Ag$_2$Se-Graphene/TiO$_2$ Nanocomposites, Sonochemical Synthesis and Enhanced Photocatalytic Properties Under Visible Light

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Ag$_2$Se-Graphene/TiO$_2$ composite was synthesized by a facile sonochemical method. The as-prepared products were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, transmission electron microscopy (TEM) and UV-vis diffuse reflectance spectrophotometer. During the reaction, both of the reduction of graphene oxide and loading of Ag$_2$Se and TiO$_2$ particles were achieved. The as-prepared Ag$_2$Se-Graphene/TiO$_2$ composites possessed great adsorptivity of dyes, extended light absorption range, and efficient charge separation properties simultaneously. Hence, in the photodegradation of rhodamine B (Rh.B), a significant enhancement in the reaction rate was observed with Ag$_2$Se-Graphene/TiO$_2$ composites, compared to the pure TiO$_2$. The high activity can be attributed to the synergetic effects of high charge mobility, and red shift in absorption edge of Ag$_2$Se-Graphene/TiO$_2$ composites.

**Key Words**: Ag$_2$Se, Graphene, UV-vis absorption spectra, Visible light, Rhodamine B

**Introduction**

Graphene is a new star on applications of condensed-matter physics, electronics, and material science after carbon nanotube and C$_60$. Because graphene is a single-atom thick sheet arranged by sp$^2$-bonded carbon atoms in a hexagonal lattice, which shows outstanding mechanical, thermal, optical, and electrical properties. Therefore, graphene-based composite materials have attracted much attention as recent studies have shown their usefulness in electronics, photocatalysis and photovoltaic devices.

It was reported that nanocarbon materials as CNT and C$_60$ have some beneficial effects on the photocatalytic activity of homogeneous and heterogeneous semiconductors by effecting electron transfer and interaction effects. Among the various semiconductors, titanium dioxide (TiO$_2$) is known to be a good catalyst for the degradation of environmental contaminants due to its high photocatalytic activity. These TiO$_2$-nanocarbon composite exhibited higher photocatalytic performance than that of bare TiO$_2$. However, some problems still hinder further promotion of eciency of TiO$_2$-nanocarbon composites, such as the weakening of light intensity arriving at surface of catalysts and the lack of reproducibility due to the preparation and treatment variation. In comparison with CNT and C$_60$, graphene has perfect sp$^2$-hybridized two-dimensional carbon structure with better conductivity and larger surface area, it seems reasonable to envision that the novel graphene-TiO$_2$ nanocomposite with high interfacial contact and potential could be much more promising to improve the photocatalytic performance of TiO$_2$. Furthermore, graphene is easy to produce from inexpensive natural graphite through intermediates product “graphite oxide”. The presence of oxygen-containing functional groups in graphene oxide (GO) and reduced graphene oxide (RGO) makes them as excellent supporters to anchor TiO$_2$ nanocrystals for the synthesis of graphene-TiO$_2$. Another important feature of the coupled semiconductor system is that the photosresponse of a large band gap semiconductor can be extended into the visible region by coupling it with a short band gap semiconductor. Metal selenides have attracted much attention during the past few years due to their special electronic and optical properties and potential applications. Silver selenide exists as a low-temperature phase ($\alpha$-Ag$_2$Se), and a high-temperature phase ($\beta$-Ag$_2$Se) with the phase transition point at 1331 °C. $\alpha$-Ag$_2$Se is a well-known superionic conductor that is useful as the solid electrolyte in photochargeable secondary batteries. $\beta$-Ag$_2$Se is a narrow-band-gap semiconductor and has been widely used for a photosensitizer in photo-graphic films or thermalchromic materials. Zhao et al. reported fabricated TiO$_2$/Ag$_2$Se interface composite film by interface reaction of AgNO$_3$ with NaSeSO$_3$ on the activated surface of porous TiO$_2$ film, which has good photovoltaic property and high photocurrent response for visible light. Cao et al. reported synthesized Single-crystalline Ag$_2$Se complex nanostructures via a solvothermal route and characterization its photocatalytic activity by photodegradation of rhodamin B (RHB) dye under ultraviolet (UV) light irradiation.

In this work, we present the studies on the preparation of Ag$_2$Se-Graphene/TiO$_2$ composites using a facile sonochemical method and utilization for photodegradation of Rh.B aqueous solution under visible light irradiation. Ag$_2$Se-Graphene/TiO$_2$ composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX) analysis, UV-vis diffuse reflectance spectra (DRS). The reasons for improving the photocatalytic activity of Ag$_2$Se-Graphene/TiO$_2$ composites were also dis-
cussed.

**Experimental**

**Materials and Reagents.** The titanium (IV) n-butoxide (TNB, C\textsubscript{10}H\textsubscript{2}O\textsubscript{2}Ti) as a titanium source for the preparation of TiO\textsubscript{2} and graphene/TiO\textsubscript{2} composites was purchased from Kanto Chemical Company (Tokyo, Japan). Silver nitrate (AgNO\textsubscript{3}), Selenium (Se) metal powder and ammonium hydroxide (NH\textsubscript{3}OH, 28\%\,) were purchased from DaeJung Chemicals & Metal Co., Ltd, Korea. Anhydrous purified sodium sulfite (Na\textsubscript{2}SO\textsubscript{3}, 95\%) was purchased from Duksan Pharmaceutical Co., Ltd, Korea. Rh.B (C\textsubscript{25}H\textsubscript{31}ClN\textsubscript{3}O\textsubscript{3}, 99.99\%\,) was used as model pollutant which purchased from Samchun Pure Chemical Co., Ltd, Korea, respectively. All chemicals used without further purification and all experiments were carried out using distilled water.

**Preparation of Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} Nanocomposite Photocatalyst.** Ag\textsubscript{2}Se-graphene/TiO\textsubscript{2} composites marked as Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} was synthesized by an ultrasonic assisted hydrothermal method\textsuperscript{25} with minor modification. GO was synthesized according to the modified Hummers-Offeman method from purified natural graphite in our previous works.\textsuperscript{26} A typical experiment for the synthesis of Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} nanocomposite is as follows: Firstly, Na\textsubscript{2}SO\textsubscript{3} (5 g) and Selenium metal powder (0.5 g) were dissolved in 30 mL distilled water and refluxed for 1 h to form Na\textsubscript{2}SeSO\textsubscript{3} solution. And 20 mg GO and 22 mg AgNO\textsubscript{3} were dispersed into a solution with the molar ratios of ethanol:H\textsubscript{2}O:TNB = 35:15:4, and nally the suspension was sonicated at room temperature for 1 h using a Controllable Serial-Ultrasound apparatus (Ultrasonic Processor, VCX 750, Korea). Then, the Na\textsubscript{2}SeSO\textsubscript{3} solution and 6 mL NH\textsubscript{3}OH (28 wt\%\,, pH = 12) were added to above system, and the mixture was stirred rapidly at 100 °C for 8 h. The reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water five times, and dried in a vacuum oven at 80 °C for 12 h before heat treatment at 500 °C for 3 h. Meanwhile, for comparison, another photocatalysts, marked as pure TiO\textsubscript{2} and GR-TiO\textsubscript{2} were prepared using similar procedure.

**Characterization of Photocatalysts.** The crystallographic structures of the composite photocatalysts were observed by using XRD (Shimatz XD-D1, Japan) at room temperature with Cu K\textalpha\, radiation (\(\lambda = 0.154056\) nm) and a graphite monochromator, operated at 40 kV and 30 mA. The BET surface areas of the photocatalysts were determined by measuring nitrogen adsorption at 77 K using a BET analyzer (Monosorb, USA). The morphologies of the photocatalysts were analyzed by SEM (JSM-5200 JOEL, Japan) at 3.0 keV. Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) with an accelerating voltage of 200 kV was used to examine the size and distribution of the photocatalysts. EDX spectra were also used for elemental analysis of the samples. Raman spectra were utilized to detect possible structural defects in the graphene akes. The measurements were carried out by using a Horiba Jobin Yvon Lab Ram system with a 100 \times objective lens and a 532 nm laser excitation. 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.

**Measurement of Photocatalytic Activities.** The photocatalytic experiments were performed at ambient temperature to test the ability of the as-prepared composites (pure TiO\textsubscript{2}, GR-TiO\textsubscript{2} and Ag\textsubscript{2}Se-GR/TiO\textsubscript{2}) to catalyze the degradation of Rh.B. The visible light sources (\(\lambda > 420\) nm, LED lamp) were used at a distance of 100 mm from the solution in a darkness box. The initial concentration of Rh.B (c\textsubscript{0}) was 2.0 \times 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 (\(\pm 5\%\)).

**Results and Discussion**

**Physicochemical Properties.** XRD analysis was used to determine the phase purity and the average crystalline properties of Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} composites are shown in Figure 1. It can be confirmed that the TiO\textsubscript{2} in the as-prepared photocatalysts is anatase-phase, while the Ag\textsubscript{2}Se appears as the predominant crystalline phase of acanthite. For these three samples, (101), (004), (211), and (204) crystal planes originated from the anatase TiO\textsubscript{2} phase while (002), (112), (121), (103), (031), (200), (213), and (134) crystal planes originated from the orthorhombic Ag\textsubscript{2}Se phase, which were in accordance with the results reported by Zhan et.al with the lattice parameters were close to a = 4.331 Å, b = 7.061 Å, and c = 7.763 Å (JCPDS card no. 14-0072).\textsuperscript{27} No impurity

![Figure 1. XRD patterns of as-prepared samples: (a) TiO\textsubscript{2}, (b) Ag\textsubscript{2}Se, (c) Ag\textsubscript{2}Se-GR/TiO\textsubscript{2}.](image-url)
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 peak appearing at around 25.88° corresponds to (002) diffraction peak of graphite from the graphene, which is partially overlapped with the (101) crystal plane of anatase TiO$_2$, resulting in the intensity of the (002) diffraction peak to be relatively weak, indicates that the GO has been reduced to graphene, which is in agreement with early reports.$^{28-30}$

The EDX spectra of pure TiO$_2$, GR-TiO$_2$ and Ag$_2$Se-GR/TiO$_2$ composites are shown in Figure 2. These spectra indicate the TiO$_2$ and Ag$_2$Se with high purity have been successfully synthesized in this study. The C element should mainly originate from graphene sheets. The oxygen and Ti element mainly comes from the TiO$_2$ nanopowder. And the strong Kα and Kβ peaks from Ti element appear at 4.51 and 4.92 keV, while a moderate Kα peak of the element O appears at 0.52 keV.$^{31}$ Figure 2 shows the presence of C, O, and Se, as major elements with strong Ag peaks. There were some small impurities, which were attributed to the use of fullerene without purification. In most samples, carbon, silver and selenium were present as major elements with small quantities of oxygen in the composite. The elemental micro-analyses (wt %) of the samples are listed in Figure 3. According to former studies,$^{8,9}$ the higher concentration of dopant in TiO$_2$ matrix can be detrimental in formation of hole/electron recombination centers and an increase of negative charge capabilities.

The typical micro-surface structures and morphologies of the as-prepared composites were characterized by SEM and TEM. The morphology of GO is observed to have aky texture, reflecting its layered microstructure, as shown in Figure 4(a). The larger interspaces of the layer and the thinner layer edges of GO can be clearly observed. Simultaneously, it is worth noting that when we used sonochemical method to synthesize control sample and Ag$_2$Se-GR/TiO$_2$...
composite, it was clear that the prepared nanoscale TiO$_2$ observed in Figure 4(b) shows a favorable morphology but a little tendency to agglomerate. Compared (b) with (c), very uniform Ag$_2$Se particles and TiO$_2$ particles can be observed and it was suggested that the graphene introduction contributed the dispersion of TiO$_2$ and Ag$_2$Se particles on graphene and made these particles appeared uniform. It is reasonable to imagine that such the structure would enable easy charge transfer between the Ag$_2$Se particles with TiO$_2$ particles and the graphene sheets. And the typical TEM image of as-obtained graphene, TiO$_2$ and Ag$_2$Se-GR/TiO$_2$ composite was displayed in Figure 4(d, e and f). The morphology of GO, consisting of thin stacked akes and having a well-defined few-layer structure at the edge, can be clearly seen in Figure 4(d). Nanoscale TiO$_2$ displayed well-dispersed nanoparticles with an average size of around 10 to 15 nm, can be clearly seen in Figure 4(e). Figure 4(f) reveals a homogeneous dispersion of TiO$_2$ and Ag$_2$Se nanoparticles attached onto the almost transparent graphene sheets, which may play a support material role in helping TiO$_2$ and Ag$_2$Se crystals growth. And the average size of well-dispersed Ag$_2$Se nanoparticles was around 25 to 30 nm. The formation mechanism of TiO$_2$ and Ag$_2$Se particles itself and the exact role of graphene sheets in this process still await further studies.

The UV-vis absorption spectra of the different samples are presented in Figure 5(a). As expected, we find that TiO$_2$, Ag$_2$Se/TiO$_2$ and Ag$_2$Se-GR/TiO$_2$ composites have great absorption in the ultraviolet region. TiO$_2$ shows the characteristic spectrum with its fundamental absorption sharp edge rising at 400 nm (E$_g$ = 3.2 eV). After the introduction of Graphene or Ag$_2$Se nanoparticles, the absorption edges of Ag$_2$Se/TiO$_2$ and Ag$_2$Se-GR/TiO$_2$ were shifted toward the visible region, which means that these composites have photocatalytic activity under visible light irradiation. This phenomenon results not only from the excellent conductivity of graphene that can facilitate the separation of photogenerated charges, but also from the introduction of the semiconductor quantum dot Ag$_2$Se by which the conduction and valence bands of TiO$_2$ are bent downward.

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

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

$$\alpha v = A(hv - E_g)^{1/2}$$

where $\alpha$, $v$, $E_g$, 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 $2\alpha$. In this case, we can use the following expression;

$$[F(R)hv]^2 = A(hv - E_g)$$

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The estimated $E_g$ value was 2.31 eV for the Ag$_2$Se/TiO$_2$ sample. This value is red shifted from the typical $E_g$ of the TiO$_2$ (3.25 eV) in Figure 5(b).

Degradation Performances.

Adsorption Ability: To evaluate the adsorption ability of the as-prepared composite catalysts, the reactor was placed...

Figure 5. (a) UV-vis absorbance spectra of pure TiO$_2$, Ag$_2$Se/TiO$_2$, and Ag$_2$Se-GR/TiO$_2$; (b) Variation of $(\alpha hv)^2$ versus photon energy ($hv$) of TiO$_2$ and Ag$_2$Se/TiO$_2$.

Figure 6. UV/Vis spectra of Rh.B concentration against the as-prepared samples after adsorption-desorption equilibrium.
was placed on the magnetic churn dasher, stirring for 30 min in the darkness box to establish an adsorption-desorption equilibrium. Two steps are involved in the photocatalytic decomposition of dyes: the adsorption of dye molecules and degradation. After adsorption in the dark for 30 min with magnetic stirring, the samples reached adsorption-desorption equilibrium. From the result shown in Figure 6, in the adsorptive step, the level of Rh.B adsorption by Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} was higher than that of the TiO\textsubscript{2} powder. This can be attributed to the big surface area of the Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} catalysts shown in Table 1, which correlates to a strong adsorption ability. And sample GR-TiO\textsubscript{2} exhibits the best adsorption effect for Rh.B dye solution because the added graphene can enhance the BET surface area which can increase the adsorption effect. After establishing an adsorption-desorption equilibrium, for GR-TiO\textsubscript{2} and Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} catalysts the Rh.B dye solution was removed 36% and 30% while Rh.B solution is removed only 16% for pure TiO\textsubscript{2}. And Figure 7 shows the time series of Rh.B degradation using Ag\textsubscript{2}Se-GR/TiO\textsubscript{2} catalyst under visible light irradiation. The spectra for the Rh.B solution after visible light irradiation are shown in Figure 6. The UV-vis absorbance spectra (Fig. 5(b)) shown that the band-gap of Ag\textsubscript{2}Se, TiO\textsubscript{2} and graphene nanosheet under visible light irradiation. Because of the inconsistency and overlapping of the conduction band (CB), valence band (VB) and band-gap of the two semiconductors, the photogenerated charge carriers can be excited from the VB of Ag\textsubscript{2}Se and then be transited to the CB of TiO\textsubscript{2} photoge-
rated holes will be left in VB of Ag$_2$Se. In addition, graphene nanosheet acting as good electron acceptors$^{34,35}$ can accept the electrons by light irradiation and the electrons exited in CB of Ag$_2$Se are also transferred to the surface of graphene. Thus the lifetime of the excited electrons (e$^-$) and holes (h$^+$) is prolonged in the transfer process, inducing higher quantum efficiency. The electrons can react with O$_2$ to generate O$_2^-$, and the holes theoretically migrate to the surface and react with OH$^-$ or H$_2$O to generate OH$^-$, these radicals can react with adsorbed pollutants. The reactions can be expressed as follows:

$$\text{Ag}_2\text{Se-TiO}_2 + h\nu \rightarrow \text{Ag}_2\text{Se}(e^-, h^+)-\text{TiO}_2$$ (6)
$$\text{Ag}_2\text{Se}(e^-, h^+)-\text{TiO}_2 \rightarrow \text{Ag}_2\text{Se}(h^+)-\text{TiO}_2(e^-)$$ (7)
$$e^- + O_2 \rightarrow O_2^-$$ (8)
$$h^+ + H_2O \rightarrow OH^-$$ (9)
$$h^+ + H_2O \rightarrow OH^- + H^+$$ (10)
$$O_2^- or OH^- + MB \rightarrow CO_2, H_2O$$ (11)

### Conclusions

In this study, we present the synthesis and characterization of Ag$_2$Se-Graphene/TiO$_2$ composites through a facile sonochemical method. The results showed that the Ag$_2$Se-Graphene/TiO$_2$ composites are able to exhibit high surface area, excellent structure, and great electrical and optical properties. The Ag$_2$Se-Graphene/TiO$_2$ composites showed an intense absorption and have a red-shifted absorption onset compared to pure TiO$_2$ and Ag$_2$Se-TiO$_2$. The excellent visible light photocatalytic activities of Ag$_2$Se-Graphene/TiO$_2$ for the degradation of Rh.B were higher than that of pure TiO$_2$. The high activity can be attributed to the synergistic effects of high charge mobility, and red shift in absorption edge of Ag$_2$Se-Graphene/TiO$_2$ composites.

### References