

Supporting Information

Advancing $n \rightarrow \pi^*$ Electron Transition of Carbon Nitride Nanotubes for H_2 Photosynthesis

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Experimental Section

Materials: All chemicals were used as received without further purification. Typically, urea and oxamide were purchased from Sigma-Aldrich with purity > 99 %.

Synthesis of CN: The typical CN photocatalyst was prepared by a traditional thermal polymerization strategy as reported previously. In a typical procedure, 10 g of urea was placed in a crucible with a cover, and then it was annealed at 550 °C for 2 h in the air. The final yellow powder was then collected and washed with DI water. After drying in vacuum oven overnight the solids were last collected for use and it was labelled as CN for simplify.

Synthesis of CN-OA-x samples: CN-OA-x samples were prepared by a facile wet-chemistry strategy followed by thermal treatment in the oven. Typically, 10 g of urea and different amounts of oxamide (0.1 g, 0.3 g, 0.5 g and 1.0 g) were mixed together with 10 mL of DI water/ethanol (1:1 in volume) in a 30 mL volume of glass bottle to form the hydrogen bond interaction. After evaporation at 100 °C, the solid powders were collected and then transferred into crucibles with cover. At last, the crucibles were heated in an air oven at 550 °C for 2 hours with a heating rate of 5 °C / min. The final products were then collected after the temperature was naturally cooled down to the room temperature and washed thoroughly with DI water. They were collected after drying in vacuum oven and denoted as CN-OA-x, where x represents the initial mass fraction of oxamide (x= 0.01, 0.03 0.05, and 0.1) for simplify. As increasing the OA amounts, the color of the polymers was changed from pale yellow to deep orange, well illustrating the successful fabrication of new carbon nitrides with high visible light absorption efficiency. For comparison, these samples were also prepared at 600 °C in the air oven with the same experimental conditions. Same color change in the apparent was also observed for the samples prepared at 600 °C.

Characterizations: Powder XRD patterns were recorded with a Bruker D8 Advance instrument with Cu K α

radiation. FTIR spectra were recorded with a Thermo Scientific Nicolet iS5 FTIR spectra meter. Optical properties of the powders were examined by a Shimadzu UV 2600 instrument. SEM images were performed on JSM-7500F (JEOL). TEM was performed on a FEI Tencai 20 microscope. Room temperature Photoluminescence spectra were monitored at a Perkin Elmer Luminescence Spectrometer (LS 50 B) with excitation wavelength of 350 nm. Average fluorescent lifetime was calculated as follows: $\tau_A = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2) / (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$. The surface area of the samples was examined by the low-temperature N₂ adsorption-desorption method with Quantachrome Quadrasorb SI porosimeter and calculated by Brunauer-Emmett-Teller (BET) model. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al K α line source (200 W). Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared on F-doped tin oxide (FTO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of FTO glass was protected using Scotch tape. The 5 mg sample was dispersed in 1 mL of DMF by sonication to get a slurry mixture. The slurry was spread onto pretreated FTO glass. After air-drying, the working electrode was further dried at 393 K for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin.

Photocatalytic tests for H₂ evolution: Photocatalytic H₂ evolution activities were evaluated in a closed system equipped with a pressure detector to examine the pressure of the evolved gases in during photocatalytic reactions. White LED light (50 W) and green LED light (50 W, $\lambda = 525 \pm 1.0$ nm) were used for photocatalytic H₂ evolution evaluation, respectively. The used volume of the reactor was 38 mL and the temperature was controlled 298 K by cycle water.

The evolved amounts of the gases were finally calculated by the Clausius-Clapeyron relation ($PV = n RT$). Typically, 50 mg of solid catalysts was dispersed into 50 mL of DI water and TEOA (10 V. %) mixture, while they were degassed in advance for use with vacuum and sonication, respectively. 3 wt. % Pt cocatalysts were deposited by a typical in-situ photodeposition strategy from H_2PtCl_6 precursor. The reaction temperature of the system was maintained at 25 °C by a flow of cooling water.

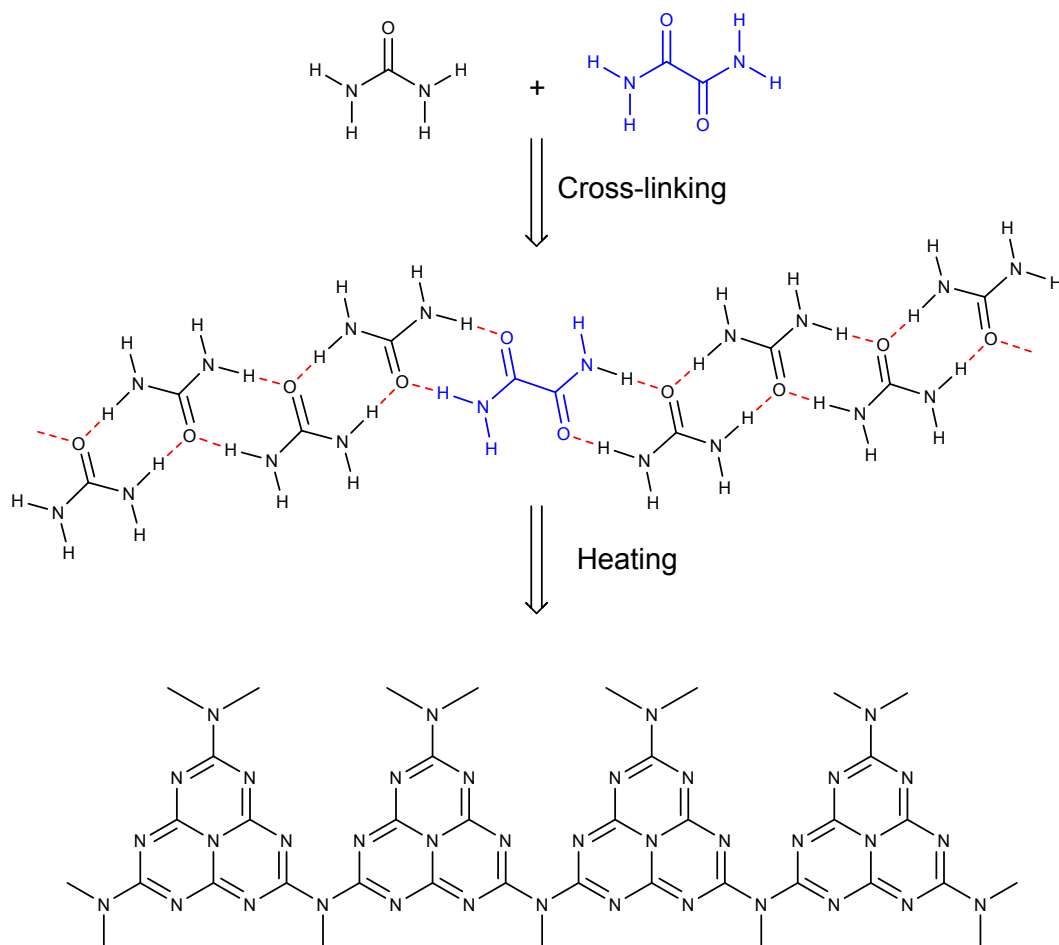
The AQY measurement and Wavelength Experiment: The apparent quantum yield (AQY) for H_2 evolution was measured using monochromatic green LED lamp (525±1.0 nm). The intensity was tested to be 4.5 mW cm⁻² and the irradiation area was controlled as 3×3 cm². Depending on the amount of hydrogen produced by the photocatalytic reaction in an average of one hour, and the AQY was calculated as follow:

$$\eta_{AQY} = \frac{N_e}{N_p} \times 100\% = \frac{2 \times M \times N_A}{\frac{E_{total}}{E_{photon}}} \times 100\%$$

$$= \frac{2M \times N_A}{S \times P \times t} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

$$h \times \frac{c}{\lambda}$$

Where, M is the amount of H_2 molecules (mol), N_A is Avogadro constant (6.022×10^{23} / mol), h is the Planck constant (6.626×10^{-34} J S), c is the speed of light (3×10^8 m/s), S is the irradiation area (cm²), P is the intensity of irradiation light (W/cm²), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).



Scheme S1. Proposed synthetic procedure of self-assembly carbon nitride nanotubes via intermolecular hydrogen bond interactions.

Table S1. Surface zeta potentials, Optical absorption under $\lambda = 420$ nm and $\lambda = 525$ nm, Photocatalytic H_2 evolution activities under white and green LED light of the CN-OA-x.

Catalysts	Zeta potentials / mV	Optical Absorption		H_2 evolution activities / $\mu\text{mol h}^{-1}$	
		$\lambda = 420$ nm	$\lambda = 525$ nm	White light	Green light
CN	-18.5	0.49	0.05	5.4	0.5
CN-OA-0.01	-19.2	0.55	0.15	9.3	2.1
CN-OA-0.03	-20.7	0.67	0.28	12.6	3.7
CN-OA-0.05	-21.9	0.85	0.46	8.3	4
CN-OA-0.1	-23.1	1.02	0.66	5.5	2.6

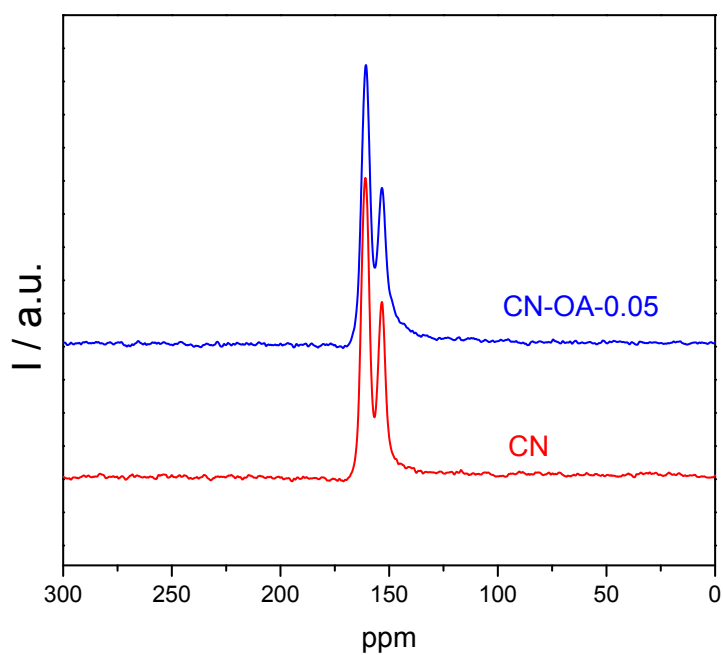


Figure S1. Solid-state C^{13} NMR spectra of CN and CN-OA samples.

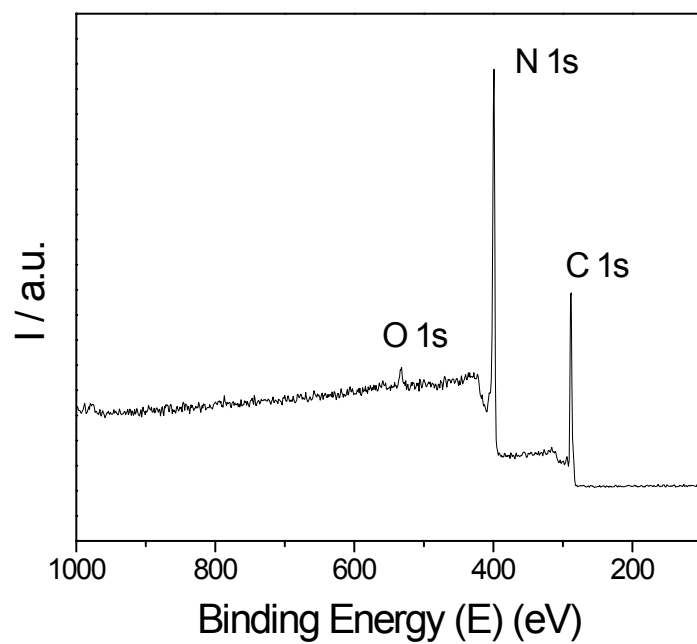


Figure S2. Survey XPS spectra of CN-OA-0.05 sample.

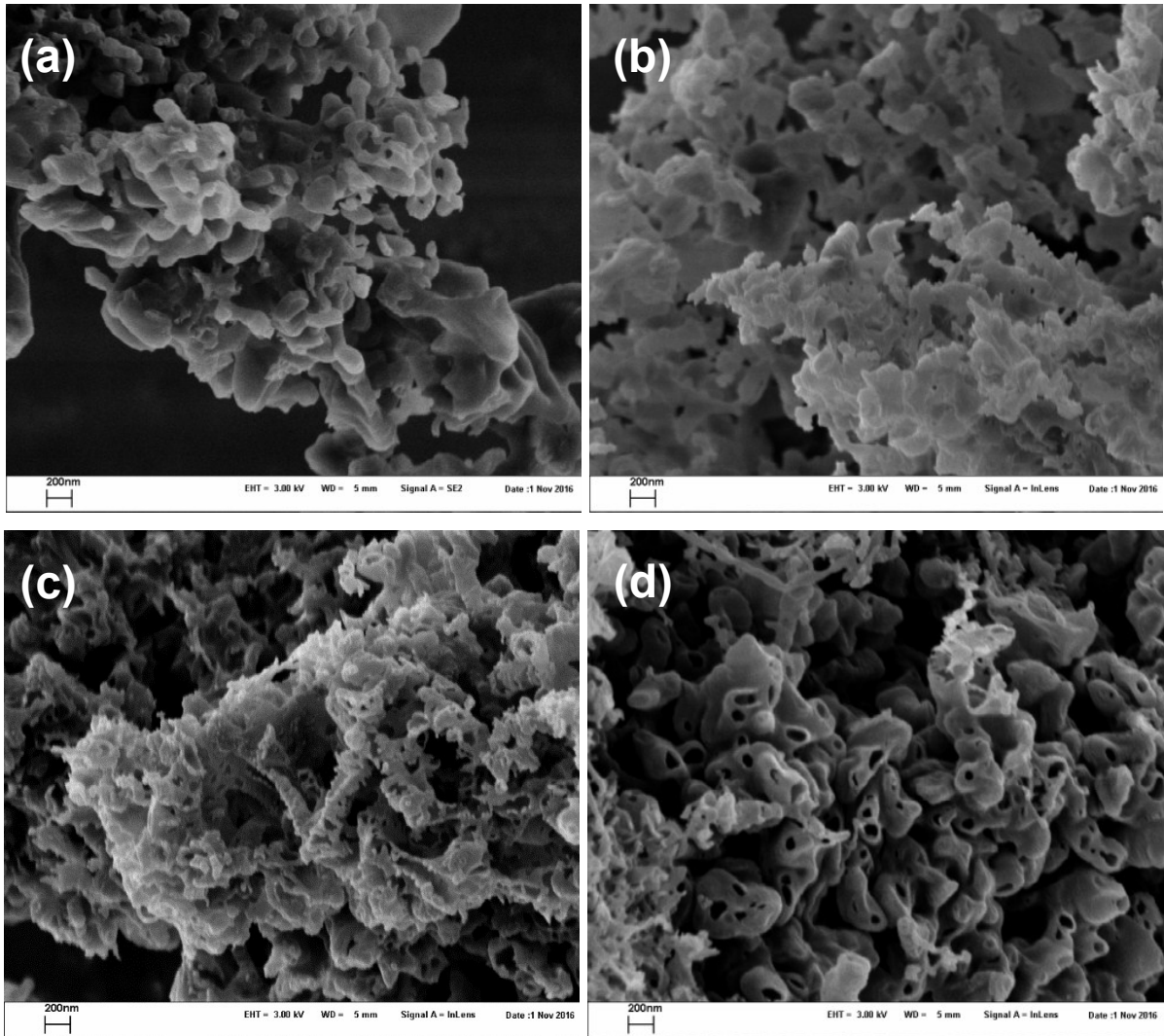
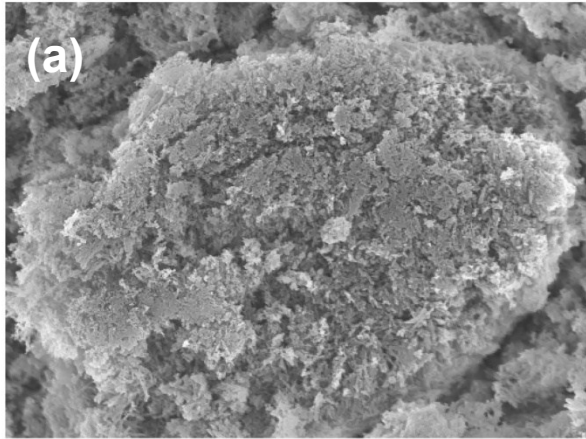
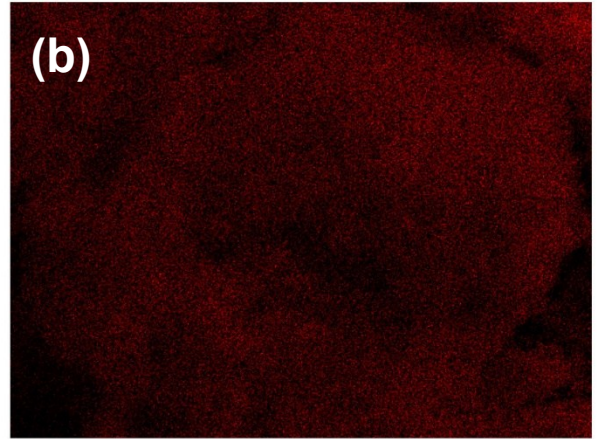


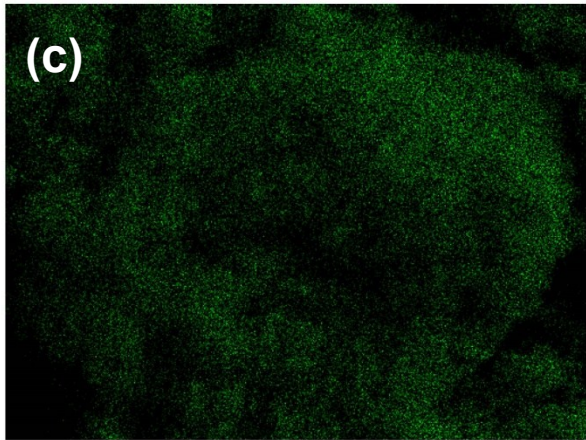
Figure S3. SEM images of (a) CN, (b) CN-OA-0.01, (c) CN-OA-0.03, and (d) CN-OA-0.1 samples.



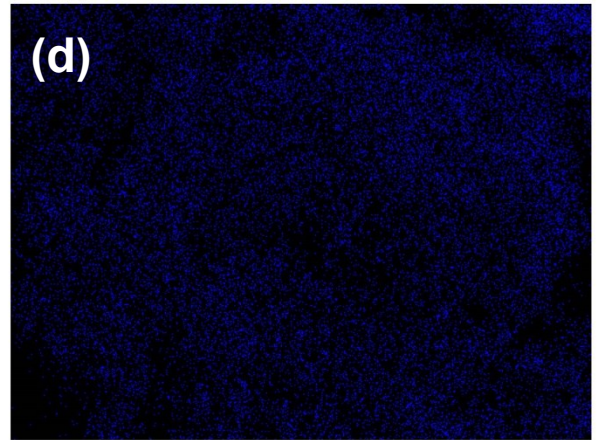
Elektronenbild 1



C Ka1_2

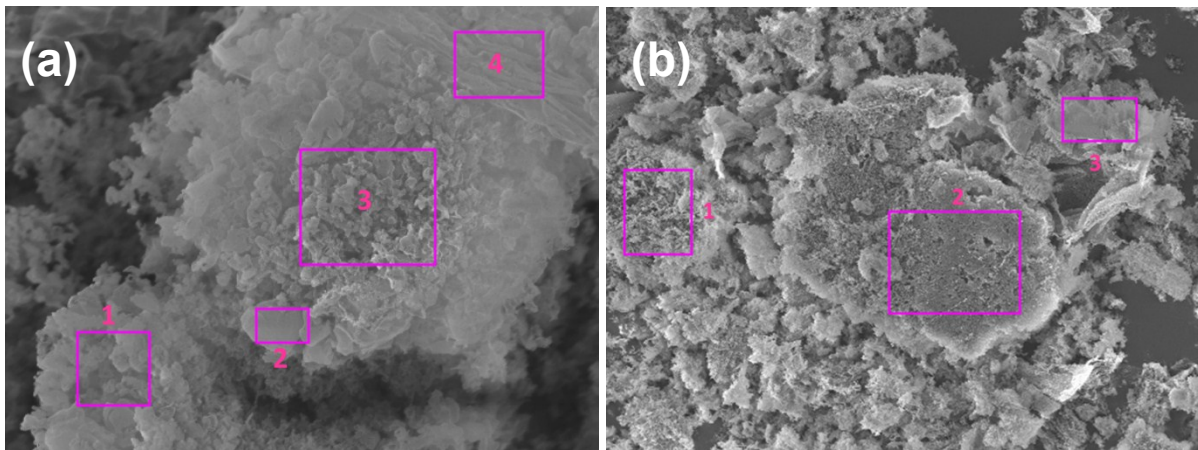


N Ka1_2



O Ka1

Figure S4. Elemental mapping images of CN-OA-0.05.



(c)

Elements	C (wt. %)	N (wt. %)	O (wt. %)	C/N (mol ratio)
Area 1	35.91	60.29	3.35	0.69
Area 2	35.94	59.99	3.27	0.70
Area 3	35.95	60.52	2.7	0.69
Area 4	36.91	58.52	4.01	0.73
Average	36.18	59.86	3.33	0.71

(d)

Elements	C (wt. %)	N (wt. %)	O (wt. %)	C/N (mol ratio)
Area 1	38.75	58.47	2.24	0.77
Area 2	37.27	59.77	2.59	0.73
Area 3	37.64	57.68	4.44	0.76
Average	37.89	58.64	3.09	0.75

Figure S5. Energy-dispersive X-ray spectroscopy (EDS) of selected areas for (a) (c) CN and (b) (d) CN-OA-0.05 samples.

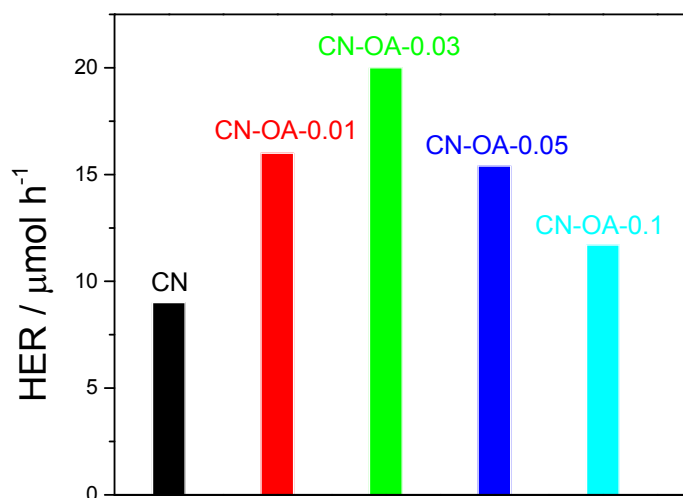


Figure S6. Photocatalytic H₂ evolution of CN and CN-OA-x samples prepared at 600 °C with white LED light irradiation ($\lambda > 420$ nm).

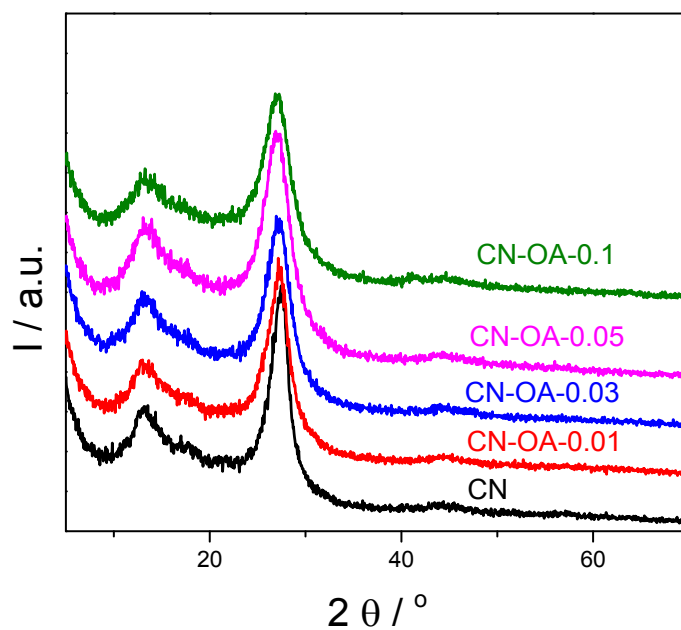


Figure S7. Powder XRD patterns of CN and CN-OA-x samples prepared at 600 °C in the air oven.

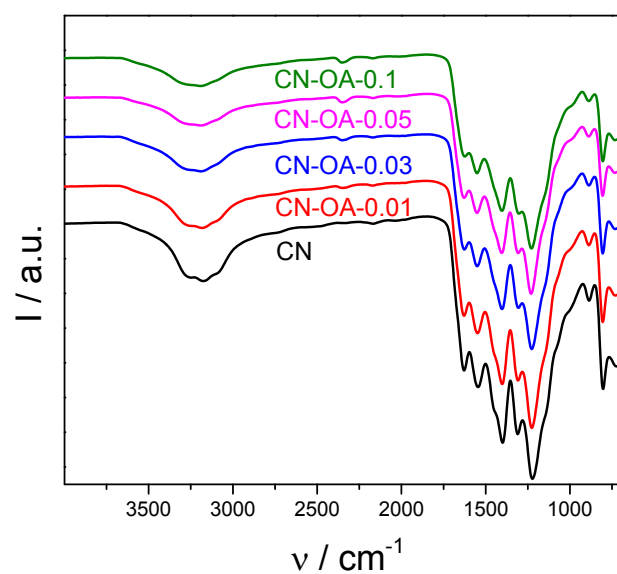


Figure S8. FT-IR spectra of CN and CN-OA-x samples prepared at 600 °C in the air oven.

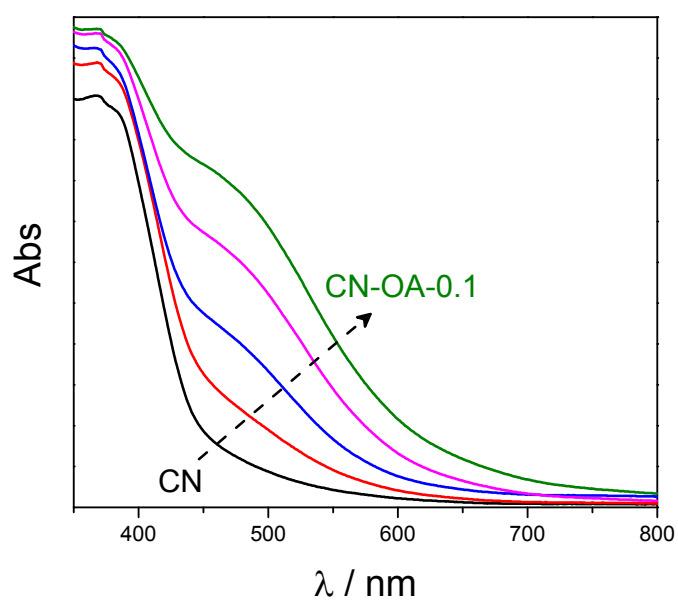


Figure S9. UV-Vis DRS spectra of CN and CN-OA-x samples prepared at 600 °C in the air oven.

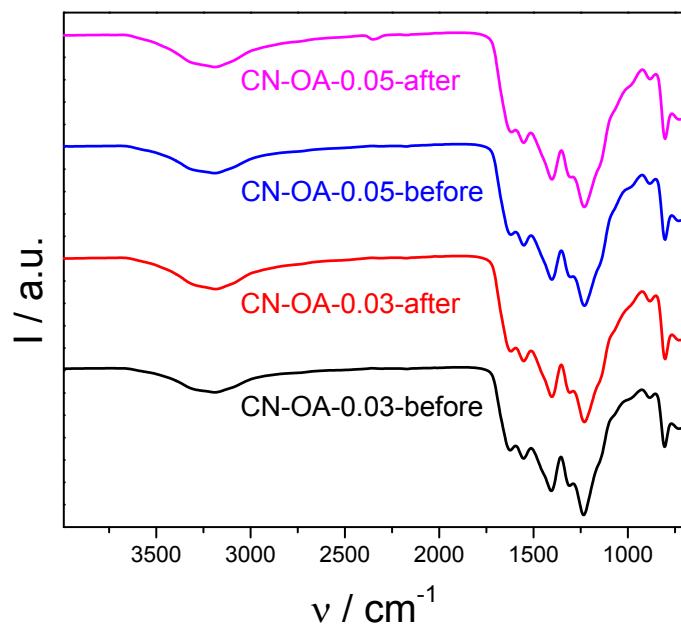


Figure S10. FT-IR spectra of both CN-OA-0.03 and CN-OA-0.05 samples tested before and after photocatalytic reaction.

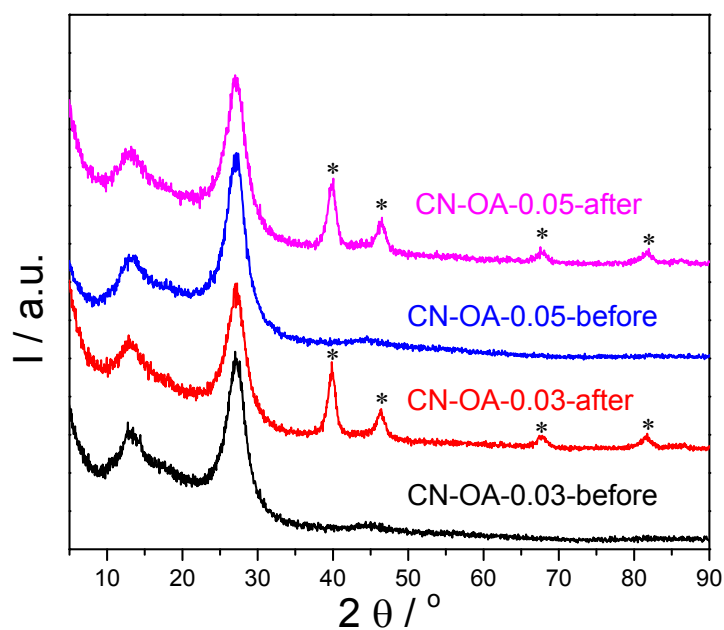


Figure S11. Powder XRD patterns of both CN-OA-0.03 and CN-OA-0.05 samples tested before and after photocatalytic reaction.

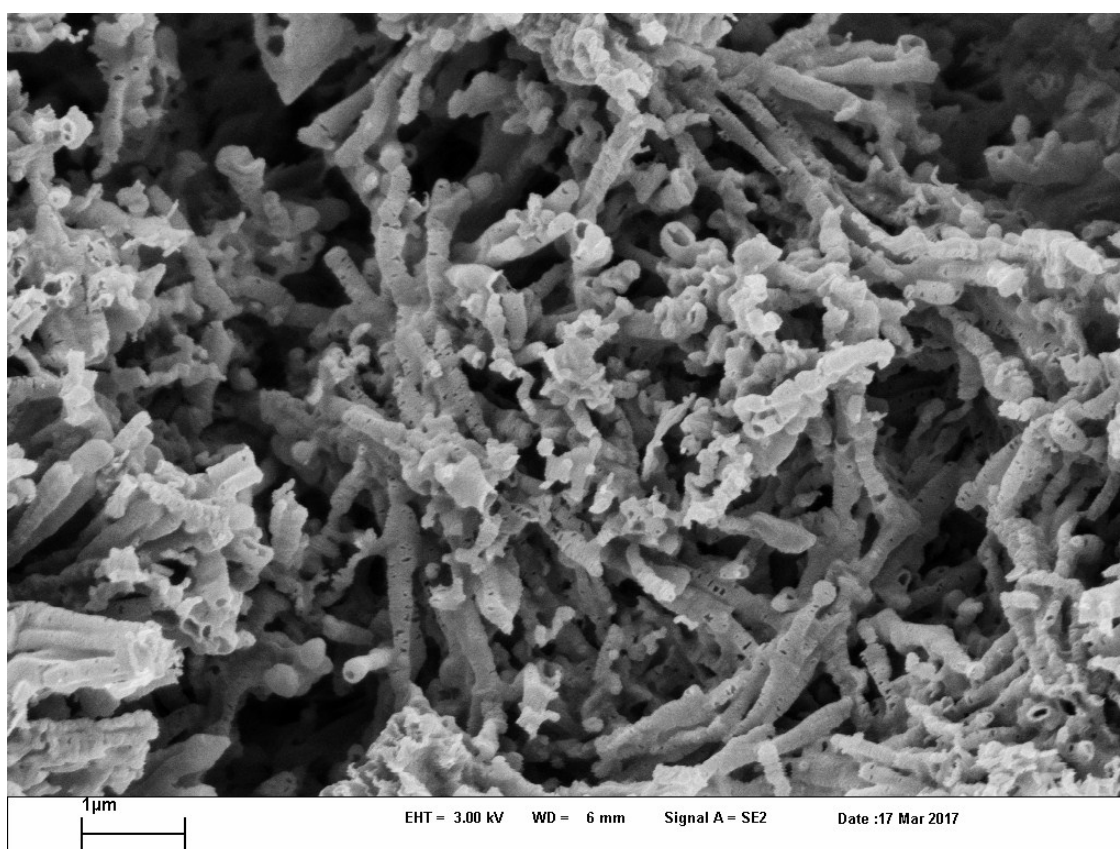
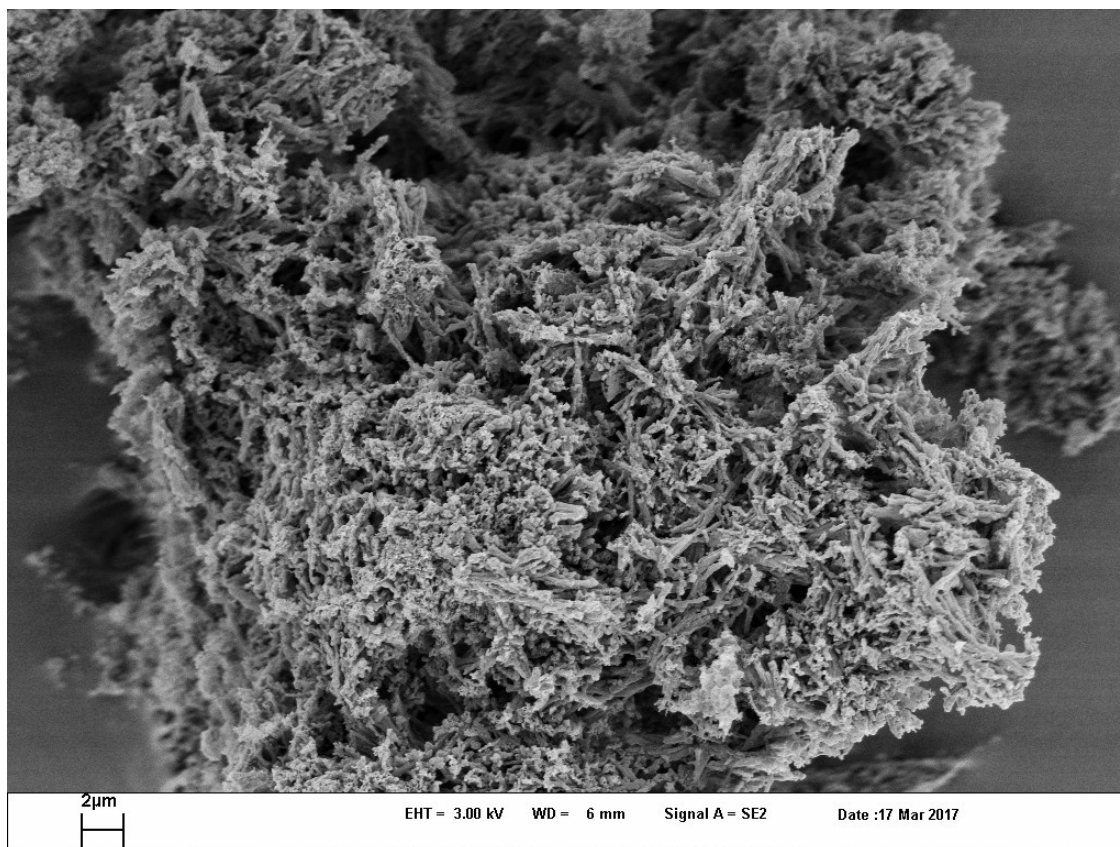


Figure S12. SEM images of CN-OA-0.05 after photocatalytic H₂ evolution reaction.