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Facile Assembly of Graphitic Carbon Nitride Film at Air/Water Interface for Photoelectrochemical NADH Regeneration

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The development of metal-free photoelectrode film is of great significance. Herein, graphitic carbon nitride (g-C₃N₄) nanosheets are first obtained in large scale by wet ball milling method, with the highest concentration up to 36 mg mL⁻¹. The obtained g-C₃N₄ nanosheets exhibit 6- and 8-times higher activity in photocatalytic H₂ evolution and nicotinamide adenine dinucleotide (NADH) regeneration than that of the bulk g-C₃N₄, respectively. Furthermore, uniform g-C₃N₄ film electrode can be fabricated by interfacial self-assembly of nanosheets at the air/water interface, which can be transferred onto various substrates. By coupling with the graphene nanosheet, g-C₃N₄/graphene hybrid film electrode is assembled at the interface, showing improved photoelectrochemical coenzyme NADH regeneration efficiency. The photoelectrochemical system uses water as the electron donor, which avoids the drawback of using additional sacrificial agents. This work presents a novel and facile method to prepare high-quality g-C₃N₄ hybrid films, and also provides a sustainable route for renewable energy conversion and biocatalytic applications.

Introduction

In recent years, metal-free graphitic carbon nitride (abbreviated as g-C₃N₄) have aroused enormous interests due to their excellent physicochemical, optical, and chemical properties, extending their exploitations beyond conventional (photo)catalysis to sensing, solar cell, ion transport and other energy-related applications.¹⁻⁶ In addition to the conventional morphology modulation (e.g., nanospheres, monolith, or nanorods) for the nanoparticle samples, the g-C₃N₄ thin films or membranes have emerged as appealing platforms for applications in photoelectrochemical reactions, gas separation, or energy devices.⁷⁻¹⁰ Converting solar energy to chemical energy using a photoelectrochemical cell is one of the most promising approaches to meet future energy demands.¹¹⁻¹³ However, the exploitation of g-C₃N₄ in photoelectrochemical cells has been limited by the difficulty in coating a layer of high-quality, homogenous g-C₃N₄ film onto a conductive substrate.¹⁴⁻¹⁵ Inspired by the conventional semiconductor photocatalysts, previous studies adopted the tedious two-step methods (e.g., spin-coating, electrophoretic deposition) to prepare the g-C₃N₄ film photoelectrodes.¹⁶⁻¹⁷ However, the poor dispersion of g-C₃N₄ materials in common solvents renders inferior thin film fabrication with the problems of inhomogeneity and being easily detached from electrodes.¹⁸ Since 2015, more and more researchers attempted to synthesize g-C₃N₄ film directly from in-situ thermal condensation of N-rich precursors onto various substrates, which avoided the poor interfacial engineering problem that usually occurred in the conventional two-step deposition methods.¹⁹,²⁰ The thickness of the g-C₃N₄ film could be controlled by applying different amount of precursors and thermal treatment time. However, this method usually requires the use of high-temperature-resistant substrates, excluding the possibility of direct deposition onto a flexible substrate. Therefore, it is still highly desired to develop a novel strategy to prepare high-quality g-C₃N₄ film under mild conditions.

Gas/liquid interface provides an ideal platform for assisting the formation of uniform thin film at the interface by self-assembly of two-dimensional nanosheets, delicately avoiding the aggregation of nanosheets during calcination or drying processes.²¹,²² Herein, we report a versatile wetting-induced transferring strategy at the air/water interface to fabricate uniform large-area ultrathin g-C₃N₄ film onto arbitrary substrates. Bulk g-C₃N₄ (BCN) is directly exfoliated into layered nanosheets through a modified wet ball milling process, obtaining a highly stable g-C₃N₄ nanosheets (CNS) dispersion with concentration up to 36 mg mL⁻¹. Due to the facile procedures of the interfacial self-assembly, the film thicknesses could be easily controlled by varying the transferring layers. Conductive graphene nanosheet was coupled with CNS during the interface assembly process to enhance the conductivity of the film electrode and improve electron–hole separation efficiency. The resulting CNS-graphene (CNS-Gr) hybrid film doubled the photoelectrochemical cofactor NADH regeneration yield in the presence of electron and proton mediator. This work opens a new route for the facile preparation of high-quality g-C₃N₄ hybrid film with enhanced conductivity and improved the separation efficiency of electron-hole pairs, which render photoelectrochemical NADH regeneration possible using water as an electron donor.²³
Experimental

Materials

Dicarboxamide, Na$_2$PO$_4$, Na$_3$HPO$_4$ and triethanolamine (TEOA) were received from Energy Chemical (China). β-NAD$^+$ and graphene were purchased from Aladdin (China). The rhodium complex was synthesized as described previously reported. All chemicals are used without further purification. FTO glasses were received from PV. Tech (China).

Preparation of BCN

Dicarboxamide was heated at 550 °C for 4 h in atmospheric environment with a ramp rate of 2 °C min$^{-1}$, and then cooled to room temperature. Finally, yellow powders were obtained.

Preparation of CNS

The CNS were prepared by grinding the BCN through ball milling at high yield. BCN was added into water, followed by grinding 1:1 mass ratio of 2 mm ZrO$_2$ ball and 0.2 mm ZrO$_2$ ball. After ball milling for 60 h, the CNS dispersion was acquired. The dispersion was centrifuged at 500 rpm for 30 min to remove unexfoliated g-C$_3$N$_4$. The supernatant was collected followed by freeze-drying to obtain CNS powders. Certain amount of CNS was dispersed into ethanol to obtain the dispersion with concentration of 20 mg mL$^{-1}$.

Self-assembly of CNS film at the air/water interface

Exfoliated CNS (20 mg mL$^{-1}$) were dispersed in an ethanol solution, and then injected the mixture into the air/water interface in a container filled with water at a certain speed. The CNS dispersion began to self-assemble into homogeneous film at the air/water interface. Then, the water surface was completely covered by CNS by increasing the injection amounts of the CNS dispersion. Afterwards, the film was transferred to an FTO substrate by lift-up technique. The FTO glasses (1×2.5 cm$^2$) were washed in advance with acetone, isopropanol, ethanol and deionized water in sequence under continuous ultrasound.

Self-assembly of CNS-Gr film at the air/water interface

The CNS-Gr suspension was prepared by adding different amount (0, 0.2, 0.5, or 0.7 mL) of graphene solution (0.5 wt.%) into the CNS dispersion (20 mg mL$^{-1}$, 3 mL). The same interface assembly method was employed to form uniform CNS-Gr hybrid film at the air/water interface followed by transferring the film onto FTO, which was further annealed at 350 °C for 2 h under air atmosphere to enhance the contact between film and substrate. The obtained films were named as CNS, CNS-Gr$_{0.2}$, CNS-Gr$_{0.5}$, and CNS-Gr$_{0.7}$, respectively.

Photocatalytic H$_2$ production test

The photocatalytic H$_2$ production experiments were performed using a photocatalytic activity evaluation system (CEAULIGHT). A 300 W Xenon arc lamp equipped with a UV-cutoff filter (λ ≥ 420 nm) as the light source. The reaction occurs in an aqueous solution (50 mL) consisting of TEOA (5 mL) and CNS or BCN (25 mg). Pt nanoparticles (3 wt.%) were deposited on g-C$_3$N$_4$ by in-situ photodeposition of H$_2$PtCl$_6$.

Photocatalytic NADH production

The photocatalytic NADH regeneration was carried out in a quartz reactor at room temperature under air atmosphere using a 36 W LED (450 nm) as the light source. The system consists of photocatalyst (BCN and CNS, 6 mg), β-NAD$^+$ (1 mmol), triethanolamine (15 wt.%), and Rhodium complex (0.25 mmol) in Na$_2$HPO$_4$/NaH$_2$PO$_4$ buffer (3 mL, 0.2 M, pH=7.4). The NADH regeneration was measured on UV-3900 spectrophotometer (UV-3900, Hitachi).

Photoelectrochemical NADH regeneration tests

The test of PEC NADH regeneration was conducted in a three-electrode configuration, in which CNS/FTO film (or CNS-Gr/FTO film) was used as the working electrode, a Pt wire as the counter electrode and Ag/AgCl as a reference electrode. The PEC NADH regeneration was carried out at room temperature under N$_2$ atmosphere using a 300 W Xenon arc lamp equipped with a UV-cutoff filter (λ ≥ 420 nm) as the light source. The NADH-regenerating PEC cell was exposed by visible light at an external bias of -0.9 V. The system was consisted of β-NAD$^+$ (1 mmol), Rhodium complex (0.25 mmol) in Na$_2$HPO$_4$/NaH$_2$PO$_4$ buffer (4 mL, 0.2 M, pH=7.4). The NADH regeneration was measured on UV-vis spectrophotometer (UV-3900, Hitachi).

Characterization

Optical transmittance test was taken with a UV-vis spectrophotometer (UV-3900, Hitachi). X-ray diffraction (XRD) was measured with Cu Ka X-ray in a scanning range from 10° to 70°. X-ray photoelectron spectroscopy (XPS) was taken with a Thermos ESCALAB 250XL. Transmission electron microscopy (TEM) was carried out on JEOL JEM-2100 Plus. The Fourier transformed infrared spectroscopy (FTIR) experiment was carried out on a Nicolet iZ10 in Thermos scientific, scanning from 4000 to 500 cm$^{-1}$. Scanning electron microscope (SEM) images were obtained from Zeiss Sigma-300. Nitrogen adsorption/desorption measurement was performed at 77 K on a Micromeritics ASAP 2460. Zeta potential was carried out on a Malvern Zeta S90. Atomic force microscopy (AFM) images were obtained using a Bruker Multimode 8. The Mott-Schottky plots were obtained on an electrochemical analyzer (Modulab ECS) with Na$_2$SO$_4$ (0.2 M) aqueous solution. The photocurrent of CNS/FTO film and electrochemical impedance spectroscopy (EIS) were measured by electrochemical analyzer (CH660E). The test was measured in a standard three-electrode system, where CNS/FTO film (or CNS-Gr/FTO film) acted as the working electrode, a Pt wire as the counter electrode and Ag/AgCl as a reference electrode. In an identical three-electrode system, the EIS measurement was carried out in a range from 1 to 100 kHz with an AC amplitude of 100 mV. Na$_2$SO$_4$ (0.2 M) salt solution was used as the electrolyte.

Results and discussion

Morphological and Structural Properties

By employing the BCN as the starting material, the CNS dispersion could be obtained from a modified wet ball milling method. The concentration of CNS reaches up to 36 mg mL$^{-1}$,
The typical Tyndall effect was observed in the CNS dispersion (Fig. 1c), suggesting the colloidal nature of the dispersion. (Table S1), making the dispersion milky white (Fig. 1a). The structure and properties of BCN and the resulting CNS were comprehensively characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), and atomic force microscopy (AFM). As shown in Fig. S1, the BCN sample possesses typical irregular morphologies, whereas the exfoliated CNS after ball milling treatment shows a thinner lamellar structure compared with the bulk counterpart, which is evidenced by the representative TEM image in Fig. 1d. As shown in the XRD spectra (Fig. 1e), the diffraction peaks of BCN with high intensity locate at 13.5° and 27.6°, ascribing to the in-plane structural repeating unit of the aromatic systems (100) and the typical graphitic interlayer (002) plane, respectively. In the case of CNS, the intensity of (002) peak significantly decreases while the peak of (100) almost disappears, indicating the efficient exfoliation of BCN into thin layers.27 This is also consistent with the SEM and TEM observations. The sheet-like morphology and thickness of g-C$_3$N$_4$ is further confirmed by AFM analysis, showing a well-defined nanosheet morphology with a thickness of ~3.85 nm corresponding to ca. 10 layers (Fig. 1f-g).28 The above results reveal that the CNS have been successfully prepared through ball milling assisted exfoliation process.

The CNS shows similar FTIR spectra with the BCN, indicating that the structure was preserved after the exfoliation process (Fig. 2a). More specifically, the peak at 810 cm$^{-1}$ can be assigned to the typical breathing mode of heptazine rings, owing to the existence of characteristic absorption peak of triazine units in carbon nitride. The peaks ranging from 1170 to 1630 cm$^{-1}$ ascribe to CN heterocycles in the melon-based framework. The broad band between 2900 and 3600 cm$^{-1}$ is attributed to the N-H stretching vibrations.29,30

Fig. 2 (a) FTIR, (b) UV-vis absorption spectra, and (c, d) C 1s and N 1s XPS spectra of BCN and CNS.

The structure and properties of BCN and CNS are determined to be -31.2 and -36.8 mV in water potential analysis. Fig. S3 shows that the Zeta potentials of BCN and CNS are determined to be -31.2 and -36.8 mV in water (pH=7), respectively. The results implied that CNS surface
possesses a much more negative potential than BCN. Additionally, the $N_2$ adsorption-desorption isotherms show that the Brunauer-Emmett-Teller (BET) specific surface area increases from 6.5 to 34.6 m$^2$ g$^{-1}$ when exfoliating BCN into CNS (Fig. S4).

**Photocatalytic Behaviors of $H_2$ Evolution and NADH Regeneration**

The photocatalytic activities of BCN and CNS were firstly evaluated by photocatalytic $H_2$ generation under visible light irradiation using TEOA as a hole sacrificial agent (see the schematic illustration in Fig. S5a). Both CNS and BCN can absorb visible light to generate the electron-hole pairs. Then, the photogenerated electrons transfer to Pt cocatalysts for reduction of $H_2O$ to $H_2$, while the remaining photogenerated holes are consumed by TEOA. Fig. S5b shows that the CNS exhibits efficient photocatalytic performance towards $H_2$ evolution, which is ~6 times higher than that of the BCN. Moreover, the stability towards photocatalytic $H_2$ evolution of CNS was demonstrated by three sequence cycling tests under same conditions, showing no obvious variation of the $H_2$ generation rate. Furthermore, the CNS was employed for cofactor (NAD(P)/NAD(P)H) regeneration, which is an important process for sustainable enzymatic synthesis. Compared with the conventional electrochemical or enzymatic regeneration, the photocatalytic regeneration method is promising using light as the only energy input. The CNS photocatalyst harvests incident visible light with electronic transition between its HOMO and LUMO orbitals, then transfers the photogenerated electrons to reduce the rhodium complex $M$ ($M = [Cp^*Rh(bpy)H_2O]^{2+}$; $Cp^*$ = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine) to $M_0$, which further accepts a proton from water. The resulting electron mediator $M_2$ selectively regenerates NADH by transferring two electrons and one proton to NAD$^+$.

The film thickness can be easily controlled by varying the amount of CNS. For example, the thickness of the CNS film increased from 1.2 to 6.2 μm when increasing the photoreactor’s settings. The higher photocatalytic activity of the CNS over the BCN is caused by the higher electron generation rate. Furthermore, the CNS was employed for cofactor (NAD(P)/NAD(P)H) regeneration, reaching 80% yield in 10 minutes, which is much higher than that of the BCN (ca. 10%) (Fig. 3b and Fig. S6). The higher photocatalytic activity of the CNS over the BCN is caused by the higher electron generation rate. Furthermore, the CNS was employed for cofactor (NAD(P)/NAD(P)H) regeneration, reaching 80% yield in 10 minutes, which is much higher than that of the BCN (ca. 10%) (Fig. 3b and Fig. S6). The higher photocatalytic activity of the CNS over the BCN is caused by the higher electron generation rate.

As a result, CNS exhibits an excellent photocatalytic activity for NADH regeneration, reaching 80% yield in 10 minutes, which is much higher than that of the BCN (ca. 10%) (Fig. 3b and Fig. S6). The higher photocatalytic activity of the CNS over the BCN is caused by the higher electron generation rate. Furthermore, the CNS was employed for cofactor (NAD(P)/NAD(P)H) regeneration, reaching 80% yield in 10 minutes, which is much higher than that of the BCN (ca. 10%) (Fig. 3b and Fig. S6). The higher photocatalytic activity of the CNS over the BCN is caused by the higher electron generation rate.
The optical properties of the CNS film with different transferring layers were shown in Fig. S9a, showing decreased transmittance upon increasing the thickness. The transient photocurrent density of the as-prepared CNS films was investigated under chopped light illumination (Fig. S9b). Although thicker film increases the light absorbance, the low conductivity of the CNS leads to larger resistance. Therefore, the optimized CNS-2 film exhibited the highest photocurrent density among three samples due to the tradeoff among the light absorbance, penetration, and conductivity. The charge separation and transfer efficiencies of the samples were further characterized by electrochemical impedance spectroscopy (EIS) measurements. Nyquist plots of CNS films under visible light irradiation are shown in Fig. S9c. CNS-1 film has the smallest arc radius among the three samples, which indicates a higher charge transfer efficiency. With increasing the films thicknesses, the arc radius of the samples increased owing to the larger charge transfer efficiency. With increasing the films thicknesses, the arc radius among the three samples, which indicates a higher charge transfer efficiency.

The flat-band potential of samples was investigated by electrochemical Mott-Schottky (M-S) plots (Fig. S9d). The flat-band potential of CNS films was measured to be -1.23 V versus Ag/AgCl, which is thermodynamically favorable for photocatalytic reduction of water and NAD$.^4,47,48$ Furthermore, the CNS-Gr$_{0.7}$ hybrid film shows a smaller semicircle arc than that of the CNS electrode (Fig. 5a), which indicates that graphene reduces the charge transfer resistance, beneficial to the separation of electron–hole from photoexcited CNS-Gr$_{0.7}$. The Nyquist plot were fitted in terms of the equivalent circuit (the inset), in which $R_s$, $R_t$, and CPE represent the solution resistance, charge transfer resistance across the interface of electrode/electrolyte, and constant phase element for the electrolyte/electrode interface, respectively.$^{49}$ The linear-sweep voltammetry (LSV) curves of CNS and CNS-Gr$_{0.7}$ photocathodes were characterized both under dark and light conditions in phosphate buffer (pH=7.4). As shown in Fig. 5b, the CNS-Gr$_{0.7}$ displays an increased cathodic photocurrent in comparison to CNS, suggesting that the hybrid of graphene with CNS can promote the charge separation and transfer.$^{23}$ In addition, UV-Vis absorption spectra clearly reveal that CNS-Gr$_{0.7}$ hybrid film on FTO red-shifts the absorption band edge to higher wavelength in comparison with that of the CNS film (Fig. 5c).$^{50}$ The CNS and CNS-Gr$_{0.7}$ films were further demonstrated to be hydrophilic by contact angle measurements (Fig. S10), which ensures good contact with the aqueous reaction system.$^{51}$

**Photoelectrochemical NADH Regeneration of CNS-Gr Hybrid Films**

Inspired by the process of natural photosynthesis that converts solar energy into chemical energy, a three-electrode PEC system is constructed for efficient coenzyme regeneration, employing CNS-Gr hybrid film as the photocathode and water as the electron donor (Fig. 6a)$^{52,53}$ In this case, the CNS or CNS-Gr film harvests incident visible light, and the resulting photogenerated electrons reduce M to M$_2$. Then, M$_2$ accepts a proton from water to generate M. NADH is regenerated when NAD$^+$ taking up two electrons and one proton from M$_2$. The sacrificial agent TEOA is not applied in this system, and the photogenerated holes are consumed by the electrons migrating through an external wire to the photocathode. Oxygen is evolved at Pt anode in the pure water reaction system.$^{54}$

The bending of energy band for CNS under applied bias greatly inhibits the recombination of the photogenerated electron-hole pairs. Cyclic voltammetry was applied to study the photoinduced electron-transfer mechanism from CNS-Gr$_{0.7}$ photocathode to M and NAD$^+$. As shown in Fig. 6b, the ternary system (CNS-Gr$_{0.7}$-M). Please do not adjust margins
In summary, we successfully synthesized homogeneous CNS film by interfacial self-assembly of nanosheet at air/water interface. The CNS dispersion was obtained via wet ball milling method in large scale, reaching up to 36 mg mL$^{-1}$. The as-prepared films could be easily transfer onto versatile substrates with good contact interface, which break the limitation of traditional in-situ thermal condensation method of N-rich precursors on the high-temperature-resistant substrates. The high-quality CNS-Gr hybrid films were further assembled on the conductive FTO at the interface, performing enhanced photoelectrochemical NADH regeneration ability employing [Cp*Rh(bpy)H]$^{2+}$ as the electron and proton mediator and water as the electron donor. The current work should shed light on the fabrication of high-performance g-C$_3$N$_4$ film catalyst and could find more application in future energy and environment related device fields.$^{59,60}$

**Conflicts of interest**

There are no conflicts to declare.

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