

Porous Graphitic Carbon Nitride Synthesized via Directly Polymerization of Urea for Efficient Sunlight-driven Photocatalytic Hydrogen Production

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Supplementary Information

Experimental

1. Catalyst preparations: Graphitic carbon nitride (g-C₃N₄) was synthesized by thermal treatment of three precursors respectively (urea, thiourea and dicyandiamide, 10 g, AR, Sinopharm Chemical Reagent Co., Ltd) in a crucible with a cover under ambient pressure in air. After dried at 80°C for 24 h, the precursor was put in a Muffle Furnace (Isotemp Programmable Muffle Furnace 650-750 Series, Fisher Scientific) and heated to 550°C for 3 hours to complete the reaction. The powders were washed with nitric acid (0.1 mol L⁻¹) and distilled water to remove any residual alkaline species (e.g. ammonia) adsorbed on the sample surface, and then dried at 80°C for 24 h. The as-prepared samples were denoted as UCN, TCN and DCN. The prepared

powders were yolk yellow/orange/bright yellow color respectively (Fig S6).

2.Characterization: The X-ray diffraction (XRD) measurements were performed with X'Pert-Pro MPD with Cu K α ($\lambda=1.5406$ Å). The surface morphologies of the polymer were determined by transmission electron microscopy (TEM) observed on Tecnai G2 F20 S-Twin (FEI, 200 kV). Chemical compositions and element binding energies of g-C₃N₄ were analyzed using X-ray photoelectron spectroscopy (XPS) on Perkin-Elmer RBD upgraded PHI-5000C ESCA system with Al K α x-ray as an excitation source. FTIR spectra were recorded on Nicolet 6700 IR spectrometer by using KBr pellets. UV-Vis diffuse-reflectance spectra (UV-Vis DRS) were recorded on Cary 5000 with Integrating Sphere Attachment (incident angle to reflecting sample: 12.5°). Photoluminescence measurements (PL) were conducted on HITACHI F-4600 fluorescence spectrophotometer. N₂ adsorption-desorption analyses were carried out at 77 K using Mocrmeritics Tristar II 3020 M.

3. Photocatalytic activity measurements: Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. Photoreduction of H⁺ to H₂ was performed in pure water, as well as aqueous solutions containing some sacrificial agent. H₂ production half reaction was performed by dispersing 80 mg of g-C₃N₄ catalyst powder in pure water (100 ml) or an aqueous solution (100 mL) containing triethanolamine (TEA, 10 vol. %) as a sacrificial reagent. In the case of deposition of Pt, an appropriate amount of H₂PtCl₆ was dissolved in the reactant solution and pre-loaded on the g-C₃N₄ under ultraviolet irradiation. The reactant solution was evacuated for one hour to remove air

completely prior to irradiation under a PLS-SXE 300 Xe lamp and a water filter. The wavelength of the incident light was controlled by using an appropriate cut-off filter to provide simulated sunlight. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography.

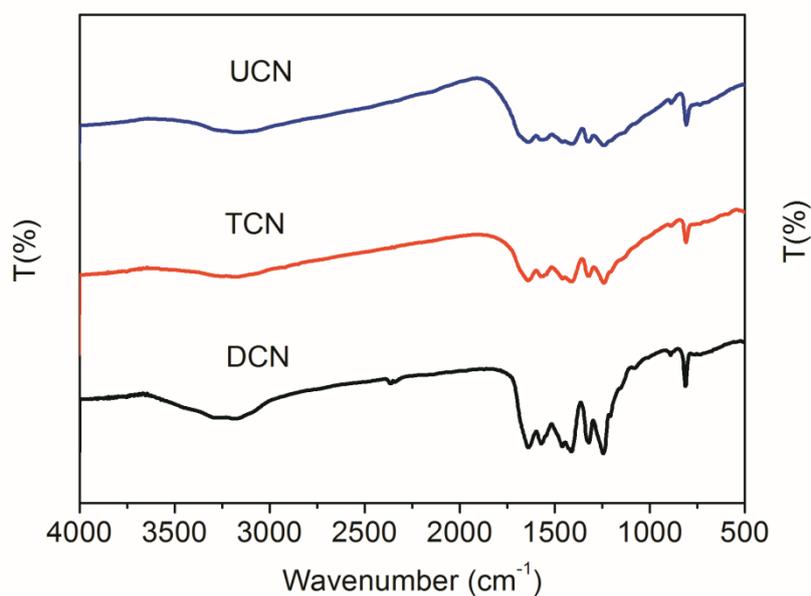


Figure S1. The FT-IR spectra of the obtained graphitic carbon nitride powders (UCN, TCN and DCN). The spectra present several major bands between 1200 cm⁻¹ and 1650 cm⁻¹ region. The peaks at about 1241, 1319, 1411, 1457, 1569, 1639 cm⁻¹, belong to the characteristic stretching modes of CN heterocycles. In addition, the breathing mode of triazine units at 809 cm⁻¹ was presented. The results are well consistent with former reports.¹

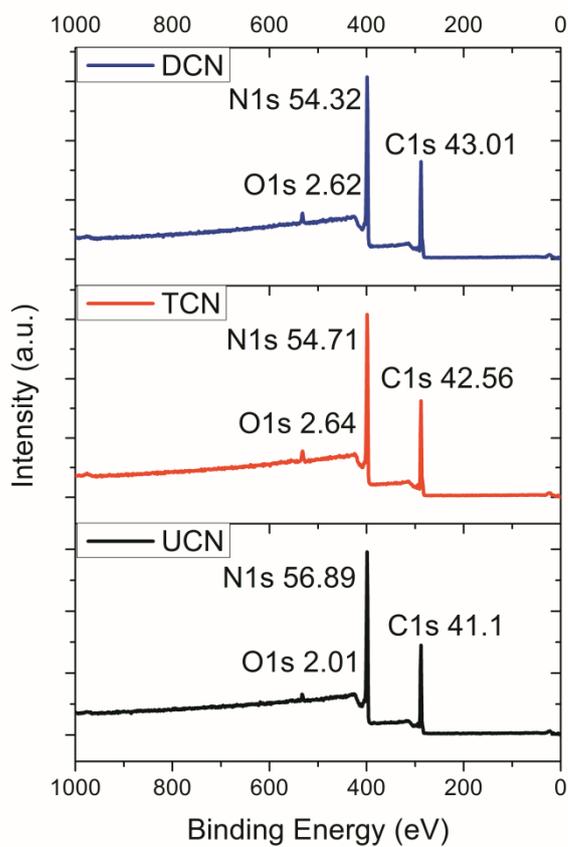


Figure S2. The XPS spectra of the powders prepared at 550°C of UCN, TCN and DCN from bottom to top.

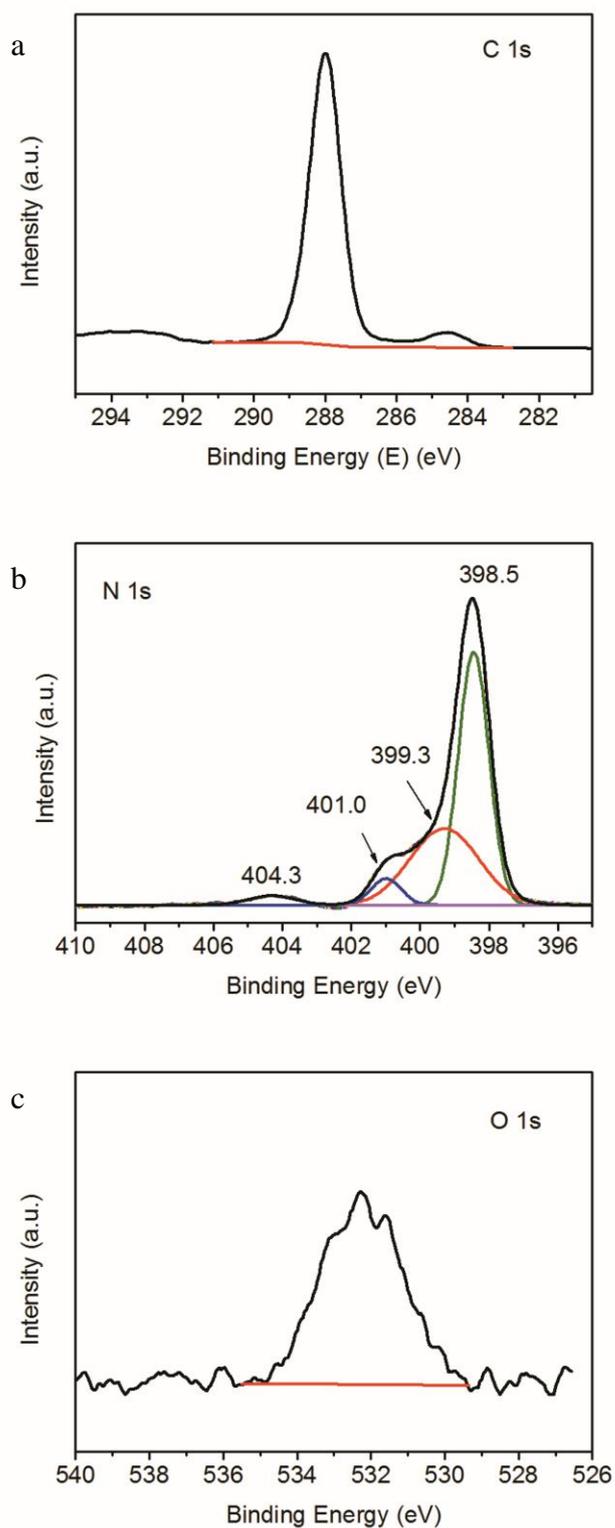


Figure S3. The XPS spectra of UCN: (a)C 1s, (b)N 1s, (c)O 1s.

XPS measurements can provide us more detailed information on the chemical composition and element status of C, N elements (Figure S3a-b). Figure S3a shows two C 1s peaks centering at 288.0 eV and 284.6 eV, corresponding to sp^2 -bonded carbon (N-C=N) and graphitic carbon respectively. In Figure S3b, the N 1s spectrum

can be fitted into four binding energies. Two main signals at 398.5 eV and 399.3 eV are exhibited. The former peak shows occurrence of C-N=C groups (denoted as N₁). The second peak relate to either tertiary nitrogen N-(C)₃ groups linking structural motif (C₆N₇) or amino functions carrying hydrogen ((C)₂-N-H) in connection with structural defects and incomplete condensation (denoted as N₂). A weak peak at 401.0 eV corresponds to N bonded three carbon atoms in the aromatic cycles. The 404.3 eV peak is attributed to the π -excitations.¹

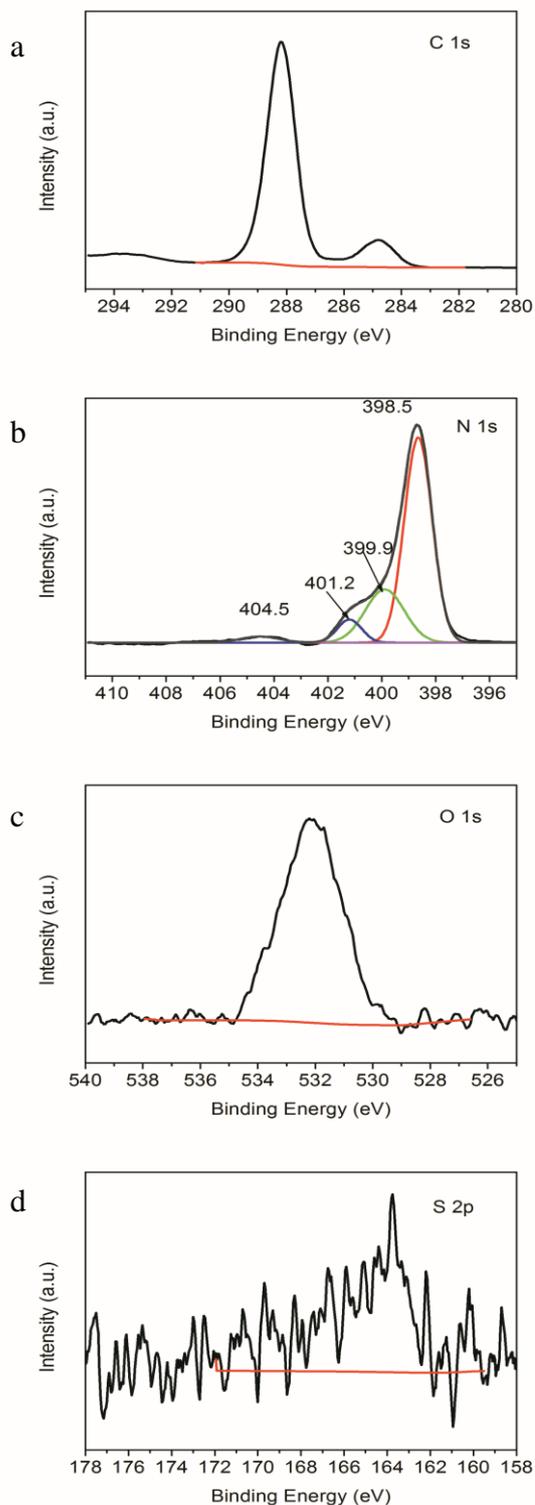


Figure S4. The XPS spectra of TCN. (a) C 1s, (b) N 1s, (c) O 1s, (d) S 2p. The spectra of TCN are similar to UCN. Careful examination of S 2p spectrum of the TCN sample (Figure S4d), the existence of sulfur is clearly evidenced.

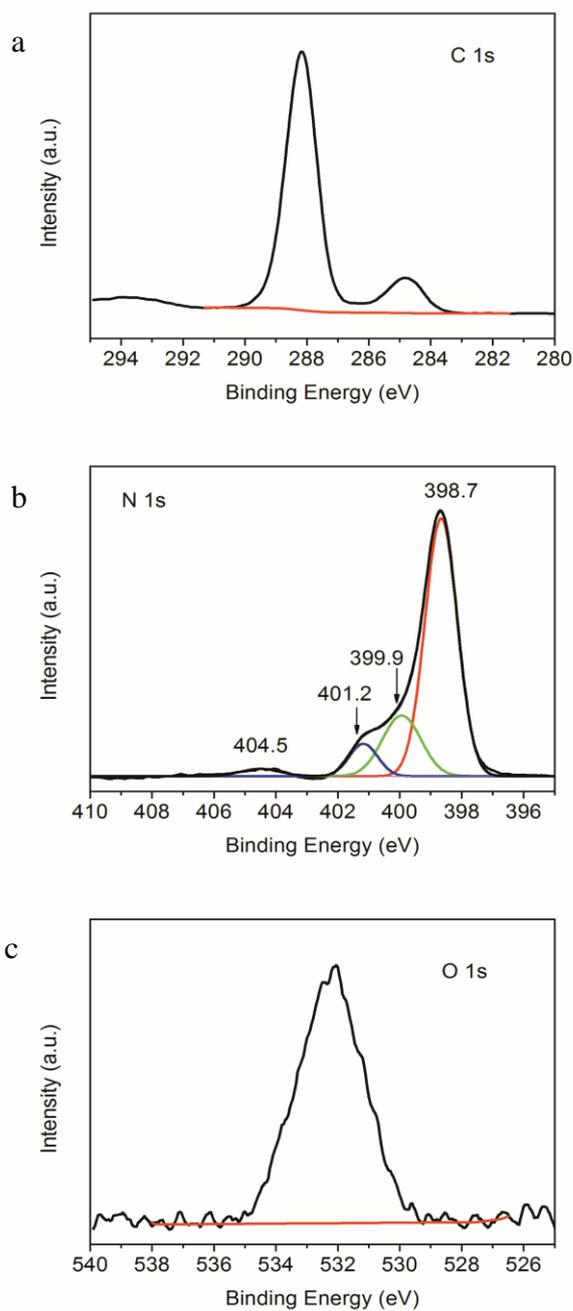


Figure S5. The XPS spectra of DCN. (a) C 1s, (b) N 1s, (c) O 1s. The spectra of DCN are similar to UCN.



Figure S6. The pictures were yolk-yellow UCN, orange TCN and bright yellow DCN from left to right.

References

- 1 J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen, *J. Mater. Chem.*, **2011**, *21*, 14398.