

Synthesis of CdSe-TiO₂ Photocatalyst and Their Enhanced Photocatalytic Activities under UV and Visible Light

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In this study, CdSe-TiO₂ photocatalyst were synthesized by a facile solvothermal method and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and UV-vis diffuse reflectance spectrophotometer. The photocatalytic activity was investigated by degrading methylene blue (MB) in aqueous solution under irradiation of UV light as well as visible light. The absorbance of degraded MB solution was determined by UV-vis spectrophotometer. The results revealed that the CdSe-TiO₂ photocatalyst exhibited much higher photocatalytic activity than TiO₂ both under irradiation of UV light as well as visible light.

Key Words : CdSe, TiO₂, UV-vis, Photocatalytic activity

Introduction

In most of the industrial wastewater treatment works, adsorption by activated carbon, advanced chemical oxidation, enhanced coagulation and photochemical processes are commonly employed technologies for removal of refractory pollutants from industrial wastes. The advance of photochemical processes has made the decomposition of synthesized refractory organics sustainable, especially with the advent of semiconductor photocatalysts.^{1,2} Several semiconductors have been developed to exhibit photocatalytic behavior. The most commonly referenced semiconductors for waste degradation are TiO₂, ZnO, CdS, etc.¹ TiO₂ is of great interest mainly due to its unique properties, such as high photoactivity and size dependent optical properties.¹ However, TiO₂ is a wide band gap semiconductor (band gap around 3.2 eV), which adsorbs light only in the UV region. To overcome this problem, various materials, like dyes and metallic nanoparticles, have been used as sensitizer to increase the photoactivity of TiO₂ in the visible range.

Compared with other materials, semiconductors have attracted considerable interest in the past two decades because of their applications in single electron transistors,³ lasers,⁴ light emitting diodes,⁵ and infrared photodetectors⁶ operating at lower currents and higher temperatures. Semiconductors have two unique advantages: (1) their band gap can be modified by varying the size to tune the visible response; (2) they can utilize hot electrons or to generate multiple charge carriers with a single highenergy photon.⁷ Various semiconductors, including CdS,⁸ PbS,⁹ Bi₂S₃,¹⁰ CdSe,^{11,12} and InP,¹³ have been investigated to sensitize TiO₂ as a visible light absorber. Among these semiconductors, Cadmium selenide (CdSe) is a kind of semiconductor with forbidden zone of 1.7 eV, 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. In addition,

CdSe exhibits much greater photostability than organic dyes when used as a photosensitizer. Therefore, many attempts have been made to use CdSe to photosensitize TiO₂ in visible light. Rincon *et al.*^{14,15} have reported the photovoltaic conversion of TiO₂ coatings sensitized with chemically deposited CdSe thin films. Fang *et al.*^{16,17} have also showed that modification of the TiO₂ electrode with CdSe particles could extend the optical absorption spectrum and photocurrent action spectrum into the visible range. However, there is no report on the utilization of CdSe/TiO₂ photocatalyst systems for environmental purification under visible light irradiation.

In this paper, CdSe-TiO₂ photocatalysts with enhanced photocatalytic activity on the degradation of organic dyes were obtained directly *via* a conventional solvothermal preparation method. The resulting photocatalysts were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and UV-vis diffuse reflectance spectrophotometer. The photocatalytic activity on the degradation of methylene blue (MB) was carried out under irradiation of UV light and visible light.

Experimental

Materials. Cadmium acetate dihydrate (Cd(CH₃COO)₂, 98%), Selenium metal powder and ammonium hydroxide (NH₄OH, 28%) were purchased from Dae Jung Chemicals & Metal Co., Ltd, Korea. Anhydrous purified sodium sulfite (Na₂SO₃, 95%) and methylene blue (MB, C₁₆H₁₈N₃S·Cl, 99.99%) were purchased from Duksan Pharmaceutical Co., Ltd, Korea. Titanium oxide nanopowder (TiO₂, < 25 nm, 99.7%) with anatase structure was purchased from Sigma-Aldrich Chemistry, USA. All chemicals used without further purification and all experiments were carried out using distilled water.

Synthesis. For the synthesis of CdSe-TiO₂ photocatalyst, two step procedures were used. In the first step, the precursor for Se that is, sodium seleno sulfite (Na₂SeSO₃) solution was prepared, which consequently allowed to react with cadmium acetate and titanium oxide in the second step.

Synthesis of Sodium Seleno Sulfite (Na₂SeSO₃) Solution: For the preparation of Na₂SeSO₃ solution, Na₂SO₃ (5 g) and Selenium metal powder (0.5 g) were dissolved in 30 mL distilled water and refluxed for 1 h. An apparent digestion of the black colored Se dispersion and the formation of a clear solution were observed. It suggested the complete conversion of Se into Na₂SeSO₃. The temperature of the solution was brought down to room temperature and used directly for further synthesis.

Synthesis of CdSe-TiO₂ Photocatalyst: For the synthesis of CdSe-TiO₂ photocatalyst, Cd(CH₃COO)₂ (0.5 g) was dissolved in 2 mL distilled water. NH₄OH (6 mL) was added to it and the mixture was stirred till it dissolved completely to form Cd(NH₃)₄²⁺ solution. Finally, the titanium oxide (0.5 g), Cd(NH₃)₄²⁺ solution and Na₂SeSO₃ 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 What-man filter paper. The solid obtained was collected and washed with distill water for 5 times. After being dried in vacuum at 353 K for 8 h, the CdSe-TiO₂ photocatalyst was obtained.

Characterization. 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 CdSe-TiO₂ photocatalyst using an electron microscope. The element mapping over the desired region of CdSe-TiO₂ photocatalyst was detected by an energy dispersive X-ray (EDX) analysis attached to SEM. UV-vis diffuse reflectance spectra (DRS) were obtained using an UV-vis spectrophotometer (Neosys-2000) by using BaSO₄ as a reference and were converted from reflection to absorbance by the Kubelka-Munk method.

Photocatalytic Activity Measurements. Photocatalytic activities of the CdSe-TiO₂ photocatalyst were evaluated by the degradation of methylene blue (MB) under irradiation of UV light (8 W, $\lambda = 365$ nm) and visible light (8W, $\lambda = 420$ nm). MB with absorption maxima $\lambda_{\text{max}} = 665$ nm^{18,19} is a model pollutant and its chemical structure is shown in Figure 1. In an ordinary photocatalytic test performed at room temperature, 0.05 g CdSe-TiO₂ photocatalyst was added to 50 mL of 1.0×10^{-5} mol/L MB solution. Before turning on the UV or visible lamp, the solution mixed with photocatalyst 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 MB concentration in solution, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 30 min, 60 min, 90 min, 120 min, 180 min and

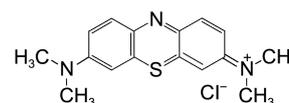


Figure 1. Molecular structure of methylene blue.

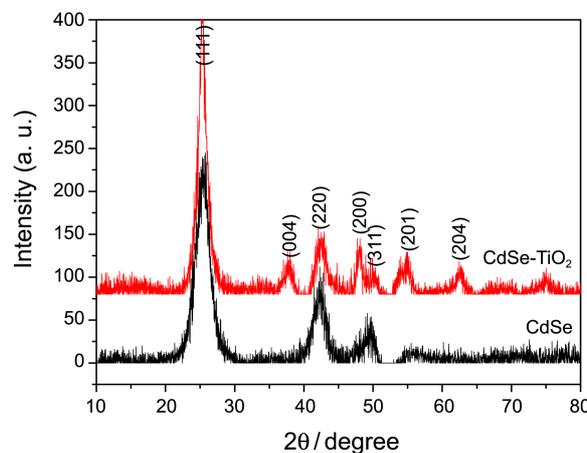


Figure 2. XRD patterns of CdSe and CdSe-TiO₂ photocatalyst.

240 min, 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 nm to 800 nm.

Results and Discussion

Characterization. XRD analysis was used to determine the phase purity of the samples. Figure 2 shows the XRD patterns of the resulting CdSe and CdSe-TiO₂ photocatalyst. As shown in Figure 2, all of the peaks around 2θ of 25.4°, 42° and 49.6°, which could 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).^{20,21} Moreover, for CdSe-TiO₂ photocatalyst, some peaks were also found at 37.9°, 47.8°, 55° and 62.7°, which could be indexed to the characteristic peaks (004), (200), (201), and (204) of anatase TiO₂ (JCPDS No. 21-1272).^{22,23} No peaks for impurities were detected.

SEM with EDX analysis provided information on the morphology, crystallinity and chemical composition of the prepared samples. Figure 3(a) and (b) shows the SEM microphotograph of CdSe particles which are spherical in shape and have homogenous particle size of about 0.5-1 μm . After introduced into TiO₂, it can be clearly seen that the TiO₂ particles homogeneously coated on the CdSe particles with particle size of 100 nm, as showed in the Figure 3(c) and (d).

Chemical composition analysis and element weight % of prepared samples was examined by EDX. The weight % and mole ratios of main element in samples CdSe and CdSe-TiO₂ photocatalyst is shown in Table 1. Main elements Cd and Se were detected in all the regions selected in the samples CdSe and CdSe-TiO₂ photocatalyst. Beside elements Cd and Se, elements Ti and O were also existed in CdSe-TiO₂

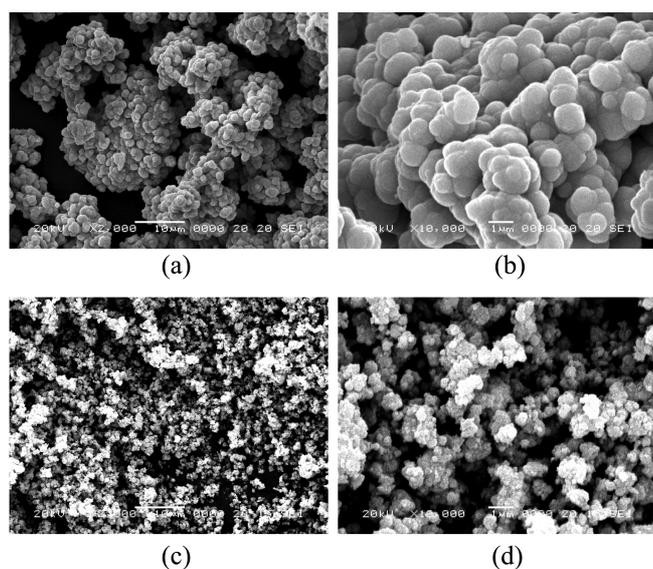


Figure 3. SEM microphotograph of CdSe (a and b) and CdSe-TiO₂ photocatalyst (c and d).

photocatalyst. The EDX results reveal the presence of CdSe and TiO₂ with high content in prepared samples.

UV-vis reflectance analysis was carried out on various systems of interest and the measurements were then converted to absorbance spectra using Kubelka-Munk method. Figure 4 shows the UV-vis diffuse reflectance spectra of the CdSe, CdSe-TiO₂ and TiO₂. As expected, the spectrum obtained from the bare TiO₂ show that TiO₂ absorbs mainly the ultraviolet light with absorption wavelength below 400 nm. After introducing of CdSe, the absorption edge is shifted toward the visible region. The CdSe exhibits the fundamental absorption edge at about 812 nm. For CdSe-TiO₂, the absorbance spectrum has two absorbance onsets at approximately 738 nm and 400 nm, corresponding to the presence of CdSe and TiO₂ particles, respectively. It is interesting to note that the onset for TiO₂ absorption was almost unchanged (at wavelength of about 400 nm) while the CdSe absorbance onset at 812 nm was blue shift to the wavelength of 738 nm. This indicated an increase in the band gap of CdSe due to the TiO₂ introduced.

The diffuse reflectance spectra of the CdSe, CdSe-TiO₂ and TiO₂ were transformed by performing the Kubelka-Munk transformation of the measured reflectance according to the following equation;

$$K = (1-R)^2/2R = F(R) \quad (1)$$

where K is reflectance transformed according to Kubelka-Munk, R is reflectancy (%), and F(R) is the so-called remission or

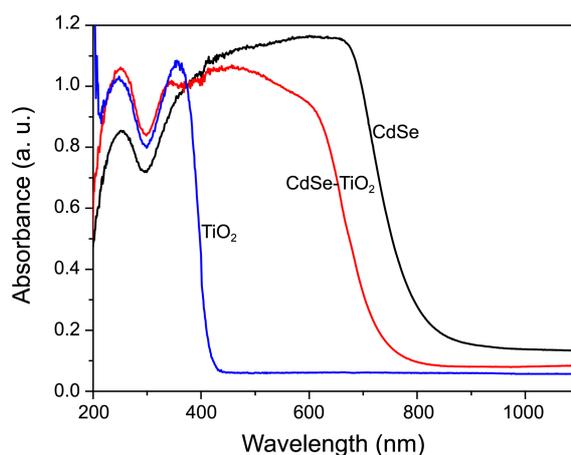


Figure 4. UV-vis diffuse reflectance spectra of CdSe, CdSe-TiO₂ and TiO₂.

Kubelka-Munk function.²⁴

It is well known that the band gap E_g , and the absorption coefficient α are related as in following equation;

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

where α , ν , E_g , and A are the absorption coefficient, light frequency, band gap, 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;

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

Therefore, the band gap energy (E_g) of the resulting samples can be estimated from a plot of $[F(R)h\nu]^2$ versus photon energy ($h\nu$). The $[F(R)h\nu]^2$ versus photon energy ($h\nu$) graph of CdSe, CdSe-TiO₂ and TiO₂ is presented in Figure 5.

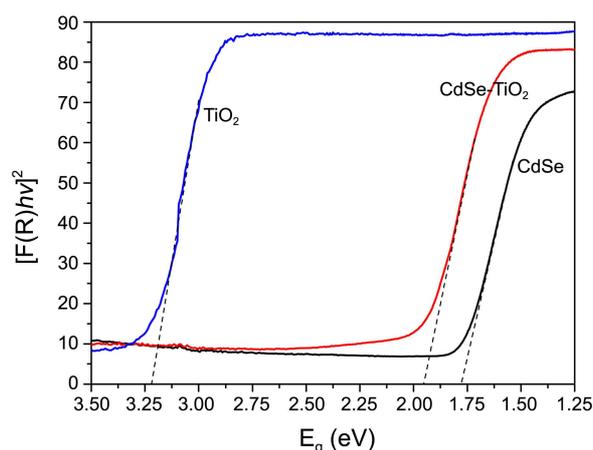


Figure 5. Variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for CdSe, CdSe-TiO₂ and TiO₂.

Table 1. The EDX microanalysis (weight %) and mole ratios of main elements in CdSe and CdSe-TiO₂

Samples	Elements (wt %)					Mole ratios
	Cd	Se	O	Ti	Others	
CdSe	49.11	39.09	7.4	-	4.4	Cd : Se : O = 1 : 1.14 : 1.07
CdSe-TiO ₂	18.34	11.36	31.06	31.98	7.26	Cd : Se : O : Ti = 1 : 0.88 : 12.13 : 4.18

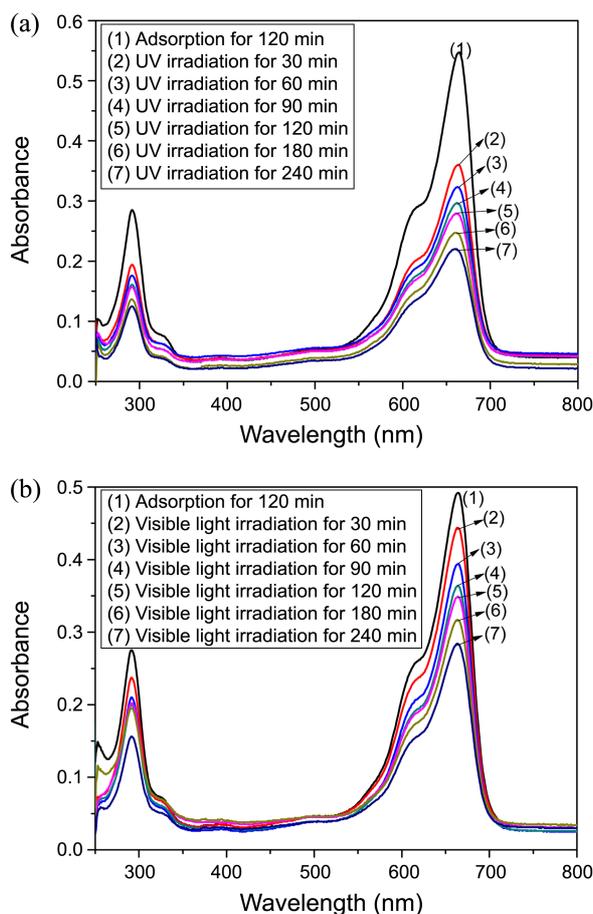


Figure 6. UV-vis absorbance spectra of MB solution degraded under the irradiation of UV light (a) and visible light (b) in the presence of CdSe-TiO₂ photocatalyst.

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 is evaluated to be 1.78 eV, which is fairly close to literature value of 1.74 eV.^{25,26} It is also found that the band gap of CdSe-TiO₂ is 1.95 eV, which is greater than the standard band gap (1.78 eV for CdSe), showing a blue shift of 0.17 eV.

Photodegradation of MB Solution. In order to investigate the photocatalytic property of prepared CdSe-TiO₂ photocatalyst, we measured the absorbance changes of MB solution in the presence of CdSe-TiO₂ photocatalyst under the irradiation of UV light as well as visible light for given times, as showed in Figure 6. Scanning was performed between 250 nm and 800 nm wavelengths. The absorption spectra corresponding to MB solution under the irradiation of UV light as well as visible light, exhibit bands in the UV and visible regions. It can be clearly seen from Figure 6 that the MB solution was characterized by two bands in the visible region at 665 nm and in the UV region at 290 nm. A significant degradation of MB solution was observed and the absorbance of MB solution decreased gradually with an increasing irradiation time both in Figure 6(a) and (b).

We performed a study as a function of time in order to examine the kinetic process of degradation versus light

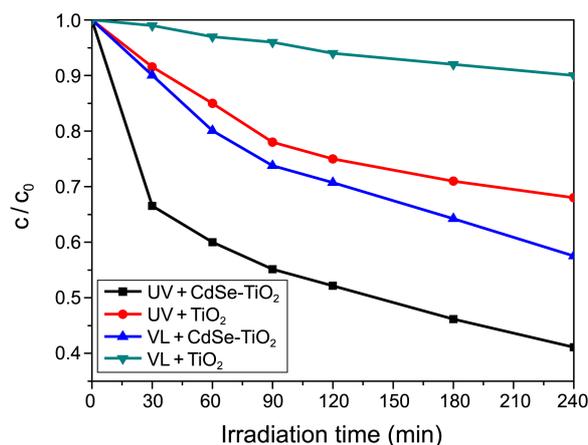


Figure 7. Comparison of photocatalytic activities of TiO₂ and CdSe-TiO₂ on the degradation of MB solution under irradiation of UV light and visible light (VL) for different times.

irradiation time. Degradation was followed by the decrease of absorbance at 665 nm for MB solution. Figure 7 depicts photodegradation *versus* time for the MB solution as the ratio expressed by (c/c_0) in the presence of CdSe-TiO₂ photocatalyst and TiO₂ under the irradiation of UV light as well as visible light. When TiO₂ existed in the system, the degradation was 32% and 10% within 240 min under the irradiation of UV light and visible light, respectively. After CdSe-TiO₂ was used as photocatalyst, the degradation of MB solution markedly enhanced under the irradiation of UV light and visible light, respectively, which were 59% and 42%, respectively. The experimental results shown in Figure 7 clearly indicate that prepared CdSe-TiO₂ photocatalyst have the excellent photocatalytic degradation activities under the irradiation of UV light as well as visible light.

The enhanced activity is probably attributed to the improved optical absorption and the heterostructure which favors the separation of photo-introduced electrons/holes pairs in CdSe-TiO₂ photocatalyst.²⁷ Figure 8 shows the scheme of excitation and charge transfer process between CdSe and TiO₂ under

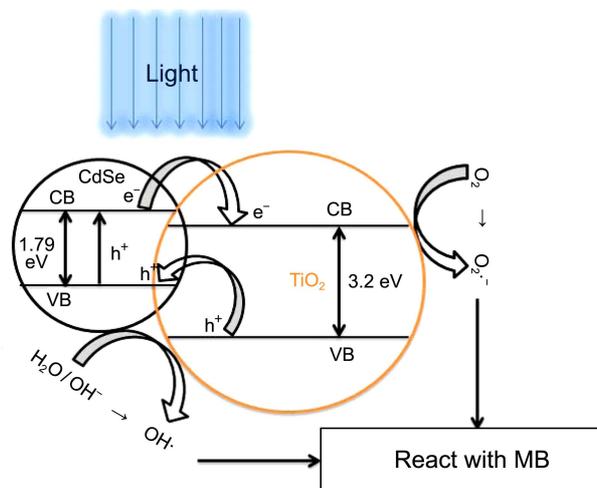
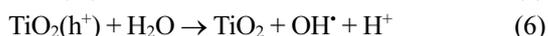
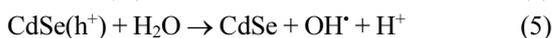
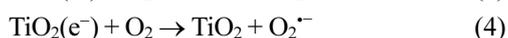
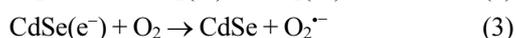
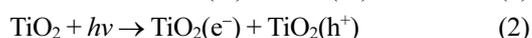
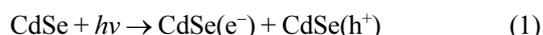


Figure 8. The scheme of excitation and charge transfer process between CdSe and TiO₂ under light irradiation.

light irradiation. Under irradiation by UV or visible lamp, both CdSe and TiO₂ can be excited (corresponding to Eq. (1) and (2), respectively), the generated electrons in CdSe and holes in TiO₂ are then immigrated to the conduction band (CB) of TiO₂ and the valence band (VB) of CdSe, respectively. This transfer process is thermodynamic favorable due to both the CB and VB of CdSe lie above that of TiO₂. 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 with dissolved oxygen molecules and produce oxygen peroxide radical O₂^{-•} (Eq. (3) and (4)), the positive charged hole (h⁺) may react with the OH⁻ derived from H₂O to form hydroxyl radical OH[•] (Eq. (5) and (6)). The MB molecule then can be photocatalytically degraded by oxygen peroxide radical O₂^{-•} and hydroxyl radical OH[•] (Eq. (7)).



Conclusions

We have successfully synthesized CdSe-TiO₂ photocatalyst by a facile solvothermal method. The cubic crystal structure of CdSe and anatase structure of TiO₂ are formed according to the XRD results. SEM microphotograph shows that the TiO₂ particles homogenously coated on the CdSe particles with particle size of 100 nm. The EDX results reveal the presence of CdSe and TiO₂ with high content in prepared samples. The diffuse reflectance spectra suggest the CdSe-TiO₂ photocatalyst shows strong photoabsorption at UV light and visible light range, with band gap is 1.95 eV. The photocatalytic activity of these CdSe-TiO₂ photocatalyst is investigated by degradation of MB in aqueous solution under UV lamp as well as visible lamp irradiation. The results reveal that CdSe-TiO₂ photocatalyst exhibit much higher photocatalytic activities than TiO₂ both under irradiation of

UV light as well as visible light.

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