TiO$_2$ nanoparticles loaded on graphene/carbon composite nanofibers by electrospinning for increased photocatalysis

Chang Hyo Kim $^a$, Bo-Hye Kim $^{b,*}$, Kap Seung Yang $^{b,c,**}$

$^a$ Department of Advanced Chemicals & Engineering, Chonnam National University, 300 Yongbong-dong, Gwangju, Republic of Korea
$^b$ Alan G. MacDiarmid Energy Research Institute, Chonnam National University, 300 Yongbong-dong, Gwangju, Republic of Korea
$^c$ Department of Polymer & Fiber System Engineering, Chonnam National University, 300 Yongbong-dong, Gwangju, Republic of Korea

ABSTRACT

Graphene/carbon composite nanofibers (CCNFs) with attached TiO$_2$ nanoparticles (TiO$_2$–CCNF) were prepared, and their photocatalytic degradation ability under visible light irradiation was assessed. They were characterized using scanning and transmission electron microscopy, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and ultraviolet–visible diffuse spectroscopy. The results suggest that the presence of graphene embedded in the composite fibers prevents TiO$_2$ particle agglomeration and aids the uniform dispersion of TiO$_2$ on the fibers. In the photodegradation of methylene blue, a significant increase in the reaction rate was observed with TiO$_2$–CCNF materials under visible light. This increase is due to the high migration efficiency of photoinduced electrons and the inhibition of charge–carrier recombination due to the electronic interaction between TiO$_2$ and graphene. The TiO$_2$–CCNF materials could be used for multiple degradation cycles without a decrease in photocatalytic activity.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

TiO$_2$ is one of the most promising catalysts because of its superior photocatalytic performance, easy availability, long-term stability, and nontoxicity [1,2]. Typically, photoexcited electron–hole pairs can be generated by irradiation with light with an energy greater than the band gap energy of TiO$_2$ ($E_{bg} = 3.2$ eV for anatase). However, several problems can arise when TiO$_2$ is applied as a photocatalyst: (1) photogenerated electron–hole pairs can recombine quickly, which affects the photocatalytic efficiency [3–7], and (2) TiO$_2$ can only be excited with ultraviolet (UV) light, which is less than 5% of solar light, because of its wide band gap [7–9]. These disadvantages of TiO$_2$ result in a low photocatalytic activity in practical application. Therefore, a number of recent studies have focused on the preparation and modification of TiO$_2$ to narrow its band gap and enhance the photocatalytic activity under visible light radiation [10–30].

Among the carbon nanostructures (e.g., C$_{60}$, carbon nanotubes, and graphenes), graphenes offer new opportunities in photovoltaic conversion and photocatalysis by the hybrid structures with a variety of nanomaterials, due to their excellent charge carrier mobility, a large specific surface area, and good electrical conductivity [31–36]. For example, TiO$_2$ combined with graphene acts as an electron trap, which promotes electron–hole separation and facilitates interfacial electron transfer [14,24–26,30]. Furthermore, graphene can help control the morphology of TiO$_2$ nanoparticles because it controls nucleation and growth of TiO$_2$ nanoparticles and allows for optimal chemical interactions and bonding between nanoparticles and graphene.
In this work, carbon nanofibers (CNFs) containing micropores were used to support TiO\textsubscript{2} because CNFs exhibit a high adsorption capability and adsorption rate due to the shallow and uniform pore structure. Shallow micropores open directly to the surface, which results in a large adsorption capacity and fast adsorption/desorption [37,38]. In addition, electrospinning has been widely used as a versatile technique to fabricate various hybrid nanofibers [39,40]. However, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. However, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrication technique to fabricate various hybrid nanofibers [39,40]. How-ever, reports have seldom been published on the fabrica

![Fig. 1 - TiO2–CCNF hybrids and its response under visible irradiation.](image-url)
The porosity was investigated from the nitrogen adsorption isotherm at 77 K (ASAP 2020, Micromeritics, USA). The specific surface area, the mesopore size distribution, and the micropore size distribution of the samples were evaluated using the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) method. Photocatalytic efficiencies were evaluated by decolorizing an aqueous solution of methylene blue (MB) under irradiation by a fluorescent lamp. A 0.1 g sample of the photocatalyst powder was dispersed in 100 mL of 15 ppm MB (Aldrich) solution by stirring with a magnetic stirrer. A 13 W fluorescent lamp (FRX 13EX-D) with light output in the 400–800 nm spectrum range was used as the visible light source. The MB concentration was measured every 30 min using a UV–Visible spectrophotometer (Shimadzu 160-A).

3. Results and discussion

Fig. 2 presents SEM images of TiO\textsubscript{2}–CCNF and TiO\textsubscript{2}–CNF hybrids prepared with and without graphene. The electrospun PAN based- and PAN/graphene based nanofibers showed a smooth surface with an average diameter of 180 and 270 nm, respectively, before coating of TiO\textsubscript{2}. It was observed that the nanoparticles were uniformly distributed across the surface of the TiO\textsubscript{2}–CCNF materials (Fig. 2a) without aggregation, whereas the TiO\textsubscript{2} on pure PAN/based fibers (TiO\textsubscript{2}–CNF) consisted of large, aggregated nanoparticles with diameters in the range of 80–110 nm (Fig. 2b). The graphene, functionalized with carboxylic acid groups, is capable of binding to metal oxide particles, such as TiO\textsubscript{2}, without aggregation effects and yields small nanoparticles [14]. Goncalves et al. [41] have shown that oxygen functionalities at the graphene surface act as reactive sites for the nucleation and growth of gold nanoparticles. They observed that the nucleation and growth of these metal nanoparticles were dependent on the density of oxygen functional groups in the graphene surface sheets [42]. TiO\textsubscript{2} nanoparticles directly grown on graphene appeared to exhibit strong interactions, which should lead to advanced hybrid materials for various applications, including photocatalysis.

TEM images, depicted in Fig. 3a, were collected to obtain microstructural information for the TiO\textsubscript{2}–CCNF materials. The images indicated that TiO\textsubscript{2} nanoparticles, with an average particle size of 10–30 nm, had been successfully grown on the surface of CNFs. SAED measurements (Fig. 3b) confirmed the nanocrystalline nature of the investigated TiO\textsubscript{2} samples. Based on the SAED ring pattern shown in Fig. 3b, the clear lattice fringes indicate that the nanoparticles have some crystallinity. In addition, the SAED patterns indicate that the nanoparticles, identified as TiO\textsubscript{2} rutile structures, reflected from the (110), (211), and (101) lattice planes as indexed in Fig. 3b. The corresponding elemental mapping of an individual TiO\textsubscript{2}–CCNF materials provided information on the distribution of Ti, O, and C atoms in the fiber (Fig. 3c).

Fig. 4 presents the XRD patterns of the TiO\textsubscript{2}–CCNF and TiO\textsubscript{2}/CNF materials. The broad peak located between 20° and 30° was attributed to the (002) plane of the carbon structure. The diffraction peaks of TiO\textsubscript{2} were also clearly observed in Fig. 4a and b. The peak locations for TiO\textsubscript{2} are cited from the Joint Committee on Powder Diffraction Standards (JCPDS) database. The peaks located at 25° correspond to the (101) plane of the anatase phase (JCPDS 21-1272), and the peaks located at 28°, 36°, 41°, and 54° correspond to the (110), (101), (111), and (211) planes of the rutile phase (JCPDS 21-1276), respectively.

Fig. 2 – SEM images of (a) electrospun PAN based nanofiber, (b) electrospun PAN/graphene based nanofiber, (c) TiO\textsubscript{2}–CNF, (d) TiO\textsubscript{2}–CCNF.
respectively [43]. All products were confirmed to be a mixture of the anatase and rutile phases. The anatase phase content for all products was calculated from the XRD patterns using the following equation: $X_a = \frac{1 + 1.26(I_r/I_a)}{C_0}$, where $X_a$ is the share of anatase in the mixture and $I_r$ and $I_a$ are the integrated intensities of the (101) reflection of anatase and the (110) reflection of rutile, respectively. TiO$_2$–CCNF has a 1:1 ratio of anatase to rutile, whereas the ratio for TiO$_2$–CNF is 1:4. Therefore, this result indicates that the addition of graphene to TiO$_2$ can effectively suppress the transformation of TiO$_2$ from an anatase to a rutile-type phase and prevents the growth of TiO$_2$ particles.

The Raman spectrum (Fig. 5) indicates the presence of TiO$_2$ crystalline nanoparticles and showed three Raman bands: 144(B$_{1g}$) for anatase and 431(E$_g$)/612(A$_{1g}$) for the rutile structure ranging between 100 and 800 cm$^{-1}$ [44]. Fig. 5 shows that the two structural types of TiO$_2$ coexist, which is consistent with the reported XRD pattern. In addition to different TiO$_2$ modes, the broad D-band (defect-induced mode) at 1340–1360 cm$^{-1}$ and G band (E$_{2g}$ graphite mode) at 1570–1590 cm$^{-1}$ were observed. The intensity ratio of D band to G band ($I_D/I_G$) is proposed to be an indication of disorder in TiO$_2$–CCNF, TiO$_2$–CNF, and CNF, originating from defects associated with vacancies, grain boundaries, and amorphous carbons. It is seen that there is little change in the $I_D/I_G$ of TiO$_2$–CCNF (1.0547) compared with TiO$_2$–CNF (1.0551) and CNF (1.0522). This result seems to indicate that graphitic (sp$^2$) nature of the carbon in the photocatalysts remained the same after loading with TiO$_2$.

XPS analysis can provide valuable insight into the surface structure of the CCNF-supported TiO$_2$ photocatalyst. The Ti2p photoelectron peaks of TiO$_2$–CCNF materials are presented in Fig. 6a. The peaks at 465.23 and 459.62 eV represent the Ti2p$_{1/2}$
and $Ti_2p_{3/2}$ of $Ti^{4+}$, respectively, and the $Ti^{3+}$ peaks at 461.90 eV ($Ti_2p_{1/2}$) and 458.58 eV ($Ti_2p_{3/2}$) were also observed. However, in the case of TiO$_2$–CCNF materials (Fig. 6b), the peaks of $Ti_2p_{1/2}$ and $Ti_2p_{3/2}$ of $Ti^{4+}$ were present, whereas the peaks of $Ti^{3+}$ in Ti$_2$O$_3$ or TiO were barely observed. The $Ti^{3+}$ species were generated for the TiO$_2$/CCNFs, which might be due to the carboxyl groups by graphene. Some of these groups combine with titanium through chelation, and then the positions of the oxygen in TiO$_2$ were occupied by carboxyl groups. The chelation effect reduce the valence of titanium, whereas increase the content of $Ti^{3+}$ [46]. Generally, the $Ti^{3+}$ state on the TiO$_2$ surface plays a dominant role in the photocatalytic activity because it can trap photogenerated electrons and leave behind unpaired charges to promote photoactivity. Therefore, the increasing $Ti^{3+}$ density promotes effective segregation of electron and cavity, interface charge transfer as well as lowered the probability of compunding cavity, and then increases the photocatalysis performance.

Fig. 7 shows the high-resolution XPS spectra of the C1s and O1s region on the surface of TiO$_2$–CCNF. The deconvolution of the C1s XPS spectrum (Fig. 7a) revealed three Gaussian curves centered at 285.0, 286.3, 287.4, and 289.1 eV, which can be assigned to graphitic carbon (C–C and CH$_n$), alcohol or ether carbon (C–OH, C–O–C), carbonyl groups (C=O), and carboxyl or ester carbon (O=C–O), respectively. The O1s core level spectrum (Fig. 7b) was deconvoluted into two peaks, indicating the presence of C=O or Ti–O bond of TiO$_2$ (530.5 eV) and C–O in ether (O$_2$, 532.2 eV) [46]. Atomic ratios of titanium to oxygen for TiO$_2$–CCNF and TiO$_2$–CNF can be calculated through the rough stoichiometry using the XPS data. The Ti:O ratios of TiO$_2$–CCNF and TiO$_2$–CNF were determined to be 1:2.63 and 1:2.50, respectively. However, it has been supposed that the titanium-oxygen ratio is less than 1:2. There is an overall increase in the Ti:O ratio, which is consistent with the increase in the proportion of oxygen in the photocatalysts. It means that there may be more oxygen species such as carboxylic acid group of graphene in the TiO$_2$–CCNF photocatalyst surface besides the crystal lattice oxygen [46,47].

The FT-IR spectrum of the TiO$_2$–CCNF was reported in Fig. 8. We can observe absorption at 3439.08 cm$^{-1}$ (OH broadened band of either alcoholic or hydroxyl groups), 1612.49/1454.33 cm$^{-1}$ (C=O and C–C stretching bands in the aromatic range, carbonyl), and 1000–1300 cm$^{-1}$ (C–O stretching band of ether). In particular, the intensity of SNF is larger than that of TiO$_2$–CCNF, which represent indirectly that TiO$_2$ nanoparticles are grown on surface of CCNF with the aid of the oxygen functionalities as reactive sites at the graphene surface. Hence, the XPS and FT-IR spectra show the presence and decrease of the oxygen functional groups, such as –C–O–, –C=O, and –O–C=O, on the TiO$_2$–CCNF catalyst after carbonization.

The photoluminescence (PL) emission spectroscopy has been widely used to study the transfer behavior of the photogenerated electrons and holes in semiconductor materials, so that it can reflect the separation and recombination of photogenerated carries. [48,49]. The measured PL-emission spectra of TiO$_2$–CCNF, TiO$_2$–CNF, and CNF in the range of 300–850 nm are presented in Fig. 9. The spectra are broad (extending from 400 to 700 nm) and centered around 485 nm (2.56 eV) for TiO$_2$–CCNF and 497 nm (2.50 eV) for TiO$_2$–CNF. The intensity of the PL-spectra decreased in the following order for the photocatalysts: CNF, TiO$_2$–CNF, and TiO$_2$–CCNF; this result indicates that the reduction of the PL-intensity shows the diminution...
of the electron/hole pairs recombination process. Generally, the lower PL intensity suggests the lower the recombination rate of photogenerated electron–hole pairs, which leads to the high the photocatalytic activity of semiconductor photocatalysts [50]. Therefore, the low PL intensity for TiO$_2$–CCNF indicates that the photocatalytic activities of TiO$_2$ may be improved due to the interactions between the excited electron of TiO$_2$ particles and the graphene.

The photocatalytic activities of the TiO$_2$–CCNF, TiO$_2$–CNF, CCNF, and CNFs were evaluated by measuring the decoloration rate of MB under visible light irradiation (Fig. 10) at $18^\circ$C. The experimental results showed that the MB decomposition rate in the samples occurred in the following order: TiO$_2$–CCNF $>$ TiO$_2$–CNF $>$ CCNF $>$ CNF. The concentration reduced rapidly over the first 30 min, and then the decomposition rate slowed down or stopped after the amount of time for all of the samples. As seen in Fig. 10a, the TiO$_2$–CCNF showed the best photocatalytic activity under visible light irradiation. The use of the TiO$_2$–CCNF catalyst yielded nearly a 100% reduction in the first 30 min of irradiation. The MB decomposition reaction followed pseudo-first-order kinetics, and the kinetic constants ($k$, min$^{-1}$) were calculated and are presented in the inset in Fig. 10a. The superior photocatalytic activity of TiO$_2$–CCNF materials was also demonstrated in the degradation of MB. The average rate constant for the TiO$_2$–CCNF ($k = 0.16$ min$^{-1}$) is much larger than those for TiO$_2$–CNF ($k = 0.012$ min$^{-1}$), CCNF ($k = 0.011$ min$^{-1}$), and CNFs.
(k = 0.003 min⁻¹). Additionally, the stability of the TiO₂–CCNF materials was examined by following the degradation of MB during a five-cycle experiment. After each run, the TiO₂–CCNF photocatalyst was evacuated for 30 min and was reused in the next run. As shown in Fig. 10b, the photocatalytic degradation of MB with TiO₂–CCNF photocatalysts under visible light irradiation was consistently effective over five degradation cycles.

In general, the efficiency of the photodegradation by TiO₂ depends on the illuminated catalyst surface area in contact with the solution and on the mass transfer to the catalyst surface [37, 38]. Nitrogen adsorption isotherms and pore size distributions for TiO₂–CCNF, TiO₂–CNF, and CNF are shown in Fig. 11. The adsorption isotherms (Fig. 11a) of TiO₂–CNF and CNF show typical type I behavior representing the microporous adsorption, and the adsorption of nitrogen was nearly complete at a low relative pressure (P/P₀ < 0.1). The adsorption isotherms of TiO₂–CCNF exhibit combined type I and type II characteristics. Hysteresis at a relative pressure higher than P/P₀ = 0.5 was observed, which was typical type II behavior of mesoporous adsorption and micropore filling were observed at a low relative pressure of P/P₀ < 0.1, which was typical type I behavior [51]. The pore size distribution in TiO₂–CCNF, TiO₂–CNF, and CNF samples based on the BJH method show a broad distribution of mesopores, with sizes ranging from 2–50 nm (Fig. 11b). In particular, TiO₂–CCNF sample has a much larger pore volume around 3.8 nm than the other samples, suggesting that the presence of mesopores can lead to adsorption of MB molecular easily. Because the molecular size of MB is 1.36 · 0.47 · 0.24 nm [20], and it can access pores with diameters larger than 1.5 nm [52]. Furthermore, as shown in Table 1, the pore characteristics of the photocatalysts decreased in the following order: TiO₂–CCNF, CNF, and TiO₂–CNF; this result indicates that the exposed CNFs surface with high surface area will be functioned as centers of condensing substrates with a physical adsorption process. Therefore, rapid decomposition of MB in the

Fig. 10 – (a) Photocatalytic degradation of MB monitored as the concentration change versus irradiation time (inset: average reaction rate constant (min⁻¹) for the photodegradation of MB with free TiO₂). (b) Photocatalytic activity of the TiO₂–CCNF hybrids for MB degradation over five degradation cycles.

Fig. 11 – (a) Nitrogen adsorption isotherms at 77 K, (b) Differential pore volume of various photocatalysts as a function of the pore diameter.
beginning is reasonably supposed to be due to further adsorption of MB into CNF layer, and the following gradual change in color could be due to consequential processes of adsorption into CNF layer and then decomposition on the surface of TiO$_2$ particle.

As CNFs and graphene of photocatalysts have some adsorption capacity for MB, as shown in Fig. 11 and Table 1, a comparison between adsorption and photocatalytic degradation of MB was carried out experimentally with and without visible light irradiation to evaluate the actual photocatalytic activity. Under the same conditions, adsorption of TiO$_2$–CCNF and TiO$_2$–CNF to MB in the dark was also tested and the results are shown in Fig. 12. When the catalyst is illuminated by visible light irradiation, the MB concentration is much higher decreased than that without visible light irradiation, indicating that MB is rapidly decomposed by the TiO$_2$–CCNF catalysts photocatalytically with visible light irradiation.

The results indicate that TiO$_2$–CCNF has a higher efficiency for the decomposition of MB than the TiO$_2$–CNF, CCNF, and CNFs. It was confirmed that the introduction of graphene and CNFs to the TiO$_2$ photocatalyst could increase the decomposition rate of some organic compounds using a photocatalytic process. The reasons for these improvements are attributed to the following functions, as shown in Fig. 13.

(i) The graphene with carboxylic acid groups is capable of binding TiO$_2$ without aggregation effects, resulting in small nanoparticles. As the particle size of TiO$_2$ becomes small, the photogenerated electrons and holes can easily migrate to reaction sites on the surface, thereby reducing the recombination probability [13,45].

(ii) In the TiO$_2$–CNF materials with a mixture of anatase and rutile structures, the graphene may act as an electron acceptor (Fig. 13a) for rutile ($E_{bg} = 3.0$ eV) and as a photosensitizer (Fig. 13b) for anatase ($E_{bg} = 3.2$ eV), which prevents the recombination of electron-hole

| Table 1 – Pore characteristics of the photocatalysts used in this study. |
|-----------------------------|-----------------|-----------------|-----------------|
| Samples        | BET surface area (m$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | Average pore diameter (nm) |
| TiO$_2$–CCNF    | 434             | 0.23            | 2.17            |
| TiO$_2$–CNF     | 361             | 0.15            | 1.60            |
| CCNF            | 447             | 0.17            | 1.58            |
| CNF             | 405             | 0.18            | 1.81            |

* Pore parameters were obtained from N$_2$ adsorption.

Fig. 12 – Adsorption behavior of MB on TiO$_2$–CCNF and TiO$_2$–CNF.

Fig. 13 – Schematic illustration of photocatalysis with TiO$_2$–CCNF hybrids.
Small TiO₂ nanoparticles were successfully deposited on electrospun CNFs by the sol–gel method, and these composites were very active photocatalysts in the photodegradation of MB under visible light irradiation. Furthermore, TiO₂–CCNF materials could be recycled without a decrease in the photocatalytic activity. The results suggest that graphene acts as an electron acceptor and a photosensitizer, which causes an increase in the photodegradation rate and reduces electron–hole pair recombination. In addition, the CNFs’ high surface area synergistically improved the photocatalytic activity of TiO₂ by enhancing the physical adsorption of the substrate. Therefore, TiO₂–CCNF materials are expected to be a promising candidate for photocatalytic processes using sunlight irradiation.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2011-0005890) and the Ministry of Education, Science and Technology (MEST) (K20903002024-11E0100-04010).

References


