

Supporting Information

Thermal reflux to synthesis C₃N₄ nanostructures with high yield
and enhanced photocatalytic activity in hydrogen evolution

*Yihang He, Mingliang Wu, and Kunquan Hong**

*Key Laboratory of Quantum Materials and Devices of Ministry of
Education, School of Physics, Southeast University, Nanjing 211189,
China*

Email: hongkq@gmail.com

Experimental section

Sample preparation:

To prepare g-C₃N₄ nanostructures, melamine (C₃H₆N₆) is used as the raw materials without further purification. At first, 2 g melamine was loaded at the bottom of a quartz tube with a length of 10 cm and diameter of 1.2 cm. The open top end of this quartz tube was partially sealed by wrapping them with aluminum foil (thickness 20 microns). Then this quartz tube was inserted into the center of a traditional horizontal tube furnace, in which the bottom located at a high temperature zone while the top end at a low temperature zone, respectively. The top end was 3 cm higher than the bottom. Then the furnace was heated to 600 °C within 20 min from room temperature and this temperature of 600 °C was held for 1 h to complete the internal material polymerization. The top end of the quartz tube was simultaneously heated to 400 °C. Finally, the furnace was let cooling to room temperature to take out the

sample. Yellow powder with the weight of 835 mg was obtained. These g-C₃N₄ nanostructures synthesized by thermal reflux method using melamine as raw materials were named sample R-M-CN. As a comparison to synthesizing g-C₃N₄ by traditional thermal polymerization method (sample T-M-CN), 2 g melamine was loaded in a ceramic crucible with a cover and warped with aluminum foil. This ceramic crucible was heated by the same furnace with the same temperature of 600°C and the procedure to obtain the powder of the sample (651 mg).

Characterization:

Scanning electron microscope (FESEM, FEI inspect F50) and transmission electron microscopy (TEM, Talos F200X) were used to analyze the morphology of the samples. X-ray diffraction (Rigaku Smartlab, Cu Ka radiation, $\lambda=0.15406$ nm) and selected area electron diffraction (SAED in TEM) were used to analyze the crystal structure of the samples. X-ray energy dispersive spectroscopy (EDX) in TEM was used to measure the composition and elements distribution. The BET surface area of the nanotubes was analyzed using a fully automatic specific surface and porosity analyzer (Micromeritics ASAP 2460). XPS (Thermo Fischer, ESCALAB 250 Xi) was used to analyze the elemental composition.

The photocatalytic H₂ evolution experiment was conducted by using a 300W Xe lamp (CEL-HXF300, China) with a 420 nm cut-off as the visible light source. 10mg of g-C₃N₄ sample was added to 30mL solution with 10 vol% triethanolamine (TEOA) as the sacrificial agent. After ultrasonic dispersion, an appropriate amount of chloroplatinic acid (H₂PtCl₆) solution was added to achieve a Pt content of 0.3 mg (3 wt%) in the solution. These Pt can be attached to the surface of photocatalysts through photodeposition [1]. Before measurement, argon gas (99.999%) flow was introduced into the reactor to fully remove the remained air for 30mins. Then the flow rate was reduced to 5

sccm (cubic centimeters per minute at STP). The light source was turned on after this flow was stabilized. The released gas passed an on-line gas chromatograph (Agilent Technologies 7890B) to analyze the component of the gas-phase products.

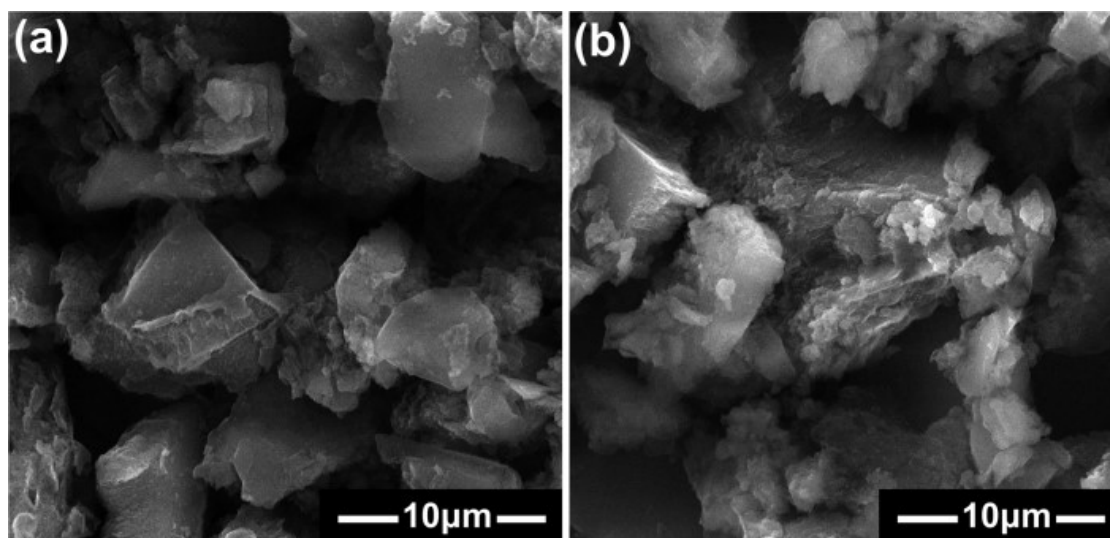


Fig. S1 SEM images of the samples. (a) R-M-CN (b) T-M-CN

Figure S1 shows the SEM images of the samples. It can be seen that when the precursor is melamine, the samples are consisted of lots of powders with a rough surface. Detail observation shows many protrusions and pores appear on the surface of these $g\text{-C}_3\text{N}_4$ powders, which improves the surface area and enhances adsorption capacity.

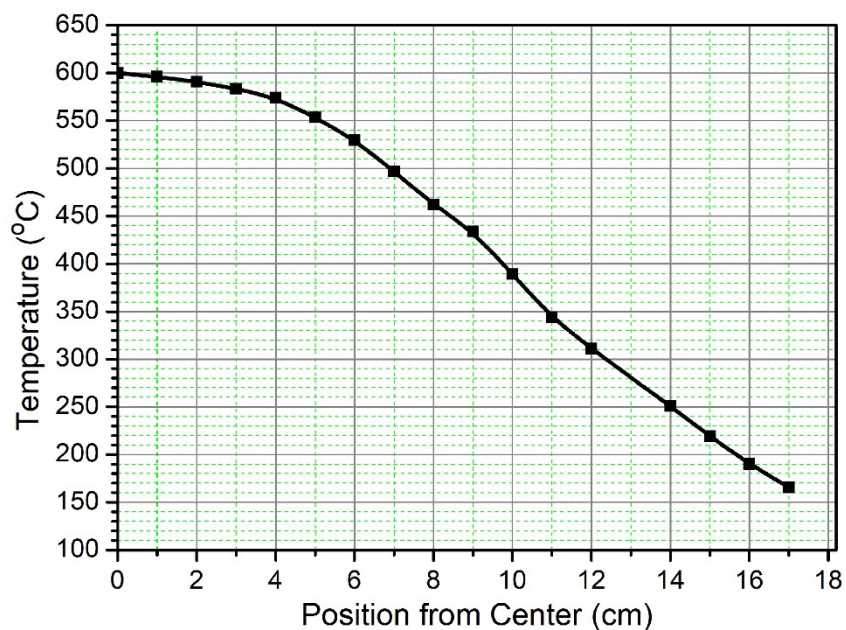


Figure S2 the temperature in the furnace as the function of distance from the centre.

Raw materials	melamine		Urea	
Sample	T-M-CN	R-M-CN	T-U-CN	R-U-CN
Mass (mg)	650.8	834.9	26.1	50.2
H ₂ rate (μmol h ⁻¹ g ⁻¹)	1459	2112	3856	7160

Table S1 the yield and H₂ evolution rate of different samples

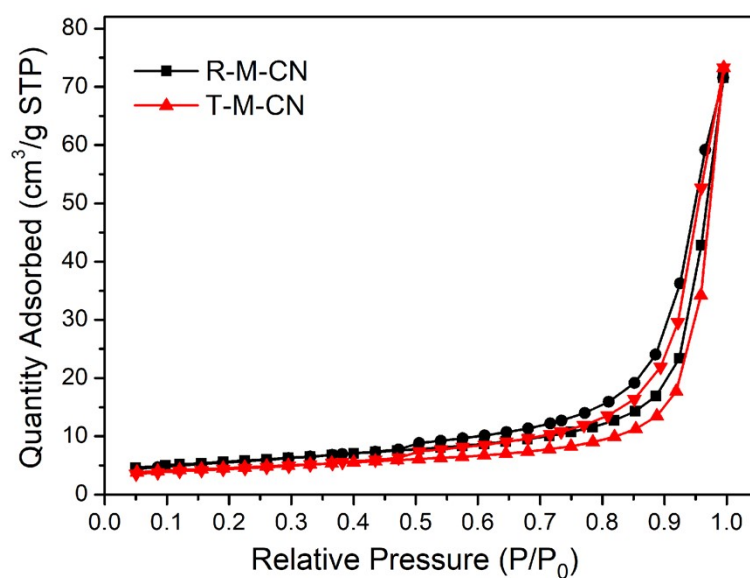


Figure S3. The N₂ isothermal absorption/desorption curves of R-M-CN and T-M-CN, which have 20.0 and 16.1 m²/g, respectively.

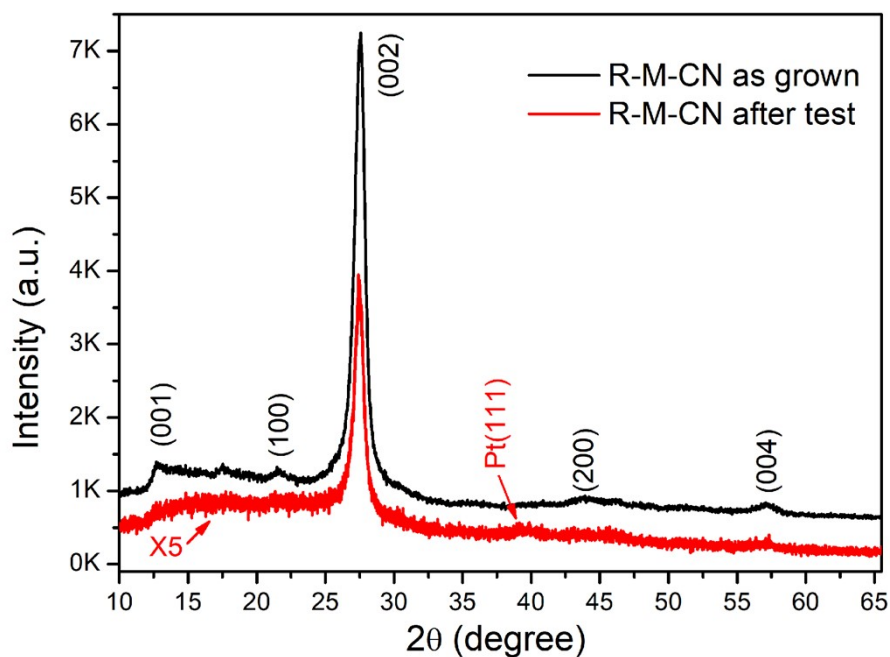


Figure S4. The XRD pattern of the sample of R-M-CN as grown and after photocatalytic test for 2 h. They have almost the same patterns except a suspected weak peak at 39° which can be indexed to Pt (111).

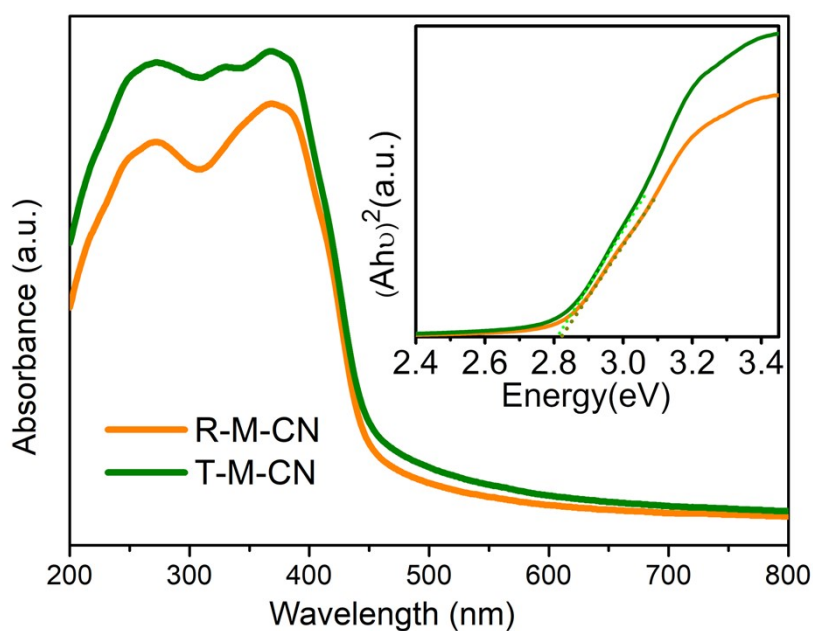


Figure S5. UV-visible diffuse reflectance spectroscopy (DRS) of the sample. The samples show the similar absorbance with band gaps of 2.82 and 2.81 eV for sample R-M-CN and T-M-CN.

References

- [1] Chen, Z., Lu, S., Wu, Q., He, F., Zhao, N., He, C., Shi, C., 2018. Salt-assisted synthesis of 3D open porous g-C₃N₄ decorated with cyano groups for photocatalytic hydrogen evolution. *Nanoscale* **10**, 3008–3013. <https://doi.org/10.1039/C7NR05927B>