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Design of Ag/g-C₃N₄ on TiO₂ Nanotree Arrays via Ultrasonic-Assisted Spin Coating as an Efficient photoanode for Solar Water Oxidation: Morphology Modification and Junction Improvement

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Graphical abstract



Highlights

- A novel hierarchical 3D TiO₂ nanotree/Ag/g-C₃N₄ photoanode was fabricated.
- 3D TiO₂ NT arrays as ETL were synthesized via a hydrothermal growth treatment.
- Ag /g-C₃N₄ was deposited on 3D TiO₂ NT with different coating methods.
- Ultrasonic assisted spin coating deposition method exhibited the best PEC performance.
- The optimized photoanode showed a photocurrent density of 1.4 mAcm⁻² at 1.23 V/RHE.

Abstract

Graphitic carbon nitride (g-C₃N₄) has been extensively studied as a model of polymeric semiconductor material in photoelectrochemical (PEC) water oxidation reaction; however, its low PEC performance is still a concern of significant importance among researchers. Herein, we did a novel host-guest design of a photoanode device comprising three dimensional (3D) TiO₂ nanotree (NT) arrays as an electron transfer layer (ESL) and Ag/g-C₃N₄ heterojunction as a photo absorber layer. In this design, 3D TiO₂ NT arrays synthesized via a hydrothermal growth treatment were deposited with an alcoholic suspension of Ag/g-C₃N₄ using different coating methods such as drop casting, spin coating, and ultrasonic assisted-spin (U-spin) coating methods. The optimized photoanode prepared via U-spin coating exhibited a remarkable photocurrent density of 1.4 mA cm⁻² at 1.23 V vs. RHE and a negatively shifted onset potential of 0.2 V in 1.0 M KOH when it was illuminated from the backside using a Xenon lamp (150 W) equipped with a 400 nm cut off filter. This hierarchical 3D design photoanode demonstrated constant stability during the water oxidation reaction for at least 8 h.

Keywords: 3D TiO₂ nanotree arrays, $Ag/g-C_3N_4$ Heterojunction, Electron transport layer, Ultrasonic-assisted spin coating, Photo water oxidation, Host-guest design

1. Introduction

Inspired by natural photosynthesis, photoelectrochemical (PEC) water splitting has attracted lots of worldwide interests in recent years [1,2]. PEC water splitting is a promising, scalable, and cost-effective method for storing solar energy in the form of chemical fuel [3,4]. The most challenging aspect of this method is the design of an efficient, low cost and robust

photoelectrode being capable of harvesting visible light efficiently and tolerating harsh PEC condition [5,6]. Considering the unusual properties and potential applications in various fields two-dimensional (2D) materials have enticed particular attention [7-9]. Among the various available 2D materials, polymeric graphitic carbon nitride (g-C₃N₄) has been more specific due to its graphene-like structure, suitable band gap energy (2.7-2.9 eV), well visible light absorption and low cost [10,11]. However, pure g-C₃N₄ still has a low efficiency of photocatalytic activity due to its bordering band gap and high rate of e^{-}/h^{+} recombination [12-14].

Various strategies have been employed to improve the PEC performance or photocatalytic activity of g-C₃N₄ [15-23]. One of the most appropriate strategies to modify carbon nitride photocatalytic properties is coupling the structure with metal nanoparticles. When a metal contact the surface of g-C₃N₄ or any other semiconductor materials, due to their different work functions a contact potential difference called the Schottky barrier will generate at their interface (metal/semiconductor) [24-26]. This potential barrier can persuade the directional transfer of photogenerated electrons from semiconductor to metal that remarkably enhance the charge separation efficiency. Meanwhile, there are two extra effects come from the metal/g-C₃N₄ coupling; the first and the most important one is the surface plasmon resonance (SPR) effect of some noble metals (such as Ag, Au, etc.) and even non-noble metals (e.g., Bi) that can enhance light absorption, and the second one is the superb catalytic activity on the surface of some noble metals (e.g., Pt) can accelerate the surface catalytic reactions [27,28].

Other drawbacks that g-C₃N₄ suffers in the role of an active photo absorber material are its limited surface area and poor light-harvesting ability. Research on photoanodes for photoelectrochemical water oxidation has introduced the concept of underlayer for the activation of ultrathin photo absorber films. Host-guest architectures (underlayer-photo absorber) are one of

the main nanostructural designs that can be used for the preparation of a thin layer of photo absorber with maximum current collection. In this way, the photo absorber material is deposited on a current collector scaffold or electron transporting layer with a high surface area. Hence, a high surface area for photo absorber (g-C₃N₄) will provide in which two different transfer pathways will effectively decouple $e^{-/}h^+$. Meanwhile, these scaffolding materials should have an almost wide band gap, good electron-transport property, and appropriate band alignment related to the photo absorber. The most studied materials in this subject were metal oxides.

One dimensional (1D) [29,30] and three dimensional (3D) [31,32] nanostructures displaying unique size-dependent features along with appropriate electrical, optical and chemical properties can be utilized as host scaffolds for g-C₃N₄ as the guest. These 1D and 3D nanostructure scaffolds can cause light-harvesting increase and e^-/h^+ recombination decrease owing to their unique morphological properties through the reduction of grain boundaries acting as the recombination sites for photo-charge carries [33-37]. Also, simple 1D nanostructures suffer from limited energy conversion efficiency due to their inadequate surface area and poor lightharvesting capability [38,39]. Then, the synthesis of hierarchically 3D structured photoanode scaffolds can be considered as a promising approach to overcome the drawbacks associated with low surface area, poor light-harvesting, and high grain boundaries.

Herein, we have fabricated a host-gust scaffold design of TiO_2 nanotree (NT) arrays and a very thin layer of Ag/g-C₃N₄. Ag/g-C₃N₄ heterojunction was prepared by a simple thermal polymerization via the mixing of urea and melamine with silver nitrate. The metallic silver nanoparticles were produced on g-C₃N₄ layers through thermal decomposition of silver nitrate under elevated temperature. TiO₂ NT arrays were hydrothermally grown on florin doped thin oxide (FTO) substrate. Then, Ag/g-C₃N₄ dispersed in ethanol was deposited on the TiO₂ NT

through drop casting, spin coating, and ultrasonic-assisted spin (U-spin) coating deposition methods. The PEC performance of the as-prepared device showed a high dependency on both the hydrothermal growth time of TiO₂ NT and the employed Ag/g-C₃N₄ deposition technique.

2. Materials and Methods

2.1. Fabrication of TiO₂ Nanotree Array

TiO₂ nanotree arrays on transparent conductive fluorine-doped tin oxide (FTO, TCE7, R:6-8ohm cm⁻²) were synthesized by a hydrothermal growth method [40]. In a typical process, the FTO substrates were first cleaned with acetone, ethanol, and deionized water, respectively, for 15 min in each solvent, and then dried in an electrical oven. The precursor was prepared by adding 1.2 mL of titanium isopropoxide (98%, Daejung, Kosdaq license) to a well-mixed solution containing 41 mL of HCl (37%, Daejung, Kosdaq license) and 59 mL of H₂O, and then the whole mixture was stirred for another 10 min until the solution became clear. The precursor was then poured into a Teflon-lined stainless-steel autoclave and the FTO substrates were immersed in the precursor solution. Hydrothermal growth was conducted at 150 °C for different times (6, 9, and 14 h) in an electrical oven. The FTO substrates were then rinsed with deionized water and dried for 1h at 70 °C. Then, TiO₂ NT arrays were immersed in a 0.2 M aqueous solution of TiCl₄ (99%, Daejung, Kosdaq license) for 2 h at 70 °C for surface modification followed by annealing at 450 °C for 30 min.

2.2. Fabrication of g-C₃N₄ and Ag/g-C₃N₄ Heterojunction

g-C₃N₄ and Ag/g-C₃N₄ were prepared using the procedure in [41]. A mixture of 2.5 g of melamine and 2.5 g of urea was placed in a crucible and was heated by a specified program; from room temperature to 300 °C with a heating rate of 8 °C min⁻¹, from 300 to 500 °C with a

heating rate of 2 °C min⁻¹, from 500 to 550 °C with a heating rate of 1 °C min⁻¹, and was finally at 550 °C for 2 h. After cooling to room temperature, the products were obtained in the powder form. Ag/g-C₃N₄ was prepared using a similar procedure for g-C₃N₄ except for the addition of 0.5 g of AgNO₃ to the melamine and urea mixture. Here, Ag nanoparticles will be produced on the surface of g-C₃N₄ layers through the thermal decomposition process of AgNO₃ at elevated temperature; qualitatively, decomposition is negligible below the AgNO₃ melting point (212 °C), but becomes appreciable around 250 °C and totally decompose at 440 °C:

 $2 \text{ AgNO}_3(l) \rightarrow 2 \text{ Ag}(s) + O_2(g) + 2 \text{ NO}_2(g)$

Thermal decomposition of metal salts is one of the easiest ways to produce metallic nanoparticles.

2.3. Fabrication of TiO₂ NT/Ag/g-C₃N₄ photoelectrodes

g-C₃N₄ and Ag/g-C₃N₄ were deposited on TiO₂ NT arrays by drop-casting, spin-coating, and U-spin coating methods. 0.05 g of g-C₃N₄ or Ag/g-C₃N₄ powders were suspended in 2 ml of ethanol through ultrasonication for 1h. Then, 100 μ l of the as-prepared suspension was drop cast or spin-coated at 3000 rpm for 30 s. In the U-spin coating method, ultrasonic waves were applied to the substrate via four ultrasonic vibrators placed beneath the substrate. Afterward, the electrodes were dried at 70 °C for 1h.

2.4. Fabrication of TiO₂ nanoparticles layer /Ag/g-C₃N₄ Photoelectrodes

To prepare TiO₂ nanoparticles (NPs) layer, 50 μ l of an ethanolic solution containing titanium isopropoxide (0.2 M) and HCl (0.2 M) was spin-coated on the cleaned FTO substrate at 3000 rpm for 30 s, followed by an annealing treatment in air at 500 °C for 30 min. Then, 0.05 g Ag/g-

 C_3N_4 powder was suspended in 2 ml of ethanol through ultrasonication for 1h and 100 µl of the as-prepared suspension was drop cast on the TiO₂ layer. The electrodes were dried at 70 °C for 1h.

2.5. Fabrication of g-C₃N₄ and Ag/g-C₃N₄ Photoelectrodes

To prepare the g-C₃N₄ and Ag/g-C₃N₄ electrodes, 5 mg of each powder and 35 μ L Nafion (5wt%, Sigma Aldrich) were dispersed in water-isopropanol solution (0.4 mL) with a volume ratio of 3:1 by sonicating for 1 h until a homogeneous ink was obtained. Then, 50 μ L ink was drop cast onto a FTO (2.0 cm×2.0 cm) substrate. After drying in the electrical oven at 70 °C for 1h, the as-prepared photoanodes were tested for PEC measurements.

2.6. Photoelectrochemical measurements

All photoelectrochemical experiments were performed in a standard three-electrode system containing the prepared photoanodes as working electrodes, Pt wire as a counter electrode, and the Ag/AgCl in 0.3 M KCl as a reference electrode. The potential of working electrode regarding the reference electrode was changed to a reversible hydrogen electrode (RHE) using the following equation:

$$E_{RHE}(V) = E_{Ag/AgCl}(V) + 0.059 \times pH + 0.197$$
(1)

where pH is the electrolyte solution pH. The PEC performance of the photoanode was measured in 1 M KOH (pH 13) under Xenon lamp (150 W) illumination equipped with a UV 400 filter (Newport 20 CGA-400). The potential was scanned from negative to positive with a scan rate of 10 mV s⁻¹. The same electrolyte solution and scan rate were used for the linear sweep voltammetry (LSV) measurements in the dark. The electrochemical impedance spectroscopy (EIS) measurements were taken in the frequency range of 0.01 Hz to 100 kHz at open circuit potential in

1M KOH solution under light illumination. The Mott-Schottky tests were conducted in the dark at a scan rate of 10 mV s⁻¹ and a frequency of 100 Hz.

2.7. Characterization equipment

The powder X-ray diffraction (PXRD) patterns of prepared nanomaterials were recorded by Bruker/D8 Advanced diffractometer in the 20 from 10.0 to 80° by step of 0.1 degrees using Cu K α radiation (λ =1.541 Å). The silicon powder was used as a standard for PXRD instrument calibration. The chemical states of elements in the samples were analyzed based on X-ray photoelectron spectroscopy (XPS) data recorded on a Thermo Scientific Sigma Probe spectrometer using a photon energy of 1486.6 eV, the spot size of 400 µm, pass energy of 200 eV and energy step size of 1.0 eV. The field emission scanning electron microscopy (FESEM) analysis of the prepared photoanodes and photocatalysts were taken by a FESEM (Model quanta 250 FEG (Field Emission Gun)). The UV–vis absorbance spectra were taken by Unico UV-2100 spectrophotometer. The spectra were recorded at room temperature in the air within the range of 200–800 nm. The suspended samples were prepared using an ultrasonic bath (Branson 5210, Branson Ultrasonic Cleaner, USA) at a frequency of 40 kHz and power of 157 W, in an inner tank sized 150x135x60 mm with a volume of 1.2 L. The photoelectrochemical analyses were performed using Versa STAT 3, Princeton Applied Research device.

3. Results and Discussion

3.1. Characterization

Fig. 1a shows the XRD patterns of prepared $g-C_3N_4$ and $Ag/g-C_3N_4$ heterojunction. No additional peaks were observed in the XRD patterns, indicating the absence of any impurity. Two diffraction peaks, at 12.8° and 27.6°, confirmed $g-C_3N_4$ formation. The intense peak at

27.6°, assigned to (002) diffraction plane, is related to the interalayer stacking of aromatic systems. The peak at 12.8°, indexed as (100) in JCPDS 87–1526, is due to the interlayer structural packing of tri-s-triazine units [41]. The four diffraction peaks of cubic Ag; (111), (200), (220), and (311) planes, are observed in the XRD pattern of Ag/g-C₃N₄ heterojunction [42]. Meanwhile, the presence of (002) plane at 27.6° confirms the existence of graphitic material. The magnified picture, Fig. S1, in the range of 2 θ (10° to 36°) confirms the presence of (100) peak at about 12.8° that could not be seen in Fig. 1a due to highly intense Ag peaks Also, Fig. 1b demonstrates the XRD patterns of TiO₂ NT/g-C₃N₄ and TiO₂ NT/Ag/g-C₃N₄ photoanodes. All the peaks of TiO₂ NT could be indexed to the formation of the tetragonal rutile phase of TiO₂ (JCPDS, no. 21-1276).



Fig. 1. X-ray diffraction patterns of (a) $g-C_3N_4$ and $Ag/g-C_3N_4$ powders, (b) $TiO_2 NT/g-C_3N_4$, and $TiO_2 NT/ Ag/g-C_3N_4$ photoanodes.

Figs. 2a and 2b exhibit the morphology and elemental mapping of the TiO_2 films respectively, which are formed via hydrothermal treatment at 150 °C for 9 h on FTO substrate. The

morphology of the TiO₂ film can be described as a branched nanorod structure or nanotree (NT), with branches of about 70-100 nm in length and 15-20.0 nm in diameter. Figs. 2c and 2d demonstrate the SEM images of TiO₂ NT/ Ag/g-C₃N₄ via a drop-casting and U-spin coating deposition methods of Ag/g-C₃N₄ suspended in ethanol on TiO₂ NT scaffold, respectively. As can be seen in Figs. 2d and 2e, a more homogeneous heterojunction was formed between TiO₂ NT and Ag/g-C₃N₄ layers through the U-spin coating method in comparison with the dropcasting method (Fig. 2c, agglomerated $Ag/g-C_3N_4$ were deposited on TiO₂ NT). This homogeneous junction formation arising of applied strong ultrasonic waves to the electrode surface during spin coating that help to a smooth spreading of Ag/g-C₃N₄ alcoholic suspension and formation of strong bonding between two different layers. Furthermore, Fig. 2f shows the cross-sectional FESEM image of TiO₂ NT/ Ag/g-C₃N₄ that is made by U-spin coating method. This figure confirmed the formation of the tree-like structure of the prepared photoanode. The elemental mapping of this photoanode was demonstrated in Fig. 2g. The absence of Ag percent in elemental mapping result is due to a very small amount of Ag in an extremely thin layer of $Ag/g-C_3N_4$ formed on TiO₂ NT, which could not be detected by this method (the XRD data has confirmed the presence of Ag atoms in the photoanode structure). The FESEM and elemental mapping of Ag/g-C₃N₄ are shown in (Fig. S2, supporting information)



Fig. 2. (a) FESEM image and (b) elemental mapping of TiO₂ NT, (c) FESEM image of TiO₂ NT/ Ag/g-C₃N₄ (drop casting), (d),(e) TiO₂ NT/ Ag/g-C₃N₄ (U-spin coating) with different magnification, (f) cross-sectional view of TiO₂ NT/ Ag/g-C₃N₄ (U-spin coating) photoanode, (g) FESEM image and elemental mapping of TiO₂ NT/ Ag/g-C₃N₄ (U-spin coating) photoanode.

The surface elemental composition and chemical states of Ag/g-C₃N₄ and g-C₃N₄ were compared by XPS technique. The XPS survey spectrum (Fig. 3a) approved the existence of the C, N, and Ag elements in the surface of the prepared photoelectrode. Figs. 3b and c show the core-level spectra of N1s and C1s for and Ag/g-C₃N₄. The XPS core-level spectra for g-C₃N₄ were shown in Fig. S3. The prevailing C1s peak at 288.1 eV is a result of C-N-C coordination in the melon structure. The N1s spectrum was deconvoluted to three main peaks of different nitrogen types at 398.2, 399.3, and 400.3 eV corresponding to pyridinic nitrogens, tertiary, and secondary and primary nitrogens in the heptazine structure. Comparing N1s core level spectra of g-C₃N₄ and Ag/g-C₃N₄ exhibited that % N2c in Ag/g-C₃N₄ is higher than that of g-C₃N₄ (29.6: 24.5) and also %N in the form of NH₂ and NH in Ag/g-C₃N₄ is much lower than that of g-C₃N₄ (6.6:11). The data were obtained via XPS analysis. Based on these results we can suggest that the

condensation process of melamine and urea was done more completed in the presence of AgNO₃ compare with in its absence. Fig 3d approved that silver element exists mainly in the form of metallic Ag^o state and partially in the form of Ag⁺ and is indicated by the Ag 3d_{5/2} at 368.2 and 371.8 eV. Also, the Ag 3d_{3/2} peaks as a result of spin-orbit splitting appeared at 6.0 eV difference compare to at Ag 3d_{5/2} [42]. The XPS results verified that most of the Ag atoms exist in the forms of Ag nanoparticles that are deposited on the g-C₃N₄ layer and also a very low amount may be doped in the nitrogen pores of the g-C₃N₄ matrix.



Fig. 3. X-ray photoelectron spectra of $Ag/g-C_3N_4$ (a) the XPS survey spectra, (b) N 1s, (c) C 1s, and (d) Ag 3d peaks.

The optical property of g-C₃N₄ and Ag/g-C₃N₄, TiO₂, and TiO₂/Ag/g-C₃N₄ were investigated via UV-Vis absorption spectroscopy. The result showed that the attachment of Ag nanoparticles on g- C_3N_4 layers has enhanced visible light harvesting along with the visible light wavelengths (absorption tail in the visible range for $Ag/g-C_3N_4$ (Urbach tail)). The band edge position for both g-C₃N₄ and Ag/g-C₃N₄ was located around 480 nm. The optical band gaps were calculated 2.94 for $g-C_3N_4$ and 2.9 for Ag/g-C₃N₄ using the Kubelka-Munk equation (Fig. S4). Meanwhile, some mid gap states will appear between the bandgap of $Ag/g-C_3N_4$ compare with $g-C_3N_4$ because of the higher absorption tail intensity. These mid gap states will provide the possibility of electron transfer with lower energy photons than the band gap. The Kubelka-Munk plot in Fig.S4b exhibited that the mid-gap states for Ag/g-C₃N₄ were located around 2.8-2.82 eV. Also, the quenching of the steady-state photoluminescence spectra for Ag/g-C₃N₄, Fig. 4b demonstrated that the e⁻/h⁺ recombination rate reduces due to the presence of metallic Ag atoms on the surface of g-C₃N₄ and this quenching increase with increasing Ag values. Ag NPs were formed on g-C₃N₄ layers easily take the electrons from the g-C₃N₄ conduction band and leave them free in their metallic free states. As a result, the e^{-/h^+} recombination rate will decrease.



Fig. 4. (a) UV-Vis absorption spectra of g-C₃N₄, Ag/g-C₃N₄, TiO₂ NT, and TiO₂ NT/ Ag/g-C₃N₄. (b) Steady-state PL spectra of g- g-C₃N₄ and Ag/g-C₃N₄ prepared with different amount of AgNO₃.

3.2. Photoelectrochemical characterization of g-C₃N₄ and Ag/g-C₃N₄ heterojunction

g-C₃N₄ and Ag/g-C₃N₄ heterojunction were synthesized via a simple thermal polymerization method and their corresponding photoelectrodes were prepared using Nafion 5% solution to evaluate the influence of $Ag/g-C_3N_4$ heterojunction formation on the g-C₃N₄ photoelectrochemical properties. As shown in Fig. 5a, the as-prepared photoelectrodes demonstrated a very low PEC performance with photocurrent density values of 1 µAcm⁻² and 2 µAcm⁻² for g-C₃N₄ and Ag/g-C₃N₄ heterojunction at the potential of 1.23 eV versus RHE, respectively. Although, UV-Vis absorption spectra, Fig.4a demonstrated that Visible light absorption has enhanced in Ag/g-C₃N₄ compare to g-C₃N₄ but it can not harvest the light efficiently and produce a high enough photocurrent density due to its limited surface areas that are exposed to the light. Also, only a limited number of holes (those are produced very near the electrode/electrolyte interface) can catch the electrode surface to participate in the photooxidation process. Due to the high recombination rate of charge carriers in the bulk, lots of the holes do not have any chance to reach the electrode surface where the water oxidation will happen. In continue, the impedance spectroscopy analysis was conducted to study the effect of metallic Ag NPs in the charge transfer process at the g-C₃N₄/electrolyte interface. The impedance analysis results demonstrated a significant difference between g-C₃N₄ and Ag/g-C₃N₄ photoanodes, Fig.5b. The low-frequency impedance results, typically associated with interfacial charge transfer phenomena, of the Ag/g-C₃N₄ photoanode, was very low in comparison with that of g-C₃N₄ photoanode. This can be attributed to the reduction of the injection barrier charge

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carriers at the electrode/electrolyte interface. Ag atoms can help the majority of carrier's separation and transportation, which scales inversely with the hole injection rate to the electrolyte and subsequently improves the electrochemical charge transfer at the electrode/electrolyte interface [43,44].



Fig. 5. (a) Linear sweep voltammetry and (b) Nyquist plot of $g-C_3N_4$ and $Ag/g-C_3N_4$ photoanodes.

3.3. TiO₂ scaffold as an electron transporting layer

To improve the photoelectrochemical properties of g-C₃N₄ and Ag/g-C₃N₄, we efficiently decreased e⁻/h⁺ recombination using an electron transporting layer (ETL) in a host- gust design [45-47]. Both g-C₃N₄ and Ag/g-C₃N₄ were deposited via a drop-casting method on TiO₂ NT arrays made by 14h hydrothermal growth treatment. As shown in Fig. 6a, the photocurrent density was much enhanced in TiO₂ NT/Ag/g-C₃N₄ photoanode compare to g-C₃N₄, which is an indication of the efficient charge recombination reduction in the Ag/g-C₃N₄ structure. Both impedance spectroscopy data and Mott-Schottky plots confirmed the improved PEC results. The

reduced Nyquist plot radius for TiO₂ 14h/ Ag/g-C₃N₄ in comparison with TiO₂ 14h/ g-C₃N₄ is an indication of decreasing charge transfer resistance at the photoanode/electrolyte interface due to the presence of Ag atoms and also effective charge carrier decoupling with the help of TiO₂ NT scaffold (Fig. 6b). Furthermore, the slope reduction of the Mott-Schottky plot in Fig. 6c for Ag/g-C₃N₄ amplifies the effect of Ag atoms in the as-prepared heterojunction as compared with that of g-C₃N₄. The plot analysis shows an increased concentration in donor density in TiO₂ NT/ Ag/g-C₃N₄ photoanode, Table S1. Also, the positive shift of the flat band potential as shown in Fig. 5c, confirms the facilitated charge carrier transport at the electrode/electrolyte interface.



Fig. 6. (a) Linear sweep voltammograms, (b) Nyquist representation of the impedance result, and (c) Mott-Schottky plot of TiO₂ NT (14 h)/g-C₃N₄ and TiO₂ NT (14 h)/ Ag/g-C₃N₄ photoanodes.

To study the effect of ETL morphology on PEC performance of Ag/g-C₃N₄, a thin film of TiO₂ NPs were deposited on FTO substrate via a simple spin coating method. The PEC performance of TiO₂ NPs/Ag/g-C₃N₄ photoanodes was evaluated via linear sweep voltammetry and Impedance spectroscopy analysis. As shown in Fig. 7a, the photocurrent density (6 μ Acm⁻² at the potential of 1.23 V vs. RHE) of the Ag/g-C₃N₄ deposited on the TiO₂ NPs was much lower than

that (approximately $30 \ \mu \text{Acm}^{-2}$) deposited on the TiO₂ NT. Moreover, the onset potential of the Ag/g-C₃N₄ deposited on the TiO₂ NPs has demonstrated an obvious positive shift that shows less electron accumulation or e⁻/h⁺ separation in the photoanode device. TiO₂ as ETL in both NPs and NT morphology could accept the photoexcited electrons from the Ag/g-C₃N₄ conduction band, and retard e⁻/h⁺ recombination on the surface area of Ag/g-C₃N₄, resulting in an improved light-harvesting capability. Meanwhile, the NT morphology can increase the electron collection efficiency by reducing the undesirable loss of electrons at the grain boundaries, which can be rolled as recombination centers of photo charge carriers of electrons and holes as redox couples [34,35]. Alternatively, it can provide a large contact area for Ag/g-C₃N₄ photo absorber and electrolyte that facilitates the hole transfer at the electrode/electrolyte interface. This hypothesis was validated by impedance spectroscopy data (Fig. 7b), where the lower impedance values in NT morphology depicted more facilitated charge carriers transport at the electrode/electrolyte interface.



Fig. 7. Linear sweep voltammograms and Nyquist representation of the impedance result of $Ag/g-C_3N_4$ deposited on TiO₂ NPs and TiO₂ NT (14h) on FTO substrate.

3.2. TiO₂ NT scaffold thickness and Ag/g-C₃N₄ deposition methods

To further optimize the PEC performance of TiO₂ NT/ Ag/g-C₃N₄ photoanode, we adjusted the TiO₂ scaffold thickness and improved the junction made between TiO₂ NT and Ag/g-C₃N₄. We modified the thickness of TiO₂ NT as an ETL by controlling he hydrothermal growth time. Then we assessed its effect on the PEC performance of the as-prepared photoanodes. Although there was almost no change in their onset potential of the prepared photoelectrodes. As shown in Fig. 8a, the photoanode with a growth time of 9h showed the greatest enhancement in the photocurrent density (150 μ Acm⁻² at 1.23 V vs. RHE).

Furthermore, to investigate the junctions that formed between $TiO_2 NT Ag/g-C_3N_4$, three different deposition methods; drop casting, spin coating, and U-spin coating were applied for the deposition of an alcoholic suspension of $Ag/g-C_3N_4$. As shown in Fig. 8b, the varying deposition method could lead to a change in both photocurrent density and onset potential. The U-spin coating method was very effective to significantly enhance the photocurrent density (300 μ A cm⁻² at 1.23 V vs. RHE) and to make a negative shift of its onset potential (0.2 V) compared to the spin coating and drop-casting. Although the spin coating method was not effective for changing the photocurrent density, its onset potential (0.2 V) showed a negative shift. In the applied spin coating, we used centrifugal force to spread the suspension on the surface of TiO₂ NT. Through this mechanism, we can make a more homogeneous layer compared with drop-casting. The obvious negative shift of the onset potential could be ascribed to the surface passivation of the prepared photoanode through making it more homogeneous and tight, however, using only spin coating for Ag/g-C₃N₄ deposition could not make a perfect junction (interface) to effectively enhance charge carrier transfer because of the pin-hole formation at the TiO₂ NT and Ag/g-C₃N₄.

Hence, the photocurrent density did not show any improvement. Meanwhile, U-spin coating method provides an external vibration when spreading the suspension on the surface. These vibrations that happen at the solid/liquid interface could affect the coating process through different mechanisms: 1) ultrasonic vibration could make very tiny droplets of the suspension that can penetrate better into the roughness of TiO₂ structure [48-50]. 2) By applying ultrasonic waves the cavitation process can happen at the solid/liquid interface [51]. Through this process, very high temperature and pressure are produced during U-spin coating. In this harsh condition, the layers of TiO₂ NT and Ag/g-C₃N₄ can join to each other very tightly through the local melting of the two layers and provide a pin-hole free interface. Both extremely perfect junction and passivated surface obtained in the U-spin coating method play an important role in producing more negative onset potential of about 0.2 mV and higher photocurrent density of 300 μ Acm⁻² at 1.23 V vs. RHE.



Fig. 8. Linear sweep voltammograms of different $TiO_2 NT/Ag/g-C_3N_4$ concerning (a) different hydrothermal growth time of $TiO_2 NT$ and (b) different $Ag/g-C_3N_4$ deposition method.

3.3. Open circuit analysis

Fig. 8 shows the steady-state open circuit potential values obtained in dark and under light illumination for TiO₂ NT/ Ag/g-C₃N₄ photoanodes with different types of Ag/g-C₃N₄ deposition methods (spin coating, U-spin coating, and drop-casting). A more negative value of $E_{OC, light}$ shows the more electron accumulation in the electrode structure [52]. As shown in Fig. 9a, both spin-coated and U-spin coated photoanodes produce the same amount of $E_{OC, light}$, which is more negative than that of the drop-casting sample. This happens because the U-spin coating method optimizes the junction formation between TiO₂ NT and Ag/g-C₃N₄ but it does not change the film thickness and surface properties compare with spin coating. As a result, the charge transfer kinetics and e⁻/h⁺ recombination rate have remained the same at the electrode interface as it has been shown before by the same value of onset potential (0.2 V) for these two photoanodes (spin-coated and U-spin coated).

Also, Fig. 9b exhibited that the TiO₂ NT/ Ag/g-C₃N₄ photoanode that deposited via U-spin coating method compare with g-C₃N₄ holds higher photovoltage and depicted slower photovoltage decay behavior after turning off the light. These characteristics are corresponding to higher charge accumulation and a longer lifetime of charge carrier.



Fig. 9. (a) Steady-state OCP values of TiO₂ NT/ Ag/g-C₃N₄ photoanodes with respect to different deposition methods of Ag/g-C₃N₄ and side illumination (frontside and backside illumination). (b) Transient OCP measurements for TiO₂ NT/ Ag/g-C₃N₄ and TiO₂ NT/ g-C₃N₄.

3.4. Light illumination direction

To study the light penetration effect into the photoanode with 3D structure design, the PEC performance was investigated by changing the light illumination direction toward the 3D structure. The hypothesis is that different degrees of availability of charge carriers generated in different zones of the photoanode. When photoanodes were irradiated from the backside of the 3D structure in TiO₂ NT Ag/g-C₃N₄ (spin coat and U-spin coat), the photocurrent density was dramatically enhanced as shown in Fig. 10a. In the spin and U-spin coated photoanodes, the identified photocurrent density reaches approximately 0.6 mA cm⁻² and 1.3 mA cm⁻² at 1.23 V vs. RHE, respectively. Also, as demonstrated in Fig. 8a, $E_{OC, light}$ shows more negative values for the light illumination from the backside, which confirms more electron accumulation in the backside of photoelectrodes during the illumination. Fig 10b. depicted the ratio of J_{front}/J_{back} vs.

potential. If the majority carriers (electrons) transport do not control the photocurrent, this ratio will equal to 1. Meanwhile, if the ratio obtains less than 1, it shows that electron generation is the dominant process for regulating the reaction rate at the electrode/electrolyte interface. Interestingly both of the prepared photoanodes demonstrated values less than 1 (0.2). Hence, the mechanism can be described as below:

As depicted in Scheme. 1 (left side), when electrons are generated near the FTO and circuit in the backside illumination, the path length for electron transportation becomes short, leading to increased photocurrent density. However, if electrons are generated far from the FTO and circuit in the frontside illumination, the path length for electron transportation becomes long, resulting in decreased photocurrent density. This resulting photocurrent density change depending on the light illumination direction validates the idea that electrons transfer efficiency can control the photoelectrochemical reaction kinetics [53].



Fig. 10. (a) Linear sweep voltammograms of $TiO_2 NT/Ag/g-C_3N_4$ photoanodes concerning $Ag/g-C_3N_4$ deposition method and light side illumination and (b) Ratio of J_{front}/J_{back} as a function of potential for $TiO_2 NT/Ag/g-C_3N_4$ (spin coat and U-spin coat).



Scheme. 1. Illustration of the mechanism behind the different sides of light illumination (front and backside) for TiO₂ NT/ Ag/g-C₃N₄ photoanodes.

3.5. Stability assessment

Long term stability of photoelectrode is one of the sensitive aspects in improving the commercial applicability of photoelectrode. To evaluate the strength of the photoanodes prepared, chronoamperometric tests were done under a constant applied potential of 1.23 V vs. RHE for 8 h. As shown in Fig. 11, during the test, the photocurrent of two photoelectrodes of TiO₂ NT/ Ag/g-C₃N₄ (spin coating, and U-spin coating) stay constant at very high value of 1.4 mA cm⁻² at 1.23 V vs. RHE and almost equal to the values recorded via linear sweep voltammetry tests. These results confirm the formation of the steady and tight junctions between the TiO₂ layer and Ag/g-C₃N₄ via both spin coating and ultrasonic-assisted spin coating methods.



Fig. 11. Extended current vs. time plot under light illumination (150 W Xenon lamp equipped with a cut off filter 400 nm) for TiO₂ NT/ Ag/g-C₃N₄ deposited via spin coating and ultrasonic-assisted spin coating) recorded with an applied bias of 1.23 V vs RHE and using 1 M KOH as the electrolyte.

4. Conclusions

This study analyzed the effects of two parameters of metal heterojunction with g-C₃N₄ and nanotree-like structure of TiO₂ as a scaffold in improving the PEC performance of an extremely thin layer of g-C₃N₄ photoanode. Even though introducing Ag NPs attached to the g-C₃N₄ layer enhanced Visible light-harvesting and facilitated charge transfer at the electrode/electrolyte interface, the PEC performance suffers from disability holes to catch the electrode surface. The combination of the Ag /g-C₃N₄ heterojunction along with the host-guest design by deposition of TiO₂ NT as an ETL exhibited a dramatic enhancement in the photocurrent density. In particular, the optimized photoanode with 9h hydrothermal growth treatment of TiO₂ NT deposited with a thin layer of Ag/g-C₃N₄ via U-spin coating method showed a great improvement in photocurrent

density of 300 μ Acm⁻² and an onset potential of 0.2 V. This study also identified the significance of the light illumination direction on improving the PEC performance. The backside illumination of the as-prepared photoanode was much more effective in increasing the photocurrent density than that of the front side. The identified effect of the light illumination direction indicates that the generation zone of the majority charge carriers (electrons) has a strong impact on PEC performance, confirming the effect of electron transport kinetics. Finally, the Ag/g-C₃N₄ photoanode with the improved heterojunction of TiO₂ NT as an electron collecting layer and the backside light illumination demonstrated extremely high stability of at least 8 h with photocurrent density of approximately 1.4 mA cm⁻² in 1.0 M KOH.

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