Enhanced Sonocatalytic Degradation of Rhodamine B by Graphene-TiO₂ Composites Synthesized by an Ultrasonic-Assisted Method

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Abstract: A series of graphene-TiO₂ composites was fabricated from graphene oxide and titanium *n*-butoxide (TNB) by an ultrasonic-assisted method. The structure and composition of the nanocomposites were characterized by Raman spectroscopy, BET surface area measurements, X-ray diffraction, transmission electron microscopy, and ultraviolet-visible absorption spectroscopy. The average size of the TiO₂ nanoparticles on the graphene nanosheets was controlled at around 10–15 nm without using surfactant, which is attributed to the pyrolysis and condensation of dissolved TNB into TiO₂ by ultrasonic irradiation. The catalytic activity of the composites under ultrasonic irradiation was determined using a rhodamine B (RhB) solution. The graphene-TiO₂ composites possessed a high specific surface area, which increased the decolorization rate for RhB solution. This is because the graphene and TiO₂ nanoparticles in the composites interact strongly, which enhances the photoelectric conversion of TiO₂ by reducing the recombination of photogenerated electron-hole pairs.

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TiO₂-based materials are the most commonly used semiconductor oxide photocatalysts because of their low environmental impact. However, there are numerous obstacles preventing the photocatalytic activity of these materials from being maximized, including low adsorption ability, detrimental recombination of charge carriers, and poor light utilization [1,2]. In the past few decades, doping with metal ions, coupling with a second semiconductor, and anchoring TiO₂ particles onto materials with a large surface area, such as mesoporous materials, zeolites or carbon-based materials, have all been used to improve the photodegradation ability of semiconductor oxide photocatalysts [3–5]. TiO₂-carbon nanotube composites show the potential as photocatalysts for use in both water and air purification [6–8]. Carbon nanotubes enhance the photocatalysis activity both by acting as an electron sink to prevent charge carrier recombination [6] and by acting a photosensitizer to generate a greater density of electron/hole pairs [7]. Carbon nanotubes also behave as impurities and form Ti–O–C bonds, which extends the absorption of light to longer wavelengths [8].

Graphene is a single-atom-thick sheet containing *sp*²-bonded carbon atoms in a hexagonal lattice and is of interest for applications in condensed-matter physics, electronics, and materials science, such as carbon nanotubes and buckminsterfullerene [9]. Such interest is because graphene shows outstanding mechanical, thermal, optical, and electrical properties. Graphene-based materials have been used

in diverse fields such as nanoelectronic devices, biomaterials, intercalation materials, drug delivery, and catalysis [10–17].

Graphene-TiO₂ composites have been successfully fabricated in various ways. Williams et al. [18] prepared a graphene-TiO₂ composite by illuminating a suspension of graphene oxide (GO) and TiO₂ under N₂ with ultraviolet (UV) light [18]. Inhibition of the UV light resulted in reducing conditions. Liang et al. [17] fabricated a graphene-TiO₂ nanocrystal hybrid material by directly growing TiO₂ nanocrystals on GO sheets. In this two-step method, TiO₂ was first coated on GO sheets by hydrolysis and then crystallized to form anatase nanocrystals by hydrothermal treatment. Wang et al. [19] prepared TiO₂-graphene composites in aqueous solution through self-assembly using anionic sulfate as a surfactant to stabilize graphene. Chen et al. [20] prepared a visible light-responsive GO-TiO₂ composite with a p-n heterojunction by adding sodium dodecyl sulfate to an aqueous of TiCl₃ and GO, in which TiO₂ could be excited by visible light > 510 nm [20]. Graphene-TiO₂ composites with high photocatalytic activity have also been fabricated from GO and TiO₂ P25 using a facile one-step hydrothermal method [21,22].

Nanosized TiO₂ powder has been used as a sonocatalyst to degrade organic pollutants under ultrasonic irradiation [23,24]. It is difficult to completely mineralize opaque or translucent wastewater by photodegradation because of the

poor ability of light to penetrate such solutions. In the few successful examples of sonocatalysis reported to date, strict conditions or special catalysts have been required [25,26]. Cavities and ‘hot spots’ appear during ultrasonic treatment of aqueous solutions, leading to the dissociation of water molecules. The hydroxyl (OH[•]) radicals formed during such ultrasonic treatment possess high oxidative activity and can degrade toxic and industrial dyes. Ultrasound has been used to degrade polymers, and has received much attention as an advanced oxidation process to remove contaminants from water. Ultrasound can allow complicated reactions to be performed using inexpensive equipment, and often requires fewer steps than conventional methods [27–29].

In this study, titanium *n*-butoxide (TNB) was used as a precursor of TiO₂ and deposited on a graphene surface by chemical reduction of GO in ethanol-water using a sonochemical method [30,31] that proceeds at high temperature. The effect of structural variation, surface state, and elemental composition on the catalytic activity of the composite was investigated. The sonocatalytic activity of the graphene-TiO₂ composite confirmed that it was an excellent catalyst.

1 Experimental

1.1 Materials

C₁₆H₃₆O₄Ti (TNB) was used as a source of titanium to prepare TiO₂ and graphene-TiO₂ composites and was purchased from Kanto Chemical Company (Tokyo, Japan). Rhodamine B (RhB, C₂₈H₃₁ClN₂O₃, 99.99%) was used as a model pollutant and was purchased from Samchun Pure Chemical Co., Ltd, Korea. TiO₂ nanopowder (< 25 nm, 99.7%) with an anatase structure used as control sample was purchased from Sigma-Aldrich, USA. All chemicals were used without further purification. Experiments were carried out using distilled water.

1.2 Synthesis of GO

GO was prepared from graphite (KS-6) according to the Hummers-Offeman method [32]. In brief, graphite powder (10 g) was dispersed in concentrated sulfuric acid (230 ml, 98 wt%) cooled in a dry ice bath. Potassium permanganate (KMnO₄, 30 g) was gradually added with continuous vigorous stirring. The temperature of the mixture was prevented from exceeding 293 K by cooling. The dry ice bath was removed and replaced with a water bath. The mixture was then heated to 308 K in 30 min under continuous stirring. Slow addition of deionized water (460 ml) caused a rapid increase in solution temperature up to a maximum of 371 K. The reaction was maintained at 371 K for 40 min to

increase the degree of oxidation of GO. The resultant bright yellow suspension was quenched by addition of distilled water (230 ml) followed by a solution of hydrogen peroxide (30%, 250 ml). The precipitate was separated by centrifugation at 3000 r/min, and then washed initially with 5% HCl until sulfate ions were no longer detectable with barium chloride. The solid was then washed three times with acetone, and dried overnight in a vacuum oven. The prepared GO was transformed into GO sheets by sonication for 30 min at 308 K [33]. This preparation procedure is outlined in Fig. 1.

Fig. 1. Flow chart outlining the synthesis of GO.

1.3 Synthesis of graphene-TiO₂ composite catalyst

The direct growth of TiO₂ on GO sheets was achieved by a sonochemical method [27,30]. TiO₂ precursors were fabricated by preparing a solution with a molar ratio of ethanol:H₂O:TNB of 35:15:4. GO (0.2 g) was added and the resulting mixture was stirred for 0.5 h at ambient temperature. The suspension was sonicated at room temperature for 3 h using a controllable serial-ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea). The products were filtered, washed repeatedly with distilled water and ethanol, and then vacuum dried at 373 K. The dried catalyst was ground in a ball mill and calcined at 773 K for 3 h to obtain a graphene-TiO₂ composite. For comparison, TiO₂ nanoparticles were prepared by a similar process without adding GO. Three kinds of graphene-TiO₂ composites were prepared by changing the amount of GO, as listed in Table 1. A proposed mechanism for ultrasonic-assisted synthesis of the composites is presented in Fig. 2.

1.4 Characterization of sonocatalysts

Raman spectra were used to detect possible structural defects in the graphene flakes. The measurements were carried

Table 1 Preparation condition and sample name

Preparation method	Sample name
Hummers-Offeman method	GO
Ethanol:H ₂ O:TNB + ultrasound	Nanoscale TiO ₂
Graphene oxide (0.2 g) + ethanol:H ₂ O:TNB + ultrasound + heat treatment	GR-TiO ₂ -1
Graphene oxide (0.3 g) + ethanol:H ₂ O:TNB + ultrasound + heat treatment	GR-TiO ₂ -2
Graphene oxide (0.4 g) + ethanol:H ₂ O:TNB + ultrasound + heat treatment	GR-TiO ₂ -3

out using a Horiba Jobin Yvon LabRAM spectrometer with a $100\times$ objective lens and 532 nm laser excitation. The crystallographic structures of the composite photocatalysts were observed by X-ray diffraction (XRD, Shimadzu XD-D1, Japan) at room temperature with Cu K_{α} radiation. Diffuse reflectance ultraviolet-visible light (UV-Vis) spectra (DRS) were obtained using a scan UV-Vis spectrophotometer (Neosys-2000) equipped with an integrating sphere assembly. The morphologies of the sonocatalysts were analyzed by a scanning electron microscope (SEM, JSM-5200 JOEL, Japan) operating at 3.0 keV that was equipped with an energy-dispersive X-ray analysis (EDX) system. A 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. The BET surface areas of the photocatalysts were determined by measuring nitrogen adsorption isotherms at 77 K using a BET analyzer (Monosorb, USA).

1.5 Ultrasonic degradation of dye solutions

A controllable serial-ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea) operating at an ultrasonic frequency of 20 kHz and output power of 750 W was used to

sonicate the RhB solution. Control sample or graphene-TiO₂ composite (0.02 g/100 ml of solution after addition of RhB solution) was added to water (90 ml) and then sonicated for 30 min to disperse the particles. RhB solution (2×10^{-4} mol/L, 10 ml) was then added to the suspension. The initial concentration of RhB (c_0) was 2.00×10^{-5} mol/L. The reactor was placed on a magnetic stirrer, and then stirred for 120 min in the dark to establish an adsorption-desorption equilibrium. The concentration of RhB was recorded as c_t , and then ultrasonic irradiation was started to induce degradation. The temperature of the reactor was controlled around room temperature (293 K) using a water bath. Degradation reactions were performed in a glass reactor (diameter = 5 cm, height = 7 cm) placed on a magnetic stirrer. The diameter of the ultrasonic tip was 1.90 cm, and the surface area of the ultrasonic probe was 26.86 cm². The mixture was exposed to ultrasound for 150 min and samples (3 ml) were withdrawn from the reactor every 30 min. Dispersed powders were removed using a centrifuge and then the filtrates were analyzed using a UV-Vis spectrophotometer (Optizen Pop Mecasys Co., Ltd., Korea).

2 Results and discussion

2.1 Physicochemical properties

Raman spectra can be used to quickly and accurately determine the number of layers and the crystal structure of graphene after chemical treatment [34]. Thus, Raman spectroscopy was used to compare the crystal structures of GR-TiO₂-2 and GO, as shown in Fig. 3. The Raman spectrum of GO contains D and G bands at 1345 and 1592 cm⁻¹, respectively. The G band is common to all materials containing sp^2 -bonded carbon atoms [35] and provides infor-

Fig. 2. Proposed formation mechanism of TiO₂ nanoparticles on graphene sheets by a sonochemical method.

Fig. 3. Raman spectra of GR-TiO₂-2 (1) and GO (2).

mation on their in-plane vibration [36]. The presence of the D band suggests the GO contains sp^3 defects [37]. The second-order D band (2D band) at about 2720 cm^{-1} is very sensitive to the stacking order of the graphene sheets along the c -axis as well as the number of layers, and becomes more structured (often a doublet) as the number of graphene layers increases. The stacking structure and agglomerated morphology of the GO nanosheets are therefore consistent with those reported previously [34,38]. In the Raman spectrum of GR-TiO₂-2, the D band is broadened and shifted to 1354 cm^{-1} compared with that for GO. The G band also shifted to around 1602 cm^{-1} . The relative intensity of the D/G bands was increased after hydrothermal reaction, which is in agreement with the results of Lambert et al. [39] and Stankovich et al. [40]. This further confirmed that GO was reduced to graphene and indicated that hydrothermal reaction considerably increased the size of the in-plane sp^2 domains and thickness of the graphitic structure.

EDX and elemental analysis (wt%) of TiO₂ and the graphene-TiO₂ composites indicate that materials with high purity were successfully synthesized. The signal for C should mainly originate from the graphene sheets, while those for O and Ti are from the TiO₂ nanoparticles. Figure 4 shows that strong K_α and K_β peaks from Ti appear at 4.51 and 4.92 keV, respectively, while a moderate K_α peak from O appears at 0.52 keV [41]. Elemental analysis (wt%) of the samples revealing the ratio of C:O:Ti are shown in Table 2. Compared with the EDX results, the intensity of the TiO₂ peak has decreased. In addition, the intensity of the signals TiO₂ decreases from GR-TiO₂-1 to GR-TiO₂-3. Therefore, introduction of graphene can prevent the growth of anatase crystals.

XRD patterns of graphene and GR-TiO₂ composites are shown in Fig. 5. For graphene, peaks were observed at 2θ of $\sim 26^\circ$ and $\sim 43^\circ$ that could be indexed to the characteristic peaks (002) and (100) plane reflections, respectively, of graphene (JCPDS 01-0646) [42]. Moreover, no typical diffraction peaks of graphite were found in these patterns, in-

Fig. 4. EDX analysis of TiO₂ (1) and composite photocatalysts GR-TiO₂-1 (2), GR-TiO₂-2 (3), and GR-TiO₂-3 (4).

Table 2 Element mass of different samples

Sample	Element mass (%)		
	C	O	Ti
TiO ₂	—	44.8	55.2
GR-TiO ₂ -1	5.1	11.0	83.9
GR-TiO ₂ -2	10.8	19.9	69.3
GR-TiO ₂ -3	29.4	38.3	32.4

dicating that GO has been reduced to graphene during hydrothermal reaction, which is consistent with previous reports [43–45]. The patterns of both the nanoscale TiO₂ and GR-TiO₂ composites exhibited diffraction peaks around 2θ of 37.9° , 47.8° , 54.3° , 55° , and 62.7° , which could be indexed to the characteristic (004), (200), (105), (211), and (204) peaks of anatase TiO₂ (JCPDS 21-1272), respectively [46]. Peaks belonging to rutile TiO₂ were not observed (JCPDS 21-1276) [47]. These results suggest that the anatase form of TiO₂ is dominant in all of the composites prepared by sonochemical reaction.

Fig. 5. XRD patterns of graphene, TiO₂, and GR-TiO₂ photocatalysts.

The surface microstructures and morphologies of the as-prepared composites were characterized by SEM and TEM (Fig. 6). GO possessed a flaky texture, reflecting its layered microstructure, as shown in Fig. 6(a). Large inter-spaces between layers and thin layer edges of GO were observed. The sonochemical method used to synthesize nanoscale TiO_2 , the GR- TiO_2 composites, produced a favorable morphology of TiO_2 with a slight tendency to agglomerate, as depicted in Fig. 6(b). Introduction of graphene caused the TiO_2 particles to disperse on the graphene so that TiO_2 appeared uniform (Fig. 6(c)). A TEM image of GO (Fig. 6(d)) showed that it consisted of thin stacked flakes with a well-defined structure containing a few layers at its edge. The nanoscale TiO_2 control sample was composed of well-dispersed nanoparticles with an average size of around 10 to 15 nm, as shown in Fig. 6(e). The graphene- TiO_2 composites exhibited a homogeneous dispersion of TiO_2 nanoparticles attached to the almost transparent graphene sheets, which may support the growth of TiO_2 crystals (Fig. 6(f–h)). In this approach, the reduction of GO and deposition of TiO_2 nanoparticles on graphene occurred simultaneously. Once the reaction was complete, decoration with TiO_2 helps to prevent both the aggregation of graphene sheets and TiO_2 . The formation mechanism of TiO_2 nanoparticles and the exact role of graphene sheets in this process require further study to be fully understood.

The light-absorbance properties of the samples were characterized by UV-Vis spectroscopy, as shown in Fig. 7. The absorption bands of GR- TiO_2 -2 were quite different from those of nanoscale TiO_2 . Because GR- TiO_2 -2 is black and absorbs strongly, the Kubelka-Munk theory could not be applied to this sample. Therefore, the DRS of TiO_2 and GR- TiO_2 -2 cannot be compared quantitatively. The enhanced light-harvesting intensity of GR- TiO_2 -2 compared with that of TiO_2 could be possibly explained by the forma-

Fig. 7. UV-Vis spectra of TiO_2 and GR- TiO_2 -2.

tion of chemical bonds between TiO_2 and graphene, i.e., Ti-O-C , which facilitate charge transfer upon light excitation [48].

2.2 Degradation of RhB

2.2.1 Adsorption ability

To evaluate the adsorption ability of TiO_2 and the GR- TiO_2 composite catalysts, the degradation of RhB was performed in the dark, as presented in Fig. 8. GR- TiO_2 adsorbed more RhB than the TiO_2 powder. This can be attributed to the large surface area of the GR- TiO_2 catalysts, as shown in Table 3, which improves adsorption ability. The enhanced adsorption ability can also be related to the amount of graphene in the GR- TiO_2 catalysts [20].

2.2.2 Sonocatalytic activity

An interesting alternative to the photocatalytic degradation of pollutants in waste water is sonocatalysis [49]. The

Fig. 6. SEM and TEM images of photocatalysts. (a, d) graphene; (b, e) nanoscale TiO_2 ; (c, g) GR- TiO_2 -2; (f) GR- TiO_2 -1; (h) GR- TiO_2 -3.

Fig. 8. UV-Vis spectra of TiO₂ and different GR-TiO₂ composite catalysts. (1) Without sample; (2) Pure TiO₂; (3) Nanoscale TiO₂; (4) GR-TiO₂-1; (5) GR-TiO₂-2; (6) GR-TiO₂-3.

Table 3 Sonocatalytic degradation rate constants (k_{app}) and specific surface areas of TiO₂ nanoparticle and GR-TiO₂ catalysts

Sample	Specific surface area (m ² /g)	k_{app}/min^{-1}
Graphene	11.63	5.41×10^{-4}
TiO ₂ nanoparticle	17.89	7.65×10^{-4}
GR-TiO ₂ -1	36.54	2.83×10^{-3}
GR-TiO ₂ -2	48.32	11.36×10^{-3}
GR-TiO ₂ -3	59.67	4.6×10^{-3}

effect of ultrasonic irradiation on RhB degradation by the TiO₂ nanoparticles and GR-TiO₂ composite catalyst were investigated, as depicted in Fig. 9. The ability of ultrasound, graphene, TiO₂ nanoparticles, and GR-TiO₂ composites to degrade RhB was compared. Figure 9(a) shows that after ultrasonic irradiation for 150 min, GR-TiO₂-2 has degraded the most RhB (88.66%), whereas GR-TiO₂-1, GR-TiO₂-2, and ultrasonic irradiation alone degraded 33.31%, 58.71%, and 4.8% of RhB, respectively. All calculated $-\ln(c/c_0)$ values were approximately linear with irradiation time, as presented in Fig. 9(b). Therefore, the sonocatalytic degradation of RhB by these catalysts obeys first-order reaction kinetics. Ultrasonic irradiation for 150 min caused a significant decrease in the concentration of RhB, which indicates that its degradation rate was quite high. The degradation rate of RhB in the presence of bare TiO₂ was lower than that with the GR-TiO₂ composite catalysts. The rate constant determined for the catalysts are presented in Table 2.

Sonocatalytic degradation of dyes in the presence of bare TiO₂ has been reported in several papers. The oxidation process of dyes is dependent on OH[•] [50,51], and can be explained by the well-known mechanism of hot spots and sonoluminescence as follows. First, the formation of cavitation bubbles can be increased by the heterogeneous nuclea-

Fig. 9. Decolorization (a) and apparent first-order reaction kinetics (b) of RhB by sonocatalysts. (1) Ultrasound; (2) Pure TiO₂; (3) Nanoscale TiO₂; (4) GR-TiO₂-1; (5) GR-TiO₂-2; (6) GR-TiO₂-3.

tion of bubbles, generating hot spots in the solution. These hot spots can cause H₂O molecules to pyrolyze to form OH[•]. Second, sonoluminescence involves intense UV light, which excites the TiO₂ particles to act as photocatalysts during sonication. Usually sonochemical reaction pathways to degrade organic compounds involve the sonolysis of water as the solvent inside collapsing cavitation bubbles under extremely high temperature and pressure (Eq. (1)) [52,53]. When a catalyst is also added, ultrasonic irradiation not only induces sonolysis of water but also couples with the catalyst to produce electron-hole pairs (Eq. (2)). The electron-hole pairs can produce OH[•] radicals and superoxide anions $\cdot\text{O}_2^-$, which can decompose dyes to CO₂, H₂O, and inorganic species (Eqs. (3)–(5)) [46,54].

A proposed mechanism for the degradation of pollutants on the GR-TiO₂ sonocatalyst under ultrasonic irradiation is shown in Fig. 10.

Fig. 10. Schematic diagram of the mechanism for the degradation of pollutants on the GR-TiO₂ composite under ultrasonic irradiation.

The catalytic activity of the GR-TiO₂ composites is mainly enhanced compared with that of TiO₂ by the high efficiency of charge separation through the synergistic effect of graphene and TiO₂. The improved ability of the GR-TiO₂ composites to adsorb RhB compared with that of TiO₂ can be ascribed to formation of π - π stacking between RhB molecules and aromatic regions of graphene, which is non-covalent [55]. GO acts as an electron acceptor to accelerate interfacial electron transfer from TiO₂, significantly hindering the recombination of charge carriers and thus improving photocatalytic activity [56]. The catalytic activity of these composites is determined by the amount of graphene to transfer photo-induced electrons and the contact area between TiO₂ and organic pollutants [57].

3 Conclusions

In this study, the graphene-TiO₂ composites were prepared from GO and *n*-butoxide by a sonochemical method. The GR-TiO₂ composites possess a high surface area, suitable structure and electrical and optical properties to act as sonocatalysts. The composites demonstrated superior adsorptivity and sonocatalytic activity under ultrasonic irradiation for the decomposition of RhB. Increasing the content of graphene resulted in higher degradation efficiencies. Adding graphene to TiO₂ enhanced its catalytic activity because graphene behaves as an adsorbent, electron acceptor, and photosensitizer to accelerate photodecomposition.

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