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March 20, 2013

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Highly visible light active Ag@TiO$_2$ nanocomposites synthesized using an electrochemically active biofilm: a novel biogenic approach†

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Titanium dioxide (TiO$_2$) nanoparticles were decorated with different amounts of silver nanoparticles (AgNPs) using an electrochemically active biofilm (EAB), which is a biogenic approach that leads to the formation of Ag@TiO$_2$ nanocomposites. UV-vis spectroscopy, photoluminescence, X-ray diffraction and electron microscopy showed AgNPs, 2–5 nm in size, well-dispersed and anchored to the TiO$_2$ surface and overall synthesis of Ag@TiO$_2$ nanocomposites. The photocatalytic performance of the as-synthesized Ag@TiO$_2$ nanocomposites was evaluated in terms of their efficiency for the photodecomposition of methylene blue (MB) in an aqueous solution under visible light irradiation. The nanocomposites showed exceptionally high photodecomposition efficiency (7 times) compared to commercial TiO$_2$ (Sigma). The enhanced photocatalytic activity was attributed to the synergistic contribution of both a delayed charge recombination rate caused by the high electronic mobility of the AgNPs and the increased surface area originating from the nanometer sized AgNPs on TiO$_2$. The nanocomposites also showed exceptionally high stability and reusability under similar experimental conditions.

1 Introduction

Titanium dioxide (TiO$_2$) is a photocatalyst used widely for the purification of water, air and other environment pollutants because of its high photocatalytic activity, exceptional chemical stability, relatively low toxicity and low cost.$^{1–3}$ On the other hand, it is active only in the UV region of the electromagnetic spectrum owing to its wide band gap energy ($\geq 3.3$ eV). Considerable efforts have been made to modify TiO$_2$ to make it more active in visible light ($\lambda > 400$ nm). Several strategies have been used to extend the photoactivity of TiO$_2$ in the visible region. These include (i) functionalization of TiO$_2$ with photosensitizers that absorb visible light,$^{4–6}$ (ii) doping TiO$_2$ with nonmetals,$^{7–9}$ and (iii) doping TiO$_2$ with metals.$^{10–14}$ The most actively followed approach is metal doping of TiO$_2$ to increase the photoactive wavelength range and enhance the photocatalytic activity under UV irradiation.$^{10–12}$ In addition, considerable efforts have been made to improve the visible light photocatalytic activity of TiO$_2$ by doping with different amounts of metal nanoparticles.$^{16–18}$ Among the doped metals, noble metals have attracted a great deal of attention because of their enhanced catalytic and photocatalytic activities on the nanometer scale.$^{9,19}$ Doping can be achieved using a range of methods including physical, chemical and biological methods.$^{8–11}$ These methods produce doped metal oxides but the overall procedure might require significant time, effort and energy input.$^{16,15}$

Recent studies have shown that metal nanoparticles, such as Ag nanoparticles (AgNPs), enhance the catalytic activity in the visible region of the electromagnetic spectrum.$^{16–18}$ The results showed that the presence of AgNPs is responsible for increasing the photocatalytic activity of TiO$_2$.$^{18}$ Several methods have been used to synthesize AgNPs. A range of materials have been used to control the growth of AgNPs.$^{17–19}$ Silver is a noble metal that does not corrode under photocatalytic conditions. The AgNPs could be anchored strongly to the TiO$_2$ surface and exhibit a characteristic surface plasmon band in the visible region due to the collective excitation of electrons in silver nanoparticles. To take full advantage of the two types of nanomaterials i.e. AgNPs and TiO$_2$, it is appropriate to synthesize novel hybrid materials, such as Ag@TiO$_2$ nanocomposites, so that the unique properties of each material can be integrated and the interactions between the two components can induce unique and novel properties. Recently, cysteine–AgNPs, gold nanoparticles and Au@TiO$_2$ nanocomposites were reported by us using an

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†Electronic supplementary information (ESI) available: The supplementary materials present further detailed information about UV-vis, FE-SEM, HAADF and EDX of 0.5 and 1.5 mM Ag@TiO$_2$ nanocomposites and UV-vis photocatalytic degradation spectra of MB. See DOI: 10.1039/c1nr00613a
electrochemically active biofilm (EAB). 15,20,21 EAB is well known for its use in microbial fuel cells for electricity production. 22 These studies prompted us to tailor Ag@TiO2 nanocomposites using an EAB.

This report presents the one-pot and one-step biogenic synthesis of Ag@TiO2 nanocomposites using an EAB. Two different Ag@TiO2 nanocomposites were synthesized with various amounts of AgNPs at a constant amount of TiO2. The present methodology does not involve any hazardous chemicals, expensive capping or reducing agents, tedious hydrothermal treatments and external energy input. This makes the present protocol highly efficient in the field of nanoparticle and nanocomposite syntheses, compared to the methodologies reported elsewhere. 4–10 TiO2 provides a large surface area for the anchoring of AgNPs and prevents its agglomeration. The as-synthesized Ag@TiO2 nanocomposites exhibit high photocatalytic activity towards MB degradation due to their large surface area and synergistic effect. The AgNPs on the TiO2 surface with good catalytic ability would offer a promising platform for the fabrication of other novel nanocomposites.

Few studies have examined the photocatalytic activity of Ag@TiO2 nanocomposites. 9,12 Therefore, the present study assessed the application of Ag@TiO2 nanocomposites as a photocatalyst. To examine the efficacy of different amounts of silver nanoparticles (AgNPs) for anchoring, Ag@TiO2 nanocomposites were synthesized and characterized by spectroscopic methods. Ultraviolet-visible (UV-vis) spectroscopy, photoluminescence (PL) and X-ray diffraction (XRD) were used to examine the effect of silver on the optical and structural properties of the TiO2 nanoparticles. In addition, the optical parameters, such as the band gap energy and absorption coefficient (α), were calculated using different methods. The photocatalytic activities of the Ag@TiO2 nanocomposites and pure TiO2 were observed by degrading MB in an aqueous solution under visible light irradiation (λ > 500 nm). The interest to use Ag@TiO2 nanocomposites as a heterogeneous catalyst in photocatalysis is to learn and explore more about it. The number of reports dealing with the photocatalytic activity of Ag@TiO2 nanocomposites is still very small, and it is of interest to expand the use of Ag@TiO2 nanocomposites as a photocatalyst.

2 Experimental

2.1 Materials

Titanium oxide (nano TiO2, size ~ 21 nm), silver nitrate (AgNO3, 99%) and methylene blue were purchased from Sigma-Aldrich. Sodium acetate was obtained from Duksan Pure Chemicals Co. Ltd., South Korea. All other chemicals were of analytical grade and used as received. All the solutions were prepared with deionized (DI) water obtained from a PURE ROUP 30 water purification system.

2.2 Methods

The diffuse reflectance UV-vis absorption spectra (DRS) of the powder Ag@TiO2 nanocomposites and pure TiO2 samples were obtained using a UV-VIS-NIR double beam spectrophotometer (VARIAN, Cary 5000, USA) equipped with a diffuse reflectance accessory. A given amount of the Ag@TiO2 nanocomposites and pure TiO2 powder was pressed uniformly in the sample holder that was placed at the integrating sphere for the reflectance measurements. A He–Cd laser (Kimon, 1 K, Japan) with a wavelength of 325 nm and a power of 50 mW was used as an excitation source for the photoluminescence (PL) measurements. X-ray diffraction (XRD, PANalytical, X’Pert-PRO MPD) was performed using Cu Kα radiation (λ = 0.15405 nm). The diffraction peaks of the crystalline phases were compared with those of standard compounds reported in the JCPDS data file. The surface morphology of the nanocomposites was observed by scanning electron microscopy (SEM; Hitachi S-4200), whereas the microstructure was examined by field emission transmission electron microscopy (FE-TEM, Teceai G2 F20, FEI, USA) operating at an accelerating voltage of 200 kV. Selected-area electron diffraction (SAED) and high angle annular dark field (HAADF) imaging are carried out by TEM. However, quantitative analysis was performed using an energy dispersive spectrometer (EDS) attached to the TEM. The photocatalytic experiments were performed using a 400 W lamp (3M, USA).

2.3 Preparation of an electrochemically active biofilm (EAB)

EAB on carbon paper was prepared using the methodology reported elsewhere. 15,20,21 Briefly, 0.2 g of sodium acetate was added as a substrate to 200 mL of mineral salt medium. 23 This was followed by the addition of 10 mL of anaerobic sludge (Biogas plant in Paju, Republic of South Korea) and sparging with N2 gas for 5 min to create strictly anaerobic conditions. Finally, the carbon paper (2.5 cm × 4.5 cm) was dipped in it and the bottle was sealed. All media, including the bacterial inoculum, were changed every two days under strict anaerobic conditions. The process was repeated for two weeks. The EAB formed on the carbon paper was confirmed using a microbial fuel cell by obtaining the appropriate voltage. The living EAB formed on the carbon paper was employed for the synthesis of Ag@TiO2 nanocomposites.

2.4 Synthesis of Ag@TiO2 nanocomposites using an electrochemically active biofilm

Two sets of 5 mM TiO2 aqueous suspensions (200 mL) were prepared and 0.2 g of sodium acetate was added to each suspension as an electron donor. 0.5 mM and 1.5 mM AgNO3 aqueous solutions were added to the above reaction mixtures. The mixtures were sparged with N2 gas for 5 min to maintain the anaerobic conditions. The EAB was hung in each reaction bottle and the systems were sealed and left for magnetic stirring at 30 °C. Within 30 minutes, the initial white color began changing to a light brown color in each case. The reaction mixture was stirred for a further ~24 h to complete the reaction. Finally, grayish brown and blackish brown precipitates were obtained in the 0.5 mM and 1.5 mM AgNO3 cases, respectively. The reaction mixtures were centrifuged and powdered Ag@TiO2 nanocomposites were isolated for further characterization and applications.
Two controlled syntheses were performed to confirm the role of the EAB. Two 5 mM TiO₂ aqueous suspensions (200 mL) were prepared. In the first controlled synthesis, a 0.2 g sodium acetate and 0.5 mM AgNO₃ aqueous solution were added, whereas in the second controlled synthesis, only a 0.5 mM AgNO₃ aqueous solution was added. Both reaction mixtures were sparged with N₂ gas for 5 min to maintain the anaerobic conditions. The EAB was hung in the second controlled synthesis only. Both systems were sealed and stirred with a magnetic stirrer at 30 °C. No changes were observed after 48 h, which shows that both the EAB and sodium acetate are necessary to complete the reactions.

2.5 Photocatalytic degradation of MB by Ag@TiO₂ nanocomposites

The photocatalytic activities of the synthesized Ag@TiO₂ nanocomposites and pure TiO₂ samples were tested for the degradation of MB and the rate of MB degradation was calculated. The photocatalytic activities of the 0.5 mM and 1.5 mM Ag@TiO₂ nanocomposites and pure TiO₂ were measured by the photodecomposition of MB with a concentration of 10 mg L⁻¹. For photodecomposition, 2 mg of each photocatalyst was suspended in 25 mL of methylene blue aqueous solution. The solutions were stirred in the dark for 30 min to complete the adsorption and obtain sorption equilibrium of the specific substrate on the Ag@TiO₂ nanocomposites and pure TiO₂. Later, each solution was sonicated for 5 min. Visible light irradiation of the solutions was performed using a 400 W lamp (λ > 500 nm). All the three sets of experiments were observed for 4 h. The rate of dye degradation was monitored by taking 2 mL of the samples from each set at every 1 h, centrifuging it, removing the catalyst and recording the UV-vis spectrum.

As a control experiment, pure TiO₂ (Sigma-Aldrich) was used and considered as a reference photocatalyst. Typically, the photocatalytic activity of any new material was compared with that of pure TiO₂ as a standard. Each experiment was performed in triplicate to ensure the photocatalytic activities of the Ag@TiO₂ nanocomposites and pure TiO₂. The stability and reusability of the Ag@TiO₂ nanocomposites were also observed in a similar manner to that mentioned above.

2.6 Stability and reusability of the Ag@TiO₂ nanocomposites

Preliminary tests for stability were performed by suspending Ag@TiO₂ nanocomposites in water and sonicking for 1 hour and AgNP leaching in the solution was observed using a UV-vis spectrophotometer which confirms the stability of the Ag@TiO₂ nanocomposites and the possibility to use them as a catalyst. The reusability of the Ag@TiO₂ nanocomposites was tested after centrifuging out the catalyst from MB solution. The isolated catalyst was washed with DI water and dried in an oven at 110 °C and reused for a second run to check its catalytic activity with MB solution under the same conditions.

3 Results and discussion

3.1 Biogenic synthesis of the Ag@TiO₂ nanocomposites and their proposed mechanism

Ag@TiO₂ nanocomposites were synthesized using an EAB as a reducing tool. This protocol does not involve any external energy input, which makes this synthesis highly useful and efficient in the field of nanoparticle and nanocomposite syntheses.15,20,21 Interestingly, this synthesis is novel and does not involve harmful chemicals, capping or reducing agents and severe treatments. The entire synthesis took place in water at room temperature. Fig. 1 shows the proposed mechanism for the synthesis of Ag@TiO₂ nanocomposites using an EAB, which is simple and easy. In this synthesis, an EAB is used as a reducing tool to provide an excess of electrons by biologically decomposing sodium acetate.15,22 The EAB generated electrons were accumulated in the conduction band (CB) of the TiO₂ nanoparticles (Fig. 1) making it highly charged with electrons. This has already been established in ref. 15 and 23. The electrons accumulated in the CB of TiO₂ nanoparticles are then transferred to reduce Ag⁺ to Ag⁰ at the surface of the TiO₂ nanoparticles, which leads to the formation of Ag@TiO₂ nanocomposites.

From the control experiment, it is clear that the presence of both EAB and sodium acetate is essential for the synthesis of Ag@TiO₂ nanocomposites. If either EAB or sodium acetate is present, the reaction will not proceed because electrons will not be available for the reduction of Ag⁺ ions. Therefore, both EAB and sodium acetate (carbon source) are needed for the synthesis of nanocomposites.15,20–22

3.2 Optical and structural properties of the Ag@TiO₂ nanocomposites

The optical diffuse reflectance spectra (DRS) of the Ag@TiO₂ nanocomposites and pure TiO₂ were measured at room temperature over the wavelength range, 200–800 nm. Fig. 2(a) presents typical reflectance spectra, showing the enhanced absorption of light in the case of Ag@TiO₂ nanocomposites. The absorption spectra of Ag@TiO₂ nanocomposites showed a shift towards the visible region (Fig. S1†). The significantly enhanced and shifted absorption spectra (Fig. S1†) towards the longer wavelength (450–550 nm) was mainly due to the surface plasmon of silver nanoparticles that depend on the particle size,
The transition of TiO2.

Photoluminescence is closely related to the surface states and stoichiometry, and is used to determine the efficiency of trapping, migration, transfer of a charge carrier, as well as to understand the fate of the electron–hole pairs in semiconductors. Fig. 3 shows the PL spectra of Ag@TiO2 nanocomposites and pure TiO2 (inset) with excitation at 325 nm at room temperature. The Ag@TiO2 nanocomposites showed an emission peak at \( \sim 475 \) nm and pure TiO2 showed an emission peak at \( \sim 512 \) nm. The emission at 475 nm was attributed to the free exciton \( O_2^{2-} \rightarrow Ti^{2+} \) charge-transfer transition. The PL intensity of pure TiO2 is apparently higher than those of the 0.5 and 1.5 mM Ag@TiO2 nanocomposites (Fig. 3). On the other hand, as the silver is anchored to TiO2, the PL intensity of the Ag@TiO2 nanocomposites (Fig. 3) evidently decreases. Similar trends were also observed by Y. L. Kuo et al. who examined the Ag–TiO2 powder. The intensity of the luminescence peak was significantly low for the 0.5 mM Ag@TiO2 nanocomposites. The intensity of the luminescence peak increased for the 1.5 mM Ag@TiO2 nanocomposites compared to that of the 0.5 mM Ag@TiO2 nanocomposites. As the PL emission is the result of the recombination of excited electrons and holes, the lower PL intensity indicates (0.5 mM Ag@TiO2 nanocomposites) a decrease in the recombination rate, i.e. higher photocatalytic activity. This can be attributed to the decreased recombination of charge-carriers, which are trapped in the Ag 3d energy level below the conduction band in the Ag anchored Ag@TiO2 nanocomposites. Therefore, the silver-loaded particles on the surface of TiO2 accept the photoinduced electrons and increase rapidly the efficiency of charge separation in the TiO2 near the surface, and decrease the quantity of the recombination of the photoinduced electron–hole pairs in TiO2, which result in the decrease of the recombination rate.

![Fig. 3 Photoluminescence spectra of the Ag@TiO2 nanocomposites and pure TiO2 (inset).](image)

The main purpose of anchoring/depositing the AgNPs on TiO2 is to enhance the photocatalytic efficiency of TiO2 in the visible region. Therefore, the band gaps of the Ag@TiO2 nanocomposites and TiO2 nanoparticles were estimated using the UV-vis reflectance spectra, as shown in Fig. 2(b). The reflectance spectra were analyzed using the Kubelka–Munk equation to convert the reflectance into the equivalent absorption coefficient \( (\alpha) \), which is proportional to the Kubelka–Munk function \( F(R) \), as follows:

\[
F(R) = \frac{(1 - R)^2}{2R} \times h\nu
\]

where \( R \) is the measured absolute reflectance of the samples. The band gap can be obtained from the plots of \([F(R)h\nu]^{1/2} \) versus \( h\nu \), as the intercept of the extrapolated linear part of the plot at \([F(R)h\nu]^{1/2} = 0 \), assuming that the absorption coefficient \( (\alpha) \) is proportional to the Kubelka–Munk function \( F(R) \). The band gap (Fig. 2(b)) of the 0.5 mM Ag@TiO2 nanocomposites (3.01 eV) and 1.5 mM Ag@TiO2 nanocomposites (2.86 eV) was shifted significantly to the visible range compared to that of pure TiO2 nanoparticles (3.33 eV). This suggests that the anchoring of AgNPs to the TiO2 surface helps to reduce the band gap of the Ag@TiO2 nanocomposites. In addition, the red shift in the band gap highlights the potential of the Ag@TiO2 nanocomposites as a promising photocatalyst.
a lower PL intensity of 0.5 mM Ag@TiO₂ nanocomposites. On the other hand, in the case of 1.5 mM Ag@TiO₂ nanocomposites, where the PL intensity was higher than the 0.5 mM Ag@TiO₂ nanocomposites, an excess of Ag in the 1.5 mM Ag@TiO₂ nanocomposites will act as a recombination center for electrons and holes, leading to a low quantum efficiency and lower photocatalytic activity.²⁷–²⁹ The same phenomenon is observed during the photocatalytic reaction of MB.

XRD was used to determine the phase and structure of the samples. Fig. 4 shows the XRD patterns, which confirm the formation of metallic AgNPs on the surface of TiO₂ as well as overall formation of Ag@TiO₂ nanocomposites and their crystalline nature. The prominent diffraction peaks were assigned to the planes of polycrystalline silver and TiO₂ (anatase and rutile phase). In the Ag@TiO₂ nanocomposite, (1 1 1), (2 0 0), (2 2 0) and (3 1 1) peaks for face-centered cubic (fcc) crystalline silver were detected at 38.05°, 44.21°, 64.38° and 77.34° 2θ, respectively (JCPDS card no. 4-783).²⁰ The peak at 38.05° 2θ is characteristic of Ag metal, which confirms the deposition of Ag on the TiO₂ lattice. Some of the peaks of Ag, such as the peak at 38.05° 2θ, overlapped with the peaks of TiO₂. The remaining peaks are the same as those of pure TiO₂ and AgNPs. As the amount of AgNPs was increased from 0.5 mM to 1.5 mM, the intensity of the silver peaks increased, which further confirms the anchoring of AgNPs to TiO₂. This is in accordance with the UV-vis and PL data (Fig. 2 and 3). The mean crystallite size of the pure TiO₂, 0.5 and 1.5 mM Ag@TiO₂ nanocomposites were calculated using the Debye–Scherrer’s formula:

\[ D = \frac{\kappa \lambda}{\beta \cos \theta} \]  (2)

where \( \kappa \) is the shape factor and has a typical value of approximately 0.9, \( \lambda \) is the wavelength (Cu Kα = 0.15405 nm), \( \beta \) is the full width at half maximum of the most intense peak and \( \theta \) is the peak position.²⁹ Using this equation, the calculated crystallite size of pure TiO₂, 0.5 and 1.5 mM Ag@TiO₂ nanocomposites was 21.2 nm, 26.5 nm and 29.0 nm, respectively, which are similar to the values determined by TEM and HR-TEM (Fig. 5 and 6). The likely reason for the increasing crystallite size of the Ag@TiO₂ nanocomposites could be the anchoring of AgNPs to the TiO₂ surface and the morphological change in TiO₂ from spherical to a rod shape in the case of 1.5 mM Ag@TiO₂ nanocomposites.¹⁵,³¹ The large size of the AgNPs increases the overall size of the nanocomposites. The broad anatase diffraction peak (25.2046° 2θ) for pure TiO₂

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**Fig. 4** XRD patterns of 0.5, 1.5 mM Ag@TiO₂ nanocomposites and pure TiO₂. The peaks marked with (*) represent the signals of Ag and the remaining peaks represent the signals from TiO₂. The inset shows the shift of the peaks.

**Fig. 5** TEM images of (a and b) 0.5 mM Ag@TiO₂ nanocomposites (c) HR-TEM of 0.5 mM Ag@TiO₂ nanocomposites, and (d) SAED of 0.5 mM Ag@TiO₂ nanocomposites.

**Fig. 6** TEM images of (a and b) 1.5 mM Ag@TiO₂ nanocomposites (c) HR-TEM of 1.5 mM Ag@TiO₂ nanocomposites, showing the rod shaped TiO₂ and (d) SAED of 1.5 mM Ag@TiO₂ nanocomposites.
suggested that the TiO₂ nanoparticles are quite small (~21.2 nm), which is consistent with the TEM observations. In contrast, in the case of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites, less broadening (Fig. 4, inset) of the anatase diffraction peaks and a shift to lower θ values were observed, which is consistent with the increase in the calculated crystallite size of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites. These observations are in accordance with an earlier report by Makinson et al.,¹¹ where faulted nanocrystals showed peak shifts due to the effects of stacking faults. In the present case, stacking faults appear to be responsible for the peak shift.¹¹

### 3.3 Morphological study of Ag@TiO₂ nanocomposites

Morphological studies of Ag@TiO₂ nanocomposites were performed by FE-SEM, FE-TEM, HR-TEM and SAED.

**TEM, HR-TEM images and SAED patterns of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites.** Fig. S2 and S5† show SEM surface images of 0.5 and 1.5 mM Ag@TiO₂ nanocomposites. Fig. 5 and 6 show TEM images of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites, respectively. The low magnification images show that the product is entirely composed of discrete Ag@TiO₂ nanocomposites. The dark spots in Fig. 5 and 6 reveal the presence of AgNPs on the surface of TiO₂. A fascinating phenomenon was observed in the case of the 1.5 mM Ag@TiO₂ nanocomposites (Fig. 6). During nanocomposite synthesis, the morphology of pure TiO₂ was modified partially from spherical to nanorods (Fig. 6(a)–(c)). This was attributed to the effect of an increase in the number of AgNPs, which affect the morphology of TiO₂. This is highly significant because this protocol does not involve any energy input, such as heating or irradiation except for magnetic stirring. Similar morphological changes in TiO₂ have been reported.¹² TEM and HR-TEM images (Fig. 6) clearly showed the modified nanorod morphology of TiO₂ and anchoring of AgNPs to TiO₂ nanoparticles. Fig. 5 and 6 show that in the case of the 0.5 mM Ag@TiO₂ nanocomposites, the size of AgNPs on the TiO₂ surface are in the range of 2–5 nm, whereas in the case of the 1.5 mM Ag@TiO₂ nanocomposites, the size of the AgNPs on the TiO₂ surface ranged from 10 to 15 nm. The SAED patterns (Fig. 5(d) and 6(d)) of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites clearly show well-resolved lattice fringes and diffraction cycles, which are indicative of the highly crystalline nature of the Ag@TiO₂ nanocomposite, and are in good agreement with the DRS (Fig. 2), PL (Fig. 3) and XRD data (Fig. 4). Fig. S3 and S6† show HAADF images of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites, respectively. Fig. S4 and S7† show the EDX spectra of the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites corresponding to the Ag (K), Ti (K), and O (K) lines. The EDX-elemental spectra were also supported by the elemental composition, as shown in Tables S1 and S2† for the 0.5 and 1.5 mM Ag@TiO₂ nanocomposites, respectively, which further confirms the anchoring of AgNPs to TiO₂. EDX revealed an increase in the silver content from the 0.5 mM Ag@TiO₂ to 1.5 mM Ag@TiO₂ nanocomposites, which is in good agreement with the DRS, PL and XRD data.

### 3.4 Visible light photocatalytic activity

As discussed previously, most of the earlier studies of Ag@TiO₂ nanocomposites were performed under UV light irradiation, which excites the TiO₂ semiconductor absorption band directly.¹³ The possibility of using the surface plasmon band of AgNPs (from 450 to 550 nm) to excite the Ag@TiO₂ nanocomposites photochemically has mostly been overlooked. Only a few reports on the visible light photoactivity of Ag@TiO₂ nanocomposites, such as in the degradation of chemical pollutants, are available.¹⁴,¹⁵ This paper reports the visible light photocatalytic activity of the Ag@TiO₂ nanocomposites. The main difference with the previous study is that AgNPs have a dual function (i) as light harvesters and injecting electrons into the semiconductor conduction band, and (ii) as catalytic sites for O₂ formation. In addition, the activity of Ag@TiO₂ nanocomposites for the visible light degradation of MB was determined. Considering the interest in silver catalysis, these findings may open new avenues for the application of this type of catalyst to photocatalysis.

The rates of degradation during the photocatalytic reactions were determined by measuring the absorbance of MB at 665 nm with a spectrophotometer. Fig. 7(a) shows the comparative visible light photocatalytic activity of the 0.5, 1.5 mM Ag@TiO₂ nanocomposites and pure TiO₂ for the degradation of MB in an aqueous solution for 4 h. The mean degradation in terms of the percentage degradation of MB in a solution can be calculated using the following formula (Fig. 7(a)):

\[
\eta = \left[ \frac{A_0 - A_t}{A_0} \right] \times 100\% \tag{3}
\]

where η is the degradation rate of MB in terms of percentage, \(t\) is the reaction time, \(A_0\) and \(A_t\) are the initial and relic MB concentration, respectively.¹³,¹⁴ The 0.5 mM Ag@TiO₂ nanocomposites showed higher catalytic activity than the 1.5 mM Ag@TiO₂ nanocomposites and pure TiO₂.

Fig. 7(b) shows a plot of ln(\(C_0/C\)) as a function of time for MB degradation by the 0.5, 1.5 mM Ag@TiO₂ nanocomposites and pure TiO₂. The photocatalytic activities for all the samples were evaluated quantitatively using the first order kinetic model derived from the Langmuir–Hinshelwood kinetic equation for the quantitative determination of the catalytic efficiency of the as-synthesized Ag@TiO₂ nanocomposites by calculating the respective first order rate constants (\(k\)) according to the following equation:

\[
\ln \left( \frac{C_0}{C} \right) = kt \tag{4}
\]

where \(C_0\) and \(C\) are the initial and reaction concentration of MB at time \(t\), respectively.¹³,¹⁴ The error bar graphs for 0.5, 1.5 Ag@TiO₂ nanocomposites and pure TiO₂ were fitted linearly (Fig. 7(b)) with correlation coefficients of \(R^2 = 0.9926, 0.9749\) and 0.9976, respectively. The rate constants (\(k\)) were determined from these linearly fitted error bar graphs. The rate constant for the 0.5 mM Ag@TiO₂ nanocomposites, \(k_{0.5}\), was 2.0519 \(\times 10^{-4}\) s\(^{-1}\), 1.5 mM Ag@TiO₂ nanocomposites, \(k_{1.5}\), was 1.0123 \(\times 10^{-4}\) s\(^{-1}\) and pure TiO₂, \(k_{TiO2}\) was 2.8629 \(\times 10^{-3}\) s\(^{-1}\). The rate constant represents the photocatalytic activities of the 0.5 and
1.5 mM Ag@TiO₂ nanocomposites. The rate of MB degradation (i.e. better photocatalytic activity) increased with increasing rate constant. In the case of MB degradation, the 0.5 mM Ag@TiO₂ nanocomposite shows an approximately 2.027 and 7.167 times higher rate of reaction than the 1.5 mM Ag@TiO₂ nanocomposite and pure TiO₂, respectively.

Fig. 7 shows that the degradation reaction followed apparent first order kinetics. Under visible light irradiation at λ > 500 nm, both the doped Ag@TiO₂ nanocomposites and pure TiO₂ showed visible light photocatalytic activities for MB degradation. The 0.5 mM Ag@TiO₂ nanocomposites showed more MB degradation than the 1.5 mM Ag@TiO₂ nanocomposites and pure TiO₂. Therefore, the small particle size of AgNPs appears to be effective in enhancing the visible light degradation of MB.

On the other hand, the 1.5 mM Ag@TiO₂ nanocomposites showed lower photocatalytic activity, which could be due to the large size of the AgNPs on the TiO₂ surface. The Ag-doped samples contained a larger amount of hydroxyl groups. Chemisorbed surface hydroxyl groups can enhance photocatalysis by trapping photoinduced holes resulting in an increase in the formation of highly oxidizing OH radicals. Ag was reported to retard the recombination of photogenerated electron hole pairs, which may be not only due to the attraction of excited electrons to silver but also due to the presence of extra hydroxyl species to delay recombination through hole trapping.

3.5 Mechanism for the photodegradation of MB
If a metal comes in contact with a semiconductor, the Fermi levels of the two systems equilibrate in such a way that they shift close to the conduction band of the semiconductor. Owing to this readjustment, the energy levels bent to higher energies, forming a Schottky barrier for trapped electrons. These trapped electrons are transferred to the MB, which are degraded further with the help of O₂ and OH radicals. The mechanism of the photochemical process indicated in Fig. 8 is due to the Ag@TiO₂ interfacial contact. Therefore, the conduction band of the semiconductor undergoes a shift toward more negative potentials. Hence, the energy levels are bent at the interface of TiO₂ by the influence of AgNPs. Consequently, the charge distribution between the AgNPs and the semiconductor causes a shift in the Fermi level toward a more negative potential.

Fig. 8 presents a schematic diagram of the enhanced photodecomposition process by Ag@TiO₂ nanocomposites compared to pure TiO₂. In the case of TiO₂, most photogenerated charges are limited in separation and transportation to the TiO₂ surface due to the high charge recombination rate. Accordingly, limited charges can generate OH radicals and O₂ intermediate species by reacting with adsorbed H₂O molecules for the photodecomposition of MB. On the other hand, in the case of the Ag@TiO₂ nanocomposites, the AgNPs act as electron acceptors with high electronic conductivity; photo-generated charges can be separated efficiently and transported to the TiO₂ for radical generation. Furthermore, the strong interaction between the aromatic regions of MB molecules leads to high affinity and adsorptivity of MB. Therefore, the use of Ag@TiO₂ nanocomposites in the photodegradation of MB shows significant improvement over pure TiO₂.

The photocatalytic activity depends on the size of the AgNPs and the amount of AgNPs anchored to TiO₂. These findings suggest that the particle size of anchored AgNPs and crystallinity of the nanocomposites play important roles in determining the photocatalytic activities of the Ag@TiO₂ nanocomposite. Therefore, it was concluded that anchoring of AgNPs of a particular size and amount to TiO₂ can enhance the photocatalytic activity of TiO₂ in visible light.

The advantage of this synthetic protocol is that DI water was used as a solvent, which does not have any adverse effects on the environment. This protocol does not involve any expensive devices or materials and energy input except for magnetic
stirring. The Ag@TiO₂ nanocomposites obtained were quite stable in the reaction mixture as well as after isolation from the reaction mixture in the solid state to air and moisture, which allows their smooth handling for a range of applications. Moreover, it was a controlled synthesis. Therefore, the dye degradation experiments showed that the Ag@TiO₂ nanocomposites exhibited enhanced photocatalytic activity compared to pure TiO₂, which was more than seven times higher that of pure TiO₂.

From the above discussion and proposed mechanism it is clear that our observations are in good agreement with UV-vis spectroscopy, PL, XRD and TEM results.\textsuperscript{25,29}

### 3.6 Stability and reusability of the Ag@TiO₂ nanocomposite

Preliminary tests for stability of Ag@TiO₂ nanocomposites revealed the stability of the Ag@TiO₂ nanocomposites and their potential use as a catalyst. The reusability of the Ag@TiO₂ nanocomposite was checked after removing the catalyst by centrifuging and using it for a second run under the same conditions. Essentially, the same kinetic profile as that shown in Fig. 7 was obtained. Moreover, after two consecutive uses, the catalyst showed similar catalytic activity to the fresh Ag@TiO₂ nanocomposite. This indicates the stability and reusability of Ag@TiO₂ nanocomposites.

### 4 Conclusions

A biogenic approach was used to synthesize Ag@TiO₂ nanocomposites for the photocatalytic degradation of MB. The proposed approach was an easy, one-pot, nontoxic, controlled and inexpensive method. Well-dispersed AgNPs with small sizes (2–5 nm) were anchored to the TiO₂ surface, which provides unique characteristics to 0.5 mM Ag@TiO₂ nanocomposites, making them highly suitable for photocatalysis. The MB degradation experiments indicated that the 0.5 mM Ag@TiO₂ nanocomposite has higher photocatalytic activity than the 1.5 mM Ag@TiO₂ nanocomposite and pure TiO₂. The rate of degradation of MB by the 0.5 mM Ag@TiO₂ nanocomposite was more than seven times higher than that of pure TiO₂. This was attributed to the small size and optimum amount of AgNPs on the TiO₂ surface. The nanocomposites showed extremely high stability and reusability under similar experimental conditions. In addition, this approach could be extended to the synthesis of other nanocomposites, such as Pd@TiO₂ and Pt@TiO₂.

### 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 (Grant no.: 2012R1A1A4A01005951).

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