Hydrothermal Synthesis, Characterization and Improved Activity of a Visible-Light-Driven ZnSe-Sensitized TiO₂ Composite Photocatalyst

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ABSTRACT

In this study, ZnSe-TiO₂ composites were synthesized by a facile hydrothermal-assisted sol-gel process and characterized by nitrogen adsorption isotherms (77 K), X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, transmission electron microscopy (TEM) and UV-vis diffuse reflectance spectrophotometry. The photocatalytic activity was investigated by decoloration methylene blue (MB), methyl orange (MO), and rhodamine B (Rh.B) in an aqueous solution under visible light irradiation. The results revealed that the photocatalytic activity of the ZnSe-TiO₂ photocatalyst was much higher than that of pure TiO₂. The ZnSe nanoparticles, which act as a photosensitizer, not only extend the spectral response of TiO₂ to the visible region but also reduce charge recombinations.

Key words: TiO₂, ZnSe, UV-vis, Hydrothermal, Visible light photocatalytic

1. Introduction

Titanium dioxide is a promising material for the conversion of photoelectrochemical solar energy and for the treatment of photocatalytic hazardous waste due to its superior photoreactivity^{1,2)}, nontoxicity³⁾, long-term stability^{4,5)} and its low price.⁶⁾ Conventionally, anatase TiO₂ only absorbs wavelengths in the near-UV region ($\lambda \leq 390$ nm), representing about 3% of the solar spectrum. Thus, solar energy cannot be utilized efficiently in real applications. An important feature of the coupled semiconductor system is that the photoresponse of the anatase TiO₂ semiconductor can be extended into the visible region by coupling it with a short-bandgap semiconductor to overcome this inherent limitation.⁷⁻⁹⁾ By coupling a second semiconductor to TiO₂, the photocatalytic efficiency and functionality can be further improved. The photocatalytic action of a semiconductor system is based on the generation of electron-hole pairs. In order to achieve a high reaction rate, the recombination of the charge carriers must be kept low. Coupling two semiconductors can result in the vectorial transfer of photo-generated electrons and holes from one semiconductor to another.

In a coupled semiconductor system, a small-bandgap semiconductor that absorbs visible light acts as a photo-

sensitizer for the TiO₂. Through the transfer of a photo-excited electron from the small-bandgap semiconductor to the TiO₂ particle, a photocatalytic redox reaction can occur. Zinc selenide (ZnSe) has a direct bandgap of ~ 2.7 eV, making it well suited for solar applications,^{10,11)} and its valence electrons can be easily evoked to the conduction band when the light wavelength of the evoking light is less than or equal to 730 nm. Moreover, it is important to note that the conduction band minimum of the small-bandgap semiconductor should be higher than that of TiO₂ so that the transfer of the photo-generated electron is allowed from the former to the latter.⁶⁾ In addition, ZnSe exhibits much greater photostability than organic dyes when used as a photosensitizer. Thus, this photosensitization property of a coupled semiconductor system provides an alternative approach in the design of efficient visible-light photocatalysts.

In order to enhance the visible-light photocatalytic activity and the dye adsorbability of TiO₂, zinc selenide (ZnSe), which acts as a photosensitizer, is introduced in this study. A ZnSe-TiO₂ composite was obtained directly via a facile hydrothermal method. The resulting composite was characterized by nitrogen adsorption isotherms (77 K), X-ray diffraction (XRD), scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX) analysis and with UV-vis diffuse reflectance spectrophotometry. The photocatalytic activities of the degradation of a methylene blue (MB), methyl orange (MO) and rhodamine B (Rh.B) solution were carried out under visible-light irradiation. The absorbance of degraded organic dyes was determined by a UV-vis spectrophotometer.

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2. Experimental Procedure

2.1. Materials

Zinc chloride (ZnCl_2), selenium metal powder and ammonium hydroxide (NH_4OH , 28%) were purchased from Dae Jung Chemicals & Metal Co., Ltd., Korea. Anhydrous purified sodium sulfite (Na_2SO_3 , 95%) was purchased from Duksan Pharmaceutical Co., Ltd., Korea. The titanium (IV) *n*-butoxide (TNB, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) used as a titanium source for the preparation of the TiO_2 nanoparticles was purchased from Kanto Chemical Company (Tokyo, Japan). The MB ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S-Cl}$, 99.99+%), MO ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, 99.99+%) and Rh.B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, 99.99+%) used as model pollutants were purchased from Duksan Pure Chemical Co., Ltd., Korea; Daejung Chemicals & Metals Co., Ltd., Korea; and from Samchun Pure Chemical Co., Ltd., Korea, respectively. Table 1 shows the structure and properties of the MB, MO and Rh.B pollutants. All chemicals were used without further purification, and all experiments were carried out using distilled water.

2.2. Synthesis of ZnSe-TiO₂ composite

TiO_2 nanoparticles were prepared according to our previous work.¹²⁾ The detailed process is described as follows: firstly, TiO_2 precursors were prepared with a molar ratio of

ethanol: H_2O : TNB of 35:15:4, and the suspension was then sonicated at room temperature for 2 h using a controllable serial-ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea). The final products were filtered and washed repeatedly and then vacuum-dried at 373 K. The dried catalyst was ground in a ball mill and calcined at 773 K for 1 h to obtain TiO_2 nanoparticles.

For the synthesis of the ZnSe-TiO₂ composite, a sodium seleno sulfite (Na_2SeSO_3) solution and a $\text{Zn}(\text{NH}_3)_4^{2+}$ solution were initially prepared. Na_2SO_3 (5 g) and selenium metal powder (0.5 g) were dissolved in 30 mL distilled water and refluxed for 1 h to form a Na_2SeSO_3 solution under certain conditions. Meanwhile, 22 mg of ZnCl_2 was dissolved in 2 mL of distilled water. NH_4OH (6 mL) was added to this and the mixture was stirred until it dissolved completely to form a $\text{Zn}(\text{NH}_3)_4^{2+}$ solution. Then, an amount of 0.5 g of TiO_2 nanoparticles was added to the $\text{Zn}(\text{NH}_3)_4^{2+}$ solution and this was followed by stirring for 2 h at an ambient temperature for the adsorption most of the $\text{Zn}(\text{NH}_3)_4^{2+}$ onto the surfaces of the TiO_2 nanoparticles. Finally, the $\text{Zn}(\text{NH}_3)_4^{2+}/\text{TiO}_2$ solution and a certain amount of Na_2SeSO_3 solution were mixed and transferred to a Teflon-lined stainless steel autoclave that was sealed afterwards. The contents were then warmed to 433 K for 8 h. The reaction mixture was allowed to cool to room temperature and the precipitate was filtered and

Table 1. The Molecular Structure and Absorbance Maximum (λ_{max}) of the Organic Dyes

Organic dyes	Molecular structure	λ_{max}
Methylene blue (MB)		665 nm
Methylene orange (MO)		465 nm
Rhodamine B (Rh.B)		554 nm

washed with distilled water five times. After being dried in a vacuum at 353 K for 8 h, the ZnSe-TiO₂ composite was obtained.

2.3. Characterization

The Brunauer-Emmett-Teller (BET) surface area of the ZnSe-TiO₂ composite was evaluated using N₂ adsorption isotherms at 77 K using a BEL Sorp analyzer (BEL). The X-ray diffraction (XRD, Shimadzu XD-D1) result was used to identify the crystallinity with Cu K α radiation. Scanning electron microscopy (SEM, JSM-5600) was used to observe the surface state and structure of the ZnSe-TiO₂ composite using an electron microscope. The element mapping over the desired region of the ZnSe-TiO₂ composite was detected by means of an energy dispersive X-ray (EDX) analysis as part of the SEM analysis. UV-vis diffuse reflectance spectra (DRS) were obtained using an UV-vis spectrophotometer (Neosys-2000) with BaSO₄ as a reference and were converted from reflection to absorbance by the Kubelka-Munk method.

2.4. Photocatalytic activity measurements

The photocatalytic activity of the ZnSe-TiO₂ composite was evaluated by the degradation of the MB, MO and Rh.B solution under irradiation with visible light (8W, $\lambda \geq 420$ nm). In an ordinary photocatalytic test performed at room temperature, 0.05 g the ZnSe-TiO₂ composite was added to 50 mL of a 2.0×10^{-5} mol/L MB, MO and Rh.B solution, which is hereafter considered as the initial concentration (c_0). Before turning on the LED visible lamp, the solution mixed with composite was kept in the dark for at least 2 h, allowing the adsorption/desorption equilibrium to be reached. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on) in order to determine the dye concentration in the solution after dark adsorption, hereafter considered as the initial concentration (c_{ads}). Samples were then withdrawn regularly from the reactor at 30 min, 60 min, 90 min, 120 min, and 150 min and immediately centrifuged to separate any suspended solids. The clean transparent solution was analyzed using a UV-vis spectrophotometer (Optizen POP) at a wavelength from 250 nm to 800 nm.

3. Results and Discussion

3.1. Characterization

The porosity of the ZnSe-TiO₂ composite was measured using the nitrogen physisorption technique. A representative nitrogen adsorption isotherm of the ZnSe-TiO₂ composite is presented in Fig. 1. It exhibits the Type-I adsorption isotherm, which indicate the presence of microporous and mesoporous. Figure 1 (inset) shows the pore size distributions of the ZnSe-TiO₂ composite measured using the BJH method. The BET surface area, average diameter of the pores and the total pore volume obtained are 101.27 m²/g, 2.9 nm, and 0.07 cm³/g, respec-

Fig. 1. Nitrogen adsorption isotherm of the ZnSe-TiO₂ composite. The inset shows the pore size distribution of the ZnSe-TiO₂ composite.

Fig. 2. XRD patterns of TiO₂ nanoparticles and the ZnSe-TiO₂ composite.

tively, which indicate that the prepared ZnSe-TiO₂ composite would have significant absorption ability.

Figure 2 shows the XRD patterns of the pure TiO₂ and prepared ZnSe-TiO₂ composite. The peaks marked by letters and symbols represent the anatase structure of the TiO₂ and the ZnSe structure, respectively. The XRD diffraction peaks around 2θ of 25.3°, 37.8°, 48.0°, 55°, and 62.5° are the diffractions of the (101), (004), (200), (201), and (204) planes of the anatase TiO₂ (JCPDS No. 21-1272)¹³⁻¹⁵ while those of the (002), (111), (220), (311), (400), and (331) of ZnSe crystal planes originate from the blende structure (JCPDS Card No. 21-1272), in accordance with the results reported by Lee *et al.* with the lattice parameters.¹⁶ The diffractogram of the prepared ZnSe-TiO₂ composite suggests the presence of the anatase structure of TiO₂ as well as the blende structure of ZnSe, and no peaks for impurities were detected.

SEM with EDX analysis provides information about the morphology, crystallinity and chemical composition of the prepared samples. Figure 3 shows a SEM microphotograph (a and b), the EDX microanalysis results (c) and the element weight % (d) of the ZnSe-TiO₂ composite. Very uniform par-

Fig. 3. SEM microphotograph (a and b), EDX microanalysis results (c) and element weight % (d) of the TiO_2 and the ZnSe-TiO_2 composite.

ticles can be observed in the low-magnification SEM image (Fig. 3 (a)), and the ZnSe particles are dispersed on the TiO_2 particles regularly. From the high-magnification SEM image (Fig. 3 (b)), it can be seen that the average size of the ZnSe-TiO_2 composite is around 200 nm.

The chemical composition and the element weight % of the prepared ZnSe-TiO_2 composite were examined by EDX. Figures 3 ((c) and (d)) show that the main elements, in this case Ti, O, Cd, and Se, are present. This indicates that a high-purity ZnSe-TiO_2 composite was successfully synthesized in this study. According to a former study, the small concentration of dopant in the TiO_2 matrix can prevent the formation of hole/electron recombination centers and an increase in the negative charge capabilities.

To obtain more detailed imagery at a higher magnification, the surface nanostructures and particle sizes of the TiO_2 and ZnSe-TiO_2 composites were studied by a TEM analysis. These results are shown in Fig. 4. The TEM images reveal, well-dispersed anatase TiO_2 nanoparticles with an average size of around 15-20 nm, as particle agglomeration was effectively inhibited by the introduction of the ZnSe nanoparticles. A few black dots can be observed in these images, corresponding to the deposition of ZnSe nanoparticles with an average size of around 15-25 nm and

Fig. 4. TEM microphotograph of the TiO_2 (a) and ZnSe-TiO_2 composite (b).

Fig. 5. UV-vis diffuse reflectance spectra of pure TiO_2 and the ZnSe-TiO_2 composite. The inset shows the variation of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for the ZnSe-TiO_2 composite.

rectangular and circular shapes. The presence of a distinct juncture between the two crystal phases further confirmed the strong interaction between the ZnSe and TiO_2 in ZnSe-TiO_2 .

Figure 5 shows the UV-vis absorbance spectra and UV-vis diffuse reflectance spectra of the pure TiO_2 and the ZnSe-TiO_2 composite. A careful study of both spectra shows an identical absorbance peak at around 250 nm, indicating that both the pure TiO_2 and the ZnSe-TiO_2 composite have activity at the UV region. However, the pure TiO_2 absorbs mainly ultraviolet light with an absorption wavelength of less than 400 nm, whereas the ZnSe-TiO_2 composite absorbs light at a wavelength shorter than 618 nm. After introducing ZnSe , the absorption edge shifted toward the visible region (red shift). The pure TiO_2 shows absorption only in the UV region due to the intrinsic bandgap of TiO_2 . The onset of the absorption spectrum of the ZnSe-TiO_2 composite is shifted towards the visible-light region, representing an emission peak from the band-edge-free excitation. The bandgap energy of a semiconductor can be calculated by the following formula:¹⁷⁾

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

Here, α , ν , E_g , and A denote the absorption coefficient, the

Fig. 6. Relative concentrations (c/c_0) of organic dye (MB, MO, Rh.B) solutions depending on the visible-light irradiation time for pure TiO_2 and the ZnSe-TiO_2 composite.

light frequency, the bandgap, and a constant, respectively. Therefore, the bandgap energy (E_g) of the ZnSe-TiO_2 composite can be estimated from a plot of $(\alpha h\nu)^{1/2}$ versus the photo energy ($h\nu$). The intercept of the tangent to the X axis would give a good approximation of the bandgap energy of the samples. The bandgap of the ZnSe-TiO_2 composite is evaluated to be 2.5 eV (Fig. 5, inset), which is smaller than the standard bandgap for TiO_2 (3.25 eV),^{1,6)} showing a blue shift of 0.75 eV.

3.2. Degradation of organic dyes

In an effort to investigate the photocatalytic activity of the prepared ZnSe-TiO_2 composite, we first measured the absorbance changes of the MB, MO and Rh.B solutions in the presence of the ZnSe-TiO_2 composite under visible light irradiation for given times. Then, we performed a study as a function of time in order to examine the kinetic process of degradation versus the light irradiation time. Degradation was followed by a decrease in the absorbance maximum (λ_{max}) at 665 nm, 465 nm, and 554 nm for the MB, MO, and Rh.B solutions, respectively. Figure 6 depicts degradation versus time for the MB, MO and Rh.B solutions as a ratio expressed by (c/c_0) in the presence of TiO_2 and the ZnSe-TiO_2 composite under UV light irradiation. After being kept in the dark for at least 2 h, the MB, MO, and Rh.B solutions became decolorized by ZnSe-TiO_2 by about 25%, 32%, and 17%, respectively. There are three tropisms when a molecule is adsorbed on a sorbent. According to Table 1, the MO molecule has obverse tropism ($1.54 \text{ nm} \times 0.48 \text{ nm}$), end tropism ($1.54 \text{ nm} \times 0.28 \text{ nm}$), and side tropism ($0.48 \text{ nm} \times 0.28 \text{ nm}$); it is the smallest among the three types of organic dyes. Thus, the pores can adsorb more MO molecules than MB or Rh.B molecules.

The concentrations of the MB, MO, and Rh.B solutions decreased with an increase in the VL irradiation time. After VL irradiation for 150 min, the MO solution was photo-

Fig. 7. The scheme of the excitation and charge transfer process between ZnSe and TiO_2 particles.

degraded by only 31%. The photocatalytic effect cannot be removed in the case of the MO molecules because most of the MO molecules had adsorbed into the pores of the ZnSe-TiO_2 composite and not on the surface of the ZnSe-TiO_2 composite. In addition, the Rh.B solution was photo-degraded by 40%. However, for the MB solution, 47% was photo-degraded by the ZnSe-TiO_2 composite. These results indicate that the prepared ZnSe-TiO_2 composite has excellent visible-light photocatalytic activity.

It is generally thought that photocatalytic performance depends on the phase structure, the absorbance, and the adsorption capacity of a photocatalyst.¹⁸⁾ In our experiments, the enhanced activity can be attributed to the improved optical absorption and the heterostructure, which favors the separation of photo-introduced electron/hole pairs in photosensitizer-titanium dioxide photocatalysts.¹⁹⁾ Meanwhile, due to the large surface area of the as-prepared composite photocatalyst, more dye molecules can be adsorbed onto the photocatalyst surface, which increases the number of photocatalytic reaction sites.²⁰⁾ The scheme of the excitation and charge transfer process between ZnSe and TiO_2 under visible-light irradiation is shown in Fig. 7. Under irradiation by a visible lamp, the generated electrons in the ZnSe and holes in the TiO_2 migrate to the conduction band (CB) of TiO_2 and the valence band (VB) of ZnSe , respectively (corresponding to Eqs. (1) and (2), respectively). This transfer process is thermodynamically favorable because both the CB and VB of ZnSe lie above those of TiO_2 . Meanwhile, the generated electrons most likely react with dissolved oxygen molecules and produce the oxygen peroxide radical $\text{O}_2^{\cdot-}$ (Eqs. (3) and (4)), the positively charged hole (h^+) may react with the OH^- derived from H_2O to form the hydroxyl radical $\text{OH}^\cdot$ (Eqs. (5) and (6)). It is well known that $\text{O}_2^{\cdot-}$ and $\text{OH}^\cdot$ are powerful oxidizing agents capable of degrading most pollutants.²¹⁾ The dye molecule then can be photo-degraded by the oxygen peroxide radical $\text{O}_2^{\cdot-}$ and the hydroxyl radical $\text{OH}^\cdot$ to CO_2 , H_2O or other mineralization products (Eq. (7)).

4. Conclusions

In this study, a ZnSe-TiO₂ composite was successfully synthesized by a simple hydrothermal method. The BET surface area, average diameter of the pores, and the total pore volume of the prepared ZnSe-TiO₂ composite are 101.27 m²/g, 2.9 nm and 0.07 cm³/g, respectively. From the XRD patterns, the blend crystal structure of ZnSe and the anatase structure of TiO₂ can be observed. SEM and TEM microphotographs show that TiO₂ particles are homogeneously coated with ZnSe particles with a uniform particle size. The diffuse reflectance spectra suggest that the ZnSe-TiO₂ photocatalyst shows strong photoabsorption in the UV light and visible light ranges, with a bandgap of 2.5 eV. The photocatalytic activity of the ZnSe-TiO₂ photocatalyst was investigated by the degradation of MB, MO and Rh.B in aqueous solutions under irradiation using a visible lamp. The results reveal that the ZnSe-TiO₂ composite exhibits much higher photocatalytic activity than pure TiO₂ under visible-light irradiation in MB and Rh.B solutions.

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