

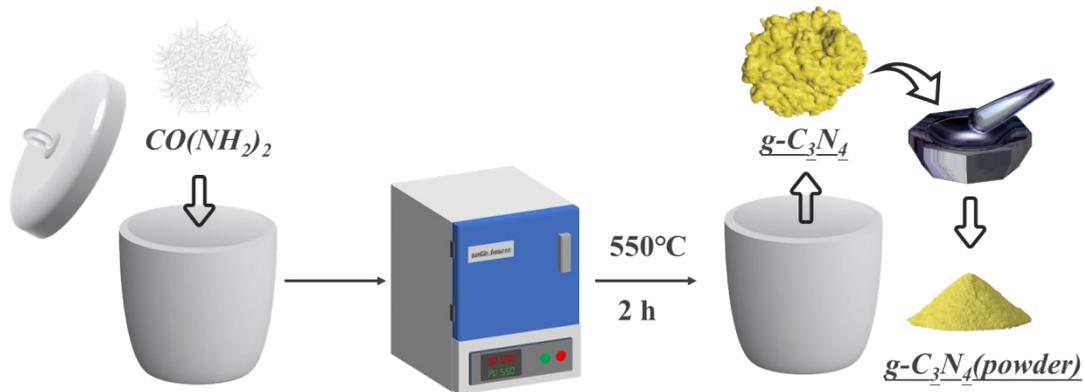
## **Band structure engineering in porous g-C<sub>3</sub>N<sub>4</sub> via tailoring surface carbon for enhanced photocatalytic hydrogen evolution**

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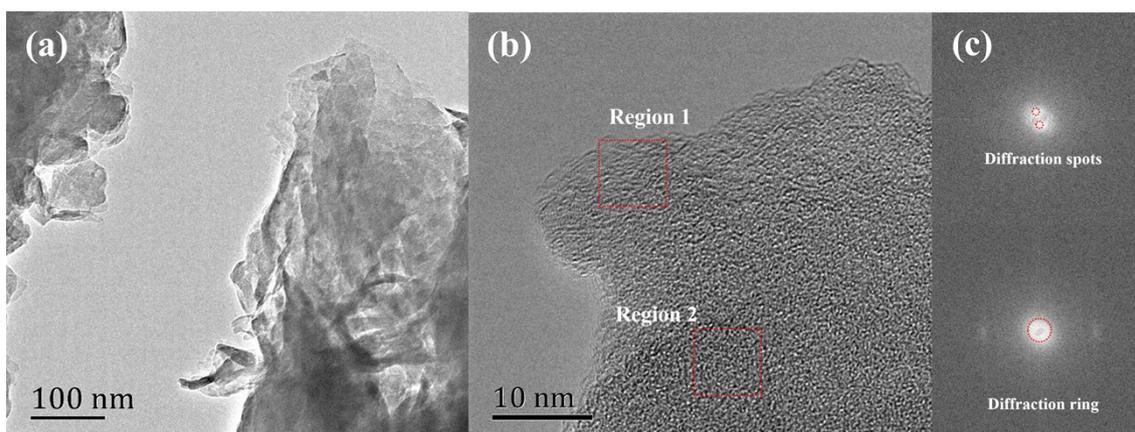
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**Fig. S1.** Schematic diagram of the synthesis process of g-C<sub>3</sub>N<sub>4</sub>

**Fig. S2.** The SEM images of (a) CNP350, (b) CNP400, (c) CNP450, (d) CNP500.



**Fig. S3.** (a) TEM and (b) HRTEM image of CNP550.(c) Selected area FFT analysis on CNP550

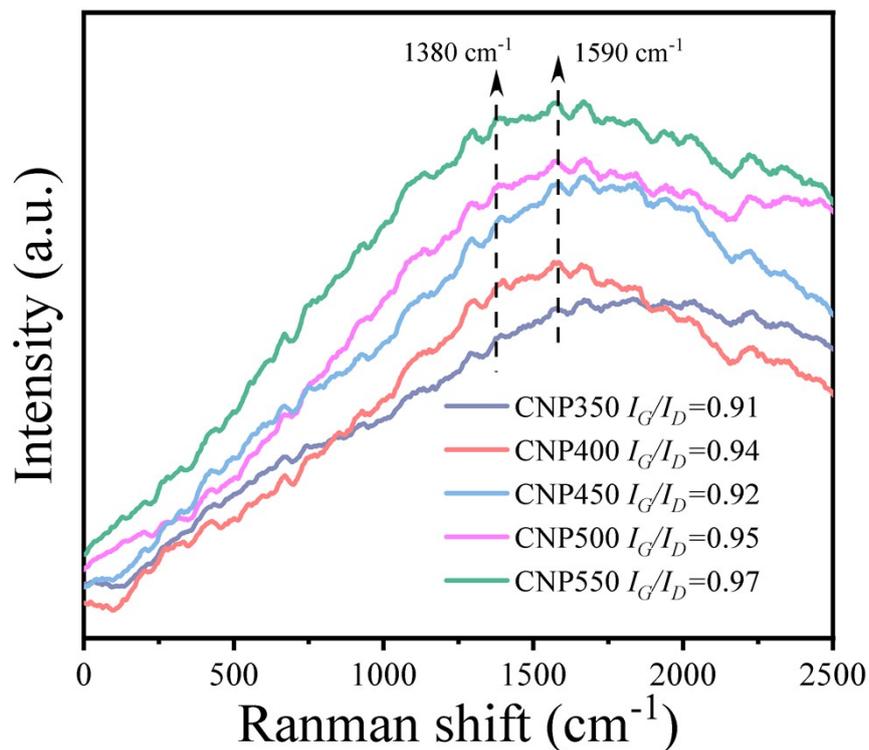


Fig. S4. The Raman spectra of CNP350, CNP400, CNP450, CNP500 and CNP550.

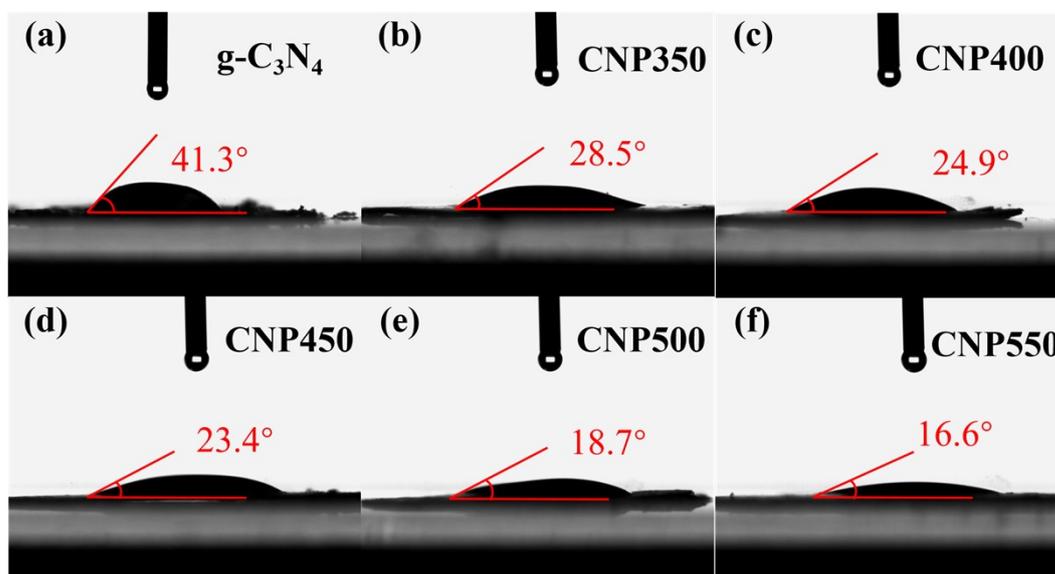


Fig. S5. Complementary contact angle measurements on the sample series.

Table S1. Atomic contents of C, N and O elements and N/C in g-C<sub>3</sub>N<sub>4</sub> and CNP samples with different prepared temperatures on the basis of XPS measurement

| Sample | g-C <sub>3</sub> N <sub>4</sub> | CNP350 | CNP400 | CNP450 | CNP500 | CNP550 |
|--------|---------------------------------|--------|--------|--------|--------|--------|
|--------|---------------------------------|--------|--------|--------|--------|--------|

|          |       |       |       |       |       |       |
|----------|-------|-------|-------|-------|-------|-------|
| C (at.%) | 42.56 | 58.18 | 59.26 | 60.93 | 61.90 | 62.65 |
| N (at.%) | 56.75 | 41.13 | 40.34 | 38.51 | 37.79 | 37.16 |
| O (at.%) | 0.69  | 0.69  | 0.40  | 0.56  | 0.31  | 0.19  |
| N/C      | 1.333 | 0.707 | 0.681 | 0.632 | 0.610 | 0.593 |

**Table S2.**  $S_{\text{BET}}$ , pore volume and pore size of each sample

| Samples                         | $S_{\text{BET}}$<br>( $\text{m}^2\cdot\text{g}^{-1}$ ) | Pore volume<br>( $\text{cm}^3\cdot\text{g}^{-1}$ ) | Pore size<br>(nm) |
|---------------------------------|--|--|-------------------|
| g-C <sub>3</sub> N <sub>4</sub> | 68.4   | 0.56   | 3.83              |
| CNP350                          | 60.2   | 0.60   | 1.42              |
| CNP400                          | 74.0   | 0.67   | 1.42              |
| CNP450                          | 89.2   | 0.74   | 1.42              |
| CNP500                          | 108.9  | 1.51   | 3.81              |
| CNP550                          | 378.0  | 8.6  | 3.81              |

**Table S3.** Comparison table of hydrogen evolution performance between this work and similar recent work

| Sample | HER activity | HER activity ratio | Ref. (year) |
|--------|--------------|--------------------|-------------|
|--------|--------------|--------------------|-------------|

|  |  | with bulk g-C <sub>3</sub> N <sub>4</sub> |           |
|--|--|---|-----------|
| HB/g-C <sub>3</sub> N <sub>4</sub>                     | 216.8 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  | 2.9                                       | S1 (2019) |
| CDCN-20  | 1266.8 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ | 3.4                                       | S2 (2020) |
| C-CN   | 40.37 $\mu\text{mol}\cdot\text{h}^{-1}$                    | 2.9                                       | S3 (2018) |
| C quantum dots/C doped g-C <sub>3</sub> N <sub>4</sub> | 205 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$    | 9   | S4 (2022) |
| C7.5-MA  | 8998.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ | 7.3                                       | S5 (2024) |
| CCN  | 1224 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$   | 4.5                                       | S6 (2021) |
| U-ECN  | 836 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$    | 8.2                                       | S7 (2021) |
| PAN pyrolysis gas                                      | 688.2 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  | 7.8                                       | This work |

**Table S4.**  $E_g$ ,  $E_{VB}$  and  $E_{CB}$  of g-C<sub>3</sub>N<sub>4</sub> and CNP samples with different prepared temperatures

| Sample               | g-C <sub>3</sub> N <sub>4</sub> | CNP350 | CNP400 | CNP450 | CNP500 | CNP550 |
|----------------------|---------------------------------|--------|--------|--------|--------|--------|
| $E_g$ (eV)           | 2.87                            | 2.70   | 2.68   | 2.48   | 2.33   | 1.94   |
| $E_{VB}$ (V vs. NHE) | 1.91                            | 1.87   | 2.01   | 2.05   | 1.91   | 1.39   |
| $E_{CB}$ (V vs. NHE) | -0.96                           | -0.83  | -0.67  | -0.43  | -0.42  | -0.55  |

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