiO}_2 > \text{TiO}_2$, which suggests that the $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ nanocomposite is a much more efficient catalyst for the degradation of Rh.B under UV light irradiation than the other composites. Similarly, the degradation efficiencies of Rh.B under visible light are ordered as follows: $\text{Ag}_2\text{S-TiO}_2/\text{CNT} > \text{CNT}/\text{TiO}_2 > \text{Ag}_2\text{S}/\text{TiO}_2 > \text{TiO}_2$. Combining TiO_2 with both MWCNTs and Ag_2S nanoparticles, the $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composites result in the best photocatalytic activity, which is much better than pure TiO_2 under UV and visible light irradiation.

Therefore, we compare the UV and visible light photodegradation efficiencies of Rh.B for pure TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, CNT/TiO_2 , and $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$, as shown in Figure 6(c). Pure TiO_2 shows much lower photoactivity under visible light irradiation than it does under UV light. As mentioned in Figure 6, the absorption edge of the light plays an important role in the photocatalysis under visible light irradiation. However, the visible light photocatalytic activity of CNT/TiO_2 was obviously lower than that of $\text{Ag}_2\text{S}/\text{TiO}_2$ composites. It is noteworthy that the good degradation

(a)

(b)

FIGURE 5: (a) UV-vis absorbance spectra of pure TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, CNT/TiO_2 , and $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$. (b) Variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of TiO_2 and $\text{Ag}_2\text{S}/\text{TiO}_2$.

activity of $\text{Ag}_2\text{S}/\text{TiO}_2$ composites could be attributed to the excellent electrical characteristics of semiconductor Ag_2S . Also, the photodegradation activity of CNT/TiO_2 could be ascribed to its good adsorption ability, which was shown in Figure 6(d). As mentioned above in Table 2, the adsorption abilities of pure TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, CNT/TiO_2 , and $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composites were evaluated after stirring for 30 min in the dark. The degradation efficiency of Rh.B of the CNT/TiO_2 composites was higher than that of any other photocatalyst in Figure 6(e). This was attributed to the high porosity of the CNT/TiO_2 surface due to the introduction of MWCNTs, which correlated with an increase in adsorption ability.

FIGURE 6: Photocatalytic degradation behaviors of Rh.B for the as-prepared photocatalysts under (a) UV light and (b) visible light irradiation. (c) Comparison of photocatalytic degradation behaviors of Rh.B for the as-prepared photocatalysts under UV and visible light. (d) Adsorption capabilities of TiO₂, Ag₂S/TiO₂, CNT/TiO₂, and Ag₂S-TiO₂/CNT samples for Rh.B under dark conditions. (e) UV/Vis spectra of Rh.B concentration against the as-prepared samples after adsorption-desorption equilibrium.

TABLE 3: UV and visible light photodegradation rate (k_{app}) constants of pure TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, CNT-TiO_2 , and $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ catalysts.

Catalysts	k_{app} (min^{-1})	
	UV light	Visible light
TiO_2	9.01×10^{-4}	0
$\text{Ag}_2\text{S}/\text{TiO}_2$	1.97×10^{-3}	1.67×10^{-3}
CNT-TiO_2	2.48×10^{-3}	2.02×10^{-3}
$\text{Ag}_2\text{S-TiO}_2/\text{CNT}$	5.32×10^{-3}	3.18×10^{-3}

Photocatalytic reactions with different photocatalysts can be expressed by the Langmuir-Hinshelwood model [30]. The photocatalytic degradation of Rh.B containing different photocatalysts under visible light obeys pseudo-first-order kinetics with respect to the concentration of Rh.B:

$$-\frac{dc}{dt} = k_{app}c. \quad (4)$$

Integration of this equation (with the restriction of $c = c_0$ at $t = 0$, with c_0 being the initial concentration in the bulk solution after dark adsorption and t the reaction time) will lead to the following expected relation:

$$-\ln\left(\frac{c_t}{c_0}\right) = k_{app}t, \quad (5)$$

where c_t and c_0 are the reactant concentrations at times $t = t$ and $t = 0$, respectively, and k_{app} and t are the apparent reaction rate constant and time, respectively. According to this equation, a plot of $-\ln(c_t/c_0)$ versus t will yield a slope of k_{app} . The results are displayed in Figure 7 and also summarized in Table 3. The Rh.B degradation rate constant for $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composites reaches $5.32 \times 10^{-3} \text{ min}^{-1}$ under UV light and $3.18 \times 10^{-3} \text{ min}^{-1}$ under visible light, both of which are much higher than the corresponding values for pure TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$ and CNT/TiO_2 . The above results suggest that the $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composite are much more effective photocatalysts than any other composite. The excellent photocatalytic activity could be attributed to the synergetic effects of high charge mobility and the red shift in the absorption edge of the $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ composites.

The excitation scheme and charge transfer process between Ag_2S , TiO_2 , and MWCNTs under light irradiation are shown in Figure 8. Under irradiation by UV and visible light, both Ag_2S and TiO_2 can be excited (corresponding to (6) and (7), resp.). The generated electrons in Ag_2S and the holes in TiO_2 are then migrated to the conduction band (CB) of TiO_2 and the valence band (VB) of Ag_2S , respectively. This transfer process is thermodynamically favorable because both the CB and VB of Ag_2S lie above those of TiO_2 . In addition, MWCNTs acting as good electron acceptors can accept the electrons excited by light irradiation and the electrons excited into the CB of TiO_2 are also transferred to the surface of MWCNTs (see (8) and (9)). Thus the lifetime of the excited electrons (e^-) and holes (h^+) is prolonged in the transfer process, inducing higher quantum efficiency. Meanwhile, the generated electrons probably react

FIGURE 7: Apparent first-order kinetics of Rh.B degradation for TiO_2 , $\text{Ag}_2\text{S}/\text{TiO}_2$, CNT/TiO_2 , and $\text{Ag}_2\text{S-TiO}_2/\text{CNT}$ photocatalysts under UV (a) and visible light (b) irradiation.

with dissolved oxygen molecules to produce oxygen peroxide radicals $\text{O}_2^{\cdot-}$ (see (10), (11), and (12)), whereas a positively charged hole (h^+) may react with the OH^- derived from H_2O to form the hydroxyl radical $\text{OH}^\bullet$ (see (13) and (14)). The Rh.B molecule then can be photocatalytically degraded by the oxygen peroxide radical $\text{O}_2^{\cdot-}$ and the hydroxyl radical $\text{OH}^\bullet$ to CO_2 , H_2O , or other mineralization (15) [31, 32]:

FIGURE 8: The possible photocatalytic mechanism of Ag₂S-TiO₂/CNT nanocomposites.

4. Conclusions

In this study, the Ag₂S-TiO₂/CNT composites are able to exhibit high surface area, excellent structure, and great electrical and optical properties. The Ag₂S-TiO₂/CNT composites showed an intense absorption and have a red-shifted absorption onset compared to pure TiO₂. The Ag₂S-TiO₂/CNT inhibited an enhanced rate and a very high efficiency for the decoloration of Rh.B under UV and visible light compared with Ag₂S/TiO₂, CNT/TiO₂, and pure TiO₂ photocatalysts.

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