Minimization of Recombination Losses in 3D Nanostructured TiO₂ Coated with Few Layered g-C₃N₄ for Extended Photo-response

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ABSTRACT

We have successfully fabricated 3D (3-dimensional) nanostructures of TiO₂ coated with a g-C₃N₄ layer via hydrothermal and sintering methods to enhance photoelectrochemical (PEC) performance. Due to the coupling of TiO₂ and g-C₃N₄, the nanostructures exhibited good performance as the higher conduction band of g-C₃N₄, which can be combined with TiO₂. To fabricate 3D nanostructures of g-C₃N₄/TiO₂, TiO₂ 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-C₃N₄ layer was coated on the TiO₂ 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-C₃N₄/TiO₂ film was found to exhibit the highest current density of 0.12 mA/cm², along with a long-term stability of 5 h. Compared to the pristine TiO₂, and to the 0.25 g, 0.75 g, and 1 g g-C₃N₄/TiO₂ films, the 0.5 g of g-C₃N₄/TiO₂ sample was coated with a thin g-C₃N₄ 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 : TiO₂, 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 TiO₂,³⁾ Fe₂O₃,⁴⁾ WO₃,⁵⁾ or ZnO⁶⁾ have been studied as efficient materials in this field. Among those materials, TiO₂ 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, TiO₂ 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, TiO₂ has been synthesized with various doping materials or heterogeneous structures including narrow band gap semiconductors such as ZnFe₂O₄,⁷⁾ CuS,⁸⁾ Cu₂O⁹⁾ or Bi₂S₃,¹⁰⁾ etc.

Recently, polymeric materials of g-C₃N₄ (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-C₃N₄ is a

stable structure in acid or alkaline based solutions because of the strong covalent bonding of the C-N atoms.¹⁵⁾ However, g-C₃N₄ exhibits fast recombination of electron and hole pairs, which leads to low efficiency in photocatalysis applications. To diminish the defects of g-C₃N₄, there have been several attempts to construct a unique composite. Hence, it has been reported that g-C₃N₄ possesses a higher conduction band than that of TiO₂; this high conduction band is attributed to the couple g-C₃N₄/TiO₂ composite as a stable heterojunction structure.¹⁶⁻¹⁹⁾ In addition to this, to achieve better photocatalytic performance, 1D (1-dimensional) aligned TiO₂ 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-C₃N₄/TiO₂ film. To control the band gap energy and to diminish the recombination rate as an effective method of separating electron-hole pairs, g-C₃N₄ is coated on double layer TiO₂ structures. Through the mechanism of its 3D nanostructure, g-C₃N₄/TiO₂ can be used to demonstrate its potential. By loading a

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thin $\text{g-C}_3\text{N}_4$ layer on TiO_2 double layer structures, electron scattering and absorption degree will increase more than is the case for a thick $\text{g-C}_3\text{N}_4$ layer because of the transmittance of incident light. Therefore, the use of a $\text{g-C}_3\text{N}_4/\text{TiO}_2$ 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 $\text{g-C}_3\text{N}_4$ on TiO_2 film

The coating of the $\text{g-C}_3\text{N}_4$ layer was conducted in a crucible with a cover via a sintering process. For the formation of $\text{g-C}_3\text{N}_4$, a melamine precursor was obtained from Junsei Chemicals. Using this precursor, sample amounts of melamine of 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 $\text{g-C}_3\text{N}_4$ layers; the heating rate was 10°min^{-1} . Consequently, 0.25 g, 0.5 g, 0.75 g, and 1 g $\text{g-C}_3\text{N}_4/\text{TiO}_2$ 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_2SO_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 K α 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 $\text{g-C}_3\text{N}_4$, 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 $\text{g-C}_3\text{N}_4$. 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 $\text{g-C}_3\text{N}_4$. PEC and LSV analyses were conducted using a potentiostat (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 $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$, the morphologies of the resulting mixtures revealed that $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ was added to the TiO_2 rod layer. Only 0.5 g and 1 g of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ were needed to uniformly cover the $\text{g-C}_3\text{N}_4$ on the TiO_2 bottom layer. Moreover, 1 g of the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ structure was present as a film that was thicker than the other $\text{g-C}_3\text{N}_4/\text{TiO}_2$ films. According to these results, we can confirm that $\text{g-C}_3\text{N}_4/\text{TiO}_2$ structures were well-constructed with increasing of the added amounts of $\text{g-C}_3\text{N}_4$.

3.1.2 TEM analysis

To accurately determine the size of the $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4/\text{TiO}_2$ 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

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), (c) 0.5 g g-C₃N₄/TiO₂, and (d) *d*-spacing of TiO₂.

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

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.

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 *d*₁₁₀ = 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. 4. (a) Optical absorbance and (b) calculation of the band gap energy of TiO₂, g-C₃N₄, and 0.25 g, 0.5 g, 0.75 g, and 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 TiO₂ film exhibited an absorbance edge at around 420 nm. The film of 0.5 g g-C₃N₄/TiO₂ has an absorbance edge at 440 nm; this means that there is higher absorbance in the visible range. Pure g-C₃N₄ and 1 g g-C₃N₄/TiO₂ 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 TiO₂, g-C₃N₄, 0.25 g g-C₃N₄/TiO₂, 0.5 g g-C₃N₄/TiO₂, 0.75 g g-C₃N₄/TiO₂, and 1 g g-C₃N₄/TiO₂, respectively. The band gap transitions are obviously revealed to depend on the amount of g-C₃N₄ added. Clearly, it can be seen that band gap energy can be adjusted according to the thickness of the g-C₃N₄ 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-C₃N₄ was confirmed using the FT-IR spectrum (Fig. 5). The bands of g-C₃N₄ 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-C₃N₄. The band at around 3000 cm⁻¹ was found to correspond to H₂O molecules adsorbed on the surface of the g-C₃N₄. The band at 805 cm⁻¹ is indicated to the s-triazine ring vibrations of g-C₃N₄. However, 0.25 g g-C₃N₄/TiO₂ and 0.75 g g-C₃N₄/TiO₂ have no distinctive g-C₃N₄ peaks due to their insufficient coating on TiO₂; the low degree of coating can be seen in the SEM images (Figs. 1(b)-(d)). Thus, the existence of g-C₃N₄ was directly confirmed through an observation of the chemical bonding.

Fig. 5. FT-IR analysis of TiO₂, g-C₃N₄, and 0.25 g, 0.5 g, 0.75 g, and 1 g of g-C₃N₄/TiO₂.

3.5. Photoluminescence

The possibility of charge separation due to g-C₃N₄ 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-C₃N₄. 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-C₃N₄ film was found to exhibit the highest intensity of around 500 nm. Then, the loadings of g-C₃N₄ were decreased from 1 g, to 0.75 g, and to 0.5 g of g-C₃N₄/TiO₂. Fig. 6(b) shows that 0.5 g of g-C₃N₄/TiO₂ film has the lowest intensity of PL due to the low recombination of charge carriers. Only the TiO₂ and the 0.25 g g-C₃N₄/TiO₂ films have almost no emission (Fig. 6(c)). The small PL intensity of the TiO₂ film is the result of its relatively porous structure.²¹⁾ On the other hand, due to the low level of loading of g-C₃N₄, the 0.25 g g-C₃N₄/TiO₂ film showed trends similar to those of TiO₂. Therefore, we identify that the 0.5 g g-C₃N₄/TiO₂ 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-C₃N₄/TiO₂ films.

Fig. 6. Photoluminescence of TiO₂, g-C₃N₄, and 0.25 g, 0.5 g, 0.75 g and 1 g of g-C₃N₄/TiO₂.

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-C₃N₄/TiO₂ film at 0.12 mA/cm². The second highest current density value was found in the 0.25 g and 0.75 g g-C₃N₄/TiO₂ films, which both had a value of 0.1 mA/cm². The TiO₂ film and the 1 g g-C₃N₄/TiO₂ film showed current density values of 0.075 and 0.03 mA/cm², respectively. Interestingly, the thicker g-C₃N₄ film, namely the 1 g g-C₃N₄/TiO₂ film, has the lowest current value, lower than even that of the TiO₂ film. This trend could be seen to indicate that the addition of a larger amount g-C₃N₄ 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-C₃N₄/TiO₂ 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 TiO₂ micro/nanorods; 0.5 g g-C₃N₄/TiO₂ seems to be a suitable material to enhance the PEC properties. Therefore, it is proved that an efficiently applied 0.5 g g-C₃N₄/TiO₂ 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 TiO₂ only and g-C₃N₄/TiO₂ composite films under a visible lamp. The TiO₂ film shows a 0.8 mA/cm² current density, which is the lowest value among the samples. After loading the g-C₃N₄ on TiO₂, a 1 g g-C₃N₄/TiO₂ thick coating film leads to a current density value of 0.12 mA/cm². Then, the thinner 0.5 g g-C₃N₄/TiO₂ coating film has a value of 0.21 mA/cm² for current density; this is approximately 3 times

Fig. 7. (a) *I*-*t* curves of TiO₂, and of 0.25 g, 0.5 g, 0.75 g, and 1 g of g-C₃N₄/TiO₂; (b) Stability test of 0.5 g g-C₃N₄/TiO₂ for 5 h.

higher than the value of pristine TiO₂ films (0.8 mA/cm²). The 0.25 g and 0.75 g g-C₃N₄/TiO₂ films showed lower current density versus potential values than that of the 0.5 g g-C₃N₄/TiO₂ film; however, this film did show a higher current density value than that of the 1 g g-C₃N₄/TiO₂ film. Similar results for PEC and LSV also demonstrated that a thin

Fig. 8. LSV measurements of TiO_2 , and of 0.25 g, 0.5 g, 0.75 g, and 1 g of $\text{g-C}_3\text{N}_4/\text{TiO}_2$.

Scheme 1. Schematic mechanism of 3D nanostructure 0.5 g $\text{g-C}_3\text{N}_4/\text{TiO}_2$ film.

coating of $\text{g-C}_3\text{N}_4$ can be used to enhance the current density. Once thick layers are coated on the TiO_2 micro/nanorods, light was not able to reach the TiO_2 surface. The electronic interaction between the TiO_2 and the $\text{g-C}_3\text{N}_4$ 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.

4. Conclusions

We successfully coated a $\text{g-C}_3\text{N}_4$ layer on 3D nanostructure grown TiO_2 films via sintering method. Through microstructural and morphological analyses, it was clearly seen that the 3D structure of TiO_2 was grown as a double layer with a flower-like shape on aligned rods. Additionally, a $\text{g-C}_3\text{N}_4$ layer was coated onto the TiO_2 double structure. From the FT-IR results, we confirmed the chemical bonding of $\text{g-C}_3\text{N}_4$ and the elements Ti, O, N, and C in the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ film. The $\text{g-C}_3\text{N}_4/\text{TiO}_2$ films are used to extend the band gap into the visible range. Based on the optical absorbance property and PEC, the recombination rate for electron-hole pairs

was found to have decreased. We can definitely prove that proper layer coating is necessary; thus, a 0.5 g $\text{g-C}_3\text{N}_4/\text{TiO}_2$ film can lead to reduced recombination and enhanced electron transfer properties.

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