

Electronic Supplementary Information

Post-annealing Reinforced Hollow Carbon Nitride Nanospheres for Hydrogen Photosynthesis

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Experimental section

Instruments

Thermogravimetric analysis (TGA) was performed on TG209 (NETZSCH Co.). The nitrogen adsorption–desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Transmission electron microscopy (TEM) was obtained by Zeis 912 microscope. Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with Cu K α radiation ($k = 1.5406 \text{ \AA}$). Fourier transformed infrared (FTIR) spectra were recorded on BioRad FTS 6000 spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al K α line source (200 W). The solid-state ^{13}C -NMR spectra were collected using a Bruker Advance III 500 Spectrometer. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were performed on Varian Cary 500 Scan UV–visible system. Photoluminescence spectra were recorded on an Edinburgh FI/FSTCSPC 920 spectrophotometer. Electron paramagnetic resonance (EPR) measurements were performed using a Bruker model A300 spectrometer. Photocurrent performance was conducted with a BAS Epsilon Electrochemical System.

Synthesis of HCNS. HCNS was prepared by thermal polymerization according to the literature. First, the monodisperse SiO_2 template were synthesized according to the Stöber method. Briefly, 3.10 g of aqueous ammonia (32 wt%, Sigma-Aldrich) and 10 g of deionised water were added in 58.5 g of ethanol to form a

mixture solution after stirring for 30 min at 30 °C. 5.6 ml of tetraethoxysilane (TEOS, Sigma-Aldrich) was added to the above solution with vigorous stirring and was left stationary for 1 h to yield uniform nonporous silica spheres. A mixture of adequate TEOS and n-octadecyltrimethoxysilane (C18TMOS, Sigma-Aldrich) was then added dropwise to the above solution with magnetic stirring, sat quietly maturing for another 3 h at ambient temperature. The nanostructured silica was centrifuged, dried at 70 °C and calcined at 550 °C for 6 h in air. The as-prepared monodisperse SiO₂ templates were neutralized with a 1-M HCl solution and then dried at 80 °C overnight. Then, these monodisperse silica nanoparticles were used as a template to prepare HCNS. 2 g of the SiO₂ template was added to 10 g of cyanamide (Alfa Aesar), and kept under sonication and vacuum at 60 °C for 2 h. After that, the mixture was dissolved and stirred at 60 °C overnight, which was then centrifuged, dried, and calcined at 550 °C for 4 h. The obtained powder was treated with 4 M NH₄HF₂ for 12 h to remove the silica template, then centrifuged and washed three times with distilled water and once with ethanol. The final yellow HCNS powders were obtained by drying at 80 °C in a vacuum oven overnight.

Synthesis of HCNS-T. Prepared HCNS samples were placed in a glass bottle to calcine in a furnace at different temperatures of 300, 400, 500, 550 and 600 °C for 2h, respectively. Then, the final post-annealed HCNS samples were obtained, denoted as HCNS-T, where T (300, 400, 500, 550, 600) refers to the post-annealing temperature.

Synthesis of 3% Co₃O₄/HCNS-550. We prepared Co₃O₄ according to the literature before. In brief, 0.1g hollow carbon nitride nanospheres powder was impregnated into 4 mL water containing certain amount of CoCl₂.6H₂O and the resulting solution was kept in ultrasonic bath for 10 second. After drying, the resulting mixture was calcined in air at 300 °C for 1h. The loading amount was based on cobalt oxide.

Photocatalytic activity. Photocatalytic H₂ production was carried out in a Pyrex top-irradiation reaction

vessel connected to a glass-closed gas circulation system. For each reaction, 20 mg well-ground catalyst powder was dispersed in an aqueous solution (100 mL) containing triethanolamine (10 vol.%) as sacrificial electron donor. 3 wt.% Pt was photodeposited onto the catalysts using H_2PtCl_6 dissolved in the reactant solution. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 300W Xe lamp and a water-cooling filter. The wavelength of the incident light was controlled by using an appropriate long pass cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) with argon as the carrier gas.

Photocatalytic O_2 production was measured in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. For each reaction, 20 mg catalyst powder was well dispersed in an aqueous solution (100 mL) containing AgNO_3 (0.01M) as an electron acceptor and La_2O_3 (0.2g) as a pH buffer agent. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xe lamp and a water-cooling filter. The wavelength of the incident light was controlled by using an appropriate long pass cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector. O_2 selectivity was calculated by $100[M_{\text{O}_2}/(M_{\text{O}_2}+M_{\text{N}_2})]$ (Where M = Molar quantity).

Table S1. Physicochemical properties and photocatalytic activities of the HCNS and HCNS-T samples.

Sample	Yield [%]	C/N atomic	SA ^{a)} [m ² g ⁻¹]	BE [eV]	HER ^{b)} [μ mol h ⁻¹]
HCNS	100	0.73	80	2.82	128
HCNS-300	93.1	0.73	96	2.87	202
HCNS-400	83.8	0.73	102	2.89	148
HCNS-500	74.7	0.72	159	2.90	171
HCNS-550	57.7	0.72	221	2.92	275
HCNS-600	0	0	0	0	0

^{a)}Surface area; ^{b)} H₂ evolution rate.

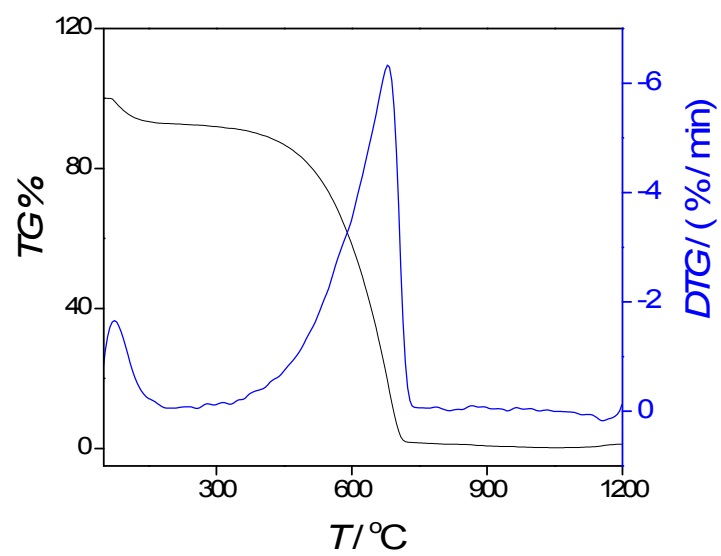


Figure S1. TGA-DTA curves of the as-synthesized HCNS sample.

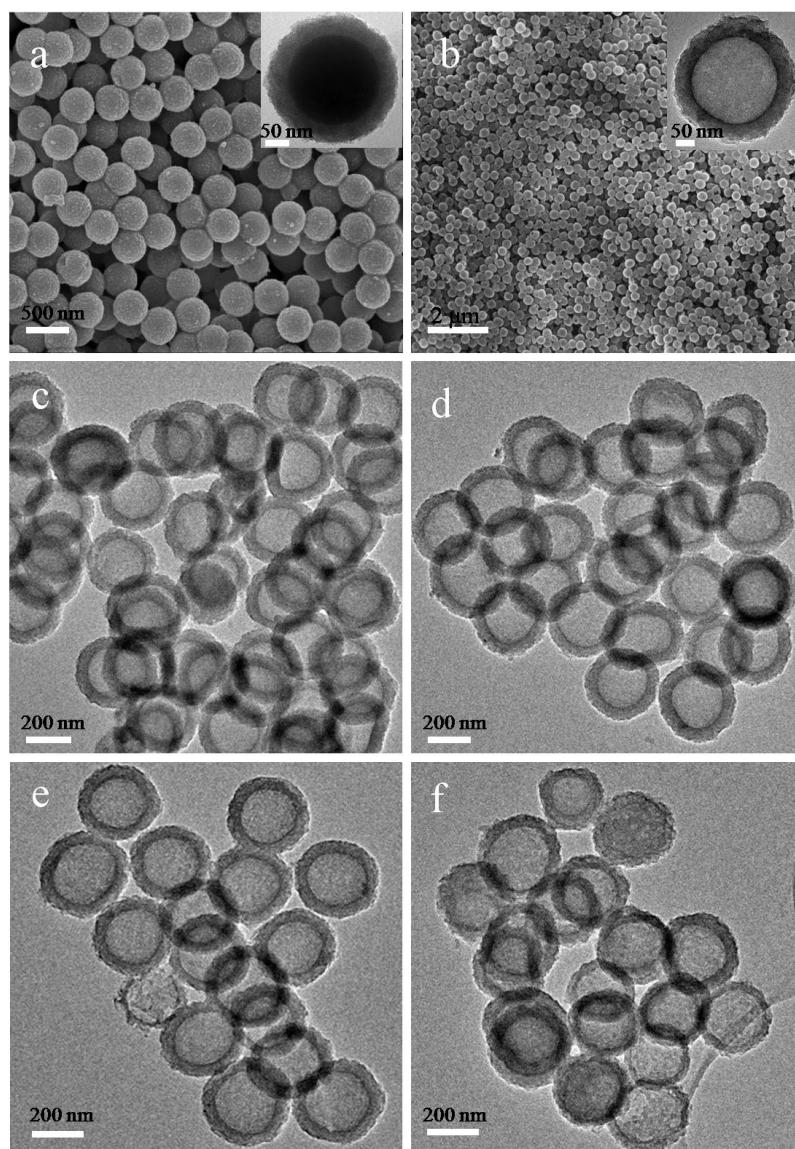


Figure S2. The SEM of a) monodisperse SiO₂ templates and b) HCNS, the insets in a) and b) are TEM of monodisperse SiO₂ templates and HCNS, respectively; c), d), e) and f) are the TEM images HCNS-T with T=300, 400, 500 and 550 °C, respectively.

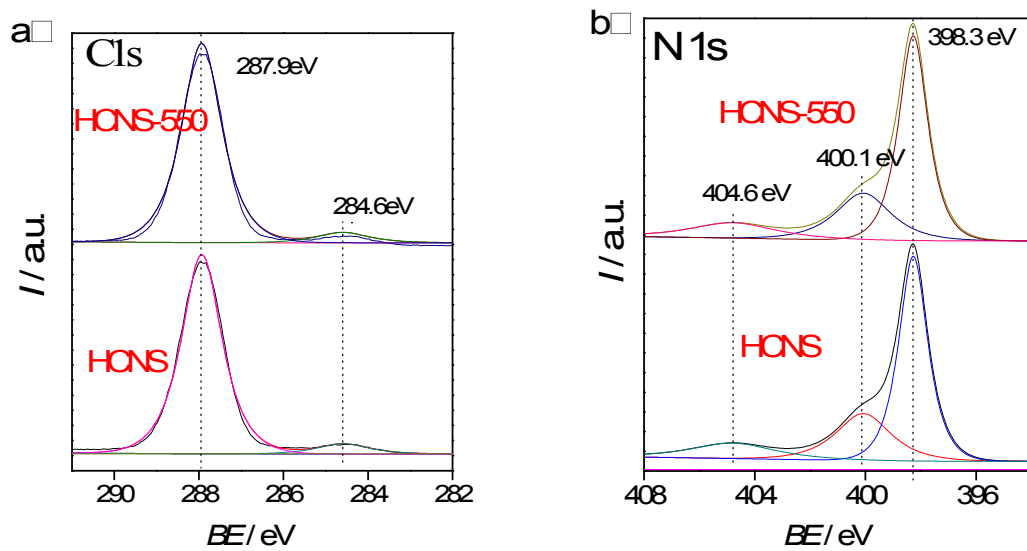


Figure S3. XPS analysis of HCNS-550 and HCNS, with the corresponding high-resolution spectra of C1s (a) and N1s (b).

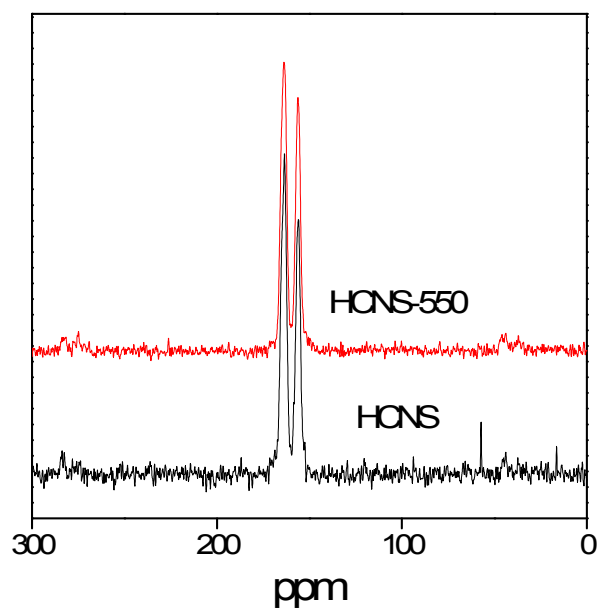


Figure S4. Solid-state ^{13}C NMR spectra of HCNS-550 and HCNS.

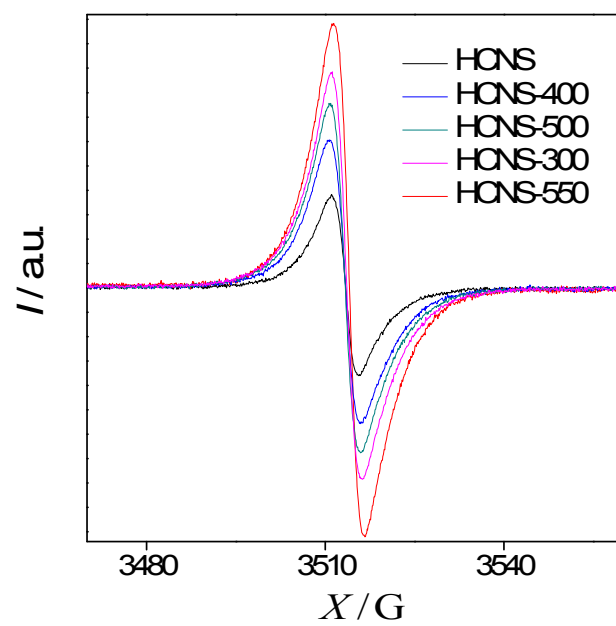


Figure S5. EPR spectra of HCNS-T and HCNS samples.

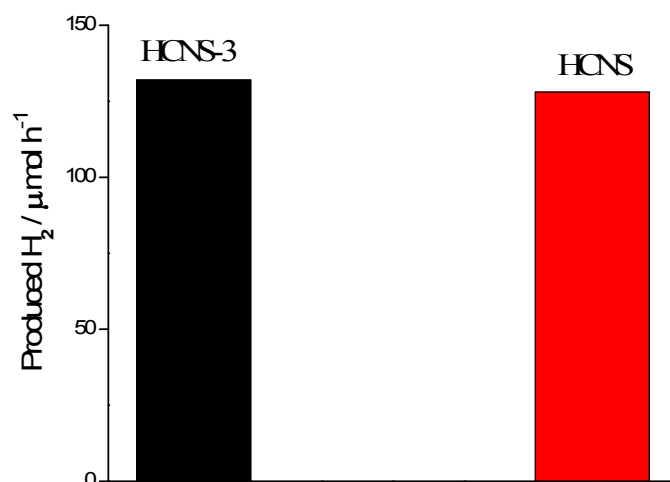


Figure S6. Photocatalytic hydrogen evolution of HCNS-3 in the nature publication at present experimental conditions and HCNS in this paper, respectively, under visible light irradiation.

In this paper, the HER of pristine HCNS is $128\mu\text{molh}^{-1}$, less than $180\mu\text{molh}^{-1}$ of HCNS-3 in the nature publication. This is due to the variation of the experimental equipment with a long time use. Such as the light intensity of Xe lamp is weaken with prolonged use. We have tested the same samples of HCNS-3 in the nature publication at the present experimental conditions, the result of HER is $132\mu\text{molh}^{-1}$, close to the HER of pristine HCNS in this paper.

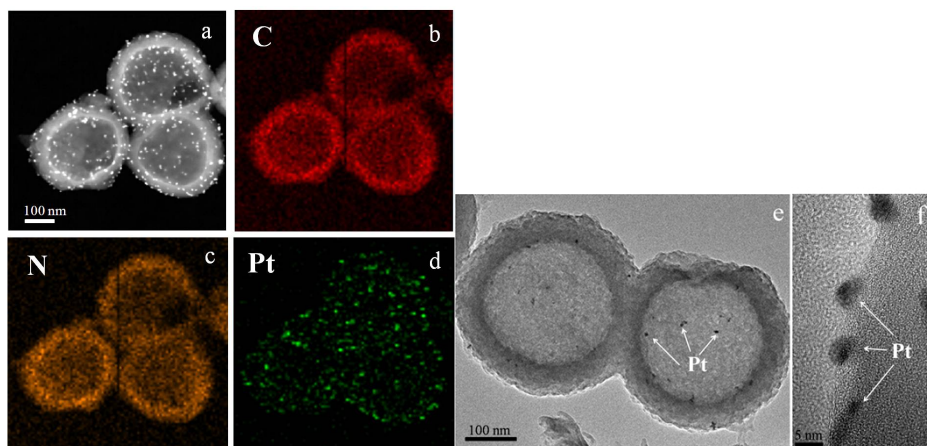


Figure S7. Elemental mapping (a-d) and TEM images (e-f) of the Pt/HCNS-550 sample recovered after the photocatalytic reaction.

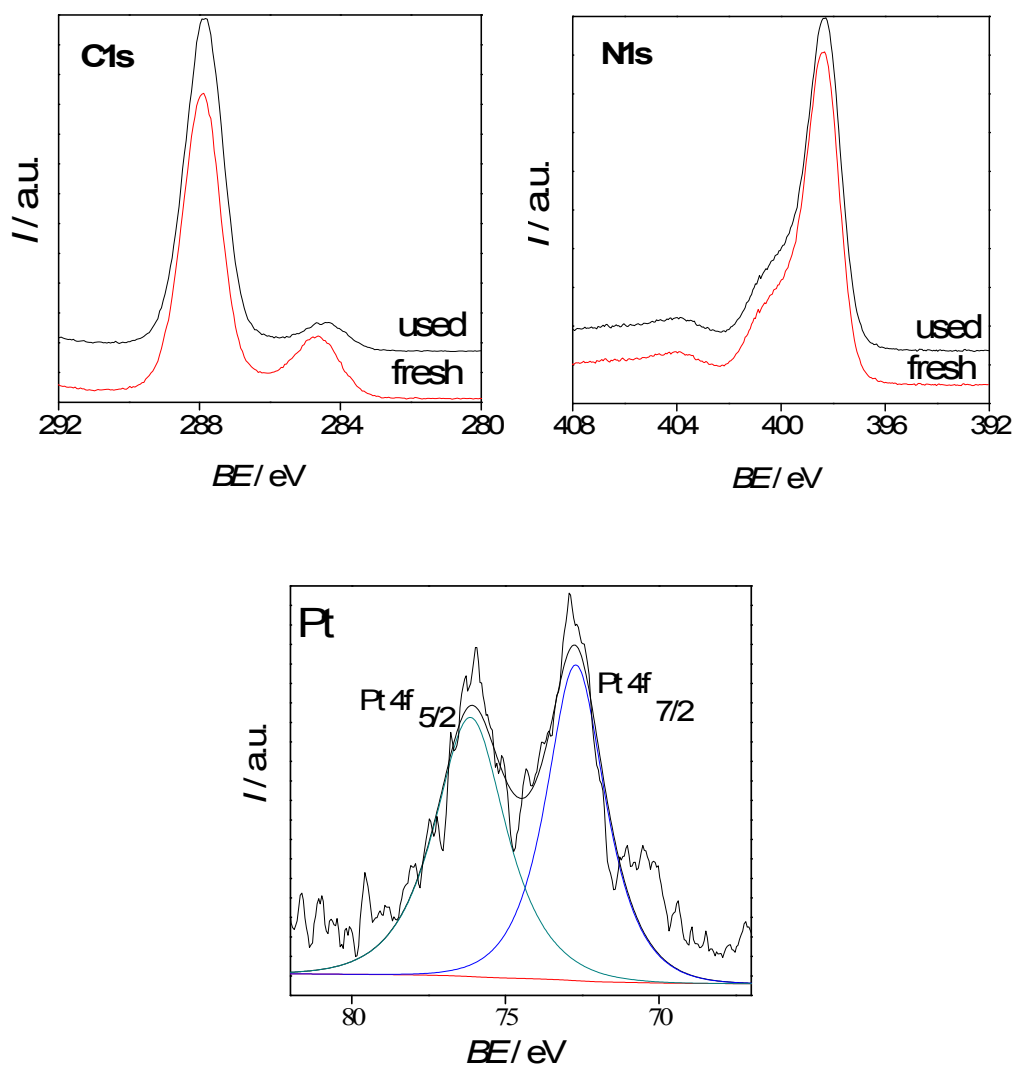


Figure S8. XPS spectra of C1s and N1s for HCNS-550 before and after used for the photocatalytic hydrogen production under visible light illumination.

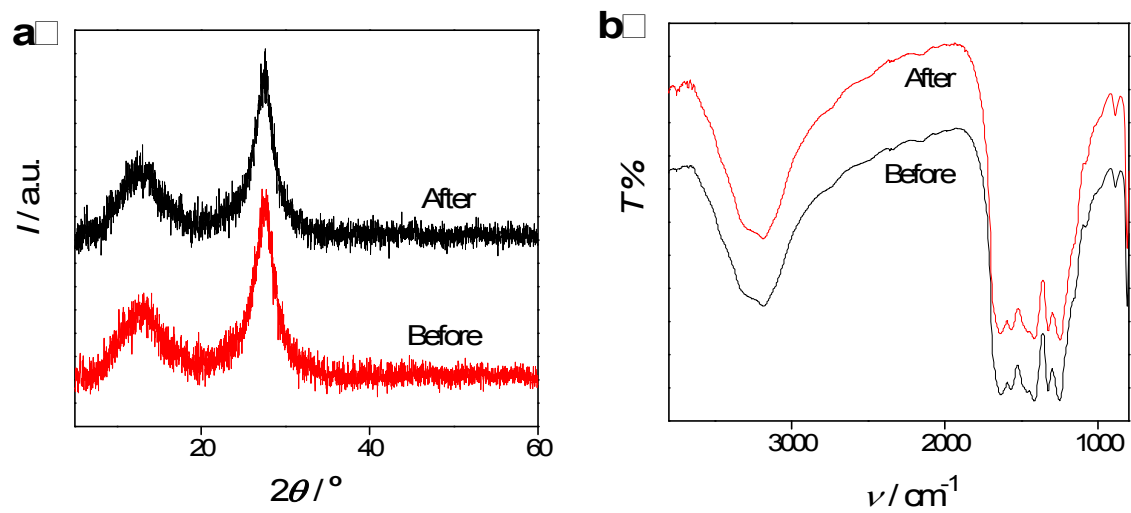


Figure S9. Structure of HCNS-550 after the photochemical reaction. a) XRD pattern; b) FTIR spectra.

Catalyst	O ₂ ($\mu\text{mol h}^{-1}$)	N ₂ ($\mu\text{mol h}^{-1}$)	O ₂ selectivity
HCNS	1.2	3.6	25.0%
3wt%Co ₃ O ₄ /HCNS	4.3	2.6	62.3%
HCNS-550	3.4	2.7	55.7%
3wt%Co ₃ O ₄ /HCNS-550	9.2	0.9	91.1%

Table S2. Ubiquity enhanced activities of photocatalysis water oxidation promoted by Co₃O₄ for HCNS and HCNS-550 photocatalysts. Reactions were taken under UV irradiation ($\lambda > 300 \text{ nm}$).