

### Supporting materials (†)

#### **A superficial intramolecular alignment of carbon nitride through conjugated monomer for optimized photocatalytic CO<sub>2</sub> reduction**

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## 1. Chemical used

Analytical grade chemicals were used, from the Sigma Aldrich company china 2, 2-bipyridine, cobaltous chloride, urea was ordered. An organic solvent namely tetrahydrofuran, methanol, dimethyl sulfoxide, acetonitrile, dimethylformamide and trichloromethane were purchased from Sinopharm Chemical Limited China. High grade CO<sub>2</sub> gas with 99.99% purity taken from Fuzhou Lianzhong Industrial Gases Ltd and <sup>13</sup>CO were ordered from Beijing Hess Chemical Industries

## 2. Preparation of photocatalysts

Preparation of TDP was carried out by the reported literature [1].

### 2.1. The synthesis of CN and CN-TDP

In typical procedure CN samples were synthesized taking urea as the main precursor by heating (15 g) of its amount directly at 600 °C (5 °C per minute) for 2 hours under air furnace and were denoted by CN. To prepare TDP modified CN, 15g of urea and various amount of TDP liquified in 15 ml of purified water and kept in glycerol oil bath at heating rate of 90 °C by continuous stirring for day and night by completely evaporate the water. After the solid residues were shifted into crucibles and keep for calcination in simple Air furnace at same temperature of 600 °C for 2 hours at heating rate 5 °C. After cooling to room temperature, the as-prepared samples were grounded into power and were used for further techniques and characterization. The as-prepared material was identified referred to be CN-TDP<sub>x</sub>, (x = 7.0, 12.0 mg).

## 3. Characterization

The as-prepared pristine CN and modified CN-TDP<sub>x</sub> samples were characterized by using powder X-ray diffraction and conducted from Bruker D8 diffractometer with Cu Kα1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The Fourier transform infrared spectra (FT-IR) were carried out by Biorad FTS 6000 spectrometer. Further UV-Visible diffuse reflectance (DRS) was carried by Varian Cary 500 Scan system. Photoluminescence analysis was examined by Edinburgh FI/FSTCSPC-920 spectrophotometer. Thermo ESCALAB-250 machine were utilized to measure X-ray photoelectron with AlKα line source (200 W) and Bruker Model A-300 spectrometer were used to study the electron paramagnetic resonance for the samples. Filed Scanning Emission Microscope was carried out on Hitachi SU8010. Transmission electron microscope were conducted on FEI Tencai 20 microscope. The photoluminescence (PL) spectra were characterized on an Edinburgh FI/FSTCSPC 920 spectrophotometer. For porosity analysis and the surface are, N<sub>2</sub> adsorption-desorption isotherm recorded on micromeritics ASAP-2020 at 77K. over

Bruker Advance III-500 MHz  $^{13}\text{C}$  NMR was measured. By using BAS Epsilon CHI electrochemical system with Pt counter electrode, A/AgCl reference and working electrode (as-prepared samples) with electrolytic solution of sodium sulphate, the electrochemical measurements were analyzed. An Agilent 7820A gas chromatography machine was used as for the detection of gases evolved during Carbon dioxide reduction ( $\text{CO}_2$ ).

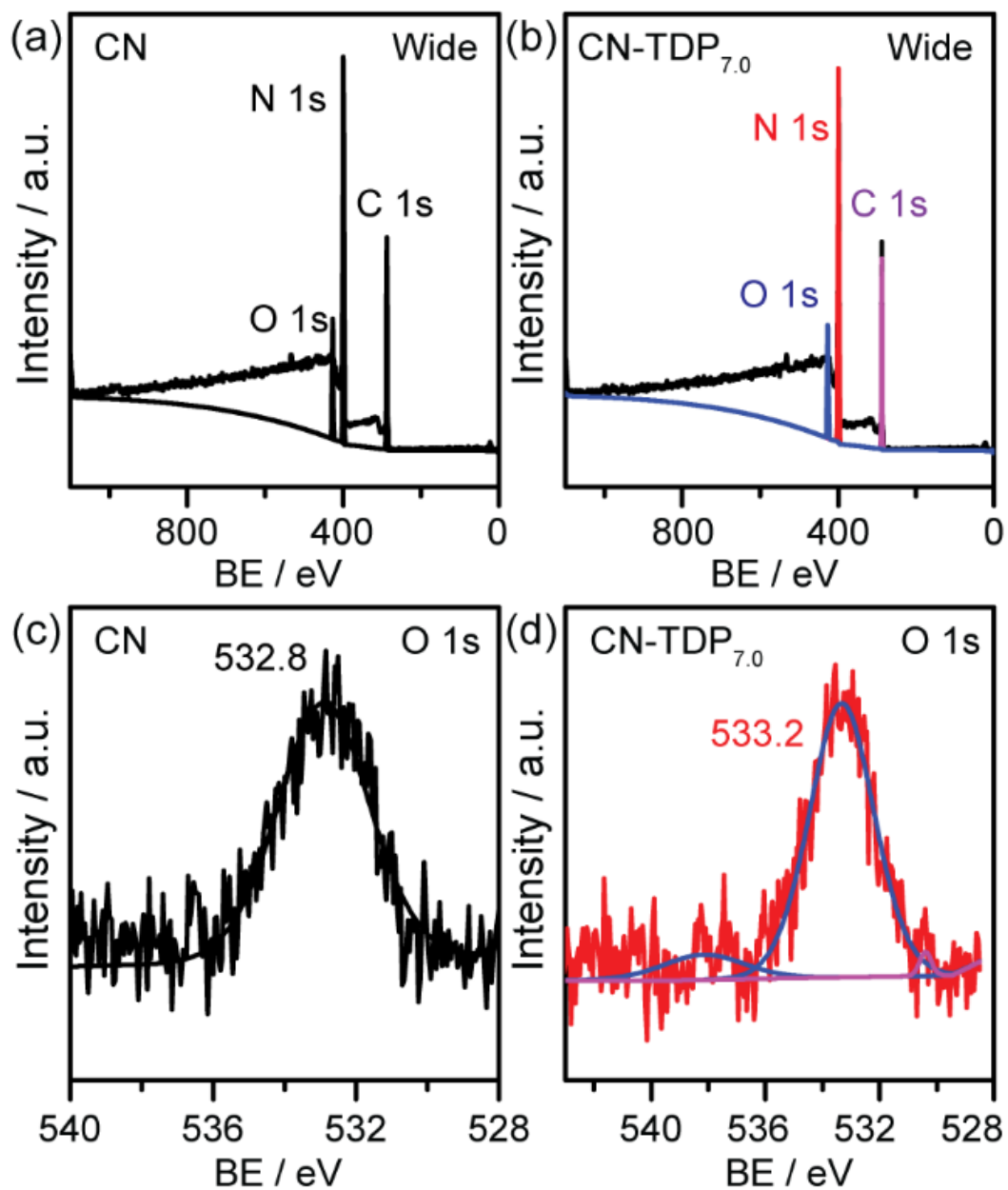
### 3.1. Photocatalytic $\text{CO}_2$ reduction reaction

$\text{CO}_2$  reduction was carried out with self an adaptable two necks Schlenk flask having 80 mL of its total volume by means of 300 W light source of Xe lamp under visible light. Typically, 30 mg fine crushed as-prepared catalyst was spared in 5 ml of solvent containing  $1\ \mu\text{mol}$  of cobalt chloride ( $\text{CoCl}_2$ ), 1 ml of triethanolamine (TEOA) and 15 mg of 2, 2-bipyridine respectively. The whole mixture system was employed to vacuum degassing for about three times by continuous vigorous stirring and after degassing backfilling the Schlenk flask with pure  $\text{CO}_2$  gas (1 bar). Later the system was photocatalytically kept under 300 W lamp (Xe) having 420 nm cutoff filter underneath dynamic shaking and system temperature was stabilized at  $30\ ^\circ\text{C}$  through continuous movement of chilling water system. After irradiation, produced gases ( $\text{CO}$ ,  $\text{H}_2$ ) were detected by gas chromatography (An Agilent 7820A gas chromatography) having Argon (Ar) was utilized as transporter during detection. After all, in the isotopic experiments  $^{13}\text{CO}_2$  (98% in purity, 1bar) was used as a reactant source and all experiments were conducted photo catalytically under same condition and the produced  $^{13}\text{CO}$  was detected through gas chromatography mass spectrometer.

### 3. 2. Electrochemical Measurements

Fluoride tin oxide (FTO) glasses were utilized for electrochemical measurement, before paste the as-prepared materials onto the conductive surface of the FTO glasses, it was washed three times through deionized water, acetone and finally with ethanol with continuous ultra-sonication, later keep in an oven for dry. After, 50 mg of well ground as prepared materials was dispersed in DMF (2 ml) with ultra-sonication. The side portions of glasses were covered by Scotch tape and deposit samples onto the glasses and keep at room temperature for dry. The glasses after dried were kept for calcinations into Air furnace at  $200\ ^\circ\text{C}$  for 2 hours to improve adhesion. After calcinations, we obtained the FTO glasses of pure CN and copolymerized CN-TDP<sub>7.0</sub> electrodes. The bare portion of as-prepared glasses electrodes were about  $0.25\text{cm}^2$  and hence epoxy resin was used to cover the uncoated area of each electrode. The electrochemical experiments were carried out with counter (Pt), reference (Ag/AgCl) and

working electrodes respectively. The supporting electrolyte solution of sodium sulfate (0.2 M) was used and working electrode (as-prepared sample) were immersed into the electrolyte solution having counter Pt plate and reference Ag/AgCl electrodes. The visible light basis (300 W, Xe lamp) with 420 nm cutoff filter and chopped manually. The electrochemical impedance spectroscopy (EIS) measurement of CN and CN-TDP<sub>7.0</sub> were conducted by using sodium sulphate (50 ml, 0.2M) at -0.4 V against Ag/AgCl in dark. For EIS measurement the perturbation signal was 20mV between 200 KHz to 10 MHz frequency. In the photocurrent experiment, the working electrode was irradiated from backside FTO substrate in order to minimize the thickness effect of semiconductor layer and photocurrent response of CN and CN-TDP<sub>7.0</sub> modified FTO, potential range between -0.3 to 0.8 V bias against Ag/AgCl, also an alarm signal was also 20 mV having frequency from 200 KHz to 100 Hz.



**Figure S1.** (a-b) wide range XPS spectra of CN and CN-TDP<sub>7.0</sub> and (c-d) XPS of O 1s respectively.

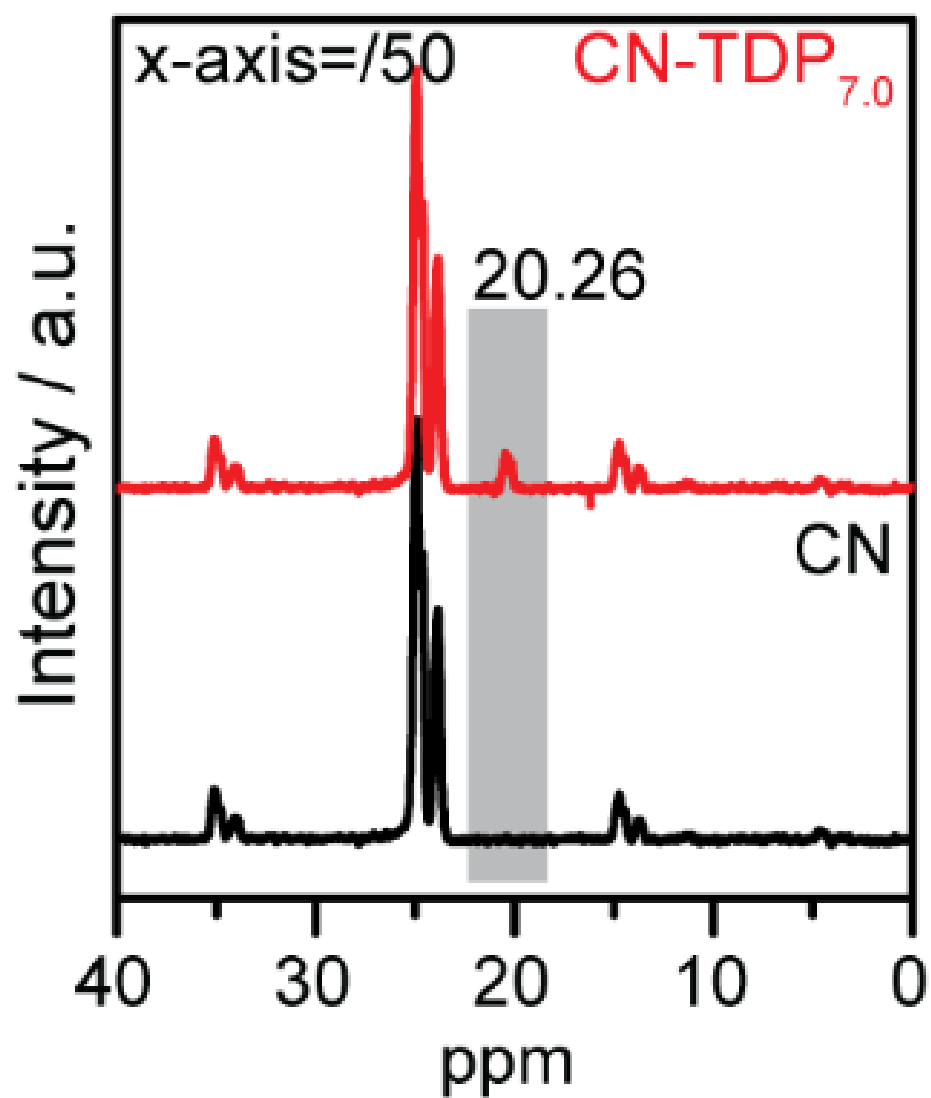


Figure S2. NMR spectra of CN and CN-TDP<sub>7.0</sub>.

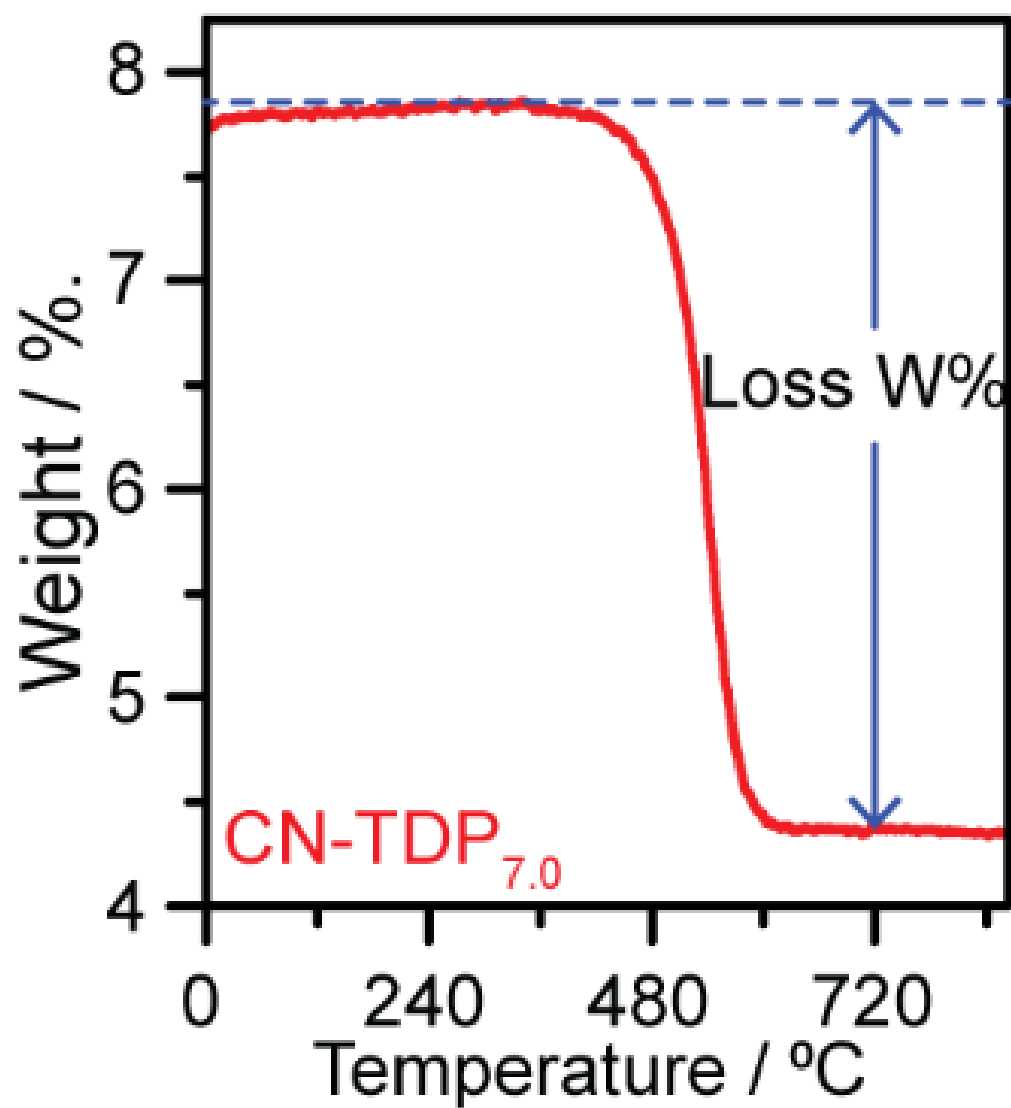


Figure S3. TGA spectra of CN-TDP<sub>7.0</sub>.

**Table S1:** Physicochemical properties and CO and H<sub>2</sub> evolution during CO<sub>2</sub> reduction of as-prepared samples.

| <b>Sample</b>           | <b>Surface<br/>area<br/>(m<sup>2</sup>g<sup>-1</sup>)[a]</b> | <b>Pore<br/>volume<br/>(cm<sup>3</sup>/g)</b> | <b>Pore<br/>diameter<br/>(nm)</b> | <b>C/N<br/>molar<br/>ratio<sup>[b]</sup></b> | <b>H<sub>2</sub><sup>[c]</sup><br/>evolution<br/>(μmole/h<sup>-1</sup>)</b> | <b>CO<sup>[c]</sup><br/>evolution<br/>(μmole/h<sup>-1</sup>)</b> |
|-------------------------|--|---|-----------------------------------|--|---|--|
| CN                      | 50   | 0.32  | 25.2                              | 0.64   | 0.2   | 3.9  |
| CN-TDP <sub>7.0</sub>   | 101  | 0.44  | 19.4                              | 0.65   | 4.4   | 17.85  |
| CNU-TDP <sub>12.0</sub> | 102  | 0.45  | 19.9                              | 0.65   | 5.2   | 20.6   |

**[a]** Calculated from N<sub>2</sub> absorption–desorption isotherms.

**[b]** From elemental analysis spectra.

**[c]** From CO<sub>2</sub> reduction-controlled experiments.



**Table S2.** Study of various conditions on controlled experiments<sup>[a]</sup>.

| Entry             | CO( $\mu$ mol)       | H <sub>2</sub> ( $\mu$ mol) | CO+H <sub>2</sub> ( $\mu$ mol) | Sel.(%) <sup>[b]</sup> |
|-------------------|----------------------|-----------------------------|--------------------------------|------------------------|
| 1                 | 23.9                 | 5.4                         | 29.3                           | 81.56                  |
| 2 <sup>[c]</sup>  | n. d. <sup>[d]</sup> | n. d.                       | -                              | -                      |
| 3 <sup>[e]</sup>  | n. d.                | n. d.                       | -                              | -                      |
| 4 <sup>[f]</sup>  | n. d.                | 0.89                        | 0.89                           | -                      |
| 5 <sup>[g]</sup>  | n. d.                | 0.7                         | -                              | -                      |
| 6 <sup>[h]</sup>  | n. d.                | <0.1                        | <0.1                           | -                      |
| 7 <sup>[i]</sup>  | n. d.                | <0.1                        | <0.1                           | -                      |
| 8 <sup>[j]</sup>  | n. d.                | <0.1                        | <0.1                           | -                      |
| 9 <sup>[k]</sup>  | n.d..                | 0.3                         | 0.3                            | -                      |
| 10 <sup>[l]</sup> | 1.2                  | 0.42                        | 1.62                           | -                      |
| 11 <sup>[m]</sup> | 1.9                  | 1.08                        | 2.98                           | -                      |

**[a]** Reaction conditions: CN-TDP<sub>7.0</sub> (30 mg), bpy (15 mg), COCl<sub>2</sub> (1 $\mu$ mol), TEOA (1ml), solvent (MeCN 5ml), and  $\lambda > 420$ nm, 30 °C, 1 h. **[b]** Selectivity =  $n_{(CO)}/n_{(CO+H_2)} \times 100$ . **[c]** Without CN-TDP<sub>7.0</sub>. **[d]** Not determined. **[e]** In dark. **[f]** Using Ar instead of CO<sub>2</sub>. **[g]** Without TEOA. **[h]** Without bpy. **[i]** Without CoCl<sub>2</sub>. **[j]** Without bpy and CoCl<sub>2</sub>. **[k]** Using N<sub>2</sub> instead of CO<sub>2</sub>. **[l]** Using of lactic acid as a sacrificial agent instead of TEOA. **[m]** using of formic acid as a sacrificial agent instead of TEOA.