Electrospinning Preparation of Nanostructured g-C₃N₄/BiVO₄ Composite Films with an Enhanced Photoelectrochemical Performance

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Supporting Information

ABSTRACT: Nanostructured g-C₃N₄/BiVO₄ composite films with an enhanced photoelectrochemical (PEC) performance have been fabricated via the facile electrospinning technique. The g-C₃N₄ nanosheets can not only form heterojunctions with BiVO₄ but also prevent the agglomeration of BiVO₄, helping the formation of nanostructures. The as-prepared g-C₃N₄/BiVO₄ films exhibit good coverage and stability. The PEC performance of the g-C₃N₄/BiVO₄ films is much more enhanced compared with that for individual BiVO₄ films because of the enhanced electron–hole separation. The photocurrent density is 0.44 mA/cm² for g-C₃N₄/BiVO₄ films at 0.56 V in the linear sweep current–voltage test, over 10 times higher than that of individual BiVO₄ films (0.18 mA/cm²). The effects of the preparation conditions including the g-C₃N₄ content, collector temperature, calcination temperature, and electrospinning time on the PEC performance were investigated, and the reasons for the effects were proposed. The optimal preparation condition was with 3.9 wt % g-C₃N₄ content in the electrospinning precursor, 185 °C collector temperature, 450 °C calcination temperature, and 40 min electrospinning time. The excellent PEC performance and the facile preparation method suggest that the g-C₃N₄/BiVO₄ films are good candidates in energy and environmental remediation area.

INTRODUCTION

Recently, the photoelectrochemical (PEC) process has been widely studied in energy and environmental areas.^{1,2} In PEC systems, the photogenerated electron–hole separation was enhanced by an external electric field, hence improving the catalytic activity.³ Meanwhile, the photocatalysts are immobilized on the FTO glass, thus its separation and reclaim process is easier compared to the conventional suspended photocatalysts.⁴

The choice of photoelectrode is crucial in the PEC system.^{5–7} Semiconductors with a band gap width suitable to absorb visible light are attractive to be used as photoelectrodes.⁸ Bismuth vanadate (BiVO₄) possesses good catalytic ability with visible light, suitable conduction band edge position for H₂ evolution, and nontoxic and good chemical stability properties and has been extensively researched as a photocatalyst and a photoelectrocatalyst.^{9,10} Up to now, various methods for synthesizing BiVO₄ films including drop casting,¹¹ electrodeposition,^{10,12} spin coating,¹³ and electrospraying¹⁴ have been developed. In addition, diverse modifications such as Co₃O₄/BiVO₄,¹² WO₃/BiVO₄,¹⁵ and SnO₂/BiVO₄¹⁶ films have been studied to enhance the photocatalytic performance of the

semiconductors. These studies proved that BiVO₄ is a promising material in the PEC applications.

Metal-free graphitic carbon nitride (g-C₃N₄) is a good visible-light photocatalyst with nontoxic properties and good thermal and chemical stabilities,^{17–19} and it is widely used to construct heterostructured photocatalysts with other semiconductors.^{20–24} The construction of heterojunctions by coupling of different semiconductors can not only enhance the utilization of sunlight but also create sufficient built-in potentials, which is beneficial for the separation of electron–hole pairs for redox reactions.^{25–28} Modification of BiVO₄ with g-C₃N₄ has been reported, and the catalytic performance has been found to be improved compared with individual BiVO₄.^{11,29–33} However, most of these studies are based on modifying powder-form BiVO₄, and the powder-form-modified BiVO₄ was then prepared as films on conductive substrates by the immersion method when needed.¹¹ The conventional spin-coating and immersion method may lead to cracks and the

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Figure 1. Schematic illustration of the formation of g-C₃N₄/BiVO₄ films.

presence of large particles in the films.⁴ Hence, more efforts are needed to study the development of facile methods for directly modifying BiVO₄ films with g-C₃N₄ and preparing evenly nanostructured g-C₃N₄/BiVO₄ films.

The electrospinning technique offers a simple, convenient, and low-cost method to fabricate nanostructured materials.³⁴ In this work, nanostructured g-C₃N₄/BiVO₄ films on FTO substrates were fabricated via the electrospinning method. The films possess good coverage, good stability, and enhanced PEC performance. The preparation process is easy, and can directly synthesize the g-C₃N₄/BiVO₄ composite films by adding the g-C₃N₄ nanosheets into the BiVO₄ precursor. The excellent PEC performance of the g-C₃N₄/BiVO₄ films and the facile preparation method offer a reference route for the construction of g-C₃N₄/BiVO₄ composite films.

EXPERIMENTAL SECTION

Synthesis of g-C₃N₄ Nanosheets. Preparation of g-C₃N₄ nanosheets was according to a previous report.⁴ Briefly, dicyandiamide was heated in a muffle furnace at 550 °C to obtain the bulk g-C₃N₄. A certain amount of bulk g-C₃N₄ was dispersed in H₂SO₄ (98%, AR), stirred for 8 h, washed with deionized water, and then dried at 80 °C to obtain g-C₃N₄ nanosheets.

Synthesis of g-C₃N₄/BiVO₄ Films. The g-C₃N₄ nanosheets were dispersed in acetic acid, stirred, and sonicated for 1 h. Then, a certain amount of bismuth (III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, ≥98%, Sigma-Aldrich) and vanadium (III) acetylacetonate (C₁₅H₂₁O₆, 97%, Sigma-Aldrich) were mixed, and the solution was stirred for 2 h. The detailed dosages are listed in Table S1.

The precursor was electrospun with the parameters of 0.08 mm·min⁻¹ push speed in 2.5 mL plastic syringe, 7.0 cm receiving distance, and 12 kV applied voltage. The FTO glass was placed on the alumina foil collector, and the precursor film was directly coated on the FTO glass. The precursor films were calcined in a muffle furnace at a heating rate of 10 °C·min⁻¹ from room temperature to the target temperatures and maintained at this temperature for 30 min. Films with 0.075, 0.125, and 0.175 g of g-C₃N₄ in the precursor were finally obtained and were denoted as CN/BV-1, CN/BV-2, and CN/BV-3, respectively.

Characterization. A field emission scanning electron microscope (SEM, SU-8020, Hitachi, Japan) and transmission electron microscope (TEM, H7500, Hitachi, Japan) instruments were used to characterize the morphology of the films. The X'pert PRO MPD PC system with Cu Kα (λ = 0.15, 418 nm, 40 kV, 40 mA) as the X-ray source was used to get the X-ray diffraction (XRD) patterns. X-ray photoelectron spectroscopy (XPS) was recorded on a Phi Quantern instrument with reference to the C 1s peak (284.8 eV). A Mettler TGA-1 thermogravimetric analyzer was used to test the thermogravimetric and differential scanning calorimetry (TG–DSC) at 10 °C min⁻¹ to 800 °C in air. The diffuse reflectance absorption spectra (DRS) were recorded on a Maya 2000 Pro (Ocean Optics Inc) spectroscope. The photoluminescence (PL) spectra were recorded on an FLSP920 (Edinburgh, UK) spectroscope. The excitation wavelength was 330 nm.

PEC measurements of the prepared films were taken on a CHI 660B electrochemical workstation (CH Instruments, Inc.). In the conventional three-electrode system, the working electrode was a g-

C₃N₄/BiVO₄ film, the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a Pt wire. The working electrode was irradiated using a Xe lamp (BoPhila Technology Co., LTD, electric power: 300 W, luminous power: 50 W) with a 420 nm optical filter. The electrolyte was a potassium phosphate buffer solution (KH₂PO₄, 0.5 M, PH 7), and sodium sulfite (Na₂SO₃, 1 M) was added in some cases as a hole scavenger. The electrolyte was purged with N₂ before tests. Degradation of bisphenol A (BPA) was performed in the above three-electrode system by adding 10 mM H₂O₂, using the CN/BV-2 film calcined at 450 °C as photoanode; the initial BPA concentration was 5 mg/L, solution volume was 100 mL, photoanode area was 6.25 cm², and the bias potential was 0.5 V versus SCE.

RESULTS AND DISCUSSION

Fabrication and Characterization of g-C₃N₄/BiVO₄ Films. The formation of g-C₃N₄/BiVO₄ films is illustrated in Figure 1. Before preparing the g-C₃N₄/BiVO₄ electrospinning precursor, the bulk g-C₃N₄ was exfoliated to g-C₃N₄ nanosheets using strong acids. The exfoliated g-C₃N₄ nanosheets exhibit intrinsic semiconductive features and good electron mobility because of their highly opened-up flat structure and large surface area.³⁵ Hence, g-C₃N₄ nanosheets are intensively researched in surface-engineered applications, such as the construction of g-C₃N₄/inorganic semiconductor heterojunctions.³⁵ Moreover, it is reported that concentrated strong acids, such as H₂SO₄ and HNO₃, may chemically protonate g-C₃N₄ to sol process a stable g-C₃N₄ colloidal suspension.³⁶ It is easy to fabricate thin films from the stable g-C₃N₄ colloidal solution, and because of the polymer system of g-C₃N₄ colloids, g-C₃N₄ can couple with other semiconductor materials.³⁶

In the precursor, the vanadium(III) acetylacetonate mainly existed in the form of complexation molecules, bismuth nitrate pentahydrate turned into Bi³⁺ and NO₃⁻, and the g-C₃N₄ nanosheets were highly dispersed. All species were intimately mixed in the precursor. During the electrospinning process, the solvent evaporated quickly and V(C₅H₇O₂)₃, Bi³⁺, NO₃⁻, and g-C₃N₄ nanosheets were electrospayed onto the FTO glass, resulting in the formation of nanostructured precursor films (Figure S1). The FTO glass was heated to a temperature near the melting point (181–184 °C) of V(C₅H₇O₂)₃, which is good for the cohesiveness of the film. After calcinations, Bi³⁺ and V(C₅H₇O₂)₃ were reacted to form crystallized BiVO₄. The calcination temperature was chosen above the BiVO₄ crystallization temperature (392 °C) and below the g-C₃N₄ burning temperature (450 °C) according to the TG–DSC results (shown in Figure S1B). BiVO₄ was formed in the gaps of g-C₃N₄ nanosheets, which could prevent the agglomeration of BiVO₄ nanoparticles and thus are favorable for the formation of nanostructured g-C₃N₄/BiVO₄ composite films.

The SEM images of the individual BiVO₄ and g-C₃N₄/BiVO₄ films are presented in Figure 2. Both of the films are well-covered on the FTO glass and integrated (Figure 2A and Figure 2C). However, the BiVO₄ film is composed of agglomerated particles with sizes over 500 nm. In the g-C₃N₄/BiVO₄ film,

Figure 2. SEM images of the films on FTO glass: an individual BiVO_4 film (A,B) and a $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ film (C,D).

BiVO_4 particles are much smaller and distributed between the nanosheets, implying that the agglomeration of BiVO_4 is well-prevented by their nearby $\text{g-C}_3\text{N}_4$ nanosheets. TGA tests for CN/BV-1, -2, and -3 and pure BiVO_4 were performed to confirm the weight ratio of $\text{g-C}_3\text{N}_4$ in the films. As shown in Figure 3, there is no weight loss for pure BiVO_4 , whereas the

Figure 3. TG curves of the samples.

weight losses are 2.55, 3.25, and 4.05%, respectively, for CN/BV-1, -2, and -3. TAs shown in Figure 3, there is no weight loss for pure BiVO_4 , whereas there are obvious weight losses for $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films. The weight loss is due to the burning of $\text{g-C}_3\text{N}_4$; hence, the weight ratios of $\text{g-C}_3\text{N}_4$ are 2.55, 3.25, and 4.05% in the CN/BV-1, CN/BV-2, and CN/BV-3 films, respectively.

Figure 4 presents the TEM and high-resolution TEM (HRTEM) images of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ sample. The samples were scraped off the FTO glass and distributed in water to adapt for the test. In Figure 4A, the nanoparticles and the nanosheets are observed, which were inferred to be BiVO_4 and $\text{g-C}_3\text{N}_4$, respectively. The nanoparticles are well-adhered on the nanosheets. Phase distribution could be observed in the HRTEM images (Figure 4B). The clear lattice structures with spacing values of 0.340 nm correspond to the 113 lattice plane of monoclinic BiVO_4 , whereas the blurry lattices correspond to $\text{g-C}_3\text{N}_4$ because of its low crystallinity characteristics. The close contact of BiVO_4 and $\text{g-C}_3\text{N}_4$ suggests the formation of $\text{BiVO}_4/$

Figure 4. (A) TEM and (B) HRTEM images of $\text{g-C}_3\text{N}_4/\text{BiVO}_4$.

$\text{g-C}_3\text{N}_4$ heterojunctions and is beneficial for the charge carrier separation. The energy-dispersive spectrometry (EDS) analysis is presented in Figure 5. The uniformly distributed N element confirmed that the dark nanosheet is $\text{g-C}_3\text{N}_4$, and the distribution of Bi element suggests that the bright nanoparticles are BiVO_4 . The results further confirmed that the BiVO_4 nanoparticles are adhered onto the $\text{g-C}_3\text{N}_4$ nanosheet, which is in accordance with the TEM analysis.

Figure 6 presents the XRD analysis of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films with various $\text{g-C}_3\text{N}_4$ contents and calcination temperatures. As shown in Figure 6A, the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films with various $\text{g-C}_3\text{N}_4$ contents calcined at 450°C all exhibit the same diffraction patterns as those of individual BiVO_4 , which correspond to monoclinic BiVO_4 (JCPDS: 14-0688). In Figure 6B, the intensity of the diffraction patterns increases with the increasing calcination temperature; especially, for the films calcined at 400°C , the intensity of the diffraction patterns is small and the peak width is wide, indicating that a weak crystallization occurred at this temperature. For the films calcined at 450 and 500°C , the diffraction patterns become sharper, indicating the high crystallinity of the films calcined at these temperatures. The crystal sizes for all of these samples calculated according to Debye–Scherrer formula are between 15 and 40 nm (Table S2). In addition, no $\text{g-C}_3\text{N}_4$ diffraction patterns are observed because of the low content, uniform dispersion, ultrathin nature, and the typical low crystallinity characteristics of $\text{g-C}_3\text{N}_4$.¹¹

The specific chemical environments and oxidation states of the elements in the films were characterized using XPS. In Figure 7, the peaks centered at 159.1 and 164.5 eV, respectively, correspond to $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$ of Bi^{3+} and the peaks at 516.9 and 524.5 eV are, respectively, assigned to $\text{V } 2p_{3/2}$ and $\text{V } 2p_{1/2}$ of V^{5+} . Meanwhile, the characteristic peak for N-C=N in $\text{g-C}_3\text{N}_4$ is clearly observed at 288.2 eV in C 1s spectra. The N 1s spectra were deconvoluted into three typical peaks at 398.3, 399.2, and 400.7 eV, which, respectively, correspond to the N 1s core level in the C-N=C bond, the bridging N atoms bonded to three C atoms (N-[C]_3), and the N atoms in the C-N-H bonds.³⁷ These results further confirm that both BiVO_4 and $\text{g-C}_3\text{N}_4$ exist in the films.

The band gap energy (E_g) of the samples was characterized using the UV/vis DRS. As shown in Figure 8, the absorption edge and intensity of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films are almost the same as that of an individual BiVO_4 film. The band energy levels of the samples were calculated from the Tauc plot³⁸

$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

where α , h , ν , E_g , and A are the absorption coefficient, Planck's constant, light frequency, optical band gap, and a constant,

Figure 5. EDS of the g-C₃N₄/BiVO₄ films.

Figure 6. (A) XRD results of various samples calcined at 450 °C and (B) CN/BV-2 calcined at various temperatures.

Figure 7. XPS spectra of (A) Bi 4f, (B) V 2p, (C) C 1s, and (D) N 1s.

respectively, and the n value depends on the characteristics of the type of optical transition in the semiconductor.³⁸ For BiVO₄ and g-C₃N₄, $n = 1$ for an indirect semiconductor.^{39,40} The band gap energies of g-C₃N₄, BiVO₄, and CN/BV-2 films are, respectively, 2.94, 2.53, and 2.51 eV. The scarce difference on the band gap energies was due to the large band gap energy of the g-C₃N₄ nanosheets, and the results are consistent with those of previous reports.¹¹

The PL spectra were investigated to shed some light on the recombination of free-charge carriers. As shown in Figure 9, the emission peaks are, respectively, centered at 438 and 558 nm

Figure 8. (A) UV/vis diffuse reflectance spectra of various samples and (B) the corresponding Tauc plots.

Figure 9. (A) PL spectra of individual BiVO₄ and g-C₃N₄/BiVO₄ films. (B) Proposed schematic band structure and the charge separation diagram.

for g-C₃N₄ and BiVO₄, which are attributed to the band gap recombination of charge carriers.³³ The g-C₃N₄/BiVO₄ composite film exhibits a similar emission peak position with BiVO₄, which is consistent with the banding energy analyzed in the UV-DRS results (Figure 8). Meanwhile, the peak intensity of the g-C₃N₄/BiVO₄ film is much weaker than that of BiVO₄, indicating that the g-C₃N₄/BiVO₄ film possesses a more efficient charge-carrier separation and a lower direct recombination of the photogenerated electron–hole pairs.

The potentials of the conductive band (CB) and the valence band (VB) of g-C₃N₄ and BiVO₄ were calculated according to the empirical eqs reported previously (see in Supporting Information).^{41,42} As shown in Figure 9B, the CB and VB potentials are, respectively, 0.27 and 2.80 eV for BiVO₄ and are, respectively, −1.24 and 1.70 eV for g-C₃N₄; these values are almost the same as those of previous reports.^{29,38,43} The staggered energy band could build up internal electric fields at the interface between g-C₃N₄ and BiVO₄, and thus, there is diffusion of photogenerated electrons and holes between the two catalysts,^{26,44} especially the photogenerated electrons on CB transfer from g-C₃N₄ to BiVO₄ and the holes on VB transfer from BiVO₄ to g-C₃N₄. Hence, the recombination of electron–hole pairs is reduced for the g-C₃N₄/BiVO₄

heterojunction photocatalyst. Moreover, the smaller size of the nanostructured g-C₃N₄/BiVO₄ could also facilitate the electron–hole separation because of the shorter charge transport distance.⁴⁵ Therefore, there are more charge carriers under visible-light irradiation for g-C₃N₄/BiVO₄ films than for BiVO₄ films, which will lead to an enhancement in the PEC performance for the g-C₃N₄/BiVO₄ films.

PEC Performance of the g-C₃N₄/BiVO₄ Films. The PEC properties of the films were evaluated using the linear sweep current–voltage (LSV) method under alternating on and off conditions for vis-light illumination, which is widely used to investigate the photocurrent response ability.⁴⁶ As shown in Figure 10, both potentials versus reversible hydrogen electrode

Figure 10. Current–voltage (I – V) curves under chopped visible light in 0.5 M phosphate buffer (pH 7) with (A) and without (B) Na₂SO₃. The inset in A is a magnification of the g-C₃N₄ current–voltage curve.

(RHE) and potentials versus SCE are shown in the current–voltage (I – V) curves according to the relationship $E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \times \text{pH} + 0.2438$, where E_{RHE} is the potential versus RHE, E_{SCE} is the potential versus SCE, and pH is the pH value of the Na₂SO₄ electrolyte solution.⁴⁷ For comparison, the g-C₃N₄ film was prepared by the doctor-blading method using the g-C₃N₄ nanosheets. As shown in Figure 10A, the photocurrents of the g-C₃N₄, BiVO₄, and g-C₃N₄/BiVO₄ films all promptly increase when the light is on and drops when the light is off over a wide potential range, implying that the photocurrent is generated under irradiation. The current of the g-C₃N₄/BiVO₄ film is anodic in the present potential range, indicating that the g-C₃N₄/BiVO₄ film is an n-type semiconductor.⁴⁸ The (photo)current is very small (on the microamps level) for the g-C₃N₄ film because of its weak electron transfer ability, which is consistent with the previously reports.^{19,33} Notably, compared with g-C₃N₄ and BiVO₄ films, the photocurrents are much higher in the whole potential range for the g-C₃N₄/BiVO₄ film. For example, at 0.56 V, the photocurrents are 0.00015, 0.03, and 0.44 mA/cm² for the g-C₃N₄, BiVO₄, and g-C₃N₄/BiVO₄ films, respectively. The photocurrents of the g-C₃N₄/BiVO₄ film are over 10 times higher than that for a BiVO₄ film. The onset photocurrent potentials were -0.35 and -0.45 V for BiVO₄ and g-C₃N₄/BiVO₄ films, respectively (Figure S2). The slightly negative shift for g-C₃N₄/BiVO₄ may be caused by the compact contact of g-C₃N₄ with BiVO₄, which is favorable for the fast transfer of the photogenerated holes from BiVO₄ to the reaction interface.¹¹ Figure 10B presents the LSV curves of the g-C₃N₄/BiVO₄ films with various electrospinning times in the electrolyte without the Na₂SO₃ hole scavenger. The rapid responses with light on and off were observed, and the overall photocurrent responses are almost the same as that tested in

the electrolyte containing Na₂SO₃ (Figure 10A). The photocurrent densities varied with the electrospinning time, indicating that the preparation conditions are important for the PEC performance of the g-C₃N₄/BiVO₄ films.

The effect of the preparation conditions on the photocurrent responses of the g-C₃N₄/BiVO₄ composite films was further investigated by the photocurrent responses versus time (i – t curves) under chopped visible-light irradiation, which is commonly used to evaluate the separation and migration efficiency of photogenerated carriers.⁴⁹ As shown in Figure 11A, the photocurrent density of CN/BV-2 was 0.36 mA/cm²,

Figure 11. Periodic on/off photocurrent responses: (A) films with various g-C₃N₄ contents, (B) various collector temperatures, (C) various calcination temperatures, and (D) various spinning times. All measurements were performed at 0.5 V bias potential under visible-light irradiation ($\lambda > 420$ nm) in 0.5 M phosphate buffer (pH 7) containing 1 M Na₂SO₃.

higher than that of CN/BV-1 (0.34 mA/cm²) and CN/BV-3 (0.28 mA/cm²), indicating that the optimal g-C₃N₄ proportion in the electrospinning precursor was 3.9 wt %. The hypocontent of g-C₃N₄ in the precursor may not form enough heterojunctions, whereas the excessive g-C₃N₄ amount could affect the light absorption and photoresponse ability because the activity of g-C₃N₄ is weaker than that of BiVO₄.^{50,51} Figure 11B presents the effect of collector temperature on the photocurrent responses of the CN/BV-2 films. The photocurrent densities were 0.29, 0.36, and 0.25 mA/cm² for the collector temperature of 130, 185, and 220 °C, respectively. The 185 °C collector temperature is just above the melting point of vanadium acetylacetonate (181 °C); hence, some vanadium acetylacetonate was melted on the FTO glass during electrospinning, which improved the cohesiveness of the films. The 130 °C collector temperature is too low to ensure the cohesiveness, whereas there may be deterioration of the precursor at 220 °C. Therefore, the film prepared at 185 °C collector temperature exhibits optimal photocurrent responses.

The effect of calcination temperature on the photocurrent responses of the films is presented in Figure 11C. The photocurrent densities were 0.09, 0.36, and 0.22 mA/cm², respectively, for the films calcined at 400, 450, and 500 °C. According to the TG–DSC curves (Figure S1B) and XRD

results (Figure 6) as analyzed previously, the crystallinity of BiVO_4 is not very good because of the low calcination temperature at 400°C , whereas the $\text{g-C}_3\text{N}_4$ will be burned off at a high temperature of 500°C . Thus, the optimal calcination temperature was 450°C . In addition, the electrospinning time also affects the photocurrent response of the films because the thickness is related to the photocurrent responses of the films and the thickness increases with the increase in electrospinning time.⁴ As shown in Figure 11D, the photocurrent densities were 0.36, 0.26, 0.25, and 0.14 mA/cm^2 , respectively, for the films with the electrospinning time of 40, 60, 20, and 10 min. An overly thick film leads to a poor migration of photogenerated electrons to the external circuit, whereas an overly thin film contains too little catalysts to generate enough photoelectrons. In this experiment, the optimal thickness of the film is with an electrospinning time of 40 min. The above results ensure the optimal conditions to prepare the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ hybrid films with a high photocurrent generation efficiency, providing a certain foundation on its PEC applications.

The interfacial charge transfer processes were investigated using electrochemical impedance spectroscopy (EIS). In EIS spectra, the high-frequency arc is assigned to the charge-transfer limiting process, and the electrodes with better charge-transfer abilities exhibit a smaller semicircle radius. As presented in Figure 12A, the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films all exhibit a smaller

Figure 12. (A) Electrochemical impedance spectra and (B) MS plots of various films.

semicircle radius than the individual BiVO_4 films, indicating that the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films possess a more efficient electron–hole separation and a faster interfacial charge transfer than that of individual BiVO_4 films. The results are in accordance with the higher PEC activity of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films. From the Mott–Schottky (MS) plots (Figure 12B), it is observed that the slopes of the linear region for both $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ and BiVO_4 films are positive, indicating that the films are n-type semiconductors.⁵² Moreover, the slope of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ film is smaller than that of the BiVO_4 film, suggesting that the photogenerated electron–hole separation of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ film is faster.

The stability of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ film was investigated by sustained $i-t$ testing for 4000 s. As shown in Figure 13A, the photocurrent density has no significant change until 4000 s and remained at the value of 0.35 mA/cm^2 . The inset in Figure 13 indicates that the film after testing was still with good coverage, further demonstrating the good stability of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ film. The above results suggest that the electrospun $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films are good candidates as photoanodes in PEC-related applications.

Herein, the degradation performance of BPA, which is a typical endocrine disrupter, was evaluated in the presence of 10

Figure 13. (A) Time-dependence photocurrent density and (B) degradation of BPA with 10 mM H_2O_2 using the CN/BV-2 film under vis-light (initial BPA concentration: 5 mg/L; solution volume: 100 mL; photoanode area: 6.25 cm^2 ; and bias potential: 0.5 V vs SCE).

mM H_2O_2 under visible-light irradiation. As shown in Figure 13B, the removal percentages of BPA were 32, 38, and 93%, respectively, by the $\text{g-C}_3\text{N}_4$, BiVO_4 , and $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ photoanodes. Obviously, the PEC degradation performance of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ composite films is significantly enhanced, and the enhancement is consistent with the photocurrent results as previously analyzed (Figure 10). These results further demonstrate that the electrospun $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ composite films possess good potentials in many PEC-related areas.

CONCLUSIONS

In summary, the nanostructured $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films with high PEC performances were successfully fabricated via the facile electrospinning method. The $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films are with good coverage and composed of nanoparticles. The contact between $\text{g-C}_3\text{N}_4$ and BiVO_4 is compact, indicating that $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ heterojunctions are formed, which is favorable for the transfer of the photogenerated carriers. The PEC activity of the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films is much more enhanced compared with those of individual BiVO_4 films. The preparation process is facile and easy to scale up. The good PEC performance and the facile preparation method suggest that the $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ films are good candidates for PEC applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b00893.

Figures showing the SEM image and TG-DSC curves of the precursor films as well as magnified current–voltage curves of the samples under chopped visible light in 0.5 M phosphate buffer (pH 7) with and without Na_2SO_3 ; tables showing detailed dosages for the preparation of $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ sol and the crystal sizes of various samples; and the previously reported empirical equations to calculate the potentials of the conductive and valance bands of $\text{g-C}_3\text{N}_4$ and BiVO_4 (PDF)

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Notes

The authors declare no competing financial interest.

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