

Supplementary information

**Enhanced Photoresponse and Fast Charge Transfer: Three-Dimensional Macroporous g-C<sub>3</sub>N<sub>4</sub>/GO-TiO<sub>2</sub> Nanostructure for Hydrogen Evolution**

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## 1. Methods

### 1.1 Materials.

Graphite powder ( $\leq 20 \mu\text{m}$ , 99.90 %), concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98.0 %), sodium nitrate ( $\text{NaNO}_3$ , A.R.), potassium permanganate ( $\text{KMnO}_4$ , A.R.), hydrogen peroxide ( $\text{H}_2\text{O}_2$  30 %), hydrochloric acid ( $\text{HCl}$ , 37 %), melamine ( $\text{C}_3\text{H}_6\text{N}_6$ , C.R.),  $\text{NH}_4\cdot\text{OH}$  (25%, A.R.), tetraethoxysilane (TEOS, A.R.), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , A.R.), butyl titanate (TBOT, A.R.), absolute ethanol (EA, A.R.), potassium ferricyanide ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ , A.R.), sodium sulfate ( $\text{Na}_2\text{SO}_4$ , A.R.), Nafion D-250 dispersion and triethanolamine (TEOA, A.R.) were purchased from Aladdin (Shanghai, China). Ultrapure water is produced by laboratory ultrapure water machine.

### 1.2 Synthesis of $\text{SiO}_2$ NPs.

The  $\text{SiO}_2$  microspheres were synthesized by a typical sol-gel method. Concretely, 8 mL TEOS was added dropwise to the mixed solution of 200 mL ethanol and 100 mL deionized water, then 5 mL  $\text{NH}_4\cdot\text{OH}$  was added to the mixed solution under mechanical agitation at 300 rpm. After being stirred for 6 h at 30 °C, the product was separated by centrifugation and washed to neutral with ethanol and deionized water. Finally, the  $\text{SiO}_2$  microspheres with particle size of 100 nm were obtained after drying for 12 h in a freeze-dryer.

### 1.3 Preparation of anatase $\text{TiO}_2$ NPs.

The anatase  $\text{TiO}_2$  NPs were prepared by hydrolysis-calcining method. 28 mL of TBOT was added

dropwise to 400 mL deionized water and stirred continuously for 2 h at 60 °C, then the as-prepared white gel particles were rinsed with deionized water for several times and dried overnight at 60 °C. Then, the dried powder was calcined for 4 h at 550 °C (10 °C/min) under N<sub>2</sub> atmosphere to obtain the anatase TiO<sub>2</sub> NPs.

#### **1.4 Preparation of 3D CNG.**

3D CNG composite was prepared by calcination method. 1.5 g of melamine and certain amount of GO (0.0050 g/0.0075 g/0.0100 g) were dissolved and dispersed in 50 mL deionized water at 90 °C and kept for 1~2 h to remove the water. Then the dried mixture was calcined for 4 h at 550 °C (10 °C/min) under N<sub>2</sub> atmosphere, and the resulting products were marked as 3D CNG- $\alpha$  ( $\alpha = 1$  (0.0050 g), 2 (0.0075 g) and 3 (0.0100 g)).

#### **1.5 Electrochemical measurements.**

Platinum electrode and Ag/AgCl electrode were used as the counter electrode and reference electrode, and ITO glass (15 mm × 15 mm) coated with tested sample was used as the working electrode. Then, a three-electrode system was built in a quartz cell with 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution as electrolyte. The preparation method of working electrode is as follows: 10 mg tested sample was ultrasonically dispersed in 1 mL absolute ethanol with 1  $\mu$ L Nafion solution, then 500  $\mu$ L above uniform dispersion was coated on the conductive surface of ITO glass and naturally dried at room temperature. In testing process, 300 W Xenon lamp (PLSSXE300) with 420 nm filter was used as the

light source. Linear sweep voltammetry (LSV), Tafel plots (TP), Mott-Schottky curves (M-S) and transient photocurrent densities of the samples were measured by using 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution as electrolyte.

In impedance testing process, the electrolyte was the K<sub>3</sub>[Fe(CN)<sub>6</sub>] solution (0.02 M). The offset potential, amplitude, initial frequency, final frequency, logarithmic current, step/decade and frequency step were 0 V, 0.01 V, 100000 Hz, 1 Hz, 100 mA, 12 and 0, respectively.

In amperometric i-t curves testing process, the initial potential, sample interval, quiet time and sensitivity were set as -0.1 V, 0.1 s, 1 s and 10 μA, respectively.

In the Tafel plots testing process, the initial potential, final potential, final potential hold time, scan rate, sweep segments, sample interval, quiet time and sensitivity were -1 V, 2 V, 0 s, 0.1 V/s, 1, 0.001 V, 1 s and 100 μA, respectively.

In linear sweep voltammetry (LSV) curves in dark testing process, the initial potential, final potential, scan rate, sample interval, quiet time and sensitivity were -1 V, 0.2 V, 0.01 V/s, 0.001 V, 1s and 100 μA, respectively. Under interrupted illumination, the above parameters were -0.4 V, 2 V, 0.02 V/s, 0.001 V, 1s and 10 μA, respectively.

In the Mott-Schottky (M-S) plots at different frequencies (1 kHz, 1.5 kHz and 2 kHz) testing process, the initial potential, final potential, increment potential, amplitude, cycles, quiet time and sensitivity were 0 V, 1 V, 0.01 V, 0.01 V, 10, 0 s and 1 mA, respectively.

## 1.6 Equations of average hydrogen evolution rate.

$$V_{H_2} = 485.11 A_s \quad (1)$$

In this formula,  $V_{H_2}$  and  $A_s$  are the volume mass of the generated hydrogen and chromatographic peak area of the generated hydrogen samples, respectively. According to mass of the catalysts ( $m_{cat}$ ) and the volume of standard hydrogen ( $V_m$ ) during the experiment, the final formula can be calculated as was shown as below:

$$R_e = \frac{A_s}{485.11 m_{cat} \cdot V_m} \quad (2)$$

## 2. Results and Discussion

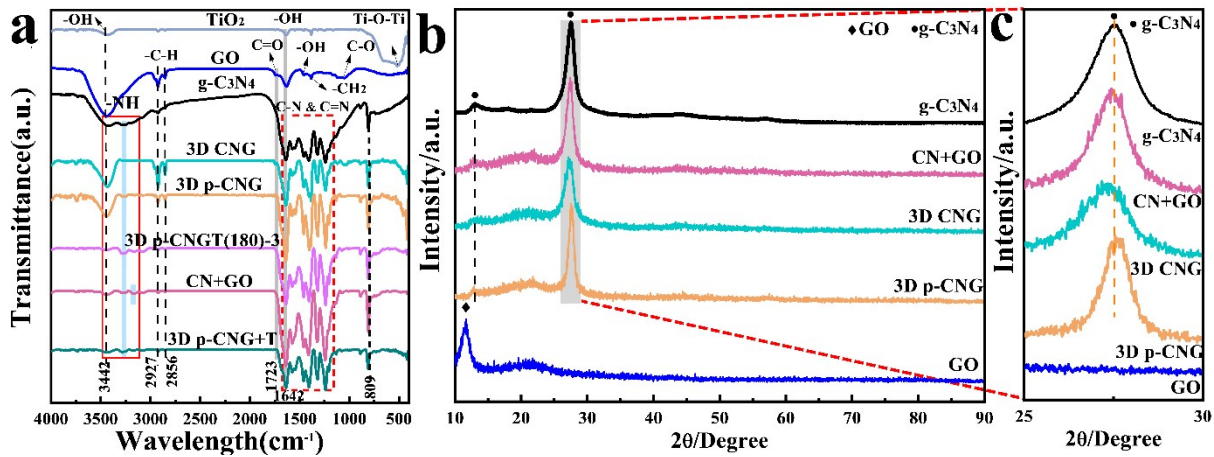


Fig.S1(a) FTIR spectra of the samples. (b) XRD patterns of the g-C<sub>3</sub>N<sub>4</sub>, CN+GO, 3D CNG, 3D p-CNG and GO. (c) Partial magnification of panel (b) at  $2\theta = 25 \sim 30^\circ$ .

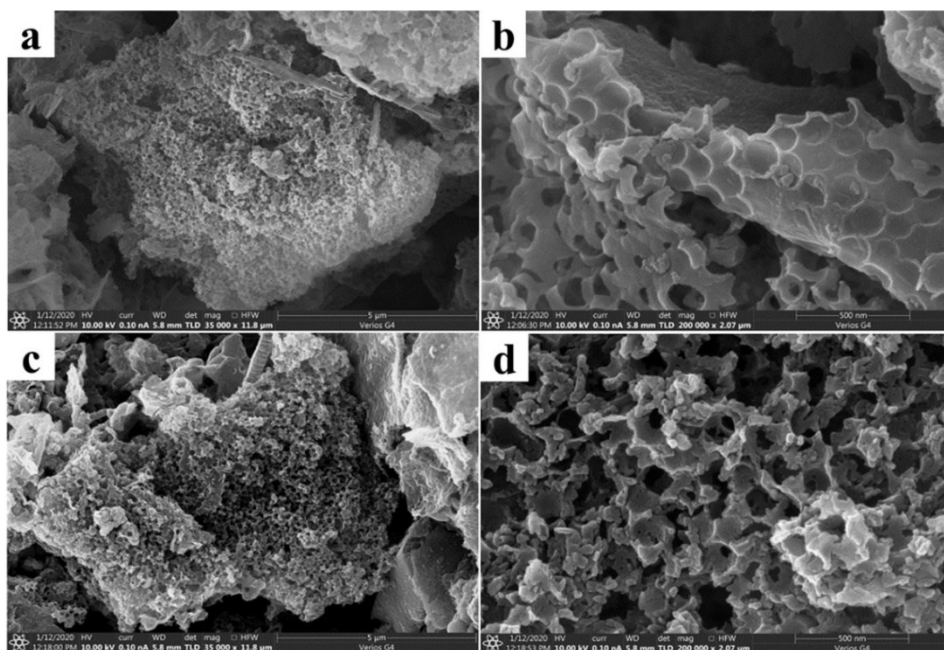


Fig.S2 SEM images of 3D p-CNG skeleton (a,b) and 3D p-CNGT(180)-3 catalyst (c,d).

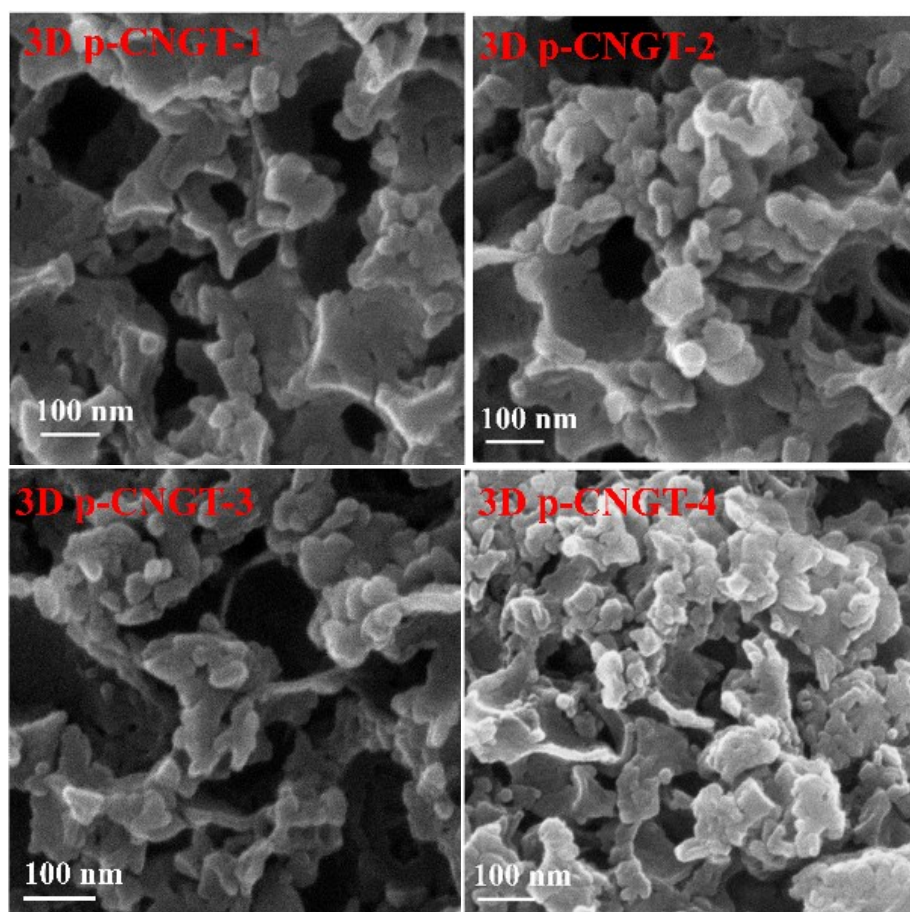
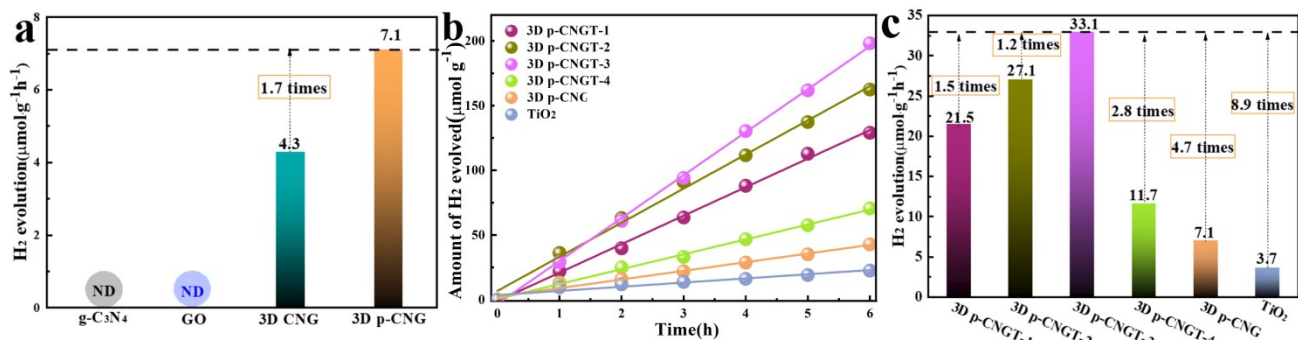
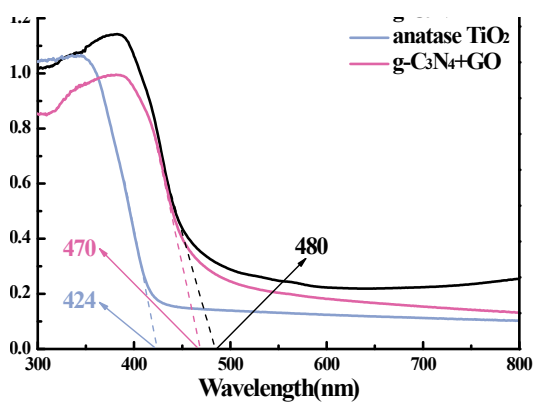


Fig.S3 SEM images of 3D p-CNGT catalysts with different amount of TiO<sub>2</sub> NPs. The synthetic temperature is 180 °C.



**Fig.S4 (a)** HER rates of g-C<sub>3</sub>N<sub>4</sub>, GO, 3D CNG and 3D p-CNG under simulated solar light. **(b)**

Amounts of evolved H<sub>2</sub> and **(c)** HER rates on different catalysts.



**Fig.S5** UV-vis absorption spectra of g-C<sub>3</sub>N<sub>4</sub>, anatase TiO<sub>2</sub> NPs and physically mixed g-C<sub>3</sub>N<sub>4</sub> and GO.