Supporting Information

Coordination Chemistry Engineered Polymeric Carbon Nitride Photoanode with Ultralow Onset Potential for Water Splitting

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Experimental Section

Chemicals and materials: Dicyandiamide (99%), Urea (99.0%-100.5%), Melamine (99%), H$_2$SO$_4$, Na$_2$SO$_4$ and NaOH were purchased from Sigma Aldrich and used without any further purification. High purity water (18.2 MΩ • cm) was prepared by a UP water Purification System. Fluorine doped tin oxide (FTO, 15*50*2.3 mm, 15 Ω sq$^{-1}$) coated glass were used for the conductive substrate. They were ultrasonically cleaned in acetone, ethanol, and high purity water for 30 min, respectively, and then dried with nitrogen gas before use.

Preparation of polymeric carbon nitride (PCN) photoanodes: A layer with 25 nm thickness of Ti film was deposited on FTO by magnetron sputtering (AJA ATC 2200 sputtering system), the as-prepared substrate was named Ti-FTO. For urea and dicyandiamide-derived PCN, the Ti-FTO glass was positioned at the bottom of a porcelain boat (30*60*15 mm) with the conductive side facedown, next a certain amount of precursor (6 g of urea, or 5 g of dicyandiamide) was put into the crucible above the Ti-FTO glass (gap exists between the bottom of crucible and the Ti-FTO glass). For melamine-derived PCN, 6 g of melamine powder was put into the crucible firstly and then the conductive side of the Ti-FTO glass was positioned on the top of the melamine powder. The crucible was heated to 250 °C for 2h and then 550 °C for another 2h under slowly flowing Argon atmosphere, the heating rate was 3 °C/min for both steps. After cooling down, the as-prepared PCN photoelectrodes could be obtained by removing the PCN aggregates on the backside of the FTO side with blade. The dicyandiamide, urea and melamine-derived carbon nitride films are denoted as DPCN, UPCN and MPCN, respectively.

Preparation of carbon nitride powder photoanodes: DPCN powder was synthesized by the above-mentioned procedure without Ti-covered FTO substrate. It was deposited on FTO glass by an electrophoretic method. Specifically, 40 mg of DPCN powder was dispersed in 50 ml of acetone containing 40 mg of iodine, the deposition was carried out in a two-electrode electrochemical cell by applying a constant voltage of 10 V for 10 min between two vertically aligned FTO glasses with 1 cm of distance. The electrode was extracted from the suspension after deposition and heated to 200 °C for 2h to strengthen the interaction between DPCN powder and FTO glass.

Characterization: The morphology and thickness of CN photoanodes were observed by a field emission scanning electron microscope (SEM, JEOL, JSM-7100F) and a Transmission electron microscope (TEM, HITACHI, HT7700A). The crystalline phases were characterized by X-ray powder diffraction (XRD, Bruker D8 Advance) with Cu Kα (λ=0.15406 nm) radiation. The chemical bond information was conducted by a Fourier transform infrared spectrometer (FT-IR, Agilent CARY 630). The UV-vis absorption spectra measurements were carried out by a JASCO V-650 spectrophotometer. X-ray photoelectron spectroscopy (XPS) with an Al Kα (hν=1253.6 eV) radiation source (Kratos Axis Supra) was used to investigate the chemical composition of the samples. All the binding energies were calibrated by using C 1s (284.8 eV) as a reference. Photoluminescence (PL) spectra and fluorescence lifetime spectra were recorded at room temperature with a Fluorescence spectrophotometer (Edinburgh FLSP-920). Nano-scratch tests were performed on a Hysitron Triboscope.
(Hysitron Inc., Minneapolis, MN, USA) with a conical tip of 20 μm diameter. A confocal microscope (LEXT OLS4100, Olympus, Japan) was used to take the surface image after scratching.

**(Photo)electrochemical measurements:** The PEC water splitting experiments were carried out in a standard three-electrode electrochemical cell on an electrochemical workstation (CHI 660d, CH Instruments, Inc) with Pt wire as counter electrode and KCl saturated Ag/AgCl electrode as reference electrode. The photocurrent was measured under a 150W Xenon lamp illumination mounted with an AM 1.5 G filter (100 mW/cm²). All PEC experiments were performed at room temperature and purged with argon gas for 30 min prior to the tests. The photoelectrodes were irradiated from the backside. Aqueous solutions of 0.5 M H₂SO₄, 0.5 M Na₂SO₄, 1 M NaOH were used as electrolytes for photoelectrochemical measurements.

Mott-Schottky (MS) curves were measured in 0.5 M H₂SO₄ aqueous solution at frequencies of 1000, 1500 and 2000 Hz. Electrochemical impedance spectra (EIS) were measured at 1.23 V RHE in 0.5 M H₂SO₄ aqueous solution under 1 sun illumination. For OCP measurements, O₂ gas was bubbled into the electrolyte firstly, then recording was started after a equilibration process (~30 min with constant stirring).

The measured potential vs. Ag/AgCl was converted to reversible hydrogen electrode (RHE) through the Nernst equation:

\[
E_{RHE} = E^\theta_{AgCl/Ag} + E_{AgCl/Ag} + 0.059 \text{ pH}
\]

Where \( E_{RHE} \) refers to the converted potential vs RHE. \( E^\theta_{AgCl/Ag} \) represents the saturated electrode potential of AgCl/Ag and the value is 0.197 V at room temperature. \( E_{AgCl/Ag} \) represents the experimentally measured potential vs. \( E^\theta_{AgCl/Ag} \).

**Un-biased PEC water splitting:** Test was conducted in a two-electrode cell comparted by a Nafion proton exchange membranes (PEM), in which the counter electrode is platinum wire. The cell was purged with argon for 30 min before and throughout the test.
Figures/Tables and discussion

Table S1. Summary of preparation methods and PEC activity of PCN photoanodes.

| PCN Photoanodes | Preparation methods | j at 1.23V_{RHE} (μA/cm²) | E_{onset} (V_{RHE}) | Electrolyte | Reference |
|-----------------|---------------------|--------------------------|--------------------|-------------|-----------|
| DPCN            | Ti-induced deposition | 242                     | -0.38              | 0.5M H₂SO₄  | This work |
| CNₜm            | Thiourea-seeded deposition | 353                     | 0.32               | 0.1M KOH    | Nature Communications, 2020, 4701 |
| CN-MSG/M        | Doctor-blade/Thermal vapor deposition | 270                     | 0.0012             | 0.1M KOH    | Nano Lett. 2020, 20, 4618–4624[1] |
| CNₙW            | Microwave induced deposition | 38                      | None               | 0.1M KCl    | Angew. Chem. Int. Ed. 2020, 59, 1139 –1143[2] |
| CN-rGO          | Doctor-blade technique | 124                     | 0.35               | 0.1M KOH    | J. Mater. Chem. A, 2019, 7, 11718–11723[3] |
| Compact PCN     | Thermal vapor deposition | 230                     | ~0.05*             | 0.5M Na₂SO₄ | Catal. Sci. Technol., 2019, 9, 425-435[4] |
| Porous PCN      | Melamine-seeded deposition | 116                     | 0.25               | 0.1M KOH    | Angew. Chem. Int. Ed. 2018, 57, 15807-15811[5] |
| PCN nanotube    | Confined polymerization within AAO template | 120.5                   | ~0.3*              | 0.1M Na₂SO₄ | Nano Lett. 2018, 18, 5954-5960[6] |
| Crystal-Face Tailored PCN | Thermal vapor deposition | 228.2                   | ~0.5*              | 0.2M Na₂SO₄ | ChemSusChem 2018, 11, 2497-2501[7] |
| B-doped PCN     | Rapid thermal vapor deposition | 103.2                   | ~0.4*              | 0.1M Na₂SO₄ | Angew. Chem. Int. Ed. 2017, 56, 8221-8225[8] |
| Compact PCN | Thermal vapor deposition | 63 | ~0.2* | 0.1M Na₂SO₄ | Carbon 2017, 117, 343-350[9] |
|------------|--------------------------|----|--------|-------------|-------------------------------|
| CoS₂-merged PCN | In-situ thermal polymerization | 200 | ~0.13* | 1M NaOH | ChemSusChem 2022, 15, e20220033[10] |

* Estimated from LSV curves.

**Figure S1.** As-prepared UDCN film on Ti-coated FTO with different thickness of Ti (10 nm, 20 nm and 25 nm from left to right). Clearly the 25 nm Ti-covered FTO resulted in PCN film with largest coverage.

**Figure S2.** (a) UV-Vis diffuse reflectance spectrum (inset: digital image), and corresponding Tauc plot (b) of the DPCN photoelectrode. The bandgap is determined by the intersection point of the dashed tangent line and the horizontal axis.
Figure S3. Cross-sectional SEM image of the DPCN photoelectrode.

Figure S4. Ti2p core-level spectrum of the sputtered Ti film on FTO.
Figure S5. (a) Equivalent circuit for fitting the Nyquist plots and (b) corresponding fitting results for the DPCN and the DPCN powder photoelectrodes. $R_s$ represents the series and solution resistances, while $R_{\text{bulk}}$ and $R_{\text{ct}}$ represent the charge transfer resistance in the bulk film and at film/electrolyte interface, respectively. CPE$_{\text{bulk}}$ and CPE$_{\text{ct}}$ represent space-charge capacitance in the bulk film and the Helmholtz capacitance at film/electrolyte interface, respectively.

| Sample      | $R_s$ (Ω) | $R_{\text{bulk}}$ (kΩ) | $R_{\text{ct}}$ (kΩ) | CPE$_{\text{bulk}}$ (µF) | CPE$_{\text{ct}}$ (µF) |
|-------------|-----------|------------------------|-----------------------|---------------------------|------------------------|
| DCN         | 49.0      | 1.6                    | 78.0                  | 11.2                      | 5.6                    |
| DCN powder  | 20.3      | 21.6                   | 4046.4                | 1.9                       | 1.2                    |

Figure S6. (a) Room-temperature steady-state PL spectra, (b) fitted PL lifetime of the DPCN and the DPCN powder photoelectrodes. The excitation wavelength is 375 nm.

| Sample          | $\tau_1$ (ns-Rel%) | $\tau_2$ (ns-Rel%) | $\tau_3$ (ns-Rel%) | $\tau_{\text{total}}$ (ns) |
|-----------------|--------------------|--------------------|--------------------|----------------------------|
| DPCN            | 1.29-17.17         | 4.14-56.48         | 17.82-26.35        | 7.26                       |
| DPCN Powder     | 1.95-24.94         | 5.59-50.28         | 38.26-24.78        | 12.77                      |
**Figure S7.** (a) Linear Sweep Voltammetry (LSV) curves of the DPCN photoelectrode in 0.5 M H$_2$SO$_4$ under 1 sun illumination. Inset: LSV curves of the calcined Ti-FTO substrate. (c) Mott-Schottky plots of the DPCN photoelectrode at varied frequencies. (c) LSV curves of the DPCN photoelectrode in 0.5 M H$_2$SO$_4$ aqueous solution with/without 20 vol% MeOH under 1 sun illumination. (d) LSV curves of the DPCN photoelectrode in 0.5 M Na$_2$SO$_4$ and 1 M NaOH aqueous solution under 1 sun illumination.
Figure S8. Long-term stability of the DPCN photoelectrode in 75mL of 0.5M H₂SO₄ (with/without 20 vol% MeOH) aqueous solution under 1 sun illumination (zero bias).

Figure S9. Interfacial (PCN/Ti) Ti2p core-level spectrum of the DPCN photoelectrode after stability test.
Figure S10. Cross-sectional and top-view SEM images of the MPCN (a and b, respectively), and the UPCN (c and d, respectively) photoelectrodes. Insets in (a) and (c): the corresponding digital images; Inset in (d): TEM image of the UPCN nanotubes. (e) XRD patterns of the MPCN and the UPCN photoelectrodes. (f) FT-IR spectra of the MPCN and the UPCN powders scratched from each photoelectrodes.

Morphology/thickness: The MPCN film has a thickness of ~150 nm (Figure S10a) and is regionally smooth and uniform (Figure S10b), the obvious cracks may be caused of thermal stress during temperature increase/decrease. The UPCN film (~75μm, Figure S10c) is composed of interconnected irregular nanotubes (Figure S10d) with a diameter of ~200-300 nm.

XRD pattern (Figure S10e) and FT-IR spectra (Figure S10f): For the XRD pattern of the UPCN, the curved characteristic of nanotube structure deteriorates the in-plane periodicity (210) and thin tube layers also makes its (002) peak less pronounced; The MPCN is too thin to exhibit any XRD peaks assigned to PCN. Both films show characteristic FT-IR peaks ascribed to PCN: Stretching vibration modes of heptazine units at 1200-1700 cm⁻¹, their breathing modes (at 809 cm⁻¹ for the UPCN and at 796 cm⁻¹ for the MPCN), and stretching vibration modes of the -NH₂ groups and the -OH groups originated from H₂O molecules at 2800-3400 cm⁻¹.
**Figure S11.** XRD pattern (a) and TEM image (b) of the intermediate obtained after calcination of urea at 250 °C for 2h.

Formation mechanism of PCN nanotubes: It is reported that thermal decomposition of urea at temperature ranging from 250°-350° leads to melamine and cyanuric acid\textsuperscript{[11]}. Accordingly, in this case, supramolecular melamine-cyanuric acid (MCA) nanorods in-situ formed at 250 °C through a self-assembly process, as confirmed by XRD pattern and TEM image of the supramolecular intermediate in Figure S9a and b, respectively. Then the MCA nanorods transformed into PCN nanotubes after a thermal polycondensation process at 550 °C.

Note: It was demonstrated that PCN nanotubes can be obtained by thermal treatment of MCA nanorods\textsuperscript{[12]}. MCA nanorods were usually synthesized by hydrothermal treatment of precursors like melamine and urea, whereas here MCA was in-situ obtained by thermal treatment of urea. The method presented in this work is one of the most facile ways reported to prepare PCN nanotubes.
Figure S12. LSV curves of the MPCN and the UPCN photoelectrodes in 0.5 M H$_2$SO$_4$ under 1 sun illumination.
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