■ Synthesis Design

Facile Electrospinning Synthesis of Carbonized Polyvinylpyrrolidone (PVP)/g-C₃N₄ Hybrid Films for Photoelectrochemical ApplicationsYan Wang,^[a] Xu Zhao,^{*[a]} Yang Tian,^[b] Yanbin Wang,^[a] Abdul Khaliq Jan,^[a] and Yutong Chen^[a]

Abstract: The film-forming ability and conductivity of graphitic carbon nitride (g-C₃N₄) are still unsatisfying, despite much progress having been made in g-C₃N₄-related photocatalysts. New methods for synthesizing g-C₃N₄ films coupled with excellent conductive materials are of significance. Herein, a facile method for synthesizing novel carbonized polyvinylpyrrolidone (PVP)/g-C₃N₄ (C_{PVP}/g-C₃N₄) films have been developed through an electrospinning technique. Nanocarbons are generated by in situ carbonization of PVP in the films, which could enhance the photoelectrochemical (PEC) performance of the films due to its good conductivity. The coverage of the C_{PVP}/g-C₃N₄ film is good and the films

exhibit excellent PEC performance. Furthermore, the thickness of the films can be adjusted by varying the electrospinning time and substantially controlling the PEC performance, of which the photocurrent densities under visible-light irradiation are 3.55, 4.92, and 6.64 $\mu\text{A cm}^{-2}$ with spinning times of 40, 70, and 120 min, respectively. The photocurrent does not decrease until testing at 4000 s and the coverage is still good after the tests, which indicates the good stability of the films. The excellent PEC performance of the films and facile preparation method enables promising applications in energy and environmental remediation areas.

Introduction

Recently, graphitic carbon nitride (g-C₃N₄) has been widely studied due to its unique electronic features and good stability as a metal-free visible-light catalyst.^[1–3] The application of g-C₃N₄ has expanded from traditional areas to many newly disclosed areas, such as bioimaging, sensing, and novel solar energy exploitations.^[4] g-C₃N₄ can also be applied to modify fluorine-doped tin oxide (FTO) electrodes, which can be used for electro-regeneration of reduced nicotinamide adenine dinucleotide phosphate (NADH).^[5] Bulk g-C₃N₄ is generally synthesized by thermal condensation of carbon- and nitrogen-rich monomers, such as melamine, dicyanamide, and cyanamide,^[6] and a variety of approaches, including copolymerization,^[7] metal doping, nonmetal doping,^[8–10] and the formation of composites and heterojunctions,^[11,12] have been used to enhance its photocatalytic activity. Nevertheless, most of these studies are based on the powder form, which is usually suspended in water and requires extensive separation procedures. Moreover, the continuous g-C₃N₄ film is preferred for many ap-

plications, such as water electrosplitting, fuel cells, and solar cells.

The photoelectrochemistry of g-C₃N₄ has been widely studied since it was reported by Zhang et al.^[13,14] g-C₃N₄ could be reversibly protonated by strong mineral acids and g-C₃N₄ could be formed directly on films by sintering protonated powders, of which the photoconductivity was measured.^[13] Moreover, the photocurrent could reach 150 $\mu\text{A cm}^{-2}$ under visible-light irradiation by using a standard photoelectrochemical (PEC) cell configuration;^[14] this demonstrates the good photocurrent generation ability and promising PEC application potential of g-C₃N₄.

The PEC responses of g-C₃N₄ films are closely related to their coverage and adhesion status on commonly conductive substrates (such as indium tin oxide (ITO) or FTO glass).^[15] However, common deposition methods (spin coating or screen printing) usually result in g-C₃N₄ films with unsatisfactory coverage and adhesion due to the large particle sizes of g-C₃N₄, along with its insolubility in most solvents. The protonation of g-C₃N₄ by strong mineral acids could modify its solubility/dispersability.^[13] Recently, a stable colloidal suspension of chemically protonated g-C₃N₄ was obtained by using strong oxidizing acids (such as HNO₃), and the sol could be used to prepare thin films with enhanced PEC performance through dip-/disperse-coating techniques.^[16] In addition, a liquid-mediated pathway by using supramolecular complexes to grow g-C₃N₄ thin films has been reported,^[15] and microcontact printing-assisted access of favorable textured g-C₃N₄ films was also reported recently.^[17] The PEC performances of these films are improved relative to that of conventional deposition methods. However,

[a] Dr. Y. Wang, Prof. X. Zhao, Dr. Y. Wang, Dr. A. K. Jan, Y. Chen
Key Laboratory of Drinking Water Science and Technology
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences, Beijing 100085 (P.R. China)
E-mail: zhaoxu@rcees.ac.cn

[b] Dr. Y. Tian
Department of Chemistry, Capital Normal University
Haidian District, Beijing 100048 (P.R. China)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201604468>.

the synthetic methods are still very limited and the conductivity of individual g-C₃N₄ samples is unsatisfying, which consequently restricts PEC applications. Hence, the modification of g-C₃N₄ film is worth studying. In view of such conditions, alternative pathways for modified g-C₃N₄ film preparation are desirable.

Herein, we report a simple, convenient, and easily scalable way to fabricate carbonized polyvinylpyrrolidone (PVP)/g-C₃N₄ (C_{PVP}/g-C₃N₄) hybrid films on ITO substrates with good PEC performance through an electrospinning method. Electrospinning is a simple, versatile, and easy to scale technique to fabricate nanofibers, membranes, and films.^[18–20] PVP possesses good film-forming and adhesion properties,^[21] and it can be easily decomposed at temperatures lower than 500 °C in a nitrogen atmosphere.^[22] Furthermore, during calcination, PVP could be transformed in situ into carbon, which is a significant material for g-C₃N₄ modification due to the excellent mobility of charge carriers and environmentally friendly characteristics.^[23,24] Bulk g-C₃N₄ was delaminated to form nanosheets and carbon, which possesses a good electron-transfer ability, was filled between the g-C₃N₄ nanosheets through in situ carbonization of PVP, finally forming C_{PVP}/g-C₃N₄ films. Coverage of the as-prepared films is good and the films exhibit excellent PEC performance and good stability; this suggests that it is a good candidate for PEC applications.

Results and Discussion

Fabrication and characterization of C_{PVP}/g-C₃N₄ films

The scheme for the synthesis of C_{PVP}/g-C₃N₄ films is as follows (Figure 1): delaminated g-C₃N₄ nanosheets (Figure S1 in the Supporting Information) and PVP were used to prepare the electrospinning precursor. The proportion of g-C₃N₄ to the total weight of g-C₃N₄ and PVP was investigated by varying it over a spinnable range, namely, 20, 43, 60, and 75 wt% (see detailed dosage in Table S1 in the Supporting Information), and the corresponding films were denoted as PVP/g-C₃N₄-20, PVP/g-C₃N₄-43, PVP/g-C₃N₄-60, and PVP/g-C₃N₄-75, respectively.

Figure 1. Schematic illustration of the formation of the C_{PVP}/g-C₃N₄ film.

During the electrospinning process, PVP nanofibers were generated and most of the solvent was evaporated before being dropped onto the substrate to prevent cracks appearing in the in the films during drying. The ITO glass collector was heated to enhance the cohesiveness of PVP. The temperature of the collector was investigated from 140 to 220 °C, which was chosen according to the melting point of PVP (165 °C), along with the thermogravimetric analysis/differential thermal analysis (TGA-DTA) curves of PVP/g-C₃N₄-60 sol in air (Figure S2 in the Supporting Information; demonstrating that the decomposition of PVP and g-C₃N₄ occurred above 200 °C). The films are homogenous and completely cover the substrate. After calcination, the color of the film changes from white to black as a result of the carbonization of PVP (Figure S3 in the Supporting Information). Compared with the conventional spin-coating method, which also works for film preparation by using the same PVP/g-C₃N₄ sol, the electrospinning method could generate nanostructured PVP nanofibers, fabricate films with fewer drying cracks, and accurately control the thickness of the films (Figures S4, S5, and S7 in the Supporting Information and see the detailed comparison in the Supporting Information).

Thermogravimetry/differential scanning calorimetry (TG-DSC) curves (Figure S6A in the Supporting Information) of PVP/g-C₃N₄ films were analyzed to determine the calcination temperatures. The exothermic peak in the region from 314 to 486 °C was assigned to the decomposition of PVP and a mass loss of 50% was observed in the TG curve. The decomposition peak of PVP in the TG-DSC curves of PVP/g-C₃N₄-60 is consistent with that of individual PVP components (Figure S6B in the Supporting Information); the exothermic peak of PVP decomposition is observed from 338 to 485 °C, and 92.73 % mass loss occurred from RT to 485 °C. These results confirmed that PVP decomposed in the final film. Meanwhile, the exothermic peak from 500 to 800 °C was due to the decomposition of g-C₃N₄, accompanied by a further mass loss of 42.67%. Therefore, 500 °C was chosen as the calcination temperature to ensure the carbonization of PVP and stability of g-C₃N₄ simultaneously. After calcination, the C_{PVP}/g-C₃N₄ films were obtained.

The morphology of the C_{PVP}/g-C₃N₄ film was investigated by SEM. As shown in Figure 2, the morphology varies upon changing the proportions of g-C₃N₄. For C_{PVP}/g-C₃N₄-20, -43, and -60, the films are integrated without any defects and the g-C₃N₄ nanosheets are in good contact with each other. The pores in the films become bigger with increasing g-C₃N₄ content. From the higher magnification SEM images, it can be seen that the C_{PVP}/g-C₃N₄-20 film is mainly composed of a fibrous-like structure. It was inferred that g-C₃N₄ nanosheets could disperse in PVP fibers during the electrospinning process due to the high PVP concentration. However, when the g-C₃N₄ content increased to 43 wt%, the fibrous morphology became unapparent. The diameters of PVP fibers become smaller and the g-C₃N₄ nanosheets become dominant when the PVP concentration decreases. It is more evident for the C_{PVP}/g-C₃N₄-60 film, which is almost entirely composed of interconnected and well-contacted g-C₃N₄ nanosheets. However, for the C_{PVP}/g-C₃N₄-75 film, the coverage is not complete. It was inferred that the cohesiveness of the film was poor due to the low content

Figure 2. Top-view SEM images of the films on ITO glass: $C_{PVP}/g-C_3N_4$ -20 (a, e), $C_{PVP}/g-C_3N_4$ -43 (b, f), $C_{PVP}/g-C_3N_4$ -60 (c, g), and $C_{PVP}/g-C_3N_4$ -75 (d, h).

of PVP. In addition, the thicknesses of the films, which are 8.0, 16.4, and 21.7 μm , can be easily controlled by adjusting the electrospinning times: 40, 70, and 120 min, respectively (Figure S7 in the Supporting Information). The side-view images further demonstrate the good cohesiveness of the films on the substrate.

The elemental composition of the final $C_{PVP}/g-C_3N_4$ -60 film was tested by means of energy-dispersive X-ray spectroscopy (EDS; Figure S8 and Table S2 in the Supporting Information). The $C_{PVP}/g-C_3N_4$ -60 film was mainly composed of carbon and nitrogen, possibly along with oxygen. The concentrations detected were 40.13, 52.32, and 7.55 wt% for carbon, nitrogen, and oxygen, respectively. The weight ratio (0.77) of carbon to nitrogen is higher than that of $g-C_3N_4$ (0.64), which was caused by carbon derived from the carbonization of PVP in the films. Oxygen in the films may be derived from the incomplete carbonization of PVP, along with oxygen from ITO glass; indium and silicon from the glass were also detected (Figure S8 in the Supporting Information). Gold in the films was derived from the gold spraying pretreatment; this is a common method to enhance conductivity and obtain a clearer SEM image.

The FTIR spectra of $PVP/g-C_3N_4$ and $C_{PVP}/g-C_3N_4$ were similar to that of raw $g-C_3N_4$ nanosheets (Figure 3A), in which all of the bands were assigned to the typical $g-C_3N_4$ structure. Specifically, bands at $\tilde{\nu} = 1200\text{--}1600\text{ cm}^{-1}$ are assigned to skeletal vibrations for aromatic C–N heterocycles and the band at $\tilde{\nu} = 810\text{ cm}^{-1}$ is ascribed to the breathing vibration for tri-*s*-triazine subunits;^[25] this confirms that the structure of $g-C_3N_4$ is well retained during electrospinning and calcination process.

The crystal structures of $C_{PVP}/g-C_3N_4$ with various $g-C_3N_4$ contents were characterized by XRD (Figure 3B), which was performed by scratching numerous films from ITO glass to collect enough samples. For individual carbonized PVP (C_{PVP}), a peak at 25.8° is observed, which indicates the formation of carbon.^[26] Theoretically, $g-C_3N_4$ has two typical diffraction peaks at about 13.1 and 27.4° , corresponding to the characteristic (100) peak for the in-plane structural packing motif and the (002) peak for the layered stacking of aromatic segments structure.^[27] For $C_{PVP}/g-C_3N_4$ -20, the peak at 27.4° is weak and broad due to the low $g-C_3N_4$ content in the sample. For $C_{PVP}/g-$

Figure 3. A) FTIR spectra of a) raw $g-C_3N_4$, b) $PVP/g-C_3N_4$ -60, and c) $C_{PVP}/g-C_3N_4$ -60. B) XRD results.

C_3N_4 -43, -60, and -75 samples, the peaks at 27.4° are clearly observed; this indicates that the layered stacking of aromatic segments structure for $g-C_3N_4$ is well retained in the films. Meanwhile, minor diffraction peaks at 13.1° are also observed for the aforementioned three samples, which further demonstrates that the $g-C_3N_4$ phase was maintained well in the films.

In the Raman spectra of C_{PVP} and $C_{PVP}/g-C_3N_4$ samples (Figure 4A), two dominating bands appeared at 1340 and 1599 cm^{-1} , which demonstrated the existence of carbon after calcination. Specifically, the G band is related to the lattice phonon of sp^2 -carbon atoms, whereas the D band is assigned to defects and the disorder-activated edge phonon.^[28] The appearance of the G band suggests that some graphite exists in the film, which is beneficial for its conductivity. In contrast, the D and G bands did not appear in the spectra of raw $g-C_3N_4$ materials and $PVP/g-C_3N_4$ samples, which indicated that carbon was derived from the carbonization of PVP. High-resolution (HR) TEM images (Figure S9b in the Supporting Information) of $C_{PVP}/g-C_3N_4$ show a partially layered structure with a typical graphite distance of 0.342 nm, which further demonstrates that some graphite exists in the film. In the selected-area electron diffraction (SAED) pattern (Figure S9c in the Supporting Information), three diffraction rings, from inner to outer layers, correspond to (002), (100), and (110) crystal planes, respective-

Figure 4. A) Raman spectra of a) C_{PVP}, b) C_{PVP}/g-C₃N₄-60, c) raw g-C₃N₄ nano-sheets, and d) PVP/g-C₃N₄-60. B) UV/Vis diffuse reflectance spectra.

ly; this suggests weakly polycrystalline structures of the graphite phase.^[29]

The optical absorptions of the samples were examined by UV/Vis diffuse reflectance spectroscopy (DRS; Figure 4B). g-C₃N₄ has absorptions at $\lambda < 432$ nm, whereas C_{PVP}/g-C₃N₄ has a wider absorption region ($\lambda = 300$ –800 nm). The values of the band gap for g-C₃N₄ nanosheets and C_{PVP}/g-C₃N₄ are determined to be 2.89 and 2.38 eV, respectively, by extrapolation. The larger band gap of the g-C₃N₄ nanosheets, relative to that of bulk g-C₃N₄ reported in the literature, was ascribed to the small thickness of the g-C₃N₄ nanosheets.^[30] The carbon component (C_{PVP}) in C_{PVP}/g-C₃N₄ has a strong absorption in the visible region ($\lambda = 400$ –800 nm), which is responsible for narrowing the band gap.

The specific chemical environments and oxidation states of the C and N backbone elements in the C_{PVP}/g-C₃N₄ film were identified by X-ray photoelectron spectroscopy (XPS). In Figure 5, the peak centered at 284.82 eV is the main contribution in the C 1s spectrum, assigned to C–C bond, which is derived from carbon originating from PVP after calcination, as well as some surface contamination carbon. The typical C 1s spectrum for N=C=N at 288.05 eV is also clearly observed, corresponding to the structure of sp²-carbon atoms bonded to nitrogen inside the aromatic structure and sp²-carbon atoms in the aromatic ring attached to the –NH– or –NH₂ groups.^[31] The N 1s spectra were deconvoluted into three different peaks to shed some light on the bonding structures (Figure 5B). The peak at a binding energy (B.E.) of 400.33 eV is assigned to nitrogen atoms in the bonds of C–N–H, whereas that at

Figure 5. XPS spectra of C_{PVP}/g-C₃N₄-60: A) C 1s spectra and B) N 1s spectra.

399.20 eV corresponds to bridging nitrogen atoms bonded to three carbon atoms (N–[C]₃), and that at 398.33 eV is due to the N 1s core level in the C–N=C bond involved in the s-triazine ring.^[17] In addition, the absence of peaks above 401.0 eV indicates that the samples do not possess the N–N bonding configuration.^[32] Therefore, these results confirmed the successful synthesis of C_{PVP}/g-C₃N₄ film on ITO substrate.

PEC performance of the C_{PVP}/g-C₃N₄ films

The PEC performance of the films was investigated by the linear sweep current–voltage method under chopped visible-light irradiation over a wider potential range; this method is commonly used to evaluate the photocurrent response ability.^[33] As shown in Figure 6, in the range of positive voltage, the

Figure 6. Current–voltage (*I*–*V*) curves in 0.05 M Na₂SO₄ under chopped visible light; the arrows indicate the respective photocurrent onset potential used to estimate *E_{fb}*. A) A wide-range potential test, B) magnification of g-C₃N₄ test, and C) magnification of C_{PVP}/g-C₃N₄-60 test. The insets in A) are optical images of the pristine g-C₃N₄ film and the C_{PVP}/g-C₃N₄-60 film.

anodic photocurrents of the C_{PVP}/g-C₃N₄-60 film gradually increased with increasing bias potential. The current densities are higher under illumination than that in the dark for both g-C₃N₄ and C_{PVP}/g-C₃N₄-60 films; this indicates that photocurrent is generated over the whole voltage range. The photocurrent at 1.2 V (obtained by subtracting the dark current from the measured current) for C_{PVP}/g-C₃N₄-60 films is 12.6 μA cm⁻², which is over 60-fold higher than that for g-C₃N₄ films (0.20 μA cm⁻²). Furthermore, the dark currents are dramatically higher for C_{PVP}/g-C₃N₄-60 films than that for individual g-C₃N₄ films; this indicates the good electrochemical properties of the C_{PVP}/g-C₃N₄-60 films. The enhanced electrochemical property of the C_{PVP}/g-C₃N₄-60 film was attributed to the carbon component in the films, which could be directly determined from the optical images (the insets in Figure 6A). The color of pristine g-C₃N₄ film is white, whereas it becomes black for the C_{PVP}/g-C₃N₄-60 film due to the carbon component in the films.

From the onset photocurrent potential method (Figure 6B and C),^[34] the flat-band potential (*E_{fb}*) is –0.08 V for C_{PVP}/g-C₃N₄-60, which is negatively shifted compared with that for pristine g-C₃N₄ (0.24 V). As a result, the increase in the anodic photocurrent for C_{PVP}/g-C₃N₄-60 (compared with that of g-C₃N₄) becomes more apparent than the cathodic photocurrent

under the same bias potential range, and the results are consistent with those of a previous study.^[34] Hence, $C_{PVP}/g-C_3N_4$ was more like an n-type semiconductor due to the more apparent anodic photocurrent in the present bias potential window.^[35]

The photocurrent responses as a function of time were investigated under alternating illumination on and off cycles; these could demonstrate the separation and migration efficiency of photogenerated carriers.^[36] The results are presented in Figure 7. The individual ITO glass, $g-C_3N_4$ film obtained by the

Figure 7. Periodic on/off photocurrent responses: a) comparison samples, b–d) $C_{PVP}/g-C_3N_4$ films. b) Various collector temperatures, c) various $g-C_3N_4$ contents, and d) various spinning times. All measurements were performed at 0.5 V bias potential under visible-light irradiation ($\lambda > 420$ nm) in 0.05 M Na_2SO_4 .

doctor blading method, and $C_{PVP}/g-C_3N_4$ film obtained by the spin-coating method were tested as references, the photocurrent densities of which were 0, 0.38, and $1.4 \mu A cm^{-2}$, respectively. The resistance of ITO glass increased slightly, but still retained low values ($18 \Omega sq^{-1}$) after calcination at $500^\circ C$ in N_2 (Table S3 in the Supporting Information). These results suggested that the effect of the ITO substrate resistance variation during calcination for the photocurrent tests was negligible. The impact of collector temperature, $g-C_3N_4$ content, and spinning time on the photocurrent densities of $C_{PVP}/g-C_3N_4$ was investigated. The photocurrent density of the film obtained at a collector temperature of $180^\circ C$ ($4.21 \mu A cm^{-2}$) is higher than those of $140^\circ C$ ($3.75 \mu A cm^{-2}$) and $220^\circ C$ ($2.63 \mu A cm^{-2}$). Because $140^\circ C$ is below the melting point ($165^\circ C$) of PVP, the cohesiveness of the film towards ITO glass is unsatisfactory, leading to low conductivity of the film. Meanwhile, at temperatures higher than $200^\circ C$, the decomposition of PVP occurred, which could be confirmed from TGA-DTA (Figure S2 in the Supporting Information) curves previously analyzed. Therefore, $180^\circ C$ was the optimal collector temperature.

The proportion of $g-C_3N_4$ also affects the photocurrent densities of the $C_{PVP}/g-C_3N_4$ films (Figure 7c). For $C_{PVP}/g-C_3N_4$ -20, -43, and -60, the photocurrent densities increased with increasing $g-C_3N_4$ contents of 0.59, 2.95, and $4.62 \mu A cm^{-2}$, respectively. The increase was due to the higher proportion of $g-C_3N_4$ content in the film, which played a vital role in the photo-electroactivity of the film. Meanwhile, the high amount of PVP might lead to unwanted recombination. However, the photocurrent density decreased to $1.10 \mu A cm^{-2}$ when the $g-C_3N_4$ content increased to 75 wt%; this may be due to poorer cohesiveness of the film towards ITO glass, as analyzed previously (Figure 2). Consequently, $C_{PVP}/g-C_3N_4$ -60 exhibits the best photo-electroactivity. Furthermore, the photocurrent could be easily tuned by adjusting the spinning time. As shown in Figure 7d, the photocurrent densities (3.55 , 4.92 and $6.64 \mu A cm^{-2}$) increase with increasing spinning time (40, 70, and 120 min, respectively), with the same trend as that of the film thickness variation (Figure S7 in the Supporting Information). The photocurrent densities of these $C_{PVP}/g-C_3N_4$ films greatly exceed the value of the traditional $g-C_3N_4$ film ($0.38 \mu A cm^{-2}$). The improved efficiency of photocurrent generation proved that these $C_{PVP}/g-C_3N_4$ films could be promising candidates in PEC applications.

The films were further examined by cyclic voltammetry (CV) to give some information about the electrochemical properties of the films (Figure S11 in the Supporting Information). The reference ITO substrate exhibited substrate oxidation at about 1.0 V, whereas there were no oxidation or reduction peaks for the $g-C_3N_4$ and $C_{PVP}/g-C_3N_4$ -60 films, which suggested that the ITO substrate was almost completely covered and there was no direct connection between the solution and ITO substrate. For $g-C_3N_4$ films, the current density at -0.6 V (versus a standard calomel electrode (SCE)) was about $0.04 mA cm^{-2}$, whereas for $C_{PVP}/g-C_3N_4$ -60 films the current density increased to $0.3 mA cm^{-2}$, which was much higher than that of individual $g-C_3N_4$ films. Furthermore, the CV curve for the $C_{PVP}/g-C_3N_4$ -60 film is similar to that of a supercapacitor; this may be caused by the carbon component in the films.^[37]

To identify the stability of $C_{PVP}/g-C_3N_4$ films, the photocurrent test was sustained for 4000 s, with partial 300 and 30 s on–off irradiation tests. As shown in Figure 8, the photocurrent density did not decrease until 4000 s, and the on–off response remained fast during testing. Furthermore, under sustainable irradiation, the current slowly increased, which was presumed to be caused by carbon in the films. As it is widely known, carbon possesses electron storage abilities and is commonly used as a supercapacitor material.^[37] In this research, the CV curves (Figure S10 in the Supporting Information) of $C_{PVP}/g-C_3N_4$ exhibit supercapacitor-like curves, which suggests that the carbon component in the films could store photoelectrons. Therefore, photoelectrons are not transferred immediately to the external circuit, but result in a slow and continuous transfer process. Thus, the current under irradiation exhibits a slowly increasing process with extended irradiation time. After testing, the $C_{PVP}/g-C_3N_4$ film is still intact (Figure 8, insets). The top- and side-view SEM images of the film after testing indicate that the coverage of the film is still good, evenly distrib-

Figure 8. Time dependence of the photocurrent density of $C_{PVP}/g-C_3N_4-60$ with a spinning time of 120 min at a 0.5 V bias potential (vs. SCE) in 0.05 M Na_2SO_4 ; the insets are top- and side-view SEM images of the $C_{PVP}/g-C_3N_4-60$ film after testing.

uted, and is well adhered onto the ITO glass; this further confirms the stability of the $C_{PVP}/g-C_3N_4$ film. The high current densities and good stability of $C_{PVP}/g-C_3N_4$ films favor PEC applications.

Electrochemical impedance spectroscopy (EIS) was performed to investigate the interfacial charge-transfer process. In electrochemical spectra, the high-frequency arc corresponds to the charge-transfer-limiting process and can be attributed to the double-layer capacitance (C_{dl}) in parallel with the charge-transfer resistance (R_{ct}) at the contact interface between the electrode and electrolyte solution.^[32] The preparation of the electrodes and electrolyte used is identical; thus the high-frequency semicircle is relevant to the resistance of the electrodes. As shown in Figure 9A, the arc radii on the EIS Nyquist plot of $C_{PVP}/g-C_3N_4$ hybrid films are smaller than that of an individual $g-C_3N_4$ film, which suggests that the separation of photogenerated electron-hole pairs is more effective and interfacial charge transfer is faster for $C_{PVP}/g-C_3N_4$ films.

The mechanism for separation and transportation of electron-hole pairs at the interface of carbon and C_3N_4 hybrid films is proposed (Figure 9B). Under visible-light irradiation, electrons (e^-) are excited from the valence band (VB; N 2p orbitals) to the conduction band (CB; C 2p orbitals) of $g-C_3N_4$, creating holes (h^+) in the VB. Normally, these charge carriers quickly recombine for individual $g-C_3N_4$ films, but for $C_{PVP}/g-C_3N_4$ films the photogenerated electrons tend to transfer to carbon nearby in the film due to the excellent electronic con-

Figure 9. A) Electrochemical impedance spectra of different films in 0.05 M Na_2SO_4 , $\lambda > 420$ nm, and the insert is the corresponding high magnification. B) The proposed mechanism for separation and transportation of electron-hole pairs.

ductivity of carbon, and thus, lead to a higher e^-h^+ separation efficiency. Therefore, the $C_{PVP}/g-C_3N_4$ films generate a higher photocurrent density under visible-light irradiation, which is beneficial for PEC applications.

The above results suggest that $C_{PVP}/g-C_3N_4$ films have potential applications in many PEC-related areas. Herein, the H_2 evolution performance of the $g-C_3N_4$ and $C_{PVP}/g-C_3N_4-60$ films were evaluated. As shown in Figure 10, the H_2 evolution ability dramatically increased for the $C_{PVP}/g-C_3N_4-60$ film compared with that for $g-C_3N_4$ films: 4.35 and 0.014 μmol , respectively, within 60 min. The improved H_2 evolution ability is consistent with the photocurrent results (Figure 6) of the films, and further demonstrates that the $C_{PVP}/g-C_3N_4$ films are promising candidates in PEC applications.

Figure 10. H_2 evolution behavior over time in a 0.05 mol L^{-1} aqueous solution of Na_2SO_4 , 1.2 V bias potential versus SCE, irradiated by using a xenon lamp, 100 $mW\ cm^{-2}$, $\lambda > 420$ nm.

Conclusions

We have demonstrated a promising strategy for the fabrication of novel $C_{PVP}/g-C_3N_4$ films through an electrospinning technique. PVP could remarkably enhance the cohesiveness of $g-C_3N_4$ toward the ITO substrate and provide a carbon component in the final film. The coverage of the films is good and the films exhibit good PEC activity. This work provides an improved preparation method for synthesizing $g-C_3N_4$ -related films and also offers a reference route for the development of highly efficient carbon-modified $g-C_3N_4$ films for PEC applications.

Experimental Section

Synthesis of $g-C_3N_4$ nanosheets

Bulk $g-C_3N_4$ was prepared by heating dicyandiamide in a muffle furnace through a calcination procedure at $2^\circ C\ min^{-1}$ from RT to $500^\circ C$, then $1^\circ C\ min^{-1}$ to $550^\circ C$, and kept at this temperature for 4 h. The as-prepared bulk $g-C_3N_4$ (1.0 g) was mixed with concentrated H_2SO_4 (10 mL; 98%, AR) in a 50 mL beaker and stirred for 8 h. The solution was diluted by slowly being poured into deionized water (100 mL), and then the diluted solution was centrifuged and washed with deionized water many times, until the pH of the solution was close to seven. The precipitate was transferred to

a glass culture dish and dried overnight in an oven at 80 °C.^[38] Finally, the obtained white powders were g-C₃N₄ nanosheets.

Synthesis of C_{PVP}/g-C₃N₄ films

The electrospinning precursor was prepared by adding g-C₃N₄ nanosheets (0.1–0.15 g) and PVP (0.05–0.6 g; K90, $M_w = 1\,300\,000$) to deionized water (3 mL) and stirring for 12 h. The detailed dosages are listed in Table S1 in the Supporting Information. Then the precursor was injected into a 2.5 mL plastic syringe, which connected to a 90° bending needle. An ITO glass was put on an aluminum foil, which could be heated. The distance between the needle and collector was 6.0 cm. The push speed was 0.08 mm min⁻¹ and the applied voltage was 12 kV. After electrospinning, PVP-modified g-C₃N₄ films (PVP/g-C₃N₄ films) coated on the ITO glass formed. Subsequently, the PVP/g-C₃N₄ films were calcined in a tube furnace at a heating rate of 3 °C min⁻¹ from RT to 500 °C and kept at this temperature for 2 h in N₂.

Synthesis of individual g-C₃N₄ films by the doctor blading method

The same weights of g-C₃N₄ nanosheets (0.4 g) as that in PVP/g-C₃N₄-60 with spinning time of 70 min were put in a mortar, ethanol (0.4 mL) was added, and the mixture was milled before being uniformly covered on the ITO glass by doctor blading. The g-C₃N₄ films on ITO glass were dried at 80 °C and then calcined at 200 °C with a heating rate of 1 °C min⁻¹ for 5 h in air.

Characterization

The morphology and thicknesses of the films were observed from top- and side-view images, respectively, recorded by using a SU-8020 field-emission scanning electron microscope (Hitachi, Japan). TEM was performed by using an H7500 microscope (Hitachi, Japan). To avoid electron-beam-induced damage, a low-intensity beam was used to collect SAED data. XPS was performed on a Phi Quantern instrument. The B.E. measurements were calibrated for charging effects with reference to the C 1s peak (284.8 eV). Raman spectra were recorded on a microscopic confocal Raman spectrometer (Renishaw inVia) with an excitation laser light of $\lambda = 633$ nm. XRD results were obtained on an X'pert PRO MPD PC system by using Cu K α ($\lambda = 0.15418$ nm, 40 kV, 40 mA) as the X-ray source. TG-DSC measurements in N₂ were undertaken on a Mettler TGA-1 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ up to 1000 °C. TGA-DTA results in air were recorded on a simultaneous TGA-DTA apparatus (DTG-60) at a heating rate of 10 °C min⁻¹ up to 800 °C. FTIR spectra were recorded in the region from $\tilde{\nu} = 800$ to 4000 cm⁻¹ by using a Nicolet 8700 FTIR spectrometer (Thermo Fisher Scientific). The diffuse reflectance absorption spectra were investigated in the range from $\lambda = 200$ to 800 nm on a Hitachi U-3900 spectrometer equipped with an integrated sphere attachment and samples (12 mg) were mixed with BaSO₄ (600 mg) for testing; BaSO₄ was used as a reference.

PEC measurements were performed on a CHI 660B electrochemical workstation (CH Instruments, Inc.) by using a conventional three-electrode system consisting of the as-prepared C_{PVP}/g-C₃N₄ film as the working electrode (geometrical area of 6 cm²), SCE as a reference electrode, and Pt wire (70 mm in length with a 0.4 mm diameter) as the counter electrode. The PEC measurements of the prepared electrode were recorded in a 0.05 M aqueous solution of Na₂SO₄ irradiated by $\lambda = 420$ nm visible light (light source: Xe lamp with 300 W electrical power and 50 W luminous power; BoPhila technology co., LTD). Potentials were shown versus a reversible hy-

drogen electrode (RHE) related as $E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{ pH} + 0.244$, in which E_{RHE} was the potential versus the RHE, E_{SCE} was the potential versus the SCE, and pH was the pH value of the Na₂SO₄ electrolyte solution.

The hydrogen evolution experiment was performed by using the same three-electrode system as that used for PEC measurements, under 1.2 V bias potential, with a 0.05 mol L⁻¹ aqueous solution of Na₂SO₄, and irradiated by $\lambda = 420$ nm visible light (Xe lamp, 100 mW cm⁻²). The generated gas was collected and analyzed by GC (GC2060; Shanghai Ruimin, P.R. China) every 20 min.

Acknowledgements

This work was financially supported by projects of the National Key Research and Development Program of China (no. 2016YFA0203101) and the National Natural Science Foundation of China (no. 21377148).

Keywords: carbon • electrochemistry • photochemistry • synthesis design • superconductors

- [1] S. Cao, J. Low, J. Yu, M. Jaroniec, *Adv. Mater.* **2015**, *27*, 2150–2176.
- [2] Y. Zheng, L. Lin, B. Wang, X. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 12868–12884; *Angew. Chem.* **2015**, *127*, 13060–13077.
- [3] J. Zhang, Y. Chen, X. Wang, *Energy Environ. Sci.* **2015**, *8*, 3092–3108.
- [4] J. Liu, H. Wang, M. Antonietti, *Chem. Soc. Rev.* **2016**, *45*, 2308–2326.
- [5] R. Cazzelles, J. Liu, M. Antonietti, *ChemElectroChem* **2015**, *2*, 333–337.
- [6] Y. Zheng, Y. Jiao, M. Jaroniec, Y. Jin, S. Z. Qiao, *Small* **2012**, *8*, 3550–3566.
- [7] J. Zhang, G. Zhang, X. Chen, S. Lin, L. Möhlmann, G. Dołęga, G. Lipner, M. Antonietti, S. Blechert, X. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 3183–3187; *Angew. Chem.* **2012**, *124*, 3237–3241.
- [8] M. Wu, J.-M. Yan, X.-W. Zhang, M. Zhao, Q. Jiang, *J. Mater. Chem. A* **2015**, *3*, 15710–15714.
- [9] G. Liu, P. Niu, C. Sun, S. C. Smith, Z. Chen, G. Q. Lu, H.-M. Cheng, *J. Am. Chem. Soc.* **2010**, *132*, 11642–11648.
- [10] G. Zhang, Z.-A. Lan, L. Lin, S. Lin, X. Wang, *Chem. Sci.* **2016**, *7*, 3062–3066.
- [11] F. He, G. Chen, Y. Yu, Y. Zhou, Y. Zheng, S. Hao, *Chem. Commun.* **2015**, *51*, 6824–6827.
- [12] N. Tian, H. Huang, C. Liu, F. Dong, T. Zhang, X. Du, S. Yu, Y. Zhang, *J. Mater. Chem. A* **2015**, *3*, 17120–17129.
- [13] Y. Zhang, A. Thomas, M. Antonietti, X. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 50–51.
- [14] Y. Zhang, M. Antonietti, *Chem. Asian J.* **2010**, *5*, 1307–1311.
- [15] J. Xu, T. J. Brenner, L. Chabanne, D. Neher, M. Antonietti, M. Shalom, *J. Am. Chem. Soc.* **2014**, *136*, 13486–13489.
- [16] J. Zhang, M. Zhang, L. Lin, X. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 6297–6301; *Angew. Chem.* **2015**, *127*, 6395–6399.
- [17] J. Liu, H. Wang, Z. P. Chen, H. Moehwald, S. Fiechter, R. van de Krol, L. Wen, L. Jiang, M. Antonietti, *Adv. Mater.* **2015**, *27*, 712–718.
- [18] C. L. Zhang, S. H. Yu, *Chem. Soc. Rev.* **2014**, *43*, 4423–4448.
- [19] H. Yoon, M. G. Mali, J. Y. Choi, M. W. Kim, S. K. Choi, H. Park, S. S. Al-Deyab, M. T. Swihart, A. L. Yarin, S. S. Yoon, *Langmuir* **2015**, *31*, 3727–3737.
- [20] Y. Wang, W. Li, Y. Xia, X. Jiao, D. Chen, *J. Mater. Chem. A* **2014**, *2*, 15124–15131.
- [21] M. M. Aria, A. Irajizad, F. R. Astaraei, S. P. Shariatpanahi, R. Sarvari, *Measurement* **2016**, *78*, 283–288.
- [22] M. I. Loria-Bastarrachea, W. Herrera-Kao, J. V. Cauich-Rodríguez, J. M. Cervantes-Uc, H. Vázquez-Torres, A. Ávila-Ortega, *J. Therm. Anal. Calorim.* **2011**, *104*, 737–742.
- [23] Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Q. Lu, S. Z. Qiao, *J. Am. Chem. Soc.* **2011**, *133*, 20116–20119.

- [24] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong, Z. Kang, *Science* **2015**, *347*, 970–974.
- [25] W. Yu, D. Xu, T. Peng, *J. Mater. Chem. A* **2015**, *3*, 19936–19947.
- [26] M. H. Tai, P. Gao, B. Y. Tan, D. D. Sun, J. O. Leckie, *ACS Appl. Mater. Interfaces* **2014**, *6*, 9393–9401.
- [27] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76–80.
- [28] J. Yang, Y. Zhang, D. Y. Kim, *Carbon* **2016**, *98*, 74–82.
- [29] G. Xin, Y. Wang, J. Zang, S. Jia, P. Tian, S. Zhou, *Carbon* **2016**, *98*, 221–224.
- [30] P. Niu, Y. Yang, J. C. Yu, G. Liu, H. M. Cheng, *Chem. Commun.* **2014**, *50*, 10837–10840.
- [31] S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang, P. M. Ajayan, *Adv. Mater.* **2013**, *25*, 2452–2456.
- [32] X. Bai, L. Wang, Y. Wang, W. Yao, Y. Zhu, *Appl. Catal. B* **2014**, *152–153*, 262–270.
- [33] S. Lou, Z. Zhou, Y. Shen, Z. Zhan, J. Wang, S. Liu, Y. Zhang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 22287–22294.
- [34] J. Wang, Y. Shen, Y. Li, S. Liu, Y. Zhang, *Chem. Eur. J.* **2016**, *22*, 12449–12454.
- [35] Y. Zhang, T. Mori, L. Niu, J. Ye, *Energy Environ. Sci.* **2011**, *4*, 4517.
- [36] Y. Li, J. Wang, Y. Yang, Y. Zhang, D. He, Q. An, G. Cao, *J. Hazard. Mater.* **2015**, *292*, 79–89.
- [37] J. Cai, H. Niu, H. Wang, H. Shao, J. Fang, J. He, H. Xiong, C. Ma, T. Lin, *J. Power Sources* **2016**, *324*, 302–308.
- [38] F. Liang, Y. Zhu, *Appl. Catal. B* **2016**, *180*, 324–329.

Manuscript received: September 21, 2016

Final Article published: December 1, 2016