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Compact carbon nitride based copolymer film with controllable thickness for photoelectrochemical water splitting

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We report successful growth of high quality carbon nitride based copolymer (CNBC) films on various substrates (glass, FTO, TiO₂) through a facile solvothermal method with post-annealing. Structural characterizations of the films reveal the polymeric carbon nitride network consisting of tri-s-triazines and s-triazines bridged by different functional groups. The strong bonding between CNBC films and the substrates via covalent linkage ensures intimate contact and smooth interfacial charge transport. As such, the CNBC films exhibit excellent photoelectrochemical (PEC) performance, which is attributed to stronger visible light harvesting, better conductivity, and more efficient charge separation and transport, as compared to the reference electrode made by pasting bulk g-C₃N₄ powder. Further, we demonstrate that similar solvothermal approach can be also used to create CNBC films on TiO₂ surface, and the resulted CNBC/TiO₂ junction allows for vectorial charge transfer, giving greatly enhanced photocurrent responses. Importantly, this work provides a general guide of solvothermal methods for *in-situ* growing metal-free films on various substrates for efficient PEC water splitting.

1. Introduction

Photoelectrochemical (PEC) water splitting for conversion of solar light into chemical energy has attracted much attention as one of the most promising solutions for sustainable energy resources. Generally, the most commonly used photoelectrode materials are inorganic semiconductors including TiO₂, ZnO, BiVO₄, FeOOH, NiOOH, hematite and so on.^{1–7} In recent years, conjugated polymer-based semiconductors, despite of relatively lower photocatalytic efficiency as compared to many typical inorganic semiconductors (e.g. TiO₂, CdS etc.), have been developed for photocatalytic applications.^{8–16} Among them, graphitic carbon nitride (g-C₃N₄) is a promising metal-free photocatalyst having a great deal of advantages, including visible light absorption, tailorable band energy levels, and high stability. Some previous studies have shown that g-C₃N₄ can work as photoelectrodes for PEC applications.^{17–26} However, the previous pure g-C₃N₄ electrode presents limited PEC efficiencies due to its intrinsic drawbacks, such as poor conductivity, limited visible-light absorption up to 450 nm, and weak interfaces between the pasted bulk g-C₃N₄ layer and the

conducting substrate.

The photocatalytic activity of g-C₃N₄ is originated from the π -conjugated melem structures. As such, modifying the conjugated structure of g-C₃N₄ to extend the delocalization of π electrons would be an effective way to improve the intrinsic electronic properties of g-C₃N₄.^{27–29} It has been reported that the co-polymerization approach by coupling with structure-matching molecules can introduce functional groups into the carbon nitride matrix to adjust the π systems of conventional g-C₃N₄, which allows for tailoring its electronic properties, optical absorption, band energy levels and photocatalytic performance.^{30–32} Researchers have successfully inserted various aromatic moieties or π -rich organic groups (e.g. thiophene and diaminopyridine etc.) into the tri-s-triazine framework of g-C₃N₄.^{28,33} Indeed, the s-triazine unit, as the base for creating tri-s-triazine, is also a typical π -rich structure. Thus, it is envisaged that the delocalization of the π electrons can be further extended by simple integration of the s-triazine and tri-s-triazine units.

The fabrication of g-C₃N₄-based electrodes was commonly accomplished by gluing bulk g-C₃N₄ powder onto a conductive substrate³⁴ or pasting molecular precursors onto the substrate with post-annealing.²⁵ Both strategies usually result in thick g-C₃N₄ films with non-uniform thickness and poor contact with the substrate, which greatly restricted the film performance in the PEC tests. As is well known, semiconductor films that are directly grown on a substrate usually have intimate contact with the substrate, and very good film uniformity with tailorable thickness and controllable crystal structures. However, it is of great challenge to achieve large-area *in-situ*

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growth of uniform polymeric carbon nitride films on conductive substrates because the formation of carbon nitride framework usually requires calcination of pasted precursors at high temperature which likely causes severe agglomeration of precursor powder/crystals (during drying) and inhomogeneous polymerization/condensation of the precursors.

Herein, in this work, we developed a facile solvothermal method with post-heating for the first time to grow a carbon nitride based copolymer (CNBC) film on different substrates, (e.g. glass, FTO, and TiO_2/FTO) with desired thickness and density by controlling growth time, precursor concentration, and post-heating temperature. Significantly, the solvothermal process allows for covalent linkage of molecular precursors onto the substrate surface, allowing for strong and intimate interfacial contact. More importantly, the critical gas-liquid condition enables uniform distribution of precursors in the reactor, and thus homogeneous polymerization/condensation reactions to grow polymeric carbon nitride framework on the substrate surface. The obtained CNBC film upon post-heating exhibits enlarged conjugating structures between *s*-triazine and tri-*s*-triazine, which results in improved conductivity and the expanded visible light absorption. As a result, comparing to the reference $\text{g-C}_3\text{N}_4$ electrode obtained by pasting $\text{g-C}_3\text{N}_4$ powder onto FTO, the obtained electrodes with *in-situ* grown CNBC films showed greatly enhanced photocurrent density. Moreover, when the CNBC film was grown on the surface of TiO_2/FTO photoelectrodes, the photocurrent responses were further boosted due to vectorial charge transfer induced by the layer-by-layer configuration. This work demonstrates the feasibility of using solvothermal approach to fabricate semiconductor carbon nitride film for PEC water splitting. Significantly, the versatility and flexibility of solvothermal methods provides great potentials for uniform doping of functional groups and different elements into the carbon nitride framework by appropriately managing the precursor solution. This opens huge scope in future development of metal-free thin films towards efficient solar energy conversion.

2. Experimental

Sample preparation

All chemicals used in the experiments were reagent grade and used as received without further purification. The CNBC film on FTO (CNBC/FTO) was prepared via a solvothermal process with post annealing by using cyanuric chloride and cyanuric acid (molar ratio as ~ 1.8) as precursors. Typically, the FTO glasses ($1.0 \text{ cm} \times 2.5 \text{ cm}$) were washed in turn with acetone, ethanol and DI water under continuous sonication, and dried in N_2 flowing. Then, the washed FTO glasses were immersed in the basic piranha solution of $\text{NH}_3/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (volume ratio of 1:1:5) for 3 h at 60°C to clean the surface. After that, the treated FTO glasses were washed with DI water under continuous sonication, and dried in N_2 flowing. For growth of CNBC film, two pretreated FTO glasses were fixed on a Teflon holder and placed in a 20 ml Teflon-lined autoclave containing 15 ml solution of acetonitrile with 164 mg precursors dissolved inside. Subsequently, the autoclave was sealed and maintained

at 200°C for 20 hours. After reaction, the carbon nitride coated FTO glass with photoactive area of 1.5 cm^2 (inset of Fig. 1A) was obtained (denoted as CNBC-U/FTO), washed sequentially with distilled water and absolute ethanol, and then annealed at 450°C under Ar flow to obtain the CNBC/FTO film. The remained product in solution after solvothermal reaction, considered as un-annealed carbon nitride based copolymer, was collected via centrifugation, washed with absolute ethanol, and dried for structural characterizations. The intermediate products were also prepared through the same solvothermal reaction with reduced reaction time (4, 8, 12 and 16 hours). The same protocol was used to grow CNBC films onto the TiO_2/FTO glass (denoted as CNBC/ TiO_2/FTO after annealing), which was prepared by depositing Ti thin film via sputtering on the FTO glass followed by annealing at 500°C for 2 h in air. The standard $\text{g-C}_3\text{N}_4$ reference sample was prepared according to literatures through calcination of melamine at 550°C .⁸

Characterizations

The XRD patterns of all samples were collected on XRD-6000 X-ray diffractometer (Cu $\text{K}\alpha$ source) at a scan rate of 2° min^{-1} . SEM images were obtained by JEOL JSM-7600F scanning electron microscope at an acceleration voltage of 5 kV. UV-Vis absorption spectra were measured on Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA) with BaSO_4 reference. Fourier Transform Infrared spectra (FTIR) were recorded by Perkin Elmer Frouier Transform Infrared Spectrometer GX. X-ray Photoelectron Spectroscopy (XPS) was carried out on a VG ESCALAB 250 XPS system with a monochromatized Al $\text{K}\alpha$ X-ray source (15 kV, 200 W). Solid-state ^{13}C NMR tests were performed on a Bruker Advance DRX500 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out by using a TGA Q500 instrument in the temperature range of $20\text{--}800^\circ\text{C}$ at a scan rate of 10°C/min under nitrogen (40 ml min^{-1}) or air (60 ml min^{-1}). Elemental analysis (EA) results were collected from a Vario MICRO instrument.

Photoelectrochemical measurement

The photoelectrochemical tests were carried out by using the conventional three-electrode electrochemical cell including a working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. The prepared photoelectrodes were used as the working electrode and irradiated by simulated solar (1 sun, AM 1.5) in Na_2SO_4 solution (0.5 M). The Mott-Schottky curves were obtained through electrochemical impedance spectroscopy (EIS) by using Metrohm Autolab potentiostat (PGSTAT-30) equipped with a frequency analyser module. Potentials were applied versus the Ag/AgCl reference electrode and can be converted versus reversible hydrogen electrode (RHE) according to the Nernst equation as follows: $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + E_{\text{Ag/AgCl}} + 0.059 \text{ pH}$ ($E_{\text{Ag/AgCl}} = 0.197 \text{ V vs. SHE at } 25^\circ\text{C}$).

3. Results and discussion

Scheme 1 the copolymerization process for the formation of CNBC on FTO.

Growth of CNBC films

Growth of carbon nitride structures on FTO is initialized by grafting *s*-triazine units onto FTO surface through coupling reaction between cyanuric chloride and the hydroxyl groups on the FTO surface. During the solvothermal process, further polymerization reactions between surface *s*-triazine units and solution precursors enables continuous grafting of more *s*-triazine units (C_3N_3) onto FTO surface. In the meantime, tri-*s*-triazine units can be created through condensation of precursors, and are also capable of covalently grafting onto the FTO surface. Certainly, the grafted *s*-triazine units on FTO can also be further reacted and condensed towards tri-*s*-triazine units. Under the solvothermal conditions, the resulted carbon nitride based film is mainly composed by loosely stacked network of tri-*s*-triazines and *s*-triazines. Upon annealing at 450 °C, further condensation leads to a polymeric network structure of $(\text{C}_6\text{N}_7)_x\text{—X—}(\text{C}_3\text{N}_3)_y$, in which the tri-*s*-triazine units (C_6N_7) and *s*-triazine units (C_3N_3) are bridged by different groups (X), including —O— , —NH— , —NH—CO—NH— , and carbodiimide (—N=C=N—) groups. The route for the overall reaction process is illustrated in Scheme 1.

SEM images of the CNBC film before and after annealing are shown in Fig. 1. The un-annealed film (CNBC-U) on FTO glass shows uniform and smooth surface (Fig. 1A) with a granular size of ~ 10 nm (Fig. 1B). The cross-sectional view (Fig. 1C and D) indicates that the CNBC-U film has ~ 375 nm thickness after 20 hour reaction and contacts intimately with the FTO layer. After annealing at 450 °C, the obtained CNBC film became more compact with reduced thickness to 125 nm, suggesting

that the heat treatment led to further condensation and polymerization of CNBC-U film. In addition, the CNBC-U film thickness is directly correlated with the reaction time. Shorter reaction time from 20 to 4 hours led to reduced thickness from 375 to 65 nm (Fig. S2).

The growth of CNBC film on the TiO_2/FTO substrate followed the same reaction process. As shown in Fig. 2, the thickness of CNBC film on TiO_2 surface was around 500 nm after 20 hour reaction, and turned to ~ 105 nm upon annealing at 450 °C. The thickness difference as comparing with the film grown on FTO surface might be ascribed to the different surface reactivity of TiO_2 and SnO_2 .

Fig. 1 (A and B) SEM images of top view of CNBC-U/FTO film. (C and D) SEM images of cross-section of CNBC-U/FTO film. (E) SEM image of top view of CNBC/FTO. (F) SEM image of cross-section of CNBC/FTO. Insets of Fig. 1A and E show the digital photograph of CNBC-U/FTO and CNBC/FTO, respectively.

Fig. 2 SEM images of top view and cross-section of TiO_2/FTO film (A and B), $\text{CNBC-U}/\text{TiO}_2/\text{FTO}$ film (C and D), and $\text{CNBC}/\text{TiO}_2/\text{FTO}$ (E and F), respectively.

Structural characterizations of CNBC

To figure out the network structure of CNBC, we have characterized the obtained products by using XRD, elemental analysis, XPS, FTIR, and solid state NMR. Fig. 3A shows the XRD patterns of $\text{CNBC-U}/\text{FTO}$ and CNBC/FTO . We noted that all clear peaks are attributed to the FTO, while no peaks corresponding to carbon nitride film could be distinguished because the film is very thin with low crystallinity.

Fig. 3 (A) XRD patterns of CNBC/FTO film before and after annealing. (B) XRD patterns of $\text{g-C}_3\text{N}_4$ and CNBC before and after annealing.

As such, we have attempted to scratch the film away from the FTO substrate surface, and characterize the obtained powder (CNBC-U and CNBC). The XRD pattern of the obtained CNBC-U powder (Fig. 3B) shows a broad diffraction peak at 26.8° ($d \approx 0.332$ nm), corresponding to the stacking of the conjugated hexatomic heterocyclic system,³⁵ which is slightly shifted as comparing to the standard $\text{g-C}_3\text{N}_4$ reference (at 27.3° , $d \approx 0.323$ nm), suggesting an increased interlayer distance. There are no diffraction peaks arising from in-planar repeated packing in the crystal possibly due to the imperfect structure of CNBC-U with low polymerization degree and incomplete condensation.^{36–39} After annealing at 450°C in Ar, the CNBC powder presents a broad diffraction peak at $\sim 13.2^\circ$ ($d \approx 0.618$ nm) corresponding to the in-planar packing, and the intensity of the peak at 26.8° increases, indicating that high

temperature annealing induced further condensation of the carbon nitride matrix with improved crystallinity.

Elemental contents of the products were determined by the elemental analysis and XPS, and the results are summarized in Table S1. Elemental analysis of the CNBC-U powder reveals a N/C molar ratio of 1.09 and small amount of residual Cl (5.4 wt%). After annealing, the N/C molar ratio slightly increased to 1.1 for the CNBC powder, while the Cl element disappeared and oxygen content significantly decreased. Such N/C ratios are lower than that of standard $\text{g-C}_3\text{N}_4$ (theoretical value of N/C is 1.33) but higher than that of precursors (cyanuric chloride and cyanuric acid, C/N=1.0). This implies that the CNBC product might have a mixed network (C_9N_{10}) consisting of *s*-triazine (C_3N_3) and tri-*s*-triazine (C_6N_7). Comparing to the solution product (C/N=1.24),³⁶ the N/C molar ratio of the film is smaller, probably because the condensation of *s*-triazines towards tri-*s*-triazines is more difficult on FTO surface than in the solution phase.

Fig. 4 and Table 1 show the XPS results of CNBC films for identification of the chemical state of C, N, and O species in the films. For the CNBC-U film on FTO before annealing, the C 1s signals can be fitted into six peaks (Fig. 4A), 284.6 eV attributed to the aromatic carbon from contaminant carbon, 286.5 eV for C-Cl, 286.9 eV for -C-O-C- bridge, 287.7 eV for -C=O or -N=C=O, 288.3 eV for -N=C-N- in tri-*s*-triazine, and 289.0 eV for -NH-COO-.^{40–46} The N 1s signals can be fitted into five peaks (Fig. 4B), 398.6 eV for C=N=C in triazine, 399.0 eV for -N=C=O group, 399.8 eV for N-C₃ in tri-*s*-triazine, 400.5 eV for -NH-COO-, and 401 eV for $\text{H}_2\text{N-CN}_2$.^{38,41,43,47} Consistently, the O 1s spectrum shows two peaks at 531.8 and 533.5 eV, corresponding to C-O (C-O-C or C-OH) and C=O, respectively (Fig. 4C).^{48,49} The Cl 2p spectrum of $\text{CNBC-U}/\text{FTO}$ (Fig. 4D) shows two Cl 2p_{3/2} peaks centered at 200.3 and 196.9 eV attributed to the covalent chloride C-Cl species and ionic Cl species, respectively.^{50,51} Based upon on the above analyses and our previous studies,^{36,52,53} it can be concluded that the CNBC-U films have copolymer network structures composed by two segments, oxygen-containing tri-*s*-triazines and polymeric *s*-triazines. Both segments may have -N=C=O terminal groups, and are interconnected via -C-O-C- or -NH-COO- bridges, which can be further confirmed by FTIR and solid-state ^{13}C NMR.

For the CNBC/FTO sample after annealing, the C 1s curve (Fig. 4E) shows three distinct peaks at 286.9 eV, 287.7 eV and 288.3 eV corresponding to -N=C=N- bridges, -C=O/-N=C=O, and N=C-N in tri-*s*-triazine, respectively. The C 1s peaks at 286.5 eV and 289.0 eV (for C-Cl and -NH-COO- species in CNBC-U) disappeared and the peak at 287.7 eV (for -C=O and -N=C=O) decreased after annealing $\text{CNBC-U}/\text{FTO}$ film. The N 1s XPS curve (Fig. 4F) also can be fitted into five peaks at 398.6 eV, 399.0 eV, 399.8 eV, 400.5 eV, 401.0 eV for C=N=C in triazine (or -N=C=N-bridge), -N=C=O, N-C₃ in tri-*s*-triazine, -NH-CO-NH-, and $\text{H}_2\text{N-CN}_2$, respectively. It is clear that the N 1s peaks at 399.0 eV for -N=C=O and 401.0 eV for -NH₂ decreased after annealing, suggesting occurrence of condensation reactions by these groups. Correspondingly, the Cl 2p peaks for Cl species disappeared, and the O 1s peak at 533.5 eV for -N=C=O and -

NH-COO- species decreased (Fig. 4G and H). These results suggest that the annealing process leads to the condensation of CNBC-U through the reactions between -N=C=O , NH-COO- , -NH_2 , -Cl and -OH (the detailed route shown in Scheme 1).

Eventually, it forms a mixed network of $(\text{C}_6\text{N}_7)_x\text{-(C}_3\text{N}_3)_y$ bridged by -N=C=N- , NH-CONH- , -NH- or -C-O-C- bonds. Further analyses by FTIR and solid-state ^{13}C NMR can also support the proposed reaction processes and the resulted structures.

Fig. 4 the high-resolution C 1s, N 1s, O 1s and Cl 2p XPS spectra of CNBC-U/FTO (A, B, C, D) and CNBC/FTO (E, F, G, H).

Table 1 XPS peak positions of C1s, N1s, O 1s, and Cl 2p_{3/2} of CNBC-U/FTO and CNBC/FTO.

XPS peak	CNBC-U/FTO		CNBC/FTO	
	Peak position (eV)	Attribution	Peak position (eV)	Attribution
C 1s	286.5	C-Cl ⁴⁰	-	-
	286.9	-C-O-C ⁴³	286.9	-N=C=N- bridge ⁴³
	287.7	-C=O and -N=C=O ⁴¹	287.7	-C=O and -N=C=O ⁴¹
	288.3	-N=C-N- in tri-s-triazine ⁴³⁻⁴⁵	288.3	-N=C-N- in tri-s-triazine ⁴³⁻⁴⁵
	289.0	-NH-COO- ⁴⁶	-	-
N 1s	398.6	C-N=C in s-triazine ^{38,43}	398.6	C-N=C in s-triazine and -N=C=N-bridge ^{38,43}
	399.0	-N=C=O ^{41,43}	399.0	-N=C=O ^{41,43}
	399.8	N-C ₃ in tri-s-triazine ^{38,43}	399.8	N-C ₃ in tri-s-triazine ^{38,43}
	400.5	-NH-COO- ⁴⁷	400.5	-NH-CO-NH- ⁴⁷
	401.0	-NH ₂ ^{38,43}	401.0	-NH ₂ ^{38,43}
O 1s	531.8	-C-O-C and C-OH ^{48,49}	531.8	-C-O-C and C-OH ^{48,49}
	533.5	-N=C=O and -NH-COO- ^{48,49}	533.5	-N=C=O and -NH-COO- ^{48,49}
Cl 2p _{3/2}	196.9	ionic Cl species ⁵⁰	-	-
	200.4	C-Cl species ^{50,51}	-	-

Fig. 5A shows the FTIR spectra of the bulk $\text{g-C}_3\text{N}_4$ reference, CNBC-U, and CNBC. FTIR spectrum of CNBC-U displays two bands at 3342 and 3168 cm^{-1} in the range of 3000-3500 cm^{-1} , several characteristic bands in the range of 1200-1650 cm^{-1} , a band at 806 cm^{-1} , which can be attributed to the N-H stretches, a fingerprint region ($\nu(\text{C-NH-C})$ and $\nu(\text{C=N})$ stretching vibrations) of s-triazine ring, and the out of plane bending,⁵⁴⁻⁵⁶ respectively. In particular, the band at 2230 cm^{-1} for -N=C=O stretches indicates that the cyanuric acid can be decomposed

under solvothermal conditions to supply -N=C=O groups that are essential for other polymerization and condensation processes. Moreover, comparing to the FTIR spectrum of the reference $\text{g-C}_3\text{N}_4$, the characteristic bands for CNBC-U in the range of 1200-1650 cm^{-1} shows slightly shift and lower resolution ratio, which might be due to network of s-triazine and tri-s-triazine bridged by -C-O-C- or -NH-COO- bonds and mixture of various segments with different polymerization degree. After annealing at 450 $^{\circ}\text{C}$, the band at 2230 cm^{-1} shifts

to 2200 cm⁻¹ corresponding to the -N=C=N- bridge formed in CNBC through the reactions between -N=C=O groups or with -NH-COOH. And the further condensation/polymerization processes lead to removal of those segments with low polymerization degree, resulting in higher intensity of the bands at 1200-1650 cm⁻¹.

The solid-state ¹³C NMR spectra of the samples are shown in Fig. 5B. The CNBC-U shows a distinct peak at 162.3 ppm and a broad band in the range of 140-159 ppm which can be fitted into three peaks at 158.0 ppm, 155.0 ppm and 150.0 ppm, respectively. Among them, the two signals, 162.3 ppm for the carbon atoms bonded to three N atoms and 155.0 ppm for the carbon atoms in the N₂C-NH₂ unit^{10,57,58} (Table 2), indicate the existence of characteristic tri-*s*-triazine units in CNBC-U. The signals at 158.0 ppm and 150.0 ppm might be attributed to the -NH-COO- bridge between two *s*-triazine units,⁵⁹ and the -C=O (or -N=C=O) bonded to *s*-triazine,³⁶ respectively. Upon annealing, the signal at 150.0 ppm for -C=O (or -N=C=O) almost disappeared, which is consistent with XPS analyses showing elimination of -C=O groups. The CNBC sample presents three signals (Fig. 5B) at 163.2 ppm for tri-*s*-triazine, 157.9 ppm for the -NH-C(O)-NH- bridges,⁶⁰⁻⁶² and 155.0 ppm for the N₂C-NH₂ units or -N=C=N- bridges. These results also suggest that at 450 °C, the condensation reactions between -C=O, -N=C=O and -NH-COO- groups in CNBC-U leads to the formation of -NH-C(O)-NH- or -N=C=N- bridges.

Table 2. ¹³C NMR peaks of g-C₃N₄, CNBC-U, and CNBC.

Samples	¹³ C (ppm)	Attribution
g-C ₃ N ₄	163.2	-CN ₃ ^{10,57,58}
	155.0	N ₂ C-NH ₂ ^{10,57,58}
CNBC-U	162.3	-CN ₃ ^{10,57,58}
	158.0	-NH-COO- bridge ⁵⁹
	155.0	N ₂ C-NH ₂ , C atoms in triazine bonded with -O-C(O)-NH- bridge ^{10,57,58}
	150.0	-C=O, C atoms in triazine bonded with -N=C=O ³⁶
CNBC	163.2	-CN ₃ ^{10,57,58}
	157.9	-NH-C(O)-NH- bridge ⁶⁰⁻⁶²
	155.0	N ₂ C-NH ₂ , C atoms in triazine bonded with -NH-C(O)-NH- or -N=C=N- bridge ^{10,57,58}

The co-polymerization of *s*-triazines and tri-*s*-triazines bridged by some functional groups evidently changes the conventional π systems, band structure, electronic and optical properties. In the UV-visible absorption spectra (Fig. S4), the CNBC-U/FTO presents a long absorption edge (up to 610 nm) as compared to the reference g-C₃N₄ (having an absorption edge at ~460 nm) due to the mixed network of (C₆N₇)_x-(C₃N₃)_y-(N=C=O)_z bridged by C-O-C or NH-COO- bonds. Upon annealing at 450 °C, the CNBC/FTO shows red-shifted absorption edge to 650 nm with increased absorption intensity in the region of 600-800 nm. Because the condensation between -N=C=O and/or -NH-COOH groups leads to the formation of carbodiimide (-N=C=N-) bridge, which would greatly enlarge the conjugation system between *s*-triazines and tri-*s*-triazines.

Based on the above characterization results, the chemical reactions of the formation processes of CNBC can be illustrated in Scheme 1. Under the solvothermal condition, some cyanuric acid molecules are firstly decomposed into the cyanic acid (HN=C=O), which can be reacted with the *s*-triazine precursors (cyanuric chloride and cyanuric acid) to generate -N=C=O group bonded to *s*-triazines species. Then, the tri-*s*-triazine species are created after a series of condensation processes. Subsequently, *s*-triazine and tri-*s*-triazine units are connected via -C-O-C- or -NH-CO-O- bridges to form mixed network of (C₆N₇)_x-(C₃N₃)_y-(N=C=O)_z. Further condensation of functional groups can be initialized upon high-temperature annealing. As such, it is believed that the resulted CNBC film has the network of *s*-triazines and tri-*s*-triazines bridged by functional groups such as carbodiimide (N=C=N), NH-CO-NH and C-O-C.

Fig. 5 (A) FTIR and (B) NMR spectra of g-C₃N₄ and CNBC powders before and after annealing.

Fig. 6 (A) Linear sweep voltammetry (LSV), (B) photocurrent (i - t curve) and (C) electrochemical impedance spectroscopy (EIS) of CNBC-U/FTO, CNBC/FTO, and $g\text{-C}_3\text{N}_4/\text{FTO}$ reference; (D) Linear sweep voltammetry (LSV) and (E) photocurrent (i - t curve) of anatase TiO_2/FTO film, CNBC-U/ TiO_2/FTO film, and CNBC/ TiO_2/FTO film. (F) Mott-Schottky plots of CNBC-U/FTO, CNBC/FTO, and $g\text{-C}_3\text{N}_4/\text{FTO}$ reference.

Photoelectrochemical tests of CNBC film on substrates

The photoelectrochemical (PEC) properties of the prepared film samples as photoanode were measured by using a three electrode system in an aqueous solution containing 0.5 M Na_2SO_4 (pH $\approx$ 7.0). The $g\text{-C}_3\text{N}_4/\text{FTO}$ electrode prepared by pasting the bulk $g\text{-C}_3\text{N}_4$ powder on FTO (see supporting information for the detailed preparation process) was used for comparison. Fig. 6A shows the chopped current density-voltage (J - V) curves of different photoanode samples under simulated solar irradiation (1 sun, AM 1.5). Comparing to the reference $g\text{-C}_3\text{N}_4/\text{FTO}$, the CNBC-U/FTO photoanode presented much larger photocurrent density with a cathodic shift in the onset potential for water oxidation. The enhanced PEC activities of CNBC-U/FTO might be due to the self-sensitized structure which enables stronger visible-light harvesting and more effective charge transfer. The post-annealing of CNBC-U/FTO leads to further increased photocurrent density for the

CNBC/FTO photoanode. When the applied bias is set as 1.23 V vs SHE (theoretical value of electrochemical water splitting for O_2 evolution), the anodic photocurrent of CNBC/FTO is 8.4 times of that of $g\text{-C}_3\text{N}_4/\text{FTO}$ reference, as shown in Fig. 6B. These results indicate that the prepared CNBC/FTO film can serve as a more effective photoanode for PEC conversion of solar light into the chemical energy as compared to the traditional $g\text{-C}_3\text{N}_4/\text{FTO}$ electrode.

To understanding the charge-transport and interfacial charge-transfer process in the CNBC/FTO electrode, we carried out measurement of electrochemical impedance spectroscopy (EIS) on these photoelectrodes. Fig. 6C shows the Nyquist impedance plots for the prepared samples, which present one semicircle in the high frequency range and can represent the charge transfer resistance. In the dark, the radii of the semicircles for $g\text{-C}_3\text{N}_4$, CNBC-U/FTO, and CNBC/FTO are very large with increasing order of CNBC/FTO < $g\text{-C}_3\text{N}_4$ < CNBC-

U/FTO, suggesting that the CNBC film has comparably lower resistance. The light irradiation leads to decrease of the semicircles radii with increasing order of CNBC/FTO < CNBC-U/FTO < g-C₃N₄ (perfectly consistent with the photocurrent intensity under light irradiation). These results indicate more effective generation and transport of photogenerated charge carriers in CNBC-U and CNBC films as compared to the reference g-C₃N₄ film.

The excellent PEC performance of the CNBC/FTO sample could be attributed to the enhanced charge transport in the conjugated carbon nitride network, intimate contact between CNBC and FTO allowing for effective interfacial charge transfer, and the enhanced visible light harvesting of CNBC (Fig. S4). In particular, the post annealing leads to creation of carbodiimide (N=C=N) bridges that would greatly enlarge the conjugation system between s-triazines and tri-s-triazines, resulting in better conductivity.

The CNBC/TiO₂/FTO samples before and after annealing were also used as photoanode for PEC tests under the same conditions. The chopped current density-voltage (*J*-*V*) curves and transient photocurrent curves at a bias of 1.23 V (vs SHE) are shown in Fig. 6D and E, respectively. The reference anatase TiO₂/FTO electrode shows an onset potential of 0.53 V (vs SHE) for water oxidation under solar irradiation. After solvothermal deposition of CNBC-U film on the TiO₂/FTO surface, the obtained electrode shows decreased photocurrent, which might be ascribed to the low conductivity of CNBC-U (Fig. 6C) and mismatched band energy levels between CNBC-U and TiO₂. Upon annealing, the CNBC/TiO₂/FTO photoanode showed remarkably enhanced photocurrent density with a cathodic shift of ~0.32 V in the onset potential for water oxidation (Fig. 6D).

Fig. 7 Schematic illustration for the PEC setup and charge transfer route in the CNBC/TiO₂/FTO film.

The Mott-Schottky curves (Fig. 6F) indicate that the flat-band potentials of CNBC-U and CNBC film are -0.9 and -1.0 V vs Ag/AgCl (-4.2 and -4.1 eV vs vacuum), respectively. The valence band levels of CNBC-U and CNBC film were estimated as -7.16 and -6.74 eV (vs. vacuum), respectively, by Ultraviolet photoelectron spectroscopy (Fig. S8). The band energy level match between CNBC, TiO₂ (conduction band at -4.2 eV vs vacuum)⁶³ and FTO (work function of -4.4 eV)^{64,65} is beneficial to the interfacial charge transfer between different layers. Therefore, the photoexcited electrons can readily transfer from conduction band of CNBC to TiO₂ towards FTO substrate under solar light irradiation, as illustrated in Fig. 7. In the meantime, the photogenerated holes transport from TiO₂ to the CNBC film for water oxidation. Therefore, we believe that the CNBC film can be used as a general economic and efficient metal free photoelectrode material, and can also be grown on various semiconductor metal oxide surface to enhance their PEC efficiency because of the broad visible light-harvesting capability of CNBC film with excellent conductivity.

Conclusions

In summary, we have developed a facile solvothermal method to in-situ grow novel CNBC thin films on various substrates, such as glass, FTO, and TiO₂/FTO. The strong bonding between CNBC films and the substrates via covalent linkage ensures intimate contact and smooth interfacial charge transport. Structural characterizations of the films indicate that the resulted CNBC films are consisting of tri-s-triazines and s-triazines bridged by different functional groups including carbodiimide (N=C=N), NH-CO-NH and C-O-C. In particular, the carbodiimide (N=C=N) bridges would greatly enlarge the conjugation system between s-triazines and tri-s-triazines, resulting in better conductivity and stronger visible light harvesting. As such, the obtained CNBC films exhibit excellent PEC performance as compared to the reference electrode made by pasting bulk g-C₃N₄ powder. Further, we demonstrate that similar solvothermal approach can be also used to create CNBC films on TiO₂ surface, and the resulted CNBC/TiO₂ junction allows for vectorial charge transfer, giving greatly enhanced photocurrent responses. This work is important because it provides a general guide of solvothermal methods for in-situ growing metal-free films on various substrates for efficient PEC water splitting.

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Notes and references

- W. D. Chemelewski, H.-C. Lee, J.-F. Lin, A. J. Bard and C. B. Mullins, *J. Am. Chem. Soc.*, 2014, **136**, 2843-2850.
- F. Le Formal, S. R. Pendlebury, M. Cornuz, S. D. Tilley, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2014, **136**, 2564-2574.
- M. T. Mayer, C. Du and D. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 12406-12409.
- E. M. P. Steinmiller and K.-S. Choi, *P. Natl. Acad. Sci.*, 2009, **106**, 20633-20636.
- G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R. C. Fitzmorris, C. Wang, J. Z. Zhang and Y. Li, *Nano Lett.*, 2011, **11**, 3026-3033.
- M. Ye, J. Gong, Y. Lai, C. Lin and Z. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 15720-15723.
- T. W. Kim and K.-S. Choi, *Science*, 2014, **343**, 990-994.
- X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.
- Z. Zhang, J. Long, L. Yang, W. Chen, W. Dai, X. Fu and X. Wang, *Chem. Sci.*, 2011, **2**, 1826-1830.
- J. R. Holst and E. G. Gillan, *J. Am. Chem. Soc.*, 2008, **130**, 7373-7379.
- H. Ou, L. Lin, Y. Zheng, P. Yang, Y. Fang and X. Wang, *Adv. Mater.*, 2017, **29**, 1700008.
- D. Zheng, X.-N. Cao and X. Wang, *Angew. Chem. Int. Edit.*, 2016, **55**, 11512-11516.
- H. Ou, P. Yang, L. Lin, M. Anpo and X. Wang, *Angew. Chem. Int. Edit.*, 10.1002/anie.201705926.
- F. Guo, P. Yang, Z. Pan, X.-N. Cao, Z. Xie and X. Wang, *Angew. Chem.*, 2017, **129**, 8343-8347.
- L. Lin, H. Ou, Y. Zhang and X. Wang, *ACS Catal.*, 2016, **6**, 3921-3931.
- Z. Zhang, J. Huang, Y. Fang, M. Zhang, K. Liu and B. Dong, *Adv. Mater.*, 2017, **29**, 1606688.
- J. Bian, Q. Li, C. Huang, J. Li, Y. Guo, M. Zaw and R.-Q. Zhang, *Nano Energy*, 2015, **15**, 353-361.
- S. Lou, Z. Zhou, Y. Shen, Z. Zhan, J. Wang, S. Liu and Y. Zhang, *ACS Appl. Mater. Inter.*, 2016, **8**, 22287-22294.
- Y. P. Yuan, W. T. Xu, L. S. Yin, S. W. Cao, Y. S. Liao, Y. Q. Tng and C. Xue, *Int. J. Hydrogen Energy*, 2013, **38**, 13159-13163.
- J. Zhang, M. Zhang, L. Lin and X. Wang, *Angew. Chem.*, 2015, **127**, 6395-6399.
- J. Bian, J. Li, S. Kalytchuk, Y. Wang, Q. Li, T. C. Lau, T. A. Niehaus, A. L. Rogach and R.-Q. Zhang, *ChemPhysChem*, 2015, **16**, 954-959.
- Q. Gu, Z. W. Gao, H. Zhao, Z. Z. Lou, Y. S. Liao and C. Xue, *RSC Adv.*, 2015, **5**, 49317-49325.
- J. Xu, T. J. K. Brenner, L. Chabanne, D. Neher, M. Antonietti and M. Shalom, *J. Am. Chem. Soc.*, 2014, **136**, 13486-13489.
- J. Liu, H. Wang, Z. P. Chen, H. Moehwald, S. Fiechter, R. van de Krol, L. Wen, L. Jiang and M. Antonietti, *Adv. Mater.*, 2015, **27**, 712-718.
- M. Shalom, S. Gimenez, F. Schipper, I. Herraiz-Cardona, J. Bisquert and M. Antonietti, *Angew. Chem.*, 2014, **126**, 3728-3732.
- Y. Kikuchi, X. Chang, Y. Sakakibara, K. Y. Inoue, T. Matsue, T. Nozawa and S. Samukawa, *Carbon*, 2015, **93**, 207-216.
- W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong and S.-P. Chai, *Chem. Rev.*, 2016, **116**, 7159-7329.
- Z. Chen, P. Sun, B. Fan, Q. Liu, Z. Zhang and X. Fang, *Appl. Catal. B: Environ.*, 2015, **170-171**, 10-16.
- J. Tian, L. Zhang, X. Fan, Y. Zhou, M. Wang, R. Cheng, M. Li, X. Kan, X. Jin, Z. Liu, Y. Gao and J. Shi, *J. Mater. Chem. A*, 2016, **4**, 13814-13821.
- W. Ho, Z. Zhang, W. Lin, S. Huang, X. Zhang, X. Wang and Y. Huang, *ACS Appl. Mater. Inter.*, 2015, **7**, 5497-5505.
- S. Chen, C. Wang, B. R. Bunes, Y. Li, C. Wang and L. Zang, *Appl. Catal. A: Gen.*, 2015, **498**, 63-68.
- Y. Shiraishi, S. Kanazawa, Y. Kofuji, H. Sakamoto, S. Ichikawa, S. Tanaka and T. Hirai, *Angew. Chem.*, 2014, **126**, 13672-13677.
- J. Zhang, M. Zhang, S. Lin, X. Fu and X. Wang, *J. Catal.*, 2014, **310**, 24-30.
- Y. Zhang, A. Thomas, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 50-51.
- A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Muller, R. Schlogl and J. M. Carlsson, *J. Mater. Chem.*, 2008, **18**, 4893-4908.
- Q. Gu, Z. Gao and C. Xue, *Small*, 2016, **12**, 3543-3549.
- Y. Kang, Y. Yang, L.-C. Yin, X. Kang, G. Liu and H.-M. Cheng, *Adv. Mater.*, 2015, **27**, 4572-4577.
- Q. Han, B. Wang, Y. Zhao, C. Hu and L. Qu, *Angew. Chem. Int. Edit.*, 2015, **54**, 11433-11437.
- X. She, H. Xu, Y. Xu, J. Yan, J. Xia, L. Xu, Y. Song, Y. Jiang, Q. Zhang and H. Li, *J. Mater. Chem. A*, 2014, **2**, 2563-2570.
- A. Pérez-Cadenas, x, F. n, F. J. Maldonado-Hódar and C. Moreno-Castilla, *Carbon*, 2003, **41**, 473-478.
- E. Z. Ciftlikli, J. Lallo, E. Y. M. Lee, S. Rangan, S. D. Senanayake and B. J. Hinch, *J. Catal.*, 2012, **295**, 269-273.
- A. P. Dementjev, A. de Graaf, M. C. M. van de Sanden, K. I. Maslakov, A. V. Naumkin and A. A. Serov, *Diam. Relat. Mater.*, 2000, **9**, 1904-1907.
- H. Li, S. Gan, H. Wang, D. Han and L. Niu, *Adv. Mater.*, 2015, **27**, 6906-6913.
- P. Niu, L. Zhang, G. Liu and H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763-4770.
- J. Zhang, M. Zhang, C. Yang and X. Wang, *Adv. Mater.*, 2014, **26**, 4121-4126.
- S.-h. Hsu and W.-C. Chen, *Biomaterials*, 2000, **21**, 359-367.
- Q. Peng, X. He, Y. Li, C. Wang, R. Wang, P. Hu, Y. Yan and T. Sritharan, *J. Mater. Chem.*, 2012, **22**, 5928-5931.
- F.-X. Xiao, J. Miao and B. Liu, *J. Am. Chem. Soc.*, 2014, **136**, 1559-1569.
- D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang and G. Yu, *Nano Lett.*, 2009, **9**, 1752-1758.
- H. E. Cingil, J. A. Balmer, S. P. Armes and P. S. Bain, *Polym. Chem.*, 2010, **1**, 1323-1331.
- J. Gu, M. J. Hu, Q. Q. Guo, Z. F. Ding, X. L. Sun and J. Yang, *RSC Adv.*, 2014, **4**, 50141-50144.
- Q. Gu, J. Liu, Z. Gao and C. Xue, *Chem. Asian J.*, 2016, **11**, 3169-3173.
- Q. Gu, H. Sun, Z. Xie, Z. Gao and C. Xue, *Appl. Surf. Sci.*, 2017, **396**, 1808-1815.
- J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat. Commun.*, 2012, 1139.
- B. V. Lotsch, M. Döblinger, J. Sehnert, L. Seyfarth, J. Senker, O. Oeckler and W. Schnick, *Chem. Eur. J.*, 2007, **13**, 4969-4980.
- M. J. Bojdys, J.-O. Müller, M. Antonietti and A. Thomas, *Chem. Eur. J.*, 2008, **14**, 8177-8182.
- B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller and W. Schnick, *J. Am. Chem. Soc.*, 2003, **125**, 10288-10300.
- K. Kailasam, J. D. Epping, A. Thomas, S. Losse and H. Junge, *Energ. Environ. Sci.*, 2011, **4**, 4668-4674.
- E. M. Hampe and D. M. Rudkevich, *Tetrahedron*, 2003, **59**, 9619-9625.
- Z. Li, *J. Ind. Eng. Chem.*, 2014, **20**, 586-590.
- A. Grube and M. Köck, *Angew. Chem. Int. Edit.*, 2007, **46**, 2320-2324.

- 62 I. P. Tsypysheva, A. V. Koval'skaya, N. S. Makara, A. N. Lobov, I. A. Petrenko, E. G. Galkin, T. A. Sapozhnikova, F. S. Zarudii and M. S. Yunusov, *Chem. Nat. Compound.*, 2012, **48**, 629-634.
- 63 M. Gratzel, *Nature*, 2001, **414**, 338-344.
- 64 A. Andersson, N. Johansson, P. Bröms, N. Yu, D. Lupo and W. R. Salaneck, *Adv. Mater.*, 1998, **10**, 859-863.
- 65 X. Wang, L. Zhi and K. Müllen, *Nano Lett.*, 2008, **8**, 323-327.