

Electronic Supplementary Information

Facile synthesis of detonation nanodiamond mediated mesoporous layers of graphitic carbon nitride for efficient hydrogen evolution reaction

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Experimental Details

Materials

Urea, K₂SO₄, chloroform, acetone, ethanol, methanol, dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagents Co., Ltd. Detonation Nanodiamond (DND) was purchased from Henan Union Abrasives Co., Ltd. All chemicals were used without further purification.

Sample Preparation

For the preparation of g-C₃N₄^{1,2}, 10 g of Urea was dissolved in 10 ml of deionized water in a crucible. The crucible was covered with a lid then placed in a furnace and heated up to 550 °C at the rate of 0.5 °C/min. It was kept at 550 °C in air for 3 hours and after that it was cooled down at ambient conditions. The light yellow color powder was obtained which was further washed with distilled water to remove impurities and dried at 80 °C for 24 hours. For hybrid preparation 0.5mg DND powder was dispersed in 10mL of deionized water via sonication and then 10 g of Urea was added in it. The whole mixture was transferred in to crucible having a lid. After that it was thermally treated in the same way as the g-C₃N₄. g-C₃N₄+DND hybrids were prepared using the different concentrations of DND. The concentrations of DND used are 0.4, 1.2, 2, 6, 10, 20, and 40 weight percent (wt%) of g-C₃N₄.

Characterizations

Thermogravimetric Analysis (TGA) was done on TGA Q5000 V3.15 Build 263 (TA instruments). FTIR spectra were acquired using Thermal Fisher Nicolet 8700 (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a resolution of 0.1 cm⁻¹. X-ray diffraction (XRD) measurements were obtained on PANalytical X'Pert Pro diffractometer using Cu K α radiation ($\lambda=1.54056$ Å). Carbon and Nitrogen K-Edge X-ray absorption near edge structure (XANES) spectra were recorded in total electron yield at the beam line 4B7B in Beijing Synchrotron Radiation Facility (BSRF). X-ray Photoemission spectroscopy (XPS) experiments were performed at the Photoemission Endstation at the BL10B beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The UV-Visible diffuse reflectance spectra (UV-Vis-DRS) were acquired using Shimadzu DUV-3700 spectrophotometer. Transmission electron microscopy (TEM) was used to check the morphology and structure of the samples and images were taken on JEOL, JEM-2100F at 200 kV. The photoluminescence (PL) measurements were recorded on Jobin Yvon HORIBA FluoroLog-3-Tau spectrofluorometer using 365 nm as the excitation wavelength. Time resolved fluorescence decay spectra were recorded on HORIBA FluoroMax-4 Fluorometer using 365 nm as the excitation wavelength. Nitrogen adsorption-desorption isotherms were measured on Autosorb iQ Station 2 apparatus. Nitrogen adsorption-desorption isotherms were measured by using an adsorption apparatus (BELSORP-MAX, China) in order to determine the Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the samples. Atomic Force Microscopy (AFM) measurements were obtained using Tapping Mode on Veeco (Multimode V) AFM.

Electrochemical Measurements

The Mott-Schottky plots, Electrochemical Impedance Spectroscopy (EIS) Nyquist plots and photocurrent measurements were performed on a CHI760E electrochemical workstation using a three-electrode configuration. Fluoride-tin oxide (FTO) with sample deposited on 0.25 cm² area was used as the working electrodes, Pt foil as the

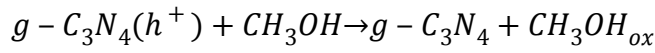
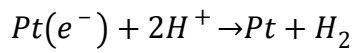
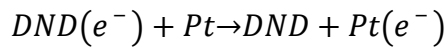
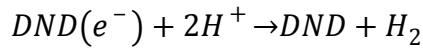
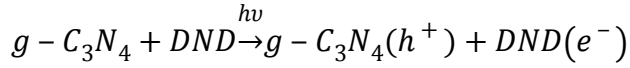
counter electrode and Ag/AgCl (3M KCl) as the reference electrode. The electrolyte was a 0.2 M K_2SO_4 aqueous solution. The working electrode was prepared on FTO conductor glass, which was cleaned by sonication in chloroform, acetone and ethanol for 30 min, respectively. 50 mg powder was mixed with 8 mL DMF under sonication for 30 min to get slurry. The slurry was spread onto FTO glass whose side parts were protected using Scotch tape. After air drying, the electrode was put at 250 °C for 30 min in air to improve adhesion. For the photocurrent measurements the working electrodes irradiated using 300 W Xe lamp (PLS-SXE300) with 420 nm cut-off filter at 1.5 V bias vs Ag/AgCl.

Photocatalytic Experiment

The photocatalytic reaction was carried out at room temperature using 300 W Xe lamp with a cut-off filter ($\lambda \geq 420$) in a Pyrex top-irradiation vessel connected to a closed gas system. In a typical photocatalytic experiment, 0.100 g of catalyst (pure g-C₃N₄ or g-C₃N₄-DND hybrid) was suspended in 100 mL solution of distilled water and Methanol (water 80 mL, Methanol 20 ml) under constant stirring. Methanol was used as a sacrificial reagent. A cocatalyst Pt (3wt%) was deposited on catalyst surface by directly adding H_2PtCl_6 in to 100 mL aqueous solution using in-situ photodeposition method. The Pyrex vessel was sealed using silicone rubber septum and catalyst was dispersed using ultrasonication bath for 30 mins. The air was completely removed before the reaction. In dark, no gas was detected for all photocatalysts. The amount of hydrogen evolved during photocatalytic reaction was determined on a gas chromatograph (GC-7900 TECHCOMP) equipped with thermal conductive detector (TCD) using N_2 as carrier gas. During the photocatalyst reaction the temperature of the solution was maintained at room temperature by a flow of cooling water and uniform suspension of photocatalyst was ensured by constant stirring at 600 rpm.

Hydrogen Evolution Reaction Mechanism

The electrons and holes produced after the absorption of visible light ($\lambda \geq 420\text{nm}$). The electrons were quickly transfer to the hydrogen generation surface sites via DND embedded in the $g\text{-C}_3\text{N}_4$ layers. The proposed reaction steps^{2,3} are given below;



Quantum Yield Calculations

The photocatalytic experiment was carried out for 8 hours to determine the Quantum Yield. The average intensity of the 300W Xe lamp with a 420nm cut off filter was recorded to be 0.0027 W/cm². The measured irradiated area was 40.71 cm². The maximum number of moles of hydrogen produced during the 8 hour experiment are 350 μmol (see Fig. 5a). The number of incident photons are calculated by using equation^{2,4} (1).

$$\begin{aligned} \text{No. of incident photons} \\ &= \frac{0.0027 \times 40.71 \times 3600 \times 8 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 6.74 \times 10^{21} \end{aligned} \quad (1)$$

The quantum yeild of our experiment was determined by using the equation^{2,4} (2).

$$\text{Quatum Yield (\%)} = \frac{2 \times \text{Number of Hydrogen molecules produced}}{\text{Number of incident photons}} \times 100 \quad (2)$$

$$\text{QY\% (} g\text{-C}_3\text{N}_4) = \frac{2 \times 6.02 \times 10^{23} \times 278 \times 10^{-6}}{6.74 \times 10^{21}} \times 100 = 4.97\%$$

$$\text{QY\% (DND0.4wt\%)} = \frac{2 \times 6.02 \times 10^{23} \times 350 \times 10^{-6}}{6.74 \times 10^{21}} \times 100 = 6.25\%$$

Additional Results

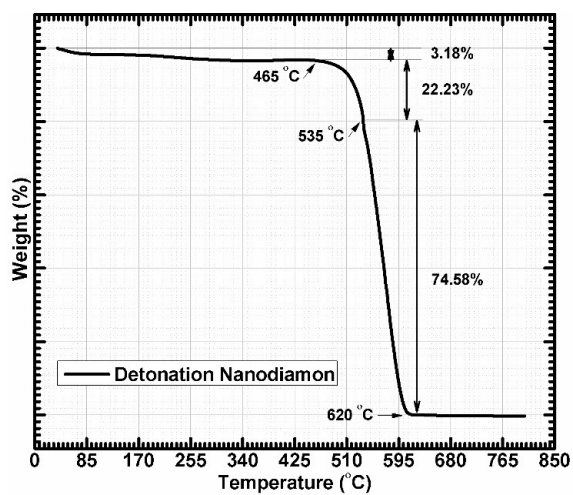


Fig. S1. TGA thermograph of DND in air

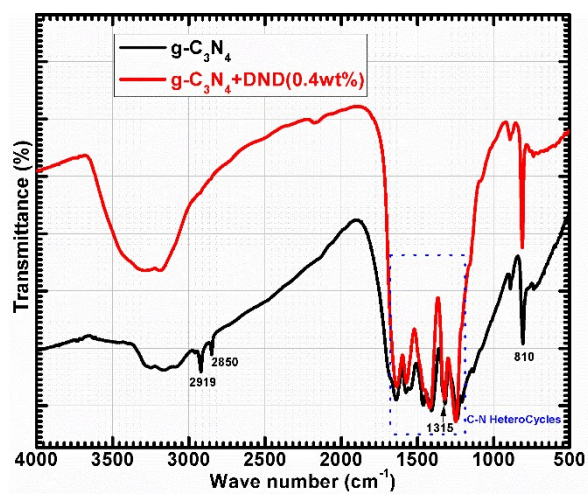


Fig. S2. FTIR spectra of of g-C₃N₄ and g-C₃N₄+DND(0.4wt%).

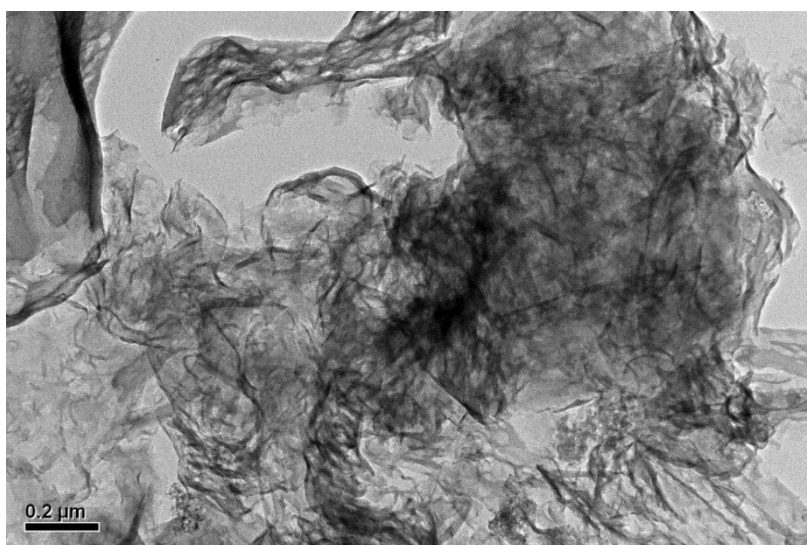


Fig. S3. TEM image of g-C₃N₄+DND(0.4wt%).

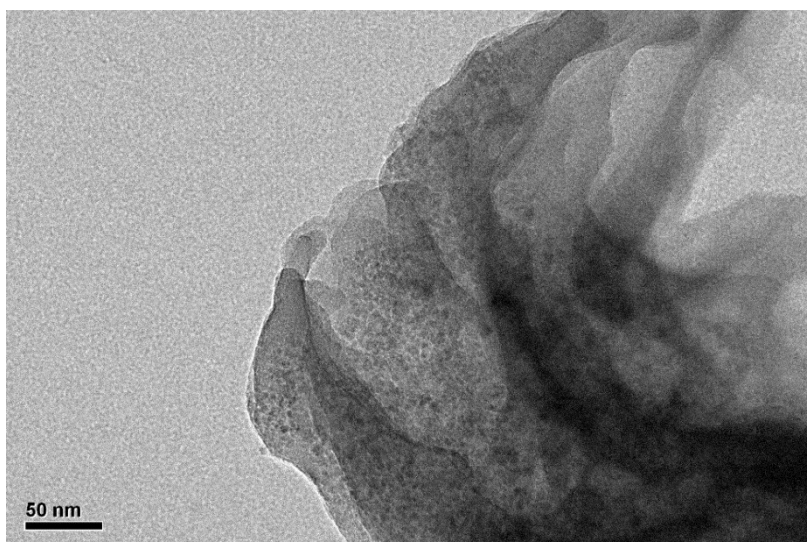


Fig. S4. TEM image of g-C₃N₄+DND(10wt%).

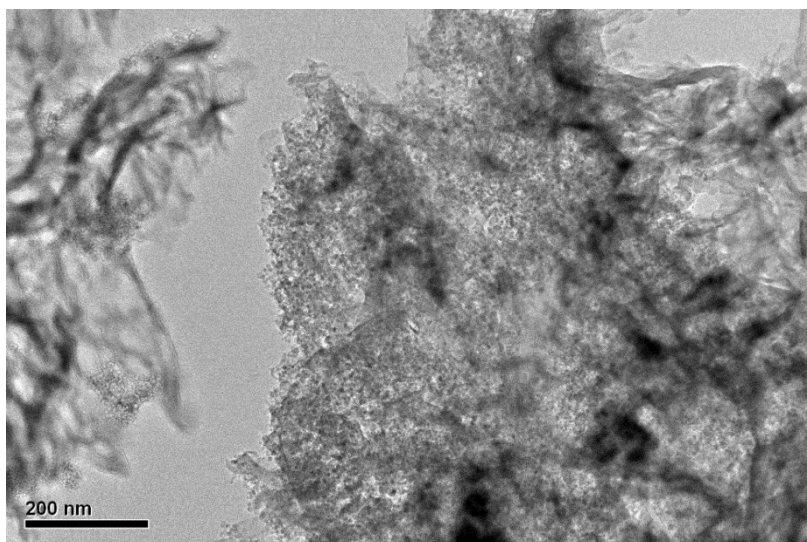


Fig. S5. TEM image of g-C₃N₄+DND(40wt%).

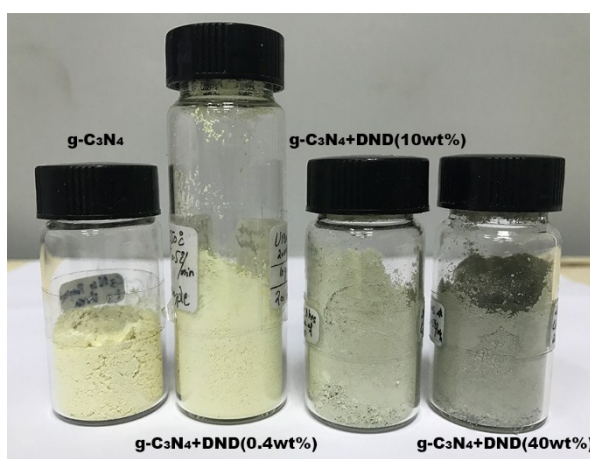


Fig. S6. Photograph of the g-C₃N₄ and g-C₃N₄+DND hybrid samples having 0.4, 10, 40 wt% of DND concentrations

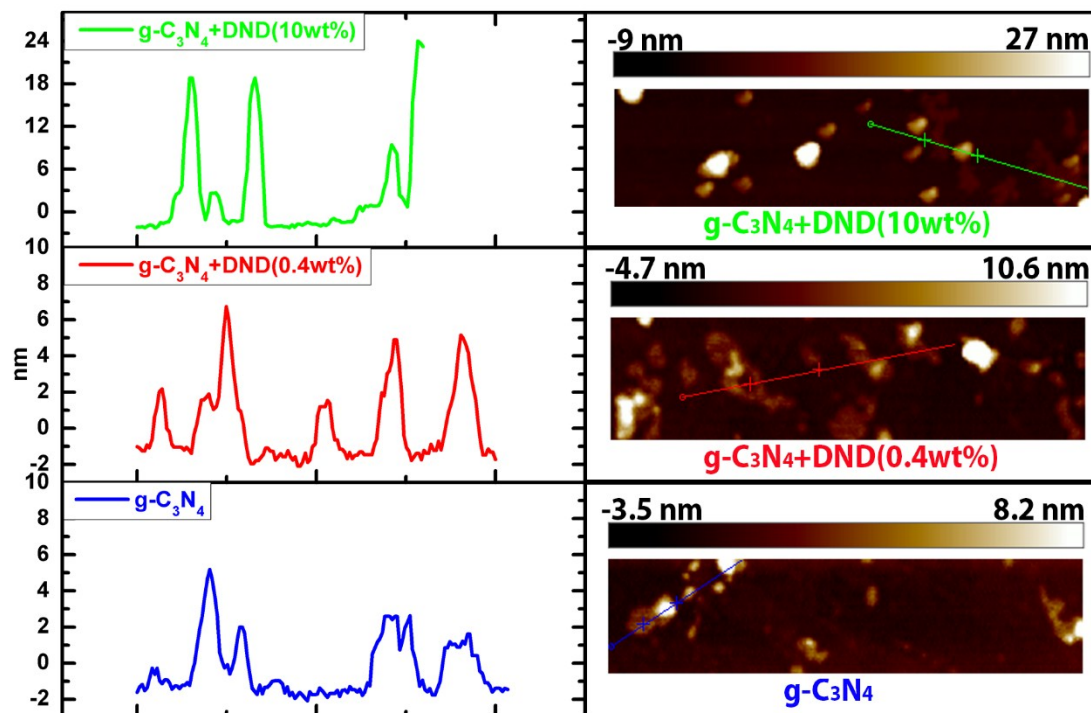


Fig. S7. AFM measurements of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4\text{+DND}(0.4\text{wt}\%)$ and $g\text{-C}_3\text{N}_4\text{+DND}(10\text{wt}\%)$.

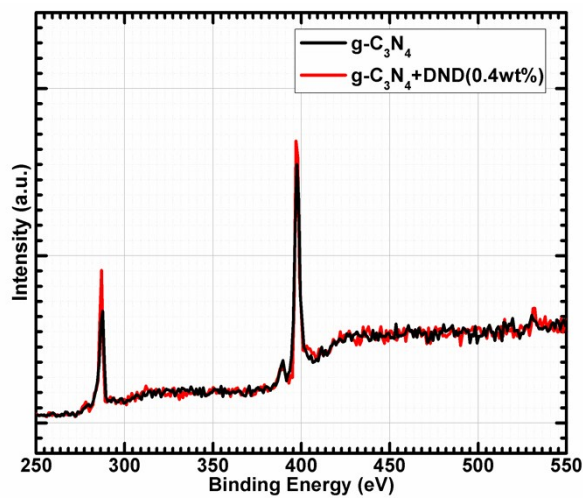


Fig. S8. XPS survey scans of $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4\text{+DND}(0.4\text{wt}\%)$.

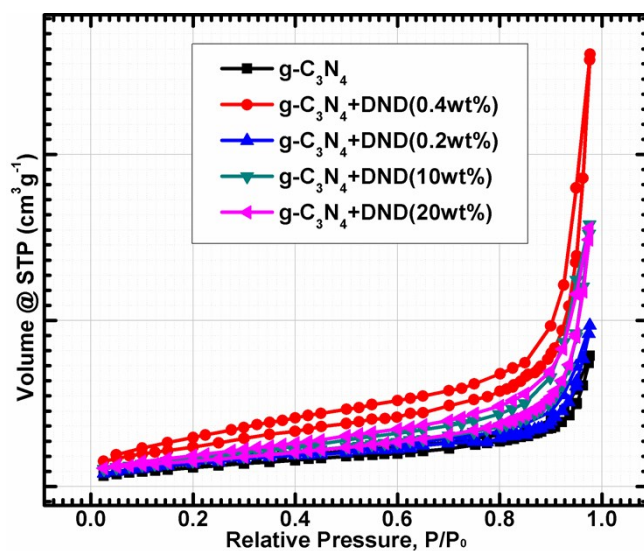


Fig. S9. N₂ absorption-desorption isotherms of g-C₃N₄ and g-C₃N₄+DND(0.4wt%).

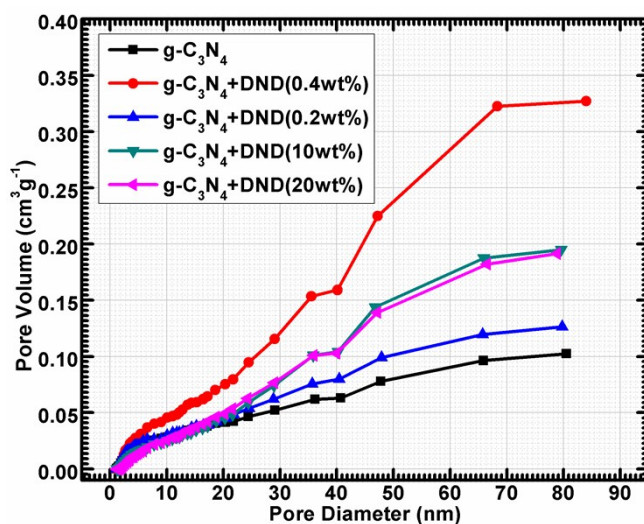


Fig. S10. Pore size distribution curves of g-C₃N₄ and g-C₃N₄+DND(0.4wt%).

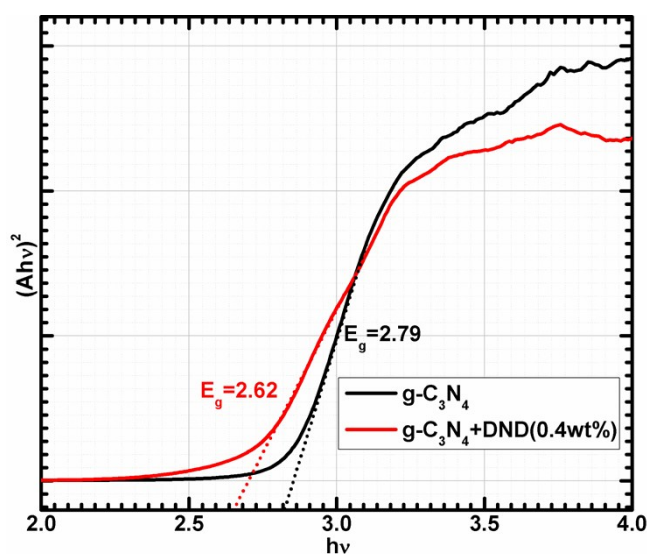


Fig. S11. Plot of $h\nu$ vs. $(Ah\nu)^2$ for direct band gap energy

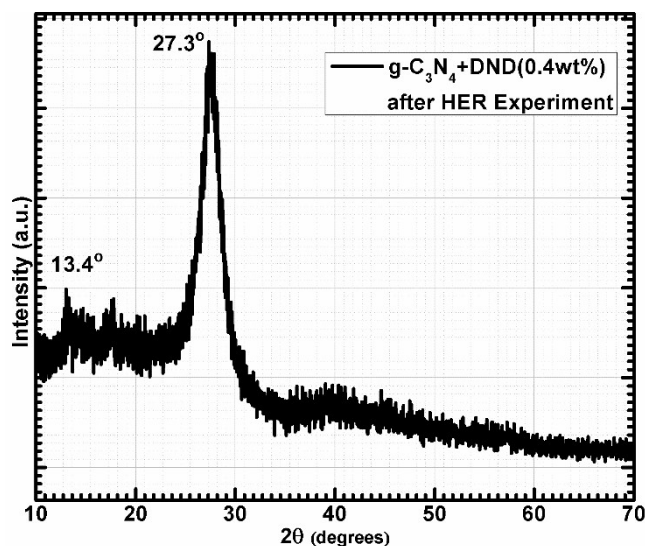


Fig. S12. XRD pattern of g-C₃N₄+DND(0.4wt%) after photocatalysis experiment.

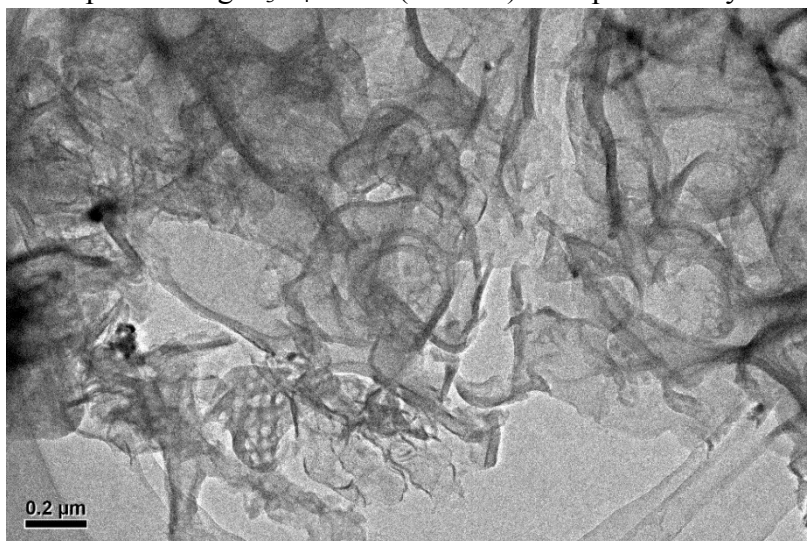


Fig. S13. TEM image of g-C₃N₄+DND(0.4wt%) after photocatalysis experiment.

References

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