Electronic Supplementary Information

Electrophoretic deposition of supramolecular complexes for the formation of carbon nitride films

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Experimental

<u>Materials</u>

All reagents and solvents (abbreviation, purity, manufacturer) were used as received: cyanuric acid (CA, 98%, Merck), melamine (M, 99%, Sigma-Aldrich), toluene (AR, LOBA Chemie), potassium hydroxide pellets (KOH, AR, 85%, LOBA Chemie), sodium sulphate anhydrous (Na₂SO₄, AR, 99%, Loba Chemie), and triethanolamine (TEOA, \geq 99.0%, Glentham Life Sciences). Deionized water (18.2 M Ω cm resistivity at 25 °C, purified using a Merck Millipore Direct-Q3 system) was used for all aqueous solutions. Fluorine-doped tin oxide coated glass (FTO, 12–14 Ω sq⁻¹, Xop Glass company – Spain) was cut, washed with an aqueous detergent solution (1% w/v Alconox), and sonicated for 20 min with acetone (AR, Bio-Lab) and ethanol (AR, Macron Fine Chemicals), subsequently.

Supramolecular precursor synthesis

A cyanuric acid–melamine (CM) supramolecular complex was prepared by mixing equal amounts of CA and M (4 mmol) in 30 mL water. The mixture was shaken for 2 h, centrifuged and dried for 24 h at 60 °C in a vacuum oven, resulting in a CM powder. *Supramolecular-films preparation*

CM powder was ground for 45 min using Fritsch Pulverisette 7 planetary ball mill (3 mm ZrO₂ balls, dry milling), washed with water, centrifuged, and dried for 24 hours at 60 °C in a vacuum oven. Next, 50 mg of ball-milled CM powder was dispersed in 5 mL of toluene to form a stable colloidal suspension (10 mg mL⁻¹). The obtained suspension was used as the deposition medium for forming CM films on top of FTO by electrophoretic deposition (EPD). The EPD setup consisted of two FTOs dipped into the deposition medium in a parallel capacitor configuration, *i.e.*, the FTO electrodes in the suspension were connected to a DC voltage using an ENDURO power supply. A constant voltage of 300 V was applied during the deposition for 2 s, 5 s, 15 s, 30 s, 45 s, 60 s, 120 s, and 180 s.

CN-films formation

Each CM_x (x = 2, 5, 15, 30, 45, 60, 120, and 180 s) electrode was placed in a glass tube (16 mm diameter × 100 mm length) along with 1.0 g melamine as a CN precursor powder for the vapor deposition. The tube was purged with N₂ for several seconds and covered tightly with an Al foil. The electrodes in each tube were calcined under N₂ atmosphere (constant flow rate of 120 mL min⁻¹), to 550 °C with a heating ramp of 5 °C min⁻¹ and kept for 4 h, resulting in CN-CM_xM electrodes. In the same calcination conditions, CM₁₂₀ electrode with CM powder (1.0 g), which was used as a CN precursor powder instead of melamine, was prepared, forming CN-CM₁₂₀CM electrode, and CM₆₀ electrodes with different amounts of melamine powder were prepared, forming CN-CM₆₀M_y electrodes (y = 0.2, 0.4, 0.6 and 0.8 g).

Characterization

FTIR spectra were obtained by using a Thermo Scientific Nicolet iS5 in the 650–4000 cm⁻¹ range using a diamond iD7 ATR. UV-vis spectra were acquired using a Cary 100 spectrophotometer equipped with a DRA (integrating sphere), in transmittance (T) and reflectance (R) modes, while the Abs(%) has calculated according to 100% - T(%) - R(%). Photoluminescence spectra were measured by using Edinburgh instruments FLS920P Fluorimeter with an excitation wavelength of λ_{ex} = 380 nm. Digital photos under UV (365 nm) illumination were taken using a TLC viewing cabinet Vilber-Lourmat CN-6. X-ray diffraction patterns (XRD) were recorded on a PANalytical's Empyrean Diffractometer equipped with a position sensitive detector X'Celerator. The data was collected for 2θ ranging from 5° to 60°, with a scanning time of ~7 min using Cu K α radiation ($\lambda = 1.54178$ Å, 40 kV, 30 mA). XPS data was collected by using an X-ray photoelectron spectrometer (Thermo Fisher ESCALAB 250) ultrahigh vacuum (1×10^{-9} bar) with an Al K α X-ray source and a monochromator. The X-ray beam size was 500 µm and survey spectra was recorded with a pass energy (PE) of 150 eV and high energy resolution spectra were recorded with a PE of 20 eV. All XPS spectra peaks were shifted relative to the C 1s peak, positioned at 284.8 eV, to correct for charging effects. The XPS results were analyzed by using the AVANTGE software. For measuring film thickness, the electrodes were scratched in three different areas on top of the same film, using a needle (1.20 mm diameter). Thickness profile was obtained by using a 3D laser microscope (LEXT OLS5000), under low magnification (×10), via focusing on a specific scan area around the scratches. The roughness from both sides of the scratch (300

 \times 200 µm) was averaged by the software, then the distance between the lowest part (FTO level), to the averaged top part of the coating (to the left and right of the scratch) has been calculated. Scanning electron microscopy (SEM) images were recorded on an FEI Verios 460L high resolution SEM, operated at 3.0 kV, and equipped with a FEG source. To avoid charging effects, the samples were coated with 10 nm of sputtered gold (for CN precursors) or a carbon (for CN).

Photoelectrochemical measurements

Photoelectrochemical analysis was performed using a three-electrode system coupled to PalmSens3 (chronoamperometry, linear sweep voltammetry) or Metrohm Autolab (Mott-Schotkky and IPCE) potentiostats. A Pt-plate (1.0 cm²), and an Ag/AgCl (saturated KCl) electrodes were used as counter and reference electrodes, respectively. The electrolyte was either a 0.1 M KOH aqueous solution (pH \approx 13) or a 0.1 M KOH solution containing 10% v/v TEOA as a hole scavenger. All the potentials *vs.* Ag/AgCl were converted with respect to a reversible hydrogen electrode (RHE), using the Nernst equation at room temperature:

$$E_{RHE}(V) = E_{Ag/AgCl}(V) + 0.197 + 0.059 \times pH$$

Chronoamperometry measurements were carried out at a bias potential of 1.23 V vs. RHE under one-sun illumination (power density of 100 mW cm⁻²), provided by a solar simulator (Newport, OPS-A500, 300 W Xe arc lamp, equipped with an air mass AM 1.5G and water filters) and calibrated using a power meter (Newport, 919P thermopile detector). The electrolyte was purged with N₂ for 15 min, followed by linear sweep voltammetry (LSV) measurements in the dark and under 1 sun illumination, at a scan rate of 10 mV s⁻¹. Mott-Schottky measurements were performed in 1 M Na₂SO₄ at a 1.0 kHz frequency. Incident photon-to-current conversion efficiency (IPCE) values at different wavelengths were calculated from the following equation:

$$IPCE \ (\%) = \frac{J_{KOH - or - TEOA} \ (A \ cm^{-2}) \times 1240}{\lambda \ (nm) \times I \ (W \ cm^{-2})} \times 100\%$$

Where *J* is the photocurrent density (J_{KOH} is the photocurrent obtained in 0.1 M KOH aqueous solution, while J_{TEOA} is the photocurrent obtained in 0.1 M KOH aqueous solution

containing 10% (v/v) TEOA; λ is the wavelength of the incident monochromatic light (400, 420, 450, and 480 nm); *I* is the light power density. Incident monochromatic light of different wavelengths was obtained by inserting a corresponding band-pass filter (Newport 10BBPF10-400, 10BBPF10-420, 10BBPF10-450, and 10BBPF10-480) between the solar simulator and the PEC cell.

The amount of photogenerated H_2 in the reactor headspace was analyzed using a gas chromatograph (Agilent 7820 GC system) equipped with a thermal conductivity detector (TCD).

Faraday efficiency (FE) was calculated using the following equation:

$$FE (\%) = \frac{m \cdot n \cdot F}{I \cdot t} \times 100\%$$

Where *m* is the number of moles of gas actually produced; *n* is the number of electrons in the electrochemical reaction; *F* is the Faraday constant; *I* is photocurrent; *t* is reaction time. This equation represents the ratio between the actual hydrogen gas evolution rate and calculated one from measuring the generated photocurrent.



Fig. S1 SEM images of CM powder assembled in water (a)–(b) before and (c)–(d) after ballmilling.



Fig. S2 Top-view SEM images of (a) CM_5 , (b) CM_{30} , (c) CM_{60} , and (d) CM_{180} electrodes.



Fig. S3 FTIR spectra of CM powders (assembled in water) before (orange) and after (rose) ball milling, and CM_{120} electrode (purple). Spectra are offset for clarity.



Fig. S4 General thickness profile of a CM_x electrode measured using a 3D laser microscope.



Fig. S5 Film thickness of the CM_x electrodes in EPD time intervals shorter than 60 s (*i.e.*, x = 2, 5, 15, 30, 45, 60) as function of deposition time.

Deposition time (s)	Average thickness of both sides (µm)	Total average thickness (µm)	Standard deviation (µm)
2	1.9	2.3	0.5
	2.8		
	2.1		
	3.6		
5	2.6	3.2	0.5
	3.3		
15	4.6	5.0	0.5
	5.5		
	4.9		
30	7.5	7.2	0.3
	7.1		
	7.0		
	8.1		
45	8.1	7.7	0.7
	6.9		
60	98		
	8 1	9.0	0.9
	0.2	9.0	0.9
120	9.5		
	/.6		
	8.3	8.2	0.6
	8.8		
	10.1		
180	9.0	8.6	1.7
	6.8		

Table S1. Statistical calculations of CM_x films thickness.



Fig. S6 Top-view SEM images of (a) CN-CM₅M, (b) CN-CM₃₀M, (c) CN-CM₆₀M, and (d) CN-CM₁₈₀M electrodes.



Fig. S7 Cross-sectional SEM images of (a) CN-CM_xM electrodes, and (b–c) CN-CM₁₂₀M.



Fig. S8 Top-view SEM images of (a) $CN-CM_{60}$ (insets: the corresponding digital photo and top-view SEM images), and (b) CN-M (insets: the corresponding digital photo and cross-sectional SEM image) electrodes.



Fig. S9 XPS analysis of CN-CM₁₂₀M electrode for (a) C1s, and (b) N1s.



Fig. S10 Final film thickness of the CN-CM_xM electrodes (after calcination), which were prepared using EPD time intervals shorter than 60 s (*i.e.*, x = 2, 5, 15, 30, 45, 60) as function of deposition time.

Deposition time (s)	Average thickness of both sides (µm)	Total average thickness (µm)	Standard deviation (µm)
2	16.8 16.9	16.9	0.05
-	16.9	10.9	0.05
	17.6		
5	17.1	17.9	1.1
-	19.2		
15	18.5		
	18.5	18.6	0.1
	18.7		
30	19.7		
	18.7	18.8	0.9
	18.0		
45	20.4		
	25.8	24.3	3.4
	26.6		
60	29.2		
	24.0	26.6	2.6
	26.6		
120	27.2		
	22.7	25.9	2.7
	27.7		
	32.1		
180	32.9	31.8	1.3
	30.4		

Table S2. Statistical calculations of CN-CM_xM films thickness.



Fig. S11 Film thickness of $CN-CM_{60}M_y$ electrodes as function of melamine powder mass in the glass tube during preparation of the electrodes.

Melamine mass (g)	Average thickness of both sides (µm)	Total average thickness (µm)	Standard deviation (µm)
	10.0		
0.2	15.5	12.8	2.7
	13.0		
0.4	18.2		
	18.7	18.9	0.8
	19.8		
	23.1		
0.6	20.5	21.7	1.3
	21.4		
0.8	26.2	25.7	0.4
	25.6		
	25.4		
	29.2		
1.0	24.0	26.6	2.6
	26.6		

Table S3. Statistical calculations of $CN-CM_{60}M_y$ films thickness.



Fig. S12 Tauc plots of CN-CM_xM electrodes (direct optical band gap, E_g).



Fig. S13 SEM image of CN-CM₁₂₀CM electrode (insets: the corresponding digital photo and cross-sectional SEM image).



Fig. S14 Optical characterization of CN-CM₁₂₀CM and CN-CM₁₂₀M electrodes: (a) UV-Vis absorptance spectra, (b) Tauc plot analysis assuming a direct E_g , and (c) photoluminescence spectra ($\lambda_{ex} = 380$ nm).



Fig. S15 Photocurrent densities at 1.23 V *vs.* RHE in 0.1 M KOH of (a) CN-CM₅M, (b) CN-CM₃₀M, (c) CN-CM₆₀M, (d) CN-CM₁₂₀M, and (e) CN-CM₁₈₀M electrodes under front- and back-illumination (1 sun), and (f) comparison of CN-CM_xM electrodes under back illumination (1 sun).



Fig. S16 Photocurrent densities of $CN-CM_{120}CM$ and $CN-CM_{120}M$ electrodes at 1.23 V vs. RHE in 0.1 M KOH under back-illumination (1 sun).



Fig. S17 Photocurrent stability of CN-CM_xM electrodes at 1.23 V vs. RHE in 0.1 M KOH aqueous solution containing 10% v/v TEOA upon continuous back-side illumination (1 sun).



Fig. S18 Mott–Schottky plots of (a) $CN-CM_5M$, (b) $CN-CM_{30}M$, (c) $CN-CM_{60}M$, (d) $CN-CM_{120}M$, (e) $CN-CM_{180}M$, and (f) $CN-CM_{120}CM$ electrodes.



Fig. S19 Proposed energy level diagram of $CN-CM_xM$ and $CN-CM_{120}CM$ electrodes with respect to water redox reactions.



Fig. S20 IPCE measurements of $CN-CM_{120}M$ electrode in 0.1 M KOH aqueous solution with and without 10% v/v TEOA upon 1 sun illumination.



Fig. S21 (a) Gas chromatograph of $CN-CM_{120}M$ as the photoelectrocatalyst biased at 1.23 V *vs.* RHE, under constant 1 sun illumination, and (b) H₂ production rates of $CN-CM_{120}M$ in 0.1 M KOH containing 10% (v/v) TEOA.