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

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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 electrospaying14 have been developed. In addition, diverse modifications such as Co₃O₄/BiVO₄,12 WO₃/BiVO₄,15 and SnO₂/BiVO₄ 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 stabilities17–19 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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Supporting Information

4694
presence of large particles in the films.\textsuperscript{4} Hence, more efforts are needed to study the development of facile methods for directly modifying BiVO\textsubscript{4} films with g-C\textsubscript{3}N\textsubscript{4} and preparing evenly nanostructured g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} films.

The electrospinning technique offers a simple, convenient, and low-cost method to fabricate nanostructured materials.\textsuperscript{34} In this work, nanostructured g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} 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-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} composite films by adding the g-C\textsubscript{3}N\textsubscript{4} nanosheets into the BiVO\textsubscript{4} precursor. The excellent PEC performance of the g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} films and the facile preparation method offer a reference route for the construction of g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} composite films.

\section{EXPERIMENTAL SECTION}

\textbf{Synthesis of g-C\textsubscript{3}N\textsubscript{4} Nanosheets.} Preparation of g-C\textsubscript{3}N\textsubscript{4} nanosheets was according to a previous report.\textsuperscript{4} Briefly, dicyandiamide was heated in a muffle furnace at 550 °C to obtain the bulk g-C\textsubscript{3}N\textsubscript{4}. A certain amount of bulk g-C\textsubscript{3}N\textsubscript{4} was dispersed in H\textsubscript{2}SO\textsubscript{4} (98%, AR), stirred, and sonicated for 1 h. Then, a certain amount of bismuth (III) nitrate pentahydrate (BiN\textsubscript{3}O\textsubscript{9}·5H\textsubscript{2}O, ≥98%, Sigma-Aldrich) and vanadium (III) acetylacetonate (C\textsubscript{5}H\textsubscript{7}O\textsubscript{2}V, 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−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\textsuperscript{-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-C\textsubscript{3}N\textsubscript{4} in the precursor were finally obtained and were denoted as CN/BV-1, CN/BV-2, and CN/BV-3, respectively.

\textbf{Characterization.} A field emission scanning electron microscope (SEM, SU-8020, Hitachi, Japan) and transmission electron microscope (TEM, H-7500, Hitachi, Japan) instruments were used to characterize the morphology of the films. The X’pert PRO MPD PC system with Cu Ka (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 Quanterm 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\textsuperscript{-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 FLS920 (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-

\section{RESULTS AND DISCUSSION}

\textbf{Fabrication and Characterization of g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} Films.} The formation of g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} films is illustrated in Figure 1. Before preparing the g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} electrospinning precursor, the bulk g-C\textsubscript{3}N\textsubscript{4} was exfoliated to g-C\textsubscript{3}N\textsubscript{4} nanosheets using strong acids. The exfoliated g-C\textsubscript{3}N\textsubscript{4} nanosheets exhibit intrinsic semiconductor features and good electron mobility because of their highly opened-up flat structure and large surface area.\textsuperscript{35} Hence, g-C\textsubscript{3}N\textsubscript{4} nanosheets are intensively researched in surface-engineered applications, such as the construction of g-C\textsubscript{3}N\textsubscript{4}/inorganic semiconductor heterojunctions.\textsuperscript{35} Moreover, it is reported that concentrated strong acids, such as H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3}, may chemically protonate g-C\textsubscript{3}N\textsubscript{4} to sol process a stable g-C\textsubscript{3}N\textsubscript{4} colloidal suspension.\textsuperscript{36} It is easy to fabricate thin films from the stable g-C\textsubscript{3}N\textsubscript{4} colloidal solution, and because of the polymer system of g-C\textsubscript{3}N\textsubscript{4} colloids, g-C\textsubscript{3}N\textsubscript{4} can couple with other semiconductor materials.\textsuperscript{36}

In the precursor, the vanadium(III) acetylacetonate mainly existed in the form of complexion molecules, bismuth nitrate pentahydrate turned into Bi\textsuperscript{3+} and NO\textsubscript{3}−, and the g-C\textsubscript{3}N\textsubscript{4} nanosheets were highly dispersed. All species were intimately mixed in the precursor. During the electrospinning process, the solvent evaporated quickly and V(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{3}, Bi\textsuperscript{3+}, NO\textsubscript{3}−, and g-C\textsubscript{3}N\textsubscript{4} 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(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{3}, which is good for the cohesiveness of the film. After calcinations, Bi\textsuperscript{3+} and V(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{3} were reacted to form crystallized BiVO\textsubscript{4}. The calcination temperature was chosen above the BiVO\textsubscript{4} crystallization temperature (392 °C) and below the g-C\textsubscript{3}N\textsubscript{4} burning temperature (450 °C) according to the TG–DSC results (shown in Figure S1B). BiVO\textsubscript{4} was formed in the gaps of g-C\textsubscript{3}N\textsubscript{4} nanosheets, which could prevent the agglomeration of BiVO\textsubscript{4} nanoparticles and thus are favorable for the formation of nanostructured g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} composite films.

The SEM images of the individual BiVO\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} 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 BiVO\textsubscript{4} film is composed of agglomerated particles with sizes over 500 nm. In the g-C\textsubscript{3}N\textsubscript{4}/BiVO\textsubscript{4} film,
BiVO₄ particles are much smaller and distributed between the nanosheets, implying that the agglomeration of BiVO₄ is well-prevented by their nearby g-C₃N₄ nanosheets. TGA tests for CN/BV-1, -2, and -3 and pure BiVO₄ were performed to prevent the weight loss for pure BiVO₄, whereas there are obvious weight losses for g-C₃N₄; hence, the weight ratios of g-C₃N₄ are 2.55, 3.25, and 4.05% in the CN/BV-1, CN/BV-2, and CN/BV-3 films, respectively.

Figure 3. TG curves of the samples.

Figure 4 presents the TEM and high-resolution TEM (HRTEM) images of the g-C₃N₄/BiVO₄ sample. The samples were characterized using XPS. In Figure 7, the peaks centered at 159.1 and 164.5 eV, respectively, correspond to Bi 4f½/2 and Bi 4f½ of Bi⁵⁺. Meanwhile, the characteristic peak for N=C=N in g-C₃N₄ is clearly observed at 288.2 eV in C 1s spectra. The N 1s spectra were deconvoluted into three typical chemical environments and oxidation states of N atoms in g-C₃N₄.11 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 Bi 4f½/2 and Bi 4f½ of Bi⁵⁺ and the peaks at 516.9 and 524.5 eV are, respectively, assigned to V 2p½ and V 2p½ of V⁵⁺. Meanwhile, the characteristic peak for N=C=N in g-C₃N₄ 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.12 These results further confirm that both BiVO₄ and g-C₃N₄ exist in the films.

The band gap energy (E GAP) of the samples was characterized using the UV/vis DRS. As shown in Figure 8, the absorption edge and intensity of the g-C₃N₄/BiVO₄ films are almost the same as that of an individual BiVO₄ film. The band energy levels of the samples were calculated from the Tauc plot18

\[
\alpha h\nu = A(h\nu - E_G)^{n/2}
\]

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

Figure 2. SEM images of the films on FTO glass: an individual BiVO₄ film (A,B) and a g-C₃N₄/BiVO₄ film (C,D).

Figure 4. (A) TEM and (B) HRTEM images of g-C₃N₄/BiVO₄.
respectively, and the \( n \) value depends on the characteristics of the type of optical transition in the semiconductor.\(^{38}\) For BiVO\(_4\) and g-C\(_3\)N\(_4\), \( n = 1 \) for an indirect semiconductor.\(^{39,40}\) The band gap energies of g-C\(_3\)N\(_4\), BiVO\(_4\), 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-C\(_3\)N\(_4\) 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 for g-C\(_3\)N\(_4\) and BiVO\(_4\) which are attributed to the band gap recombination of charge carries.\(^{33}\) The g-C\(_3\)N\(_4\)/BiVO\(_4\) composite film exhibits a similar emission peak position with BiVO\(_4\), which is consistent with the banding energy analyzed in the UV-DRS results (Figure 8). Meanwhile, the peak intensity of the g-C\(_3\)N\(_4\)/BiVO\(_4\) film is much weaker than that of BiVO\(_4\), indicating that the g-C\(_3\)N\(_4\)/BiVO\(_4\) 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 valance band (VB) of g-C\(_3\)N\(_4\) and BiVO\(_4\) 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 BiVO\(_4\) and are, respectively, −1.24 and 1.70 eV for g-C\(_3\)N\(_4\); 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-C\(_3\)N\(_4\) and BiVO\(_4\) and thus, there is diffusion of photogenerated electrons and holes between the two catalysts,\(^{45,44}\) especially the photogenerated electrons on CB transfer from g-C\(_3\)N\(_4\) to BiVO\(_4\) and the holes on VB transfer from BiVO\(_4\) to g-C\(_3\)N\(_4\). Hence, the recombination of electron–hole pairs is reduced for the g-C\(_3\)N\(_4\)/BiVO\(_4\) composite.
heterostructured g-C3N4/BiVO4 could also facilitate the electron–hole separation because of the shorter charge transport distance. 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. As shown in Figure 10, both potentials versus reversible hydrogen electrode (RHE) and potentials versus SCE are shown in the current–voltage (I–V) curves according to the relationship $E_{RHE} = E_{SCE} + 0.0591 \times pH + 0.2438$, 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. 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 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. 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 reported results. Notably, compared with g-C3N4 and BiVO4 films, the photocurrents are much higher in the whole potential range over a wide potential range, implying that the PEC performance of the g-C3N4/BiVO4 films.

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.

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 ($> 420$ nm) in 0.5 M phosphate buffer (pH 7) containing 1 M Na2SO3.

The PEC performance 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. As shown in Figure 11A, the photocurrent density of CN/BV-2 was 0.36 mA/cm², 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 electrosprinning 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 photoreaction ability because the activity of g-C3N4 is weaker than that of BiVO4. The photoresponse of the CN/BV-3 film prepared at 185 °C is just above the melting point of vanadium acetylacetonate (181 °C); hence, some vanadium acetylacetonate was melted on the FTO glass during electrosprinning, which improved the cohesiveness of the films. The 130 °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 electrosprinning, which improved the cohesiveness of the films. The 130 °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 electrosprinning, which improved the cohesiveness of the films. The 130 °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 electrosprinning, which improved the cohesiveness of the films. The 130 °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 electrosprinning, which improved the cohesiveness of the films.

The effect of collector temperature on the photocurrent responses of CN/BV-2 films. 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.

| Collector Temperature | Photocurrent Density (mA/cm²) |
|-----------------------|-------------------------------|
| 130 °C                | 0.36                          |
| 185 °C                | 0.34                          |
| 220 °C                | 0.28                          |

The onset photocurrent densities varied with the electrospinning time, indicating that the preparation conditions are important for the PEC performance of the g-C3N4/BiVO4 films.
thickness is related to the photocurrent responses of the time. As shown in Figure 11D, the photocurrent densities were and the thickness increases with the increase in electrospinning 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. As shown in Figure 11D, the photocurrent densities were 0.36, 0.26, 0.25, and 0.14 mA/cm², respectively, for the films with the electrospinning time of 40, 60, 20, and 10 min. A overly thick film leads to a poor migration of photogenerated electrons to the external circuit, whereas a 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 g-C3N4/BiVO4 hybrid films with a high photocurrent generation efficiency, providing a certain foundations 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 g-C3N4/BiVO4 films all exhibit a smaller semicircle radius than the individual BiVO4 films, indicating that the g-C3N4/BiVO4 films possess a more efficient electron–hole separation and a faster interfacial charge transfer than that of individual BiVO4 films. The results are in accordance with the higher PEC activity of the g-C3N4/BiVO4 films. From the Mott–Schottky (MS) plots (Figure 12B), it is observed that the slopes of the linear region for both g-C3N4/BiVO4 and BiVO4 films are positive, indicating that the films are n-type semiconductors. Moreover, the slope of the g-C3N4/BiVO4 film is smaller than that of the BiVO4 film, suggesting that the photogenerated electron–hole separation of the g-C3N4/BiVO4 film is faster.

The stability of the g-C3N4/BiVO4 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/cm². The inset in Figure 13 indicates that the film after testing was still with good coverage, further demonstrating the good stability of the g-C3N4/BiVO4 film. The above results suggest that the electrospun g-C3N4/BiVO4 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 mM H2O2 under visible-light irradiation. As shown in Figure 13B, the removal percentages of BPA were 32, 38, and 93%, respectively, by the g-C3N4, BiVO4, and g-C3N4/BiVO4 photoanodes. Obviously, the PEC degradation performance of the g-C3N4/BiVO4 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 g-C3N4/BiVO4 composite films possess good potentials in many PEC-related areas.

### CONCLUSIONS

In summary, the nanostructured g-C3N4/BiVO4 films with high PEC performances were successfully fabricated via the facile electrospinning method. The g-C3N4/BiVO4 films are with good coverage and composed of nanoparticles. The contact between g-C3N4 and BiVO4 is compact, indicating that g-C3N4/BiVO4 heterojunctions are formed, which is favorable for the transfer of the photogenerated carriers. The PEC activity of the g-C3N4/BiVO4 films is much more enhanced compared with those of individual BiVO4 films. The preparation process is facile and easy to scale up. The good PEC performance and the facile preparation method suggest that the g-C3N4/BiVO4 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 Na2SO3; tables showing detailed dosages for the preparation of g-C3N4/BiVO4 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 g-C3N4 and BiVO4 (PDF)

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**Notes**

The authors declare no competing financial interest.
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