Minimization of Recombination Losses in 3D Nanostructured TiO$_2$ Coated with Few Layered g-C$_3$N$_4$ for Extended Photo-response

Suhee Kang, Rajendra C. Pawar, Tae Joon Park*, Jin Geum Kim, Sung-Hoon Ahn**, and Caroline Sunyong Lee†

Department of Materials Engineering, Hanyang University, Ansan 15588, Korea
*Research Institute of Engineering and Technology, Hanyang University, Ansan 15528, Korea
**Department of Mechanical & Aerospace Engineering, Seoul National University, Seoul 08826, Korea

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ABSTRACT

We have successfully fabricated 3D (3-dimensional) nanostructures of TiO$_2$ coated with a g-C$_3$N$_4$ layer via hydrothermal and sintering methods to enhance photoelectrochemical (PEC) performance. Due to the coupling of TiO$_2$ and g-C$_3$N$_4$, the nanostructures exhibited good performance as the higher conduction band of g-C$_3$N$_4$ which can be combined with TiO$_2$. To fabricate 3D nanostructures of g-C$_3$N$_4$/TiO$_2$, TiO$_2$ was first grown as a double layer structure on FTO (Fluorine-doped tin oxide) substrate at 150°C for 3 h. After this, the g-C$_3$N$_4$ layer was coated on the TiO$_2$ film at 520°C for 4 h. As-prepared samples were varied according to loading of melamine powder, with values of loading of 0.25 g, 0.5 g, 0.75 g, and 1 g. From SEM and TEM analysis, it was possible to clearly observe the 3D sample morphologies. From the PEC measurement, 0.5 g of g-C$_3$N$_4$/TiO$_2$ film was found to exhibit the highest current density of 0.12 mA/cm$^2$, along with a long-term stability of 5 h. Compared to the pristine TiO$_2$, and to the 0.25 g, 0.75 g, and 1 g g-C$_3$N$_4$/TiO$_2$ films, the 0.5 g of g-C$_3$N$_4$/TiO$_2$ sample was coated with a thin g-C$_3$N$_4$ layer that caused separation of the electrons and the holes; this led to a decreasing recombination. This unique structure can be used in photoelectrochemical applications.

Key words : TiO$_2$, Graphitic-carbon nitride, Photoelectrochemical, Recombination, Film

1. Introduction

Photoelectrochemical (PEC) electrodes have often been applied to solve energy and environmental issues.$^{1,2}$ To produce a PEC electrode, various catalysts can be considered candidates for practical applications. Semiconductor photocatalysts such as TiO$_2$,$^3$ Fe$_3$O$_4$,$^4$ WO$_3$,$^5$ or ZnO$^6$ have been studied as efficient materials in this field. Among those materials, TiO$_2$ is one general material that has been explored as a semiconductor because of its non-toxicity, low cost, easy fabrication, and highly stable chemical and photo-response properties. However, TiO$_2$ has the drawback of a large band gap ($>3.2$ eV), and it absorbs only in the ultraviolet range, which is less than 5% of the solar spectrum. To reduce its band gap energy, TiO$_2$ has been synthesized with various doping materials or heterogeneous structures including narrow band gap semiconductors such as ZnFe$_2$O$_4$,$^7$ CuS,$^8$ CuO$^{9}$ or Bi$_2$S$_3$,$^{10}$ etc.

Recently, polymeric materials of g-C$_3$N$_4$ (graphitic-carbon nitride) are being used as photocatalysts due to their lower band gap energy ($<2.6$ eV) and excellent thermal stability at relatively high temperature.$^{11-14}$ Particularly, g-C$_3$N$_4$ is a stable structure in acid or alkaline based solutions because of the strong covalent bonding of the C-N atoms.$^{15}$ However, g-C$_3$N$_4$ exhibits fast recombination of electron and hole pairs, which leads to low efficiency in photocatalysis applications. To diminish the defects of g-C$_3$N$_4$, there have been several attempts to construct a unique composite. Hence, it has been reported that g-C$_3$N$_4$ possesses a higher conduction band than that of TiO$_2$; this high conduction band is attributed to the couple g-C$_3$N$_4$/TiO$_2$ composite as a stable heterojunction structure.$^{16-19}$ In addition to this, to achieve better photocatalytic performance, 1D (1-dimensional) aligned TiO$_2$ micro/nanorod structures have been explored for rapid electron transfer. However, these 1D structures have poor surface area and efficiency.$^{20}$ Hence, to advance the overall performance, 3D (3-dimensional) constructions, such as branched or flower-like shapes, have been under profound consideration in attempts to increase the surface area and the photo-response efficiency. Such 3D structures can be more easily used to facilitate faster movement of electrons than is possible when using 1D structures.

In the present study, using hydrothermal and sintering methods, we explore the fabrication of a g-C$_3$N$_4$/TiO$_2$ film. To control the band gap energy and to diminish the recombination rate as an effective method of separating electron-hole pairs, g-C$_3$N$_4$ is coated on double layer TiO$_2$ structures. Through the mechanism of its 3D nanostructure, g-C$_3$N$_4$/TiO$_2$ can be used to demonstrate its potential. By loading a
thin g-C$_3$N$_4$ layer on TiO$_2$ double layer structures, electron scattering and absorption degree will increase more than is the case for a thick g-C$_3$N$_4$ layer because of the transmittance of incident light. Therefore, the use of a g-C$_3$N$_4$/TiO$_2$ film as a 3D nanostructure facilitates electron transport under illumination; it is therefore possible to apply this method to PEC electrode technology.

2. Experimental Procedure

2.1. Preparation of TiO$_2$ micro/nanorods

TiO$_2$ micro/nanorods on an FTO substrate were prepared by following a basic hydrothermal process. Before employing the hydrothermal method, FTO substrates were cleaned with ethanol for 30 min. During the cleaning process, TiO$_2$ solution was prepared. First, deionized water and HCl (Hydrogen chloride, Dae-jung) were mixed at a 1:1 volume ratio. Then, to prevent agglomeration of the Ti precursors, 1 mL of TIPP (Titanium isopropoxide, Sigma-Aldrich) was added drop-wise into the above solution and resulting mixture was stirred vigorously for 30 min. The two cleaned conductive FTO substrates were placed into a Teflon-lined autoclave facing the walls and the autoclave was heated to 150°C; this temperature was maintained for 3 h. After this, the autoclave was cooled to room temperature. Finally, the grown TiO$_2$ film was rinsed with distilled water and dried at room temperature.

2.2. Sintering process for g-C$_3$N$_4$ on TiO$_2$ film

The coating of the g-C$_3$N$_4$ layer was conducted in a crucible with a cover via a sintering process. For the formation of g-C$_3$N$_4$, a melamine precursor was obtained from Junsei Chemicals. Using this precursor, sample amounts of melamine if 0.25 g, 0.5 g, 0.75 g, and 1 g were added to the crucible and the prepared TiO$_2$ film was placed facing down. The crucibles were then heated to 520°C and maintained at that temperature for 4 h to obtain uniform g-C$_3$N$_4$ layers; the heating rate was 10°C/min. Consequently, 0.25 g, 0.5 g, 0.75 g, and 1 g g-C$_3$N$_4$ /TiO$_2$ films were successfully obtained.

2.3. Photoelectrochemical performance

The photoelectrochemical (PEC) performance evaluation was conducted to measure the charge carriers under visible illumination (halogen lamp, 100 W). This process used a conventional three-electrode system. Carbon and Ag/AgCl were used for the counter and reference electrodes, respectively. 0.5 M Na$_2$SO$_4$ was used as the electrolyte. PEC was conducted with 1 V of applied bias potential versus the Ag/AgCl reference electrode during 4 cycles of on/off under visible light. To determine the long-term stability of the samples, a stability test was carried out for 5 h under the same conditions. LSV (Linear Sweep Voltammetry) analysis was carried out at a 20 mV/s scan rate and -1 to 1 V of potential range.

2.4. Characterization

XRD (X-Ray Diffraction; model D/Max–2500/PC, Rigaku, USA; Cu Ka source) measurement was performed to determine the crystalline structure properties of the TiO$_2$ phase. The surface morphologies, used to differentiate between TiO$_2$ and g-C$_3$N$_4$, were obtained by SEM (Scanning Electron Microscopy; model S4800, Hitachi, Japan) and TEM (Transmission Electron Microscopy; model JEM 2100F, JEOL, Japan). To observe and calculate the band gap energy of the films, optical absorbance measurement was conducted using UV spectroscopy (UV–Vis; model V650, JASCO, Japan); BaSO$_4$ was used as the reference sample. FT-IR (Fourier-transform infrared spectroscopy; model iS10, Thermo Fisher Scientific, UK) measurement was conducted for observation of the chemical formation of g-C$_3$N$_4$. PL (Micro confocal Photoluminescence; model MonoRa750i, DongWoo Optron Co. Ltd, Korea) spectra measurement using a 325 nm excitation light source was conducted to determine the recombination rates of TiO$_2$ and g-C$_3$N$_4$. PEC and LSV analyses were conducted using a potentiotstat (model VersaSTAT4, Princeton Applied Research, USA).

3. Results and Discussion

3.1. Structural morphologies

3.1.1 SEM analysis

The surface morphologies of the distinctive g-C$_3$N$_4$ and TiO$_2$ structures were observed using SEM. In Fig. 1(a), it can be seen that TiO$_2$ micro/nanorods grew as double layer structures; these structures are present in rod shape in the bottom layer and in flower-like shape at the top of the layer. The overall length of the double layer was determined to have an average of 3 µm. Double layer structures are expected to accelerate the movement of electrons and to assist in improving the scattering effect. When the melamine powders were added to the TiO$_2$ films to form the g-C$_3$N$_4$, the morphologies of the resulting mixtures revealed that g-C$_3$N$_4$ sheets were coated on the TiO$_2$ surfaces according to the varying amounts of melamine of 0.25 g, 0.5 g, 0.75 g, and 1 g (Figs. 1(b) ~ (e)). From these microstructures, we can confirm that g-C$_3$N$_4$ was added to the TiO$_2$ rod layer. Only 0.5 g and 1 g of g-C$_3$N$_4$/TiO$_2$ were needed to uniformly cover the g-C$_3$N$_4$ on the TiO$_2$ bottom layer. Moreover, 1 g of the g-C$_3$N$_4$/TiO$_2$ structure was present as a film that was thicker than the other g-C$_3$N$_4$/TiO$_2$ films. According to these results, we can confirm that g-C$_3$N$_4$/TiO$_2$ structures were well-constructed with increasing of the added amounts of g-C$_3$N$_4$.

3.1.2 TEM analysis

To accurately determine the size of the g-C$_3$N$_4$ layer on TiO$_2$ structure, TEM analysis was conducted, with results shown in Fig. 2. Here, we tried to compare only TiO$_2$ rods and a 0.5 g g-C$_3$N$_4$/TiO$_2$ film that we optimized as explained in later sections. As can be seen in Fig. 2(a), the average diameter was observed and found to be ~125 nm, which is in agreement with the SEM results. Importantly, coating thickness can be controlled according to the amount of
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added melamine. Figs. 2(b) and (c) shows that 0.5 g of g-C₃N₄/TiO₂ leads to an approximately thin ~ 10 nm coating on the TiO₂ rods. Further, according to the SAED (selected area electron diffraction) pattern, TiO₂ and g-C₃N₄ showed crystalline and amorphous phases, respectively. The d-spacing of the TiO₂ lattice is 0.34 nm (Fig. 2(d)). Therefore, we can confirm the crystallization of TiO₂ from the lattice diffraction pattern and the g-C₃N₄ coating layers on the TiO₂ rods.

3.2. Phase crystallization - X-ray Diffraction

XRD analysis was conducted to examine the TiO₂ crystallinity and the g-C₃N₄ phase structure. As can be seen in Fig. 3, the presence of only TiO₂ peaks indicated the formation of rutile TiO₂ phase, which is exactly correct according to JCPDS card No. 01-078-4190. Additional peaks in the TiO₂ films can be referred to the SnO₂ phase (JCPDS card No. 01-077-0449). Using XRD analysis, the TiO₂ lattice constants were calculated and found to be a = 4.62, c = 2.15 Å and d₁₁₀=3.26 Å for the tetragonal TiO₂ structure. Pure g-C₃N₄ film showed a peak at around 27°, which means it has an amorphous structure as well, as can be seen in Fig. 3(b). However, it is difficult to differentiate TiO₂ and g-C₃N₄ crystallization from Figs. 3(c) to (f) because the crystal (110) plane of TiO₂ at 27° overlapped exactly with the g-C₃N₄ plane. The amounts of g-C₃N₄ can be correlated with the broadening of the peak at 27° compared to that of the pristine TiO₂ film. Finally, it is proved that TiO₂ is well-crystallized and that the g-C₃N₄ sheet is well formed with TiO₂.

Fig. 1. Surface morphologies of (a) only TiO₂, and (b) 0.25 g, (c) 0.5 g, (d) 0.75 g, and (e) 1 g of g-C₃N₄/TiO₂ observed using SEM.

Fig. 2. TEM analysis of (a) only TiO₂, (b) 0.5 g g-C₃N₄/TiO₂, and (d) d-spacing of TiO₂.

Fig. 3. XRD analysis of (a) TiO₂, (b) g-C₃N₄, and (c) 0.25 g, (d) 0.5 g, (e) 0.75 g, and (f) 1 g of g-C₃N₄/TiO₂.
micro/nanorods.

### 3.3. Optical absorbance

The degree of absorbance under the visible range can be determined using a UV-Vis spectrophotometer. All films were prepared for measurement of the optical absorbance from 800 to 300 nm. In Fig. 4(a), the absorbance properties of each film can be seen; the TiO$_2$ film exhibited an absorbance edge at around 420 nm. The film of 0.5 g g-C$_3$N$_4$/TiO$_2$ has an absorbance edge at 440 nm; this means that there is higher absorbance in the visible range. Pure g-C$_3$N$_4$, 1 g g-C$_3$N$_4$/TiO$_2$, and 0.75 g g-C$_3$N$_4$/TiO$_2$ film have similar slopes of around 450 nm. Fig. 4(b) presents detailed data on the calculation of the band gap energy of the films. The calculated band gap energies of the samples were 2.92, 2.65, 2.88, 2.75, 2.79, and 2.61 eV for TiO$_2$, g-C$_3$N$_4$, 0.25 g g-C$_3$N$_4$/TiO$_2$, 0.5 g g-C$_3$N$_4$/TiO$_2$, 0.75 g g-C$_3$N$_4$/TiO$_2$, and 1 g g-C$_3$N$_4$/TiO$_2$, respectively. The band gap transitions are obviously revealed to depend on the amount of g-C$_3$N$_4$ added. Clearly, it can be seen that band gap energy can be adjusted according to the thickness of the g-C$_3$N$_4$ coating. From the band gap transition, because of the high optical absorbance, we can expect an effective generation of charge carriers.

### 3.4. FT-IR analysis

The existence of g-C$_3$N$_4$ was confirmed using the FT-IR spectrum (Fig. 5). The bands of g-C$_3$N$_4$ are mainly located from 1650 to 1200 cm$^{-1}$. The band at 1625 cm$^{-1}$ was assigned to a strong band of the C-N stretching modes. The other bands at 1401, 1317, and 1234 cm$^{-1}$ were related to C-N bonding and represent heterocycle stretching of g-C$_3$N$_4$. The band at around 3000 cm$^{-1}$ was found to correspond to H$_2$O molecules adsorbed on the surface of the g-C$_3$N$_4$. The band at 805 cm$^{-1}$ is indicated to the s-triazine ring vibrations of g-C$_3$N$_4$. However, 0.25 g g-C$_3$N$_4$/TiO$_2$ and 0.75 g g-C$_3$N$_4$/TiO$_2$ have no distinctive g-C$_3$N$_4$ peaks due to their insufficient coating on TiO$_2$; the low degree of coating can be seen in the SEM images (Figs. 1(b)-(d)). Thus, the existence of g-C$_3$N$_4$ was directly confirmed through an observation of the chemical bonding.

### 3.5. Photoluminescence

The possibility of charge separation due to g-C$_3$N$_4$ addition was observed using photoluminescence (PL) spectra, with results as shown in Fig. 6(a). The strength of PL intensity was found to increase according to the amount of added g-C$_3$N$_4$. This means that the recombination rate for this film is faster than that possible with any of the other films. From these results, pure g-C$_3$N$_4$ film was found to exhibit the highest intensity of around 500 nm. Then, the loadings of g-C$_3$N$_4$ were decreased from 1 g, to 0.75 g, and to 0.5 g of g-C$_3$N$_4$/TiO$_2$. Fig. 6(b) shows that 0.5 g of g-C$_3$N$_4$/TiO$_2$ film has the lowest intensity of PL due to the low recombinations due to charge carriers. Only the TiO$_2$, and the 0.25 g g-C$_3$N$_4$/TiO$_2$ films have almost no emission (Fig. 6(c)). The small PL intensity of the TiO$_2$ film is the result of its relatively porous structure. On the other hand, due to the low level of loading of g-C$_3$N$_4$, the 0.25 g g-C$_3$N$_4$/TiO$_2$ film showed trends similar to those of TiO$_2$. Therefore, we identify that the 0.5 g g-C$_3$N$_4$/TiO$_2$ film was better able to separate electron and hole pairs efficiently and to decrease the recombination rate than the 0.25 g, 0.75 g, and 1 g g-C$_3$N$_4$/TiO$_2$ films.
3.6. Photoelectrochemical analysis

3.6.1 Photocurrent-time \((I-t)\) curves

The evaluation of the PEC properties is a significant part of determining the chemical stability. The measurement of the current densities of the as-prepared films was conducted and results are shown in Fig. 7(a). Among the three films, the highest value of current density was obtained for the 0.5 g g-C\(_3\)N\(_4\)/TiO\(_2\) film at 0.12 mA/cm\(^2\). The second highest current density value was found in the 0.25 g and 0.75 g g-C\(_3\)N\(_4\)/TiO\(_2\) films, which both had a value of 0.1 mA/cm\(^2\). The TiO\(_2\) film and the 1 g g-C\(_3\)N\(_4\)/TiO\(_2\) film showed current density values of 0.75 and 0.03 mA/cm\(^2\), respectively. Interestingly, the thicker g-C\(_3\)N\(_4\) film, namely the 1 g g-C\(_3\)N\(_4\)/TiO\(_2\) film, has the lowest current value, lower than even that of the TiO\(_2\) film. This trend could be seen to indicate that the addition of a larger amount g-C\(_3\)N\(_4\) does not help the electron transfer efficiency. Moreover, a thicker coating layer might disturb the adsorption of light. Based on the PEC results, the 0.5 g g-C\(_3\)N\(_4\)/TiO\(_2\) film was used for confirmation of the photoresponse stability, as shown in Fig. 7(b). As well as a higher photoresponse under visible illumination, this film maintained a steady state of its original structure and did not decrease during the 5 h process. There needs to be a proper coating layer on the TiO\(_2\) micro/nanorods; 0.5 g g-C\(_3\)N\(_4\)/TiO\(_2\) seems to be a suitable material to enhance the PEC properties. Therefore, it is proved that an efficiently applied 0.5 g g-C\(_3\)N\(_4\)/TiO\(_2\) film can retain stability and can be used for PEC water splitting.

3.6.2 LSV

Figure 8 shows linear sweep voltammetry measurement results for TiO\(_2\) only and g-C\(_3\)N\(_4\)/TiO\(_2\) composite films under a visible lamp. The TiO\(_2\) film shows a 0.8 mA/cm\(^2\) current density, which is the lowest value among the samples. After loading the g-C\(_3\)N\(_4\) on TiO\(_2\), a 1 g g-C\(_3\)N\(_4\)/TiO\(_2\) thick coating film leads to a current density value of 0.12 mA/cm\(^2\). Then, the thinner 0.5 g g-C\(_3\)N\(_4\)/TiO\(_2\) coating film has a value of 0.21 mA/cm\(^2\) for current density; this is approximately 3 times higher than the value of pristine TiO\(_2\) films (0.8 mA/cm\(^2\)). The 0.25 g and 0.75 g g-C\(_3\)N\(_4\)/TiO\(_2\) films showed lower current density versus potential values than that of the 0.5 g g-C\(_3\)N\(_4\)/TiO\(_2\) film; however, this film did show a higher current density value than that of the 1 g g-C\(_3\)N\(_4\)/TiO\(_2\) film. Similar results for PEC and LSV also demonstrated that a thin
coating of g-C₃N₄ can be used to enhance the current density. Once thick layers are coated on the TiO₂ micro/nanorods, light was not able to reach the TiO₂ surface. The electronic interaction between the TiO₂ and the g-C₃N₄ layer can be used to separate the electrons and the holes efficiently, thus reducing the recombination rate (Scheme 1). Consequently, proper and uniform thickness of the coating layer is necessary for transmission of light to that of surface.

**Scheme 1.** Schematic mechanism of 3D nanostructure 0.5 g g-C₃N₄/TiO₂ film.

was found to have decreased. We can definitely prove that proper layer coating is necessary; thus, a 0.5 g g-C₃N₄/TiO₂ film can lead to reduced recombination and enhanced electron transfer properties.

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**REFERENCES**


