Mediated Growth of Carbon Nitride Films via Spray-Coated Seeding Layers for Photoelectrochemical Applications

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Polymeric carbon nitride (CN) has emerged as a promising semiconductor in photoelectrochemical devices, thanks to its unique electronic and catalytic properties, low price, stability in various chemical environments, and benign nature. Decent progress in the deposition and growth of CN layers on substrates has been achieved using several deposition and growth methods; however, the properties of the layer, including the quality of its contact with the substrate and its structural properties, are still largely dependent on the surface properties of said substrate. Here, we introduce a new approach in which a spray-coated seeding layer composed of CN monomers directs the growth of a homogenous, thick CN layer on a substrate by calcination at high temperature in the presence of melamine vapor. Uniform CN layers with strong adhesion to the substrate were obtained. The influence of the seeding layer and the vapor composition on the photoelectrochemical, optical, and structural properties was studied in detail. The best-performing electrode, based on urea as the seeding layer, demonstrates good activity as a photoanode in photoelectrochemical cells, reaching up to $300 \mu\text{A cm}^{-2}$ in the presence of a hole scavenger.

1. Introduction

Polymeric carbon nitride materials (CNs) have emerged as low-cost, chemically stable photo- and electro-catalysts for various reactions such as water splitting, CO₂ reduction, and other organic transformation reactions.^[1-10] In the last few years, efforts to integrate carbon nitride films into photoelectronic and photoelectrochemical devices have increased, motivated by the unique photophysical properties of carbon nitride (energy band positions and tunable bandgap) and its stability under harsh chemical environments.^[11-12] However, the deposition/growth of a CN layer in intimate contact with the substrate remains an ongoing challenge.^[13-15] To this end, several gas-phase-based methods to grow CN layers on a substrate have been developed: chemical vapor deposition (CVD),^[16-17] thermal vapor condensation (TVC),^[18-21] microwave-assisted condensation,^[22] alongside others. However, in all scenarios, one of the main bottlenecks for the growth of a homogenous and firmly attached layer is the poor interaction of CN with the surface of the substrate. This is especially the case for methods involving the adsorption of a gas-phase reactant (*e.g.*, CVD) since solid-gas interactions between the substrate and the CN monomer are required for the reaction to occur.^[23] Therefore, the CN coatings obtained so far have mostly consisted of thin, poorly attached layers.

One approach to directing the growth of materials by a gas-phase reaction is to use a seeding layer to facilitate the nucleation process.^[24-27] Furthermore, a thicker layer can be prepared by this approach, owing to the large roughness induced by the seeding layer compared to a flat substrate. For a controlled gas-phase growth of a CN layer on a substrate, a homogenous seeding layer of controlled thickness consisting of CN monomers should be deposited before the thermal condensation. Spray coating is a facile, repeatable, and large-scale method to coat a substrate with a wide diversity of molecules and materials.^[28-29] In this technique, a liquid is atomized into a mist of even micron-sized droplets using ultrasonic vibrations in the nozzle; it can then be easily and controllably deposited as a layer on a variety of (possibly heated) substrates.

Herein we report the use of spray coating to deposit a seeding layer of urea and other CN monomers, for the direct growth of CN films on substrates by calcination in the presence of melamine vapor. The seeding layer provides nucleation sites promoting the growth of the CN film in the form of a homogenous layer in intimate contact with the substrate, thus improving the photoelectronic properties of the electrode. The morphology, structural properties, and optical properties of the obtained CN films were investigated. The photoelectrochemical performance was measured for a model water-splitting photoelectrochemical cell (PEC) setup; specifically, hydrogen evolution reaction in the presence of a hole scavenger was measured, which accords with the United Nation's sustainable development goals as a source of affordable and clean energy.^[30-34]

2. Results and Discussion

2.1. Preparation and Characterization of Urea Films

The synthetic route is illustrated in **Figure 1a**. The first step is the deposition of a CN-precursor seeding layer of controlled thickness. Here, an aqueous urea solution (375 g L^{-1} ; the solubility of urea at room temperature is 1096 g L^{-1})^[35] was sprayed on fluorine-doped tin oxide (FTO) coated glass using an ultrasonic spray coater, forming a uniform layer of urea on the FTO. The spraying process includes a variable number of repetitive spray cycles; several films were prepared and labeled as U_x , where x represents the number of spray cycles: 5, 10, 50, or 100. The X-ray diffraction (XRD) patterns of U_{10} and urea powder exhibit similar features (Figure 1b); the additional diffraction signals for U_{10} are attributed to the FTO substrate. The Fourier-transform infrared (FTIR) spectra of U_{10} and urea powder show similar N–H vibrations in the range of $3230\text{--}3410 \text{ cm}^{-1}$, as well as a C=O stretching band at $\sim 1660 \text{ cm}^{-1}$, which further confirms the successful deposition of urea on the FTO (**Figure S1**). Top-view and cross-sectional scanning electron microscopy (SEM) images disclose the morphology of the obtained U_x films: as the number of spray cycles increases, the layer becomes thicker and rougher (Figure 1c and **S2**).

2.2. Preparation and Characterization of CN Films

The calcination of the U_x films in the presence of melamine powder (0.5 g at the bottom of a closed, but not sealed, reaction glass tube at 550 °C under N_2 atmosphere for 4 hours) led to the formation of CN electrodes (labeled as $CN-U_xM_{0.5}$). During the thermal treatment, the melamine sublimates, and the vapor is deposited on the urea-coated FTO substrate,^[24] where the urea coating serves as a seeding layer for the growth of the CN. Motivated by the high photocurrent density of $CN-U_{10}M_{0.5}$ under operational PEC conditions (as will be shown later), we prepared another electrode by spraying 10 cycles of urea solution as a seeding layer, followed by calcination in the presence of 1.0 g of melamine (labeled as $CN-U_{10}M_1$) instead of the 0.5 g that was used in all other cases.

To evaluate its importance in the formation of the final CN film, we performed a similar calcination process in the absence of the seeding layer (namely, the CN film was created by deposition of melamine vapor on bare FTO, labeled as $CN-M_{0.5}$). Without the seeding layer, the process resulted in incomplete coverage of the substrate by the CN film. Indeed, top-view and cross-sectional SEM images show that $CN-M_{0.5}$ consists of a patchy, uneven distribution of CN structures that only partially covers the FTO surface (**Figure 2a–b**). In contrast, while $CN-U_5M_{0.5}$ has a similar morphology to that of $CN-M_{0.5}$, it provides better coverage of the substrate (**Figure S3a–b**). This difference proves the critical role of the seeding layer in the formation of a uniform CN film on the FTO. We also performed the same calcination process in the absence of melamine powder in the reaction tube; most of the urea film sublimated during calcination, and no substantial CN film was formed on the FTO. Therefore, we conclude that both the seeding layer and the melamine vapor are essential for the growth of a CN layer that fully covers the FTO.

The top-view and cross-sectional SEM images of $CN-U_xM_{0.5}$ and $CN-U_{10}M_1$ (Figure 2c–d and S3) reveal interesting outcomes. The top-view SEM images of $CN-U_{10}M_{0.5}$, $CN-U_{50}M_{0.5}$, $CN-U_{100}M_{0.5}$, and $CN-U_{10}M_1$ all show uniform coating of the FTO. However, their

cross-sectional SEM images reveal differences: CN-U₁₀M_{0.5} is very compact and has the fullest contact to the FTO and a uniform layer thickness, whereas the contact of CN-U₅₀M_{0.5} and CN-U₁₀₀M_{0.5} with the FTO is less homogenous. Besides, CN-U₁₀M₁ shows significant variations in its thickness, which is likely due to an excess of melamine powder during calcination.

The XRD patterns of the obtained CN electrodes (**Figure 3a**) exhibit two typical CN signals corresponding to an in-plane (100) diffraction at 12.8° and an interplanar stacking (002) diffraction at 27.6°.^[36] The FTIR spectra of the CN electrodes (**Figure S4**) show signals in the 1100–1700 cm⁻¹ range that correspond to C–N heterocycles stretching modes. The peaks at ~800 cm⁻¹ are attributed to the breathing vibration of the heptazine units in CN films, whereas the broad bands at ~3000–3600 cm⁻¹ match the stretching vibration of N–H in the amino groups resulting from incomplete polymerization. The X-ray photoelectron spectroscopy (XPS) spectra of CN-U₁₀M_{0.5} (**Figure S5**) confirm the successful growth of CN films. The C1s spectrum presents three peaks located at 284.9 eV, 288.0 eV, and 289.4 eV, which correspond to C–C from the carbonaceous environment, N–C=N coordination, and O–C=O, respectively, with the latter possibly resulting from partial oxidation of the CN film.^[37] The N1s spectrum reveals three peaks located at 398.4 eV, 399.5 eV, and 400.8 eV, attributed to C=N–C, N–(C)₃, and N–H, respectively. Hence, the XRD, FTIR, and XPS results confirm the formation of tri-s-triazine-based CN.

The UV-vis absorbance spectra of all CN electrodes exhibit similar features except that of CN-M_{0.5}, which displays the highest transmittance, owing to the uneven appearance of CN-M_{0.5} (**Figure 3b**). A Tauc plot analysis (**Figure 3c**) reveals an optical bandgap in the 2.60–2.64 eV range for the CN–U_xM_y films, as expected for CN materials.^[38] The CN–U₁₀M_{0.5} film has the narrowest estimated bandgap (2.60 eV). It also exhibits the lowest photoluminescence (PL) intensity (**Figure 3d**), suggesting nonradiative recombination paths of photogenerated electron-hole pairs caused by surface states.

2.3. Adhesion Test

To evaluate the mechanical stability and adhesion of the CN films to the FTO, we covered CN–U₁₀M_{0.5}, CN–M_{0.5}, and CN–U₁₀M₁ with scotch tape and placed a heavy object (*ca.* 1.5 kg) on top of each sample for two hours (**Figure S6**). Removal of the scotch tape revealed that CN–U₁₀M_{0.5} largely remained uniform, whereas CN–M_{0.5} was affected to a greater extent, clearly illustrating the benefit of using a seeding layer. CN–U₁₀M₁ peeled off partially, probably because of the thickness differences in different areas of the electrode, as its cross-sectional SEM image shows (Figure S3h).

2.4. Versatility of the Method

The deposition of a urea seeding layer by spray coating followed by the growth of a CN film from melamine vapor during calcination was also achieved on a glass slide and carbon cloth (**Figure S7a–c**). A similar procedure was successfully carried out on a 9 cm × 1.2 cm FTO slide to show the applicability of the method to larger surfaces (Figure S7d). Furthermore, for the sake of example, we successfully used thiourea and alanine instead of urea as the seeding layer (Figure S7e and S7f, respectively) and substituted thiourea for melamine as the precursor that undergoes sublimation in the test tube (Figure S7g). These proof-of-principle results indicate that the CN electrodes can be prepared from different monomers and that the seeding layer promotes the growth of a CN film regardless of the type and size of the substrate. However, further optimization is needed for each system.

2.5. PEC performance of the CN Electrodes

The activity of the CN electrodes as water-splitting photoanodes was tested in a standard three-electrode system. Chronoamperometric measurements of the CN electrodes were performed at 1.23 V *vs.* RHE in 0.1 M KOH under 1-sun front- and back-side illumination (**Figure 4a and S8**). The highest photocurrent density (*ca.* 110 $\mu\text{A cm}^{-2}$) was obtained using a CN–U₁₀M_{0.5} photoelectrode under back-side illumination. We ascribe this to the electron diffusion length being the limiting factor in charge separation and transport.^[39] Additional chronoamperometry

measurements were conducted in the presence of triethanolamine (TEOA) as a hole scavenger (10% (v/v) TEOA in 0.1 M KOH) to test the efficiency of electron transport, assuming most photogenerated holes are consumed by TEOA (Figure 4b and S9). Under these conditions, both photocurrent density values and stability were improved in all the CN electrodes, thanks to the improved hole extraction, which hinders the recombination of photogenerated electron-hole pairs and the self-oxidation of the CN layer. Linear sweep voltammetry (LSV) curves in the dark and under 1-sun back-side illumination (Figure 4c) disclose a low onset potential of 0.17 V *vs.* RHE for CN-U₁₀M_{0.5}. All the CN electrodes exhibited a linear increase in photocurrent density with increased potential—a typical PEC behavior—and a sharp increase in current at approximately 1.7 V *vs.* RHE attributed to electrocatalytic water oxidation.

The charge transfer efficiency of CN-U₁₀M_{0.5} reached up to 53% at 1.6 V *vs.* RHE (**Figure S10**). Incident photon-to-current conversion efficiency (IPCE) measurements of CN-U₁₀M_{0.5} were performed at 1.23 V *vs.* RHE in both 0.1 M KOH and 10% (v/v) TEOA in 0.1 M KOH (Figure 4d). The highest efficiency was achieved at 380 nm in both cases; the presence of a hole scavenger improved the IPCE value from 1.7% to 3.9%. In addition, CN-U₁₀M_{0.5} showed a good stability in the presence of TEOA, with a photocurrent value of *ca.* 60 $\mu\text{A cm}^{-2}$ even after 16 h of continuous illumination (**Figure S11**). Additional chronoamperometric measurements of CN-U₁₀M_{0.5} were performed at 1.23 V *vs.* RHE in a neutral aqueous solution (0.1 M phosphate buffer, pH $\approx$ 7) under 1-sun front- and back-side illumination (**Figure S12**). Under these conditions, a lower photocurrent density (*ca.* 65 $\mu\text{A cm}^{-2}$) was obtained compared to the photoanode's performance in 0.1 M KOH; no apparent change in stability was observed. Using Mott-Schottky analysis of the electrodes (**Figure S13**) and the optical band gaps (Figure 3c), we calculated the energy diagram presented in **Figure S14**, which shows the band positions of all the CN electrodes. Moreover, despite morphological changes of the CN film following PEC measurements in alkaline conditions, its contact with the substrate remained quite homogenous (**Figure S15**). The XRD patterns of CN-U₁₀M_{0.5} before and after PEC

measurements do not exhibit any significant difference (**Figure S16**), while an EDS analysis of the photoanode post-PEC measurements reveals a minor increase in oxygen quantity, suggesting oxidation of CN film during the measurements (**Figure S17** and **Table S1**).

The measured PEC performances of the various CN photoelectrodes, together with the morphology analysis of the urea films before calcination and the corresponding CN photoelectrodes, show that a seeding layer (*ca.* 12 μm) is of great benefit for the formation of a homogenous CN film firmly attached to the substrate.

3. Conclusions

To conclude, we reported a facile and scalable method to grow a homogenous CN layer on a substrate, with good adhesion, by providing nucleation sites for the growth of CN from the gas phase. To do so, we coated the substrate with CN precursors, using a spray coating technique before the thermal condensation. Our results indicate that the seeding layer promotes the growth of a uniform CN film regardless of the type and size of the substrate. The influence of the spray coating parameters (composition, thickness, and solvent) and the vapor content were studied in detail and correlated with the structural, photophysical, and photoelectrochemical properties of the CN layer. The new electrodes exhibit good performance as photoanodes in photoelectrochemical cells, *i.e.*, low onset potential, high photocurrent density, and moderate photostability. This approach facilitates the growth of CN on various substrates with controlled properties; its extension to other CN and metal-free materials on various substrates with controlled properties should accelerate their integration into photoelectrochemical devices.

4. Experimental Section

Materials:

All reagents and solvents were used as received from their respective commercial vendors, without further purification: urea (98%) and triethanolamine (TEOA, 99%) from Glentham; thiourea (99%) from Acros Organics; L-alanine (>95%) from Fisher Bioreagents; melamine

(99%) from Sigma-Aldrich. KOH (85%) and Na₂SO₄ (99%) from Loba-Chemie; Na₂HPO₄ (98+%) and NaH₂PO₄ (96%) from Alfa Aesar; acetone (99.8%) and ethanol (absolute, 99.9%) from Bio-Lab Chemicals. Deionized water (18.2 MΩ cm resistivity at 25 °C, purified using a Millipore Direct-Q3 system) was used for all aqueous solutions. Fluorine-doped tin oxide (FTO)-coated glass (12–14 Ω sq⁻¹) was purchased from Xop Glass company, Spain. Before use, the FTO was cut into rectangular pieces (1.3 cm × 2.5 cm) and sonicated with an aqueous detergent solution (Alconox, 1% m/v), acetone, and ethanol successively, for 15 min each, then dried in an air oven at 60 °C.

Preparation of urea/FTO films:

First, an aqueous urea solution (375 g L⁻¹) was prepared by dissolving 15 g of urea in 40 mL of water and then shaking the mixture for 15 min. Next, the solution was sprayed on an FTO substrate heated to 45 °C using a Sono-Tek ExactaCoat ultrasonic spray coater, with a varying number of spray cycles (5, 10, 50, or 100) and the following constant spray parameters: shaping air pressure of 0.5 psi (*ca.* 3.5 kPa), dwell time of 10 s between spray cycles, and distance of 4.0 cm between the spray nozzle and the FTO. Finally, the urea/FTO films were dried in an air oven at 60 °C (these films are denoted as U_x, *x* being the number of spray cycles). The choice of solvent and CN precursor to be sprayed is determined mainly according to solubility—urea was chosen to be deposited as a seeding layer due to its high solubility in water, which enables the formation of uniform films with controlled thickness by the spray coater.

Preparation of CN films:

Each piece of urea/FTO was inserted into a glass test tube (16 mm diameter × 100 mm length) filled with the chosen amount of melamine powder (0.5 g or 1.0 g) at its closed end. The tube was purged with N₂ for 1 min and closed with an Al foil. Lastly, the tube was submitted to a calcination process of 4 h at 550 °C with a heating ramp of 4.2 °C min⁻¹ under N₂ atmosphere to yield CN electrodes denoted as CN-U_xM_y, where *y* is the mass of melamine in the tube.

For the evaluation of the versatility of the method, we explored different materials: the growth of CN films on glass and carbon cloth substrates was achieved similarly to that of CN-U₁₀M_{0.5}, *i.e.*, deposition of a seeding layer by 10 spraying cycles of urea, then calcination in the presence of 0.5 g of melamine. For the growth of a CN film on a 9 cm × 1.2 cm FTO slide, the procedure for the preparation of CN-U₁₀M₁ was applied, only in a larger glass test tube (16 mm diameter × 150 mm length). The deposition of thiourea and L-alanine as seeding layers was achieved by spraying 10 cycles of aqueous thiourea (150 g L⁻¹) or aqueous L-alanine (125 g L⁻¹) solution, respectively.

Characterization:

The morphology of the samples was characterized using a scanning electron microscope (SEM, FEI VERIOS 460L) operated at 3.5 kV, 25 pA, and using an Everhart-Thornley secondary electron detector (ETD); the samples were sputtered with ~ 7 nm gold before analysis. Energy dispersive X-ray spectroscopy (EDS) was performed using the aforementioned microscope, operated at 6 kV with a probe current of 13 nA. X-ray diffraction (XRD) patterns were measured using a PANalytical Empyrean diffractometer (equipped with an X'celerator position-sensitive detector) with a scanning time of ~7 min for a 2θ range of 5–60°, using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$)—operation parameters: 40 kV, 30 mA. Fourier transformed infrared (FTIR) spectra were collected on a Thermo Scientific Nicolet iS5 using a diamond iD7 ATR. The chemical states of key elements were deduced from X-ray photoelectron spectroscopy (XPS) measurements conducted on a Thermo Fisher Scientific ESCALAB 250 using monochromated K α X-rays; all the binding energies in the XPS spectra were calibrated using the C 1s peak at 284.8 eV. UV-vis spectra were recorded on a Cary 100 spectrophotometer equipped with a diffuse reflectance accessory (DRA) in both transmittance (T) and reflectance (R) modes; the absorbance was calculated as: $100 - T - R$ (%). A Horiba Scientific FluroMax 4 fluorimeter

was used to collect photoluminescence (PL) spectra, with an excitation wavelength of $\lambda_{\text{ex}} = 390$ nm.

Photoelectrochemical measurements:

All photoelectrochemical measurements were performed using a three-electrode system with a Pt plate (1.0 cm²) and Ag/AgCl (saturated KCl) as the counter and reference electrodes, respectively. The electrolyte was either 0.1 M KOH aqueous solution (pH $\approx$ 13), 0.1 M KOH solution containing 10% (v/v %) TEOA or phosphate buffer (pH $\approx$ 7). All potential values versus Ag/AgCl were converted to values versus reversible hydrogen electrode (RHE) using the Nernst equation at room temperature:

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \text{ (V)} \quad (1)$$

Chronoamperometry and linear sweep voltammetry (LSV) measurements were conducted using an Ivium potentiostat (Vertex.1A). Photocurrent density was measured at a bias potential of 1.23 V vs. RHE under 1-sun illumination (power density of 100 mW cm⁻²) supplied by an LCS-100 solar simulator (calibrated using a Newport 919P power meter). LSV measurements were performed in the dark and under 1-sun illumination in the range of 0–1.8 V vs. RHE. Incident photon-to-current conversion efficiency (IPCE) and Mott-Schottky measurements were performed using an Autolab potentiostat (Metrohm, PGSTAT302N). IPCE measurements were performed under 1-sun illumination supplied by a Newport 94011A solar simulator equipped with an air mass AM1.5G filter and calibrated using a Newport 919P power meter. Values were calculated using:

$$\text{IPCE (\%)} = \frac{J(\text{A cm}^{-2}) \cdot 1240}{\lambda(\text{nm}) \cdot I(\text{W cm}^{-2})} \cdot 100 \% \quad (2)$$

Where J is the photocurrent, λ is the wavelength of the incident monochromatic light, which is controlled by different optical bandpass filters (Newport 10BBPF10 series) with a center wavelength of 380 nm, 400 nm, 420 nm, 440 nm, 460 nm, and 480 nm, and I is the light power density.

The charge transfer efficiency was calculated using:

$$\eta(\%) = \frac{J_{\text{KOH}}}{J_{\text{TEOA}}} \cdot 100\% \quad (3)$$

J_{KOH} is the photocurrent density obtained in 0.1 M KOH aqueous solution, while J_{TEOA} is the photocurrent density obtained in 0.1 M KOH containing 10% (v/v) TEOA. We assume that the extraction rate of photogenerated holes in the system is 100% after the addition of the hole scavenger. Mott-Schottky measurements were carried out in 1.0 M Na₂SO₄ aqueous solution (pH $\approx$ 6.3).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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Figure 1. (a) Digital photo of the spray coater system (left); illustration of the preparation of CN films on FTO in two steps (right): spray coating of a CN precursor (urea) serving as a seeding layer, followed by calcination under an inert atmosphere in the presence of melamine powder in a glass tube. (b) XRD patterns of FTO (bottom, black), urea powder (middle, red), and U₁₀ film on FTO (top, blue); the patterns are vertically offset for clarity. (c) Top-view SEM image of U₁₀ (insets: the corresponding digital photo and cross-sectional SEM image).

Figure 2. (a) Top-view (inset: digital photo) and (b) cross-sectional SEM images of CN-M_{0.5}.
(c) Top-view (inset: digital photo) and (d) cross-sectional SEM images of U₁₀M_{0.5}.

Figure 3. (a) XRD patterns of the CN electrodes; the diffraction signals at 26.4°, 33.6°, 37.7°, and 51.5° are from the FTO substrate, and (bottom, black) diffraction pattern of a bare FTO substrate. (b) Absorbance spectra of the CN electrodes. (c) Tauc plot analysis for the determination of the optical band gaps of the CN electrodes. (d) PL spectra of the CN electrodes; $\lambda_{\text{ex}} = 390 \text{ nm}$.

Figure 4. Characterization of PEC performance. Chronoamperometric measurements of CN electrodes (photocurrent density at 1.23 V vs. RHE) (a) in 0.1 M KOH and (b) in 0.1 M KOH aqueous solution containing 10% (v/v) triethanolamine (TEOA) as a hole scavenger. (c) LSV curves of the CN electrodes; dashed lines—in the dark; complete lines—under illumination. (d) IPCE plots of CN-U₁₀M_{0.5} at 1.23 V vs. RHE in 0.1 M KOH and in 0.1 M KOH containing 10% TEOA (the experimental points are connected as a guide for the eye); the corresponding absorbance spectrum (black) of this photoelectrode is shown (absorbance % values on the right-side y-axis).

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Mediated Growth of Carbon Nitride Films via Spray-Coated Seeding Layers for Photoelectrochemical Applications

A facile, large-scale growth of carbon nitride (CN) layer on a substrate using spray-coated seeding layer is reported. Upon calcination in the presence of melamine vapor, a homogenous, thick CN layer with strong adhesion to the substrate is obtained. The CN films exhibit good performance as photoanodes in photoelectrochemical cells, with low onset potential, high photocurrent density, and moderate photostability.

Supporting Information

Mediated Growth of Carbon Nitride Films via Spray-Coated Seeding Layers for Photoelectrochemical Applications

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Figure S1. FTIR transmittance spectra of urea powder (bottom, black) and U₁₀ film on FTO (top, red). Spectra are offset on the y-axis for clarity.

Figure S2. (a) Top-view and (b) cross-sectional SEM images of U₅; approximate height measurement of 6 μm. (c) Top-view and (d) cross-sectional SEM images of U₅₀; approximate height measurement of 68 μm. (e) Top-view and (f) cross-sectional SEM images of U₁₀₀; approximate height measurement of 89 μm.

Figure S3. (a) Top-view SEM image of CN-U₅M_{0.5} (inset: digital photo). (b) Cross-sectional SEM image CN-U₅M_{0.5}. (c) Top-view SEM image of CN-U₅₀M_{0.5} (inset: digital photo). (d) Cross-sectional SEM image of CN-U₅₀M_{0.5}. (e) Top-view SEM image of CN-U₁₀₀M_{0.5} (inset: digital photo). (f) Cross-sectional SEM image CN-U₁₀₀M_{0.5}. (g) Top-view SEM image of CN-U₁₀M₁ (inset: digital photo). (h) Cross-sectional SEM image CN-U₁₀M₁.

Figure S4. FTIR transmittance spectra of the different CN electrodes. Spectra are offset on the y -axis for clarity.

Figure S5. (a) C1s and (b) N1s XPS spectra of CN-U₁₀M_{0.5}. Experimental signal: black dashed line; fitted signal: red curve; individual deconvoluted fitted spectra are shown using full colored traces.

Figure S6. Adhesion tests. (a) Full adhesion test procedure for CN-U₁₀M_{0.5}. (b) CN-M_{0.5} and (c) CN-U₁₀M₁ before (left) and after (right) the respective adhesion tests.

Figure S7. CN films on various substrates and variation of the precursor. (a) $CN-U_{10}M_{0.5}$ on a glass substrate (microscope slide). (b) clean carbon cloth (left) and U_{10} deposited on carbon cloth (right). (c) The resulting $CN-U_{10}M_{0.5}$ film on carbon cloth. (d) $CN-U_{10}M_1$ deposited on an FTO with $9\text{ cm} \times 1.2\text{ cm}$ dimensions. CN electrodes formed by using (e) thiourea and (f) alanine as the seeding layer precursors, followed by calcination in the presence of melamine powder. (g) CN electrode prepared by using urea as a seeding layer, followed by calcination in the presence of thiourea powder (instead melamine in the standard procedure).

Figure S8. Chronoamperometric measurements (photocurrent densities at 1.23 V vs. RHE in 0.1 M KOH under front- and back-side illumination vs. time) of (a) CN-M_{0.5}, (b) CN-U₅M_{0.5}, (c) CN-U₁₀M_{0.5}, (d) CN-U₅₀M_{0.5}, (e) CN-U₁₀₀M_{0.5}, and (f) CN-U₁₀M₁.

Figure S9. Chronoamperometric measurements in the presence of a hole scavenger (photocurrent densities at 1.23 V vs. RHE in 0.1 M KOH containing 10% (v/v) triethanolamine (TEOA) under front- and back-side illumination vs. time) of (a) CN-M_{0.5}, (b) CN-U₅M_{0.5}, (c) CN-U₁₀M_{0.5}, (d) CN-U₅₀M_{0.5}, (e) CN-U₁₀₀M_{0.5}, and (f) CN-U₁₀M₁.

Figure S10. Calculated charge transfer efficiency of CN-U₁₀M_{0.5} vs. applied potential.

Figure S11. Photocurrent density of CN-U₁₀M_{0.5} at 1.23 V vs. RHE in 0.1 M KOH aqueous solution containing 10% TEOA under 16 hours of continuous 1-sun back-side illumination.

Figure S12. Chronoamperometric measurements (photocurrent densities at 1.23 V vs. RHE in 0.1 M sodium phosphate buffer solution, pH ~ 7, under front- and back-side illumination vs. time) of CN-U₁₀M_{0.5}.

Figure S13. Mott-Schottky measurements of the CN electrodes. The determined CB positions are calculated using linear extrapolation and appear in the legend.

Figure S14. Calculated electronic energy band diagrams of the CN electrodes on the RHE scale (determined by Mott-Schottky analysis and the optical band gap).

Figure S15. (a) Top-view and (b) cross-sectional SEM images of CN-U₁₀M_{0.5} post-PEC measurements.

Figure S16. XRD patterns of FTO (bottom, black), CN-U₁₀M_{0.5} before PEC measurements (middle, red), and CN-U₁₀M_{0.5} after PEC measurements (top, blue); the patterns are vertically offset for clarity.

Figure S17. EDS spectra of CN-U₁₀M_{0.5} film on FTO (a) before and (b) after PEC measurements.

Table S1. Elemental analysis of CN-U₁₀M_{0.5} obtained by SEM-EDS before and after PEC measurements.

Element	Before PEC measurements (at. %)	After PEC measurements (at. %)
C	48.0 ± 0.2	47.2 ± 0.2
N	51.7 ± 0.2	51.7 ± 0.2
O	0.34 ± 0.06	1.08 ± 0.06