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Preparation and Photocatalytic Activity of CdSe-TiO_2 Composite Designed for High Decomposition Effect

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In this study, CdSe-TiO_2 composite were synthesized by a facile sol-gel method and characterized by nitrogen adsorption isotherms (77 K), X-ray diffraction, scanning electron microscopy with energy dispersive X-ray (EDX) analysis and UV-visible diffuse reflectance spectrophotometer. The photocatalytic activity was investigated by degrading methylene blue, methyl orange and rhodamine B (Rh.B) in aqueous solution under irradiation of UV light as well as visible light. The absorbance of degraded methylene blue solution was determined by UV-visible spectrophotometer. The results revealed that the CdSe-TiO_2 composite exhibited much higher photocatalytic activity than pure TiO_2 both under irradiation of UV light as well as visible light for photodegradation of methylene blue solution.

Key Words: TiO_2, CdSe, UV-VIS, Photocatalytic activity.

INTRODUCTION

Titanium dioxide is a promising material for photoelectrochemical solar energy conversion and photocatalytic hazardous waste treatment because of its superior photoreactivity, nontoxicity, long-term stability and low price[1-6]. By coupling a second semiconductor to TiO_2, 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. Another important feature of the coupled semiconductor system is that the photoresponse of a large band gap semiconductor can be extended into the visible region by coupling it with a short band gap semiconductor[7-9]. Conventionally, anatase TiO_2 only absorbs wavelength in the near-UV region ($\lambda \leq 390$ nm), which is about 3 % of the solar spectrum. Thus, solar energy cannot be utilized efficiently in real applications. Fortunately, coupling of TiO_2 with a smaller band gap semiconductor seems to be a promising approach to overcome this inherent limitation. In a coupled semiconductor system, the small band gap semiconductor that absorbs visible light acts as a photosensitizer for the TiO_2. Through the transfer of a photoexcited electron from the small band gap semiconductor to the TiO_2 particle, a photocatalytic redox reaction can occur. Thus, this photosensitization property of a coupled semiconductor system provides an alternative approach in the design of efficient visible light photocatalysts.

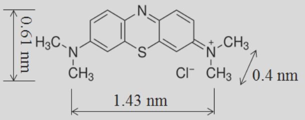
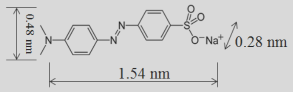
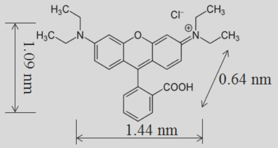
Cadmium selenide (CdSe) is a kind of semiconductor with forbidden zone of 1.7 eV, which closely matches the solar spectrum[10,11] and its valence electrons can be easily evoked to conduction band when the light wavelength of evoking light is less than or equal to 730 nm. Moreover, it is important to note that the conduction band minimum of the small band gap semiconductor should be higher than that of TiO_2 so that the transfer of the photo-generated electron is allowed from the former to the latter one. In addition, CdSe exhibits much greater photostability than organic dyes when used as a photosensitizer.

In this work, CdSe-TiO_2 composite were obtained directly *via* a facile sol-gel preparation method. The resulting composite was characterized by nitrogen adsorption isotherms (77 K), X-ray diffraction, scanning electron microscopy with energy dispersive X-ray (EDX) analysis and UV-VIS diffuse reflectance spectrophotometer. The photocatalytic activities on the degradation of methylene blue, methyl orange and rhodamine B (Rh.B) solution were carried out under irradiation of UV light and visible light. The absorbance of degraded organic dyes was determined by UV-VIS spectrophotometer.

EXPERIMENTAL

Cadmium acetate dihydrate [$Cd(CH_3COO)_2{\cdot}2H_2O$, 98 %], selenium metal powder and ammonium hydroxide (NH_4OH, 28 %) were purchased from Daejung Chemicals & Metal Co., Ltd., Korea. Anhydrous purified sodium sulfite (Na_2SO_3, 95 %) was purchased from Duksan Pharmaceutical Co., Ltd, Korea. Titanium oxide powder (TiO_2) was commercially available purchased from Duksan Pure Chemical Co., Ltd., Korea, which was composed of a single phase of anatase structure with secondary particles of about 80-150 μm aggregated from the primary particles of about 30-50 μm. The methylene blue ($C_{16}H_{18}N_3S{\cdot}Cl$, 99.99 + %), methyl orange ($C_{14}H_{14}N_3NaO_3S$, 99.99 + %) and rhodamine-B ($C_{28}H_{31}ClN_2O_3$, 99.99 + %) was used as model pollutant, which purchased from Duksan Pure Chemical Co. Ltd., Korea, Daejung Chemicals & Metals Co. Ltd., Korea and Samchun Pure Chemical Co. Ltd., Korea, respectively. Table-1 shows the structure and properties of methylene blue, methyl orange and rhodamine-B dyes. All the chemicals used without further purification and all experiments were carried out using distilled water.

TABLE-1
MOLECULAR STRUCTURE AND ABSORBANCE MAXIMUM (λ_{max}) OF ORGANIC DYES

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

Synthesis of CdSe-TiO₂ composite: For the synthesis of CdSe-TiO₂ composite, the sodium seleno sulfite (Na_2SeSO_3) solution and $Cd(NH_3)_4^{2+}$ solution was prepared at first. Na_2SO_3 (5 g) and selenium metal powder (0.5 g) were dissolved in 30 mL of distilled water and refluxed for 1 h to form Na_2SeSO_3 solution. Meanwhile, $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.5 g) was dissolved in 2 mL of distilled water. NH_4OH (6 mL) was added to it and the mixture was stirred till it dissolved completely to form $Cd(NH_3)_4^{2+}$ solution. Finally, the titanium oxide (0.5 g), $Cd(NH_3)_4^{2+}$ solution and Na_2SeSO_3 solution were mixed together and the mixture was stirred and refluxed for at least 5 h. After the temperature of the mixture was brought down to room temperature and the mixture was filtered through Whatman filter paper. The solid obtained was collected and washed with distilled water for 5 times. After being dried in vacuum at 353 K for 8 h, the CdSe-TiO₂ composite was obtained.

Characterization: The Brunauer-Emmett-Teller (BET) surface area of CdSe-TiO₂ composite was evaluated from the N_2 adsorption isotherms at 77 K using a BEL Sorp Analyzer (BEL). X-ray diffraction (XRD, Shimadz XD-D1) result was used to identify the crystallinity with CuK_α radiation. Scanning electron microscopy (SEM, JSM-5600) was used to observe the surface state and structure of CdSe-TiO₂ composite using an electron microscope. The element mapping over the desired region of CdSe-TiO₂ composite was detected by an energy dispersive X-ray analysis attached to SEM. UV-VIS diffuse reflectance spectra (DRS) were obtained using an UV-VIS spectrophotometer (Neosys-2000) by using $BaSO_4$ as a reference and were converted from reflection to absorbance by the Kubelka-Munk method.

Photocatalytic activity measurements: Photocatalytic activity of the CdSe-TiO₂ composite was evaluated by the degradation of methylene blue, methyl orange and rhodamine-B solution under irradiation of UV light (8 W, λ = 365 nm) and visible light (8 W, λ = 420 nm). In an ordinary photocatalytic test performed at room temperature, 0.05 g CdSe-TiO₂ composite was added to 50 mL of 1.0×10^{-5} mol/L methylene blue, methyl orange and rhodamine-B solution, which was hereafter considered as the initial concentration (c_0). Before turning on the UV or 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. Then, the solution was irradiated with UV or visible lamp. 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 methylene blue concentration in solution after dark adsorption, which was hereafter considered as the initial concentration (c_{ads}). Samples were then withdrawn regularly from the reactor by an order of 0.5, 1, 1.5, 2, 3 and 4 h and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-VIS spectrophotometer (Optizen POP) at wavelength from 250 to 800 nm.

RESULTS AND DISCUSSION

Characterization: The porosity of the CdSe-TiO₂ composite is measured using the nitrogen physisorption technique. A representative nitrogen adsorption isotherm of CdSe-TiO₂ composite is presented in Fig. 1. It exhibits type-II adsorption isotherm, which indicate the presence of microporous and mesoporous. Fig. 1 (inset) shows the pore size distributions of CdSe-TiO₂ composite measured using the BJH method. The BET surface area, average diameter of the pores and the total pore volume obtained are 112.73 m^2/g, 3-4 nm and 0.21 cm^3/g, respectively, which indicate the prepared CdSe-TiO₂ composite would have big absorption ability.

Fig. 2 shows the XRD patterns of pure TiO₂ and prepared CdSe-TiO₂ composite. The peaks marked by triangle (Δ) and rectangle (□) are represented to anatase structure of TiO₂ and CdSe structure, respectively. The XRD diffraction peaks around 2θ of 25.3°, 37.8°, 48.0°, 55° and 62.5° are the diffractions of (101), (004), (200), (201) and (204) planes of anatase TiO₂ (JCPDS No. 21-1272)[12-15] and peaks around 2θ of 25.4°, 42° and 49.6°, which can be indexed to the characteristic peaks (111), (220) and (311) plane reflections of cubic crystal structure CdSe with lattice constants of 6.05 Å (JCPDS No. 65-2891)[16,17]. The diffractogram of prepared CdSe-TiO₂ composite suggests the presence of anatase structure TiO₂ as well as cubic structure CdSe and no peaks for impurities are detected. This indicates that the sol-gel method used in this study is responsible for the formation of the CdSe-TiO_2 composite.

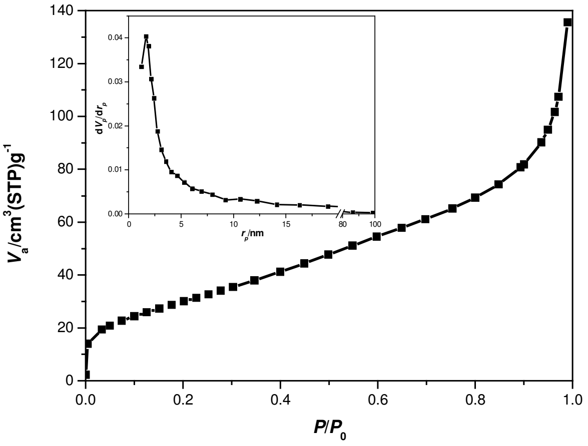


Fig. 1. Nitrogen adsorption isotherm of CdSe-TiO_2 composite. The inset is the pore size distribution of CdSe-TiO_2 composite

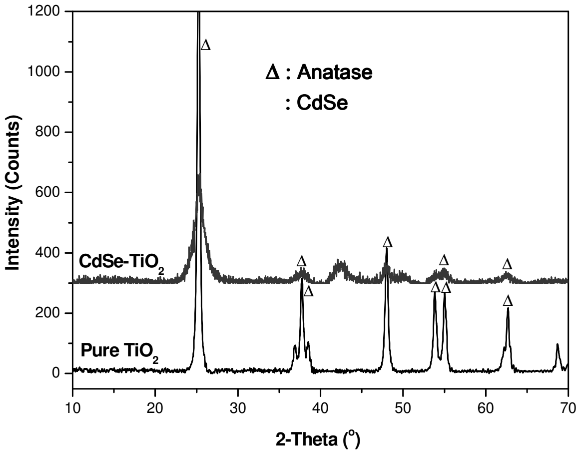
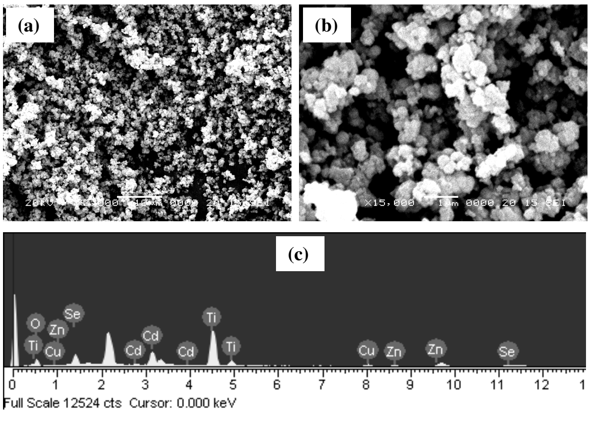


Fig. 2. XRD patterns of pure TiO_2 and CdSe-TiO_2 composite

SEM with EDX analysis provides information on the morphology, crystallinity and chemical composition of the prepared samples. Fig. 3 shows the SEM microphotograph (a and b), EDX microanalysis (c) and element weight % (d) of CdSe-TiO_2 composite. Very uniform particles can be observed from the low magnification of SEM [Fig. 3 (a)] and the TiO_2 particles are dispersed on the CdSe particles regularly. From the high magnification of SEM [Fig. 3 (b)], it can be seen that average size of CdSe-TiO_2 composite is around 200 nm.



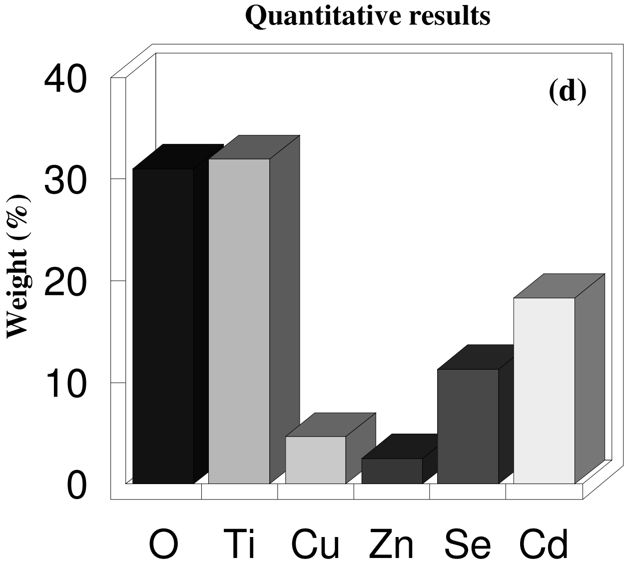


Fig. 3. SEM microphotograph (a and b), EDX microanalysis (c) and element weight % (d) of CdSe-TiO_2 composite

Chemical composition analysis and element weight % of prepared CdSe-TiO_2 composite is examined by EDX. From the Fig. 3 [(c) and (d)], it is observed that the main elements such as Ti, O, Cd and Se are existed and other impure elements such as Zn and Cu are also existed which might get from the experimental process. And the content of main elements is much more than that of impure elements. It can be indicated that the CdSe-TiO_2 composite with high purity has been successfully synthesized in this study.

Fig. 4 shows the UV-VIS diffuse reflectance spectra of pure TiO_2 and CdSe-TiO_2 composite. A careful study of both spectra shows a same absorbance peak at around 250 nm, indicating both of pure TiO_2 and CdSe-TiO_2 composite has activity at UV region. However, the pure TiO_2 absorbs mainly the ultraviolet light with absorption wavelength less than 400 nm, whereas CdSe-TiO_2 composite absorbs light at wavelength shorter than 738 nm. After introducing of CdSe, the absorption edge is shifted toward the visible region (red shift). Pure TiO_2 shows absorption only in the UV region due to the intrinsic band gap of TiO_2. The onset of the absorption spectrum of CdSe-TiO_2 composite is shifted towards visible light. It is an emission peak from band edge free excitation. The band gap energy of a semiconductor can be calculated by the following formula[18]:

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

where, α, ν, E_g and A are the absorption coefficient, light frequency, band gap and a constant, respectively. Therefore, the band gap energy (E_g) of CdSe-TiO_2 composite can be estimated from a plot of $(\alpha h\nu)^{1/2}$ *versus* photo energy ($h\nu$). The intercept of the tangent to the X axis would give a good approximation of the band gap energy of the samples. The band gap of CdSe-TiO_2 composite is evaluated to be 1.95 eV (Fig. 4 inset), which is greater than the standard band gap for CdSe (1.74 eV)[19,20], showing a blue shift of 0.21 eV.

Degradation of organic dyes: In order to investigate the photocatalytic activity of prepared CdSe-TiO_2 composite, we measured the absorbance changes of methylene blue, methyl orange and rhodamine-B solution in the presence of CdSe-

TiO_2 composite under the irradiation of UV light for given times at first. Then we performed a study as a function of time in order to examine the kinetic process of degradation versus light irradiation time. Degradation was followed by the decrease of absorbance maximum (λ_{max}) at 665, 465 and 554 nm for methylene blue, methyl orange and rhodamine-B solution, respectively. Fig. 5 depicts degradation versus time for the methylene blue, methyl orange and rhodamine-B solution as the ratio expressed by (c/c_0) in the presence of CdSe-TiO_2 composite under the irradiation of UV light. It can be clearly seen that the degradation of organic dyes was caused by two effects, one is adsorption effect and another is photodegradation effect by prepared CdSe-TiO_2 composite. After keeping in the dark for at least 2 h, the methylene blue, methyl orange and rhodamine-B solution has been degraded 22, 40 and 12 %, respectively. There are three tropisms when a molecule was adsorbed on a sorbent. According to the Table-1, the methyl orange molecule has observe tropism (1.54 nm × 0.48 nm), end tropism (1.54 nm × 0.28 nm) and side tropism (0.48 nm × 0.28 nm), which is the smallest among the three kinds of organic dyes. Thus the pores can adsorb more methyl orange molecules than that of methylene blue and rhodamine-B molecules. The photodegradation effect is carried out after turning on the UV lamp. The concentration of methylene blue, methyl orange and rhodamine-B solution is decreased by an increasing of UV irradiation time. After UV irradiation for 240 min, the methyl orange solution is photodegraded only 8 %. The photocatalytic effect cannot be taken out for methyl orange molecules due to the most of methyl orange molecules have been adsorbed into the pores of CdSe-TiO_2 composite, not on the surface of CdSe-TiO_2 composite. The rhodamine-B solution is photodegraded 15 %. However, for methylene blue solution, 48 % has been photodegraded by CdSe-TiO_2 composite. According to our previous work[21]) methylene blue solution could be photodegraded 21 % by pure TiO_2, which is more than 2 times less than CdSe-TiO_2 composite. These results can be indicated that the prepared CdSe-TiO_2 composite has excellent photocatalytic activity under UV region.

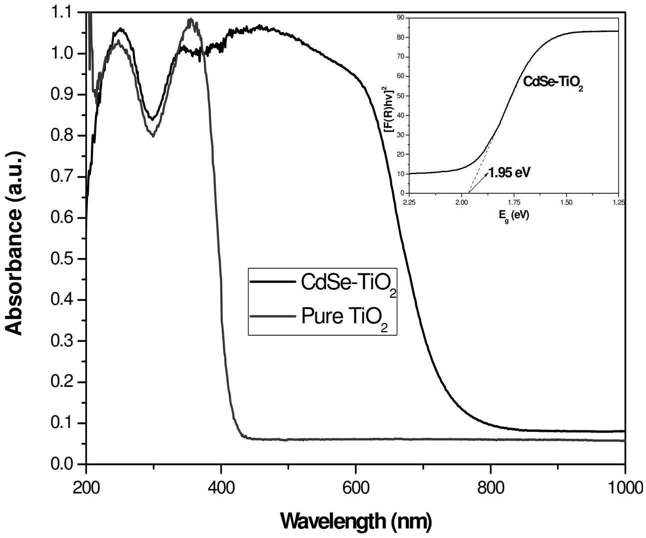


Fig. 4. UV-VIS diffuse reflectance spectra of pure TiO_2, CdSe-TiO_2 composite. The inset shows the variation of $(\alpha h\nu)^2$ *versus* photon energy (hν) for CdSe-TiO_2 composite

Due to the CdSe-TiO_2 composite has most photocatalytic activity for degradation of methylene blue solution under irradiation of UV light, so we choose the methylene blue solution to determine the photocatalytic activity of CdSe-TiO_2 composite under irradiation of visible light. As shows in Fig. 5 (inset), after visible light irradiation for 4 h, the methylene blue solution is photodegradated only 10 % by pure TiO_2. However, when prepared CdSe-TiO_2 composite is used as photocatalyst, the methylene blue solution is photodegradated 43 %, which is 4.3 times more than pure TiO_2. This can be indicated that the prepared CdSe-TiO_2 composite has also excellent photocatalytic activity under visible light region.

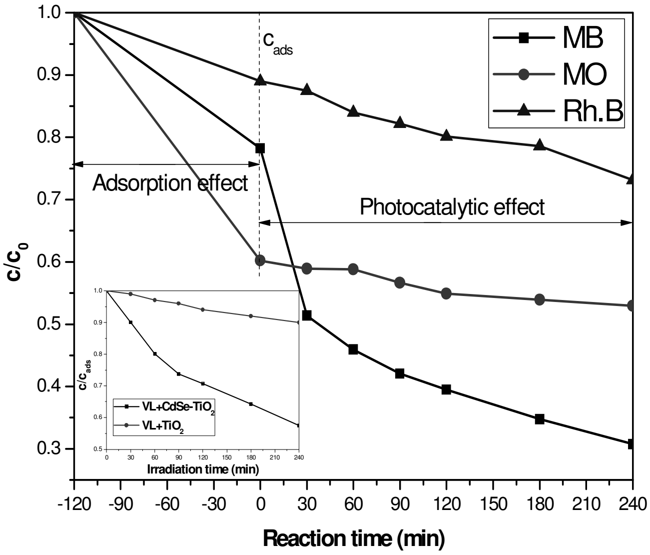


Fig. 5. Relative concentration (c/c_0) of organic dyes solution on time of UV irradiation for CdSe-TiO_2 composite. The inset shows the relative concentration (c/c_{ads}) of methylene blue solution on the time of visible light irradiation for pure TiO_2 and CdSe-TiO_2 composite

Conclusion

In this study, CdSe-TiO_2 composite was successfully synthesized by a simple sol-gel method. Brunauer-emett-teller surface area, average diameter of the pores and the total pore volume of prepared CdSe-TiO_2 composite are 112.73 m^2/g, 7.44 nm and 0.21 cm^3/g, respectively. From the XRD patterns, the cubic crystal structure of CdSe and anatase structure of TiO_2 can be observed. SEM microphotograph shows that the TiO_2 particles homogenously coated on the CdSe particles with uniform particle size. The EDX results reveal the presence of CdSe and TiO_2 with high content in prepared composite. The diffuse reflectance spectra suggest the CdSe-TiO_2 photocatalyst shows strong photoabsorption at UV light and visible light range, with band gap is 1.95 eV. The photocatalytic activity of these CdSe-TiO_2 photocatalyst is investigated by degradation of methylene blue, methyl orange and rhodamine-B in aqueous solution under UV lamp as well as visible lamp irradiation. The results reveal that CdSe-TiO_2 composite exhibit much higher photocatalytic activity than pure TiO_2 both under irradiation of UV light as well as visible light for methylene blue solution.

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