Carbon-Doped Porous Polymeric Carbon Nitride with Enhanced Visible Light Photocatalytic and Photoelectrochemical Performance

Neeta Karjule, Liel Abisdris, Adi Azoulay, Michael Volokh, and Menny Shalom*

The photocatalytic activity of polymeric carbon nitride (CN) is strongly tied to its surface area, morphology, optical, and electronic properties. Herein, a straightforward approach to adjusting the electronic properties and morphology of CN materials by fine tuning their carbon content while preserving their high surface area is proposed. To do so, supramolecular assemblies based on CN monomers together with an additional carbon-rich monomer that does not participate in the preorganization are calcinated. The use of a supramolecular assembly as the precursor endows the CN material with a high specific surface area and an ordered morphology, whereas the addition of a carbon-rich monomer provides light carbon doping. As a result, the new CN exhibits excellent activity as a photoanode material in photoelectrochemical cells and as a photocatalyst for the hydrogen evolution reaction. Detailed studies reveal that the modified CN samples show enhanced charge carrier transfer and separation efficiency, improved light absorption response, a tunable energy band structure, a higher electrochemical surface area, and better electronic conductivity compared with a reference CN.

1. Introduction

Polymeric carbon nitride (CN) semiconductor materials have attracted great interest as metal-free organic photocatalyst owing to their low cost, high chemical and thermal stability, ease of synthesis, and good catalytic activity.\(^1\) As a photocatalyst, CN has been used for the production of hydrogen (H\(_2\)) through water splitting,\(^2\) CO\(_2\) reduction,\(^3\) various organic transformations,\(^4\) and the degradation of pollutants.\(^5\) However, the intrinsic drawbacks of CN, especially large grain boundaries, small specific surface area, low density of active sites, high recombination rate of electron–hole pairs, and moderate light absorption, hinder its activity as a photocatalyst.\(^6\)

To overcome these challenges, many different strategies have been proposed, such as morphology control,\(^7\) copolymerization,\(^8\) heteroatom doping,\(^9\) and heterojunction formation.\(^10\) Among these, the copolymerization of standard CN precursors with other organic compounds is an effective route to fabricate modified CN polymers with improved photocatalytic activity.\(^11\) Hence, finding suitable comonomers with a diverse chemical composition and structure to alter the band structure and optoelectronic properties of CN is an important task.\(^12\) Carbon doping and nitrogen defects in CN have previously been shown to improve electrical conductivity, charge transfer rate, and photocatalytic activity.\(^13\) Most importantly, carbon doping can increase the size of delocalized \(\pi\)-bond networks, which favors electron transfer, modulates the band structure, and extends the optical absorption range to lower energies.\(^14\) In addition, an asymmetric distribution of C and N atoms on the surface causes charge nonuniformity, which may improve photocatalytic properties.\(^15\) However, the amount of carbon doping must be carefully adjusted to augment the activity: even a small deviation may lead to a nonactive photocatalyst. CM supramolecular complexes—composed of cyanuric acid (C) and melamine (M) connected through hydrogen bonds—are frequently used as a precursor to CN-based materials.\(^16\) The incorporation of doping molecules into the CM self-supramolecular complex was found to affect the photophysical properties of CN. Caffeine,\(^17\) phosphoric acid,\(^18\) barbituric acid,\(^19\) thymine,\(^20\) urea,\(^21\) 2,4-diamino-6-phenyl-1,3,5-triazine (Mp),\(^22\) 2,4,6-triaminopyrimidine (TAP),\(^22\) and chitosan\(^23\) are some of the precursors that were used to tune the properties of CN-based materials. Nevertheless, the incorporation of additives within the hydrogen framework of CM often leads to excessively high carbon levels in the final CN.\(^24\)

In this work, we propose a simple method for the synthesis of tetracyanoethylene (TCNE)-modified CN materials by thermally induced copolymerization of a CM supramolecular assembly and TCNE. To do so, we calcinate the CM supramolecular assembly with various amounts of added TCNE under an inert atmosphere. Unlike the incorporation of additional monomer before the supramolecular assembly in solution—typically water, in...
which the solubility of each monomer may differ significantly, the solid-state synthesis enables fine adjustments of the elemental ratio and overall properties to be made easily. The delicate carbon modification leads to better light absorption response, a tunable energy band structure, a large specific surface area, and a more effective charge carrier separation compared with a reference CN (CN-CM). As a result, TCNE-modified CN demonstrates good activity as a photocatalyst for H₂ evolution and rhodamine B degradation. Furthermore, the new CN shows high performance as a photoanode material in photoelectrochemical cells. Various

Scheme 1. CN (CM and CN-CMTₓ) synthesis at 550 °C from hydrogen-bonded supramolecular complexes and TCNE as the starting reactants.

Figure 1. Electron microscopy morphology characterization. a–d) SEM images of CN-CM and CN-CMTₓ and e–f) TEM images of CN-CM and CN-CMT₂ after condensation at 550 °C for 4 h under N₂. Optical digital photographs of the resulting powders are shown as insets in the corresponding SEM panels (a–d).
photo- and electrochemical studies reveal that the modified CN samples exhibit improved charge carrier transfer and separation efficiency, higher electrochemical surface area, and better electronic conductivity.

2. Results and Discussion

2.1. Synthesis and Characterization of Precursors

Supramolecular assemblies of hydrogen-bonded CM were formed by mixing equal amounts of cyanuric acid and melamine in water.\(^{[7,25]}\) We then calcinated mixtures of CM supramolecular preassembly as the CN precursor and TCNE as an additive (denoted as T), achieving the preparation of TCNE-modified polymeric CNs (CN-CMT\(_x\)), as shown in Scheme 1. CM and CMT\(_x\) powders were prepared by mixing CM (1.0 g) with different wt% of TCNE (\(x = 0, 0.50, 1.0, 1.5, 2.0, 2.5, \) and 10); the combination of powders was ground using a mortar and pestle to ensure thorough mixing. Scanning electron microscopy (SEM) images of the CM and CMT\(_x\) precursors (Figure S1, Supporting Information) demonstrate that the morphologies of the supramolecular assemblies were not altered by the addition of the TCNE precursor. The molecular structure of the mixtures was further characterized via Fourier-transform infrared (FTIR) spectroscopy and X-Ray diffraction (XRD). The FTIR spectra of CM and CMT\(_x\) disclose similar vibration modes, indicating that the small amount of added TCNE is insufficient to affect the structure of the CM complex (Figure S2, Supporting Information). The XRD patterns of CM and CMT\(_2\) both exhibit strong and distinct diffraction signals at 11° (corresponding to the (100) plane), 19.8° ([110] plane), 21.75° ([200] plane), and 27.5° (related to the (002) plane) (Figure S3, Supporting Information).\(^{[7]}\) Hence, XRD analysis confirms that the presence of TCNE does not alter the supramolecular structure of CM. TCNE is potentially only bound to the surface.

2.2. CN Characterization

The CM and CMT\(_x\) mixtures were each pyrolyzed at 550 °C in nitrogen atmosphere for 4 h to prepare photoactive CNs (CN-CM and CN-CMT\(_x\)). TCNE is a carbon-rich material containing only C and N (as an ideal graphitic CN) and four cyanogroups.\(^{[26]}\) During calcination, the cyanogroups of TCNE could integrate directly into the CN during the copolymerization of CM with TCNE, resulting in the formation of a C–C bond attached to the heptazine ring.\(^{[27]}\) The C–C bond linked to the heptazine ring may break during copolymerization at high temperatures because it is less stable (longer bond length) than a C–N bond, resulting in amino group vacancies, as shown in Scheme 1.\(^{[27]}\) The amino group’s absence reduces the heptazine ring's

![Figure 2.](image-url) a) FTIR spectra and b) XRD patterns of the synthesized CN materials; c) solid-state \(^{13}\)C CP MAS NMR spectra of CN-CM and CN-CMT\(_2\) (*indicates a spinning side band).
connectivity, resulting in the formation of nitrogen-poor and carbon-rich CN. This caused the CN network structure to fracture, resulting in some defects in CN-CMTx materials. The morphology and microstructure of CN-CM and CN-CMTx were investigated using SEM and transmission electron microscopy (TEM), as shown in Figure 1a–d. When the TCNE content increased, the size of the CN nanosheets decreased and higher porosity (relative to reference CN) developed, indicating that the TCNE copolymerization reaction caused nanosheets’ fragmentation and the formation of pores on the CN’s surface. The TEM images show that CN-CMT2 exhibits a much thinner and more porous layer structure than CN-CM. The increased porosity of the CN-CMTx materials could lead to an increase in the amount of catalytically active sites while shortening the diffusion path of photogenerated charge carriers.[28]

The formation of CN materials after heating was confirmed by FTIR spectroscopy and XRD analysis (Figure 2). The FTIR spectra show the typical breathing mode of the triazine units in CN at 809 cm⁻¹ and the characteristic stretching modes for the CN heterocycles from 1200 to 1600 cm⁻¹ (Figure 2a). We assigned the broad band between 3000 and 3600 cm⁻¹ to either –NH₂ groups or surface-adsorbed H₂O molecules, or both. The XRD patterns (Figure 2b) of the CNs exhibit two distinct diffractions at 13.0° and 26.7°, which we assigned to the (100) and (002) planes, indicative of a layered structure formation. For the CN-CMTx sample, the peak corresponding to (002) is broadened, which is due to the lower interaction between the layers.

The molecular structure of the different CNs was further determined by solid-state NMR (Figure 2c and S4, Supporting Information).[29] The ¹H magic-angle spinning (MAS) NMR spectra reveal two signals with peaks maxima at ≈9.4 and ≈4.3 ppm, attributable to the presence of –NH₂ groups and residual water in the heptazine lattices, respectively (Figure S4, Supporting Information)[30]; this indicates the presence of melon-like NH–bridged heptazine-based structures with some –NH and –NH₂ terminations. The slight shift in CN-CMT2 signals implies that the heptazine units have different chemical environments depending on the orientation of the adjacent layers. As a result, heptazine–based structures with some –NH and –NH₂ groups are involved in intermolecular hydrogen bonding, causing CN-CMT₂ to shift down field.[31] The ¹³C cross-polarization CP MAS NMR spectrum exhibits two clear signals at 164.5 and 157.3 ppm, which we ascribed to carbon bonded to NH₂ groups (N₂C–NH₂) and sp² carbon of the C–N bonds (CN₃) in the heptazine units, respectively.[32] CN-CMTx and CM-CN show similar peak patterns, indicating the preservation of the basic heptazine structure in CN-CMTx.

The surface chemical environments of C and N were investigated by X-Ray photoelectron spectroscopy (XPS) (Figure S5–S6 and Table S1, Supporting Information).[33] In the CN-CM

![Figure 3. a) UV–vis DRS of CNs, b) Tauc plot analysis assuming a direct-bandgap semiconductor, c) PL spectra of CNs (excited at 370 nm), and d) PL average lifetime of CN materials.](image-url)
samples, the C 1s binding energy signal at 285.1 eV is ascribed to graphite carbon atoms (C=C), whereas the peak at 288.1 eV is attributed to sp² carbon (N=C=N) present in the CN backbone. The peak at 289.4 eV belongs to C=O (surface-adsorbed atmospheric oxygen) or C–N bonds. The N 1s peak at 398.6 eV corresponds to sp³-hybridized aromatic N in tri-s-triazine rings (C≡N≡C). We assigned the peak with a high binding energy at 401.8 eV is characteristic of amino functional groups (–NH₂). Elemental analysis data (Table S2, Supporting Information) unveils only slight changes in the C/N ratio owing to the low wt% of the dopant.

The light absorption properties of CNs were investigated by UV–vis diffuse reflectance spectroscopy (DRS) (Figure 3a). The absorption edge of CN-CMTₓ is slightly redshifted and the visible light absorption is enhanced compared with the reference CN-CM. This implies that the intrinsic electronic properties of the CN materials were changed by the alteration of their elemental composition: it leads to a decrease in the bandgap of the CN-CMTₓ samples (Figure 3b), improving light harvesting. The photoluminescence (PL) intensity of all CN-CMTₓ samples is dramatically reduced compared with the reference CN-CM, indicating an alternative nonradiative path for the photogenerated electron–hole pairs (Figure 3c). We attributed this to the creation of defect levels and to the nanosheet structure of doped CN-CMTₓ, which lead to a shorter charge carrier migration path and improved electronic conductivity, thus suppressing the photoinduced recombination of electron–hole pairs.[37]

To further study the lifetime of photogenerated charge carriers in the samples, we also performed time-resolved fluorescence measurements (Figure S7, Supporting Information). CN-CMT₂ presents a faster exponential decay than CN-CM, with an average
lifetime of 22 ns versus 61 ns. Typically, a shorter lifetime implies better charge separation properties, which in turn improve photocatalytic activity.\textsuperscript{[13a]} The CN materials show n-type behavior, and the conduction band (CB) edges of CN-CM and CN-CMT\textsubscript{x} are at \(-0.6 \) and \(-0.36 \) V versus RHE (RHE = reversible hydrogen electrode), respectively (Figure S8, Supporting Information). The CB position of CN-CMT\textsubscript{x} is downshifted and remains more above the reduction potential of \( \text{H}^+ / \text{H}_2 \). \( \text{N}_2 \) adsorption–desorption isotherms (Figure S9, Supporting Information) indicate that all the CN-CMT\textsubscript{x} samples have a higher specific surface area than the reference CN-CM (\( S_A \), Figure 4a). The measured \( S_A \) of CN-CMT\textsubscript{2} is 86.2 m\textsuperscript{2} g\textsuperscript{-1}, almost twice that of the reference CN (46.6 m\textsuperscript{2} g\textsuperscript{-1}). The total pore volume of CN-CMT\textsubscript{2} (2.4 cm\textsuperscript{3} g\textsuperscript{-1}) is five times larger than that of CN-CM (0.52 cm\textsuperscript{3} g\textsuperscript{-1}).

2.3. Photocatalytic Activity

The photocatalytic hydrogen evolution experiment was performed under a white light-emitting diode (LED) illumination in a water–triethanolamine (TEOA) mixture with Pt as a cocatalyst (Figure 4b). Among all the modified CN-CMT\textsubscript{x} samples, CN-CMT\textsubscript{2} exhibited the highest photocatalytic \( \text{H}_2 \) evolution activity (1757 \( \mu \text{mol h}^{-1} \text{g}^{-1} \))—an almost fourfold increase over that of CN-CM (422 \( \mu \text{mol h}^{-1} \text{g}^{-1} \))—as shown in Figure 4b. We envision that the enhancement in activity is due to the elemental modification, which improves the electronic properties of the material, and to the increased surface area of the porous CN structure, which provides more sites for cocatalyst deposition and \( \text{H}_2 \) production.\textsuperscript{[13b]} CN-CMT\textsubscript{2} demonstrates excellent stability during \( \text{H}_2 \) evolution (Figure 4c and S10a, Supporting Information), still evolving a steady amount of \( \text{H}_2 \) after four cycles under the same reaction conditions. A wavelength-dependent \( \text{H}_2 \) generation experiment of CN shows that the variation in apparent quantum efficiency (AQE) coincides with the variation in absorption in the UV–vis spectrum (Figure S10b, Supporting Information and Figure 3a). For CN-CMT\textsubscript{2}, the AQE at 405 nm is estimated to be about 6%. The activity of the CN samples as photocatalysts for pollutant degradation was measured using the RhB dye.\textsuperscript{[7]} A proposed photocatalytic RhB dye degradation scheme over CN is shown in Figure S11, Supporting Information. As shown in Figure 4d, after 15 min of the photocatalytic reaction, CN-CM showed relatively poor RhB degradation rates. In contrast, the photocatalytic activity of the CN-CMT\textsubscript{x} samples was significantly enhanced, particularly CN-CMT\textsubscript{2}, which achieved full RhB degradation within 15 min.

Finally, we prepared CN-CM and CN-CMT\textsubscript{2} electrodes for photoelectrochemical cells by the doctor-blade method (Figure S12, Supporting Information).\textsuperscript{[33]} Photocurrent density measurements (Figure 5) at 1.23 V versus RHE in 0.1 M KOH reveal a higher and more stable photocurrent response for the CN-CMT\textsubscript{2} electrode than for reference electrode CN-CM,
indicating an enhanced charge separation and improved electronic structure. The photocurrent responses were obtained under ten cycles of illuminated/dark conditions. Figure 5a shows that CN-CMT2 exhibits an improvement in photocurrent density, reaching 60 μA cm⁻², significantly higher than that of CN-CM (21 μA cm⁻²). In the presence of a hole scavenger (TEOA), CN-CMT2 exhibits a high current density of 160 μA cm⁻² compared with CN-CM (68 μA cm⁻²) (Figure 5b). The enhancement in photogenerated charge separation and electron conductivity of the TCNE-modified CN-CMT2 electrode is further demonstrated by the improved stability of the modified CN films (Figure S13, Supporting Information). The electrochemical impedance spectroscopy (EIS) results imply an increase in hole transfer to the solution for the CN-CMT2 samples compared with CN-CM, which in turn lead to longer electron lifetime (Figure 5c).[36a] The improvement in conductivity was supported by electrochemically active surface area (ECSA) measurements of the CN films (Figure 5d), which also showed higher values for the CN-CMT2 films. The higher ECSA reflects the participation of a larger proportion of the CN surface in the photoelectrochemical process, which increases electron collection.

3. Conclusion

We introduced a facile method to synthesize a porous, highly photoactive carbon-doped CN by the surface modification of a supramolecular assembly as the reactant. To do so, we used TCNE as an additive that, upon thermal condensation, modified the structural, electronic, and catalytic properties of CN. The new TCNE-modified CN photocatalyst exhibited an improved absorption in the visible region, a modulated energy band structure, an efficient separation of photogenerated charge carriers, and a high surface area leading to more active sites. The new CN-CMT2 presents a significant enhancement in photocatalytic activity with a hydrogen evolution rate of 1757 μmol h⁻¹ g⁻¹ and a high QE of 6% at 405 nm. Furthermore, CN-CMT2 exhibits high and stable photocurrent densities when used as a photoanode material in photoelectrochemical cells. (Photo)electrochemical studies reveal a better charge separation under illumination, owing to the increased electrochemical surface area, good electronic conductivity, and improved hole extraction to the solution of CN-MT2.

4. Experimental Section

Materials: All chemicals were purchased from commercial sources and used without further purification. Melamine (99%), chloroplatinic acid solution (8 wt% H₃PtCl₆ in H₂O), and rhodamine B (RhB, 95%) were purchased from Sigma-Aldrich. Cyanuric acid (99%) and tetracyanoethylene (TCNE, 98%) were purchased from Alfa Aesar. Triethanolamine (TEOA, 99%) was purchased from Glentham Life Sciences, UK. Deionized water (DI) was purified using a Millipore Direct-Q 3 water purification system (18.2 MΩ cm resistivity). All the photocatalysis experiments were carried out under argon atmosphere.

Synthesis of Polymeric CN Materials: The CM complex was prepared by mixing cyanuric acid (C, 1 g, 7.75 mmol) and melamine (M, 0.98 g, 7.75 mmol) in a 1:1 molar ratio in 40 mL DI water in an automatic shaker. The resulting powder was filtered and washed several times with water and then dried at 60°C in a vacuum oven. CMT powders were then prepared by mixing CM (1.0 g) with x wt% of TCNE (x = 0.50, 1.0, 1.5, 2.0, 2.5, and 10). Each mixture was ground until well mixed using an agate mortar and pestle and then calcined at 550°C for 4 h under N₂ atmosphere (heating rate of 2°C min⁻¹ from room temperature to the calcination temperature). Afterward, the CN materials were collected and labelled as CN-CMTx. A CN-CM reference was prepared using the same procedure from the CM complex (free of TCNE).

Photocatalytic H₂ Evolution Reaction (HER): The production of hydrogen by CN materials was measured in a Schlenk flask thermally regulated with a cooling system and using a white LED array as the irradiation source, 3 wt% Pt as a cocatalyst, and triethanolamine (TEOA) as a hole scavenger. Photocatalytic hydrogen evolution experiments were conducted under an inert argon atmosphere at a constant temperature of 25°C. In a 50 mL Schlenk flask, 15 mg of CN was suspended in a solvent mixture (19 mL) composed of water and TEOA in a 9:1 v/v ratio and 19.6 μL of a H₂PtCl₆ solution (8 wt% in water). The mixture was then kept for 30 min in the dark under a constant argon flow to reach thermal equilibrium; the reaction was subsequently started by switching on a 100 W white LED array (Bridgelux BXRA-50C5300; λ > 410 nm). The amount of evolved gas in the headspace of the reactor was evaluated by gas chromatography (Agilent 7820 GC System). In this system, upon visible light irradiation, CN materials generated electron–hole pairs that migrated to the catalyst’s surface. The valence band (VB) holes in the VB reacted with TEOA when the electron–hole pairs separated spatially, while photexcited electrons reduced the molecular Pt salt to Pt (0), allowing subsequent electrons to reduce water molecules into H₂.

The apparent quantum yield (AQY) for H₂ evolution was determined using mounted LEDs (Thor Labs, Model no. M405L4, M430L4, and M455L4 equipped with a 405, 430, and 450 nm band-pass filter, respectively). Quantum yield measurements were performed in a sealed reactor connected to an argon line and an Agilent 7820 GC system. The reactor was continuously purged with argon (in the dark) to remove the existing hydrogen, nitrogen, oxygen, and other gases, and the purging process was monitored by automatic sampling every 11 min. After purging, the LED was switched on, and the amount of produced hydrogen gas was recorded; the integrated area was used further for the calculation of the average quantum yield (AQY%), which was calculated as follows: AQY = Nₑ/Nₚ × 100% = 2 M/Nₑ × 100%, where Nₑ is the amount of reaction electrons, Nₚ is the amount of incident photons, and M is the amount of H₂ molecules.

Photocatalytic Tests: The photocatalytic activity of the CN materials was determined by performing rhodamine B (RhB) dye degradation under a white 100 W LED (Bridgelux BXRA-50C5300; λ > 410 nm) illumination. RhB (in 20 mL water, 20 mg L⁻¹) and the photocatalyst (10 mg) were mixed in a glass vial and placed in the dark under continuous stirring until an adsorption–desorption equilibrium was reached. After a specific time of illumination duration, the samples were collected. RhB concentration was monitored by measuring the optical absorbance (utilizing the absorption maximum of RhB, λmax = 554 nm), which was plotted as a normalized concentration C/C₀.

Characterization: SEM images of the CN electrodes were obtained using a JEOL JSM-7400 F high-resolution SEM, equipped with an field emission gun source, operated at an accelerating voltage, U₀ = 3.5 kV (after sputtering with ≈10 nm Pt using a Quorum Q150T ES system). TEM images were obtained using a Tecnai (FEI) T12 200 kV Field Emission gun microscope at U₀ = 120 kV. UV–vis absorption and DRS were measured on a Cary 100 spectrophotometer in transmittance mode (10 mm quartz cuvettes) or equipped with a diffuse reflectance accessory (DRA). Fluorescence measurements were carried out on a Fluoromax 4 spectrofluorometer from Horiba Scientific. FTIR was performed on a Thermo Scientific Nicolet iS5 FTIR spectrometer (equipped with a Si ATR). XRD (XRD) were obtained using a PANalytical’s Empyrean diffractometer equipped with a position-sensitive detector X’Celerator. Data was collected with a scanning time of ≈7 min for 2θ ranging from 5° to 60° using Cu Kα radiation (λ = 1.54178 A, 40 kV, 30 mA). XPS data were obtained from an X-Ray photoelectron spectrometer ESCALAB 250 ultrahigh vacuum (1 x 10⁻⁹ bar) device with an Al Kα X-Ray source and a monochromator. The X-Ray beam size was 500 μm, survey spectra were recorded with a pass energy (PE) of 150 eV, and high-energy resolution spectra were recorded with a PE of 20 eV. To correct for charging effects, all spectra were calibrated relative.
to a carbon 1s peak positioned at 284.8 eV. The XPS results were
processed using the Thermo Scientific Avantage software. Elemental
analysis data for carbon, nitrogen, and hydrogen (CNH) was collected
using a Thermo Scientific Flash Smart elemental analyzer OEA 2000.
Nitrogen sorption measurements and Brunauer–Emmett–Teller (BET)
specific surface area calculations were performed on a Quantachrome
NOVAtouch NT LX3 system. Solid-state NMR experiments were carried
out in a Bruker Avance III 500 MHz narrow-bore spectrometer, using a
4 mm double-resonance MAS probe at a spinning rate of 8 kHz. 13C
CP MAS experiments were carried out using a 2.5 μs 90° pulse, a 2
ms mixing time, and a 3 s recycle delay between acquisitions. 1H direct
excitation experiments were carried out using a 2.5 μs 90° pulse and a 2 s
recycle delay. Time-resolved fluorescence measurements were performed
using a time-correlated single-photon counting setup with Fluorolog
Modular Spectrofluorometer. The PL decay curves were monitored at
their maximum emission wavelength under the excitation of light with
a wavelength of 370 nm. The triple-exponential function was used to
fit the decay curves. Intensity-averaged fluorescence lifetime \( \tau \)
was calculated using the equation: \( \tau = \frac{\sum_t^T \alpha_i \tau_i}{\sum_t^T \alpha_i} \), where \( \tau_i \) is the lifetime and \( \alpha_i \) is the amplitude of the \( i^{th} \) component.

CM and CMT films preparation: For the preparation of the CM and CMT supramolecular polycrystals, CM powder (1.0 g) without and with TCNE (2 w%) were blended thoroughly in ethylene glycol (2.0 mL). The pastes were then doctor-bladed onto FTO-coated glass (using 2 scotch tape layers (L) to control the film thickness and achieve a homogeneous coating). Then, the films were subsequently dried at 90°C on a hotplate and finally transferred into a closed (but not sealed) 16 mm-diameter glass test tube. All the FTO substrates were cleaned by successive sonication in an aqueous detergent solution (1% m/v Alconox), acetone, and ethanol, and were finally dried before use. For the calcination process, melanin powder (0.2 g) was placed at the bottom of a test tube, in the middle of which two electrodes (FTO substrates) were then placed. The test tube was purged with \( N_2 \) for 5 min and covered with Al foil. Finally, the samples were heated up to 550°C at a ramp rate of 5°C min\(^{-1}\) and kept at 550°C for 4 h under a flow of \( N_2 \) to obtain the CN-CM and CN-CMT2 electrodes.

All electrochemical measurements were performed using a three-electrode system on an Autolab potentiostat (Metrohm, PGSTAT302N). Pt foil (1 cm²) and Ag/AgCl (saturated KCl) were used as the counter and reference electrodes, respectively. The electrolyte was either a 0.1 M KOH aqueous solution (pH = 13.1) or a 0.1 M KOH solution containing 10% v/v TEOA. All the potentials were converted to RHE values using the equation \( V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \) (V). Photocurrents were measured at 1.23 V versus RHE under the illumination of a solar simulator (Newport 2000 W Xe arc lamp, equipped with an AM 1.5G and water filters) at a power density of 100 mW cm\(^{-2}\), which was calibrated using a thermopile power meter (Model 919-P, Newport), that is, 1 sun conditions. Nyquist plots of the samples were measured in the frequency range from 100 kHz to 10 mHz at an applied voltage of 1.23 V versus RHE. Mott–Schottky plots of CN were measured in 1 M Na₂SO₄ at 2.0 kHz frequency.

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

Acknowledgements
This project received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement no. [849068]). This work was also partially supported by the Israel Science Foundation (ISF), grant no. 601/21, and ISF-NSFC, grant no. 2969/19. The authors thank Jonathan Tzadikov, Ayelet Tashakory, and Dr. Jiawei Xia for help with material characterization. The authors thank Dr. Chabanne for fruitful discussion.

Conflicts of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
carbon nitride, photocatalytic hydrogen generation, photoelectrochemical cells, pollutant degradation, supramolecular assemblies

Received: March 14, 2022
Revised: April 17, 2022
Published online: May 8, 2022

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