Electronic Supplementary Information

Shell-Engineering of Hollow g-C_3N_4 Nanospheres via Copolymerization for Photocatalytic Hydrogen Evolution

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Experimental section

Synthesis of SiO_2 template: 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 in a beaker to from 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 (C_{18}TMOS, Sigma-Aldrich) was then added dropwise to the above solution with magnetic stirring (1000 rpm), 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.

Synthesis of HCNS: The as-prepared monodisperse SiO_2 templates were neutralized with a 1-M HCl solution for 3h and then dried at 80 °C overnight. Then, these monodisperse silica nanoparticles were used as a template to prepare HCNS. 2 g of the SiO_2 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 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 NH_4HF_2 with magnetic stirring 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 CNST: 10 g cyanamide was mixed with a certain amount of ATCN at 55 ^{o}C for 24 h under N_2 protection. Then 2.0 g HCl-treated monodisperse SiO_2 template was added to this liquid mixture, kept sonication and vacuum at 60 ^{o}C for 2 h. After that, the mixture was stirred at 60 °C overnight, which was then centrifuged, dried, and calcined at 550 °C for 4 h. The resulting powder was treated with 4 M

NH_4HF_2 solution for 12 h to remove the silica template, followed by filtration, washing with water and ethanol several times, and finally drying at 80 °C. The resultant samples were further labeled as CNST*x*, where x (0.005, 0.01, 0.05, 0.1) refers to the weighed in amount of ATCN.

Characterization: The morphology of the sample was investigated by field emission scanning electron microscopy (SEM) (JSM-6700F). Transmission electron microscopy (TEM) was obtained by Zeis 912 microscope. The nitrogen adsorption–desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Thermogravimetric analysis (TGA) was performed on TG209 (NETZSCH Co.) Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with Cu Ka1 radiation (k = 1.5406 Å). 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 Kα 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. 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 indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5 mg sample was dispersed in 1 mL of DMF by sonication to get a slurry. The slurry was spread onto pretreated ITO 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 activity for water splitting: Photocatalytic H_2 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.

Table S1. Physicochemical properties of the HCNS and CNST samples.

Sample	C/N molar ratio	Surface area (m^2g^{-1})	Pore volume (cm^3/g)	Pore diameter（nm）
HCNS	0.73	89	0.31	0.78
$CNST_{0.005}$	0.75	94	0.33	0.75
$CNST_{0.01}$	0.76	92	0.29	0.77
$CNST_{0.05}$	0.77	87	0.32	0.76
$CNST_{0.1}$	0.78	92	0.29	0.77

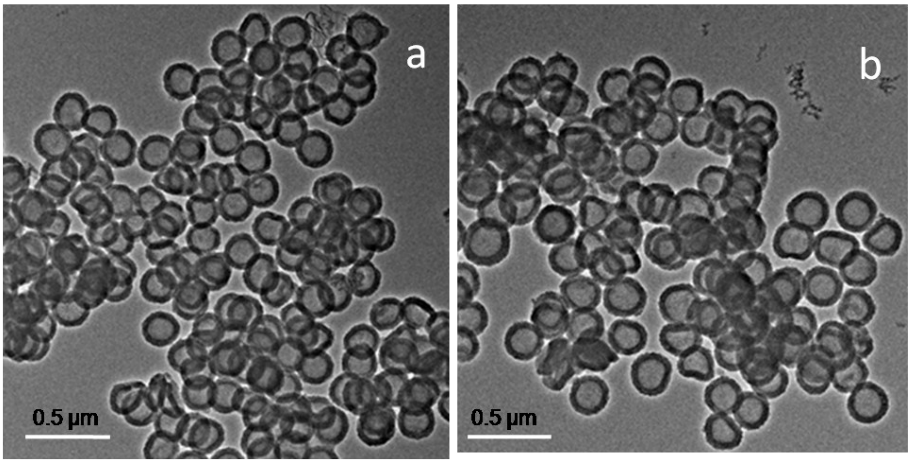

Figure S1. a) b) TEM images of HCNS-BA and HCNS-ABN samples, respectively.

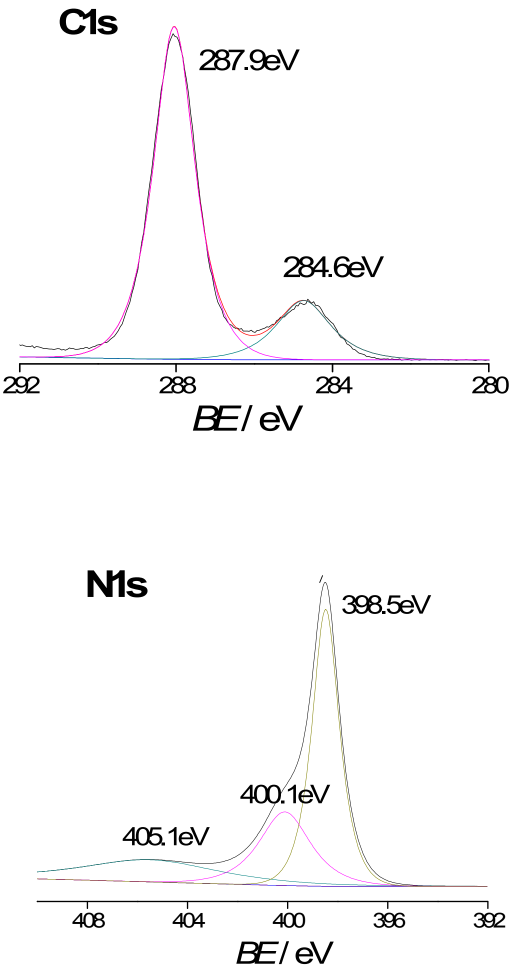

Figure S2. XPS spectra of C1s and N1s for $CNST_{0.05}$.

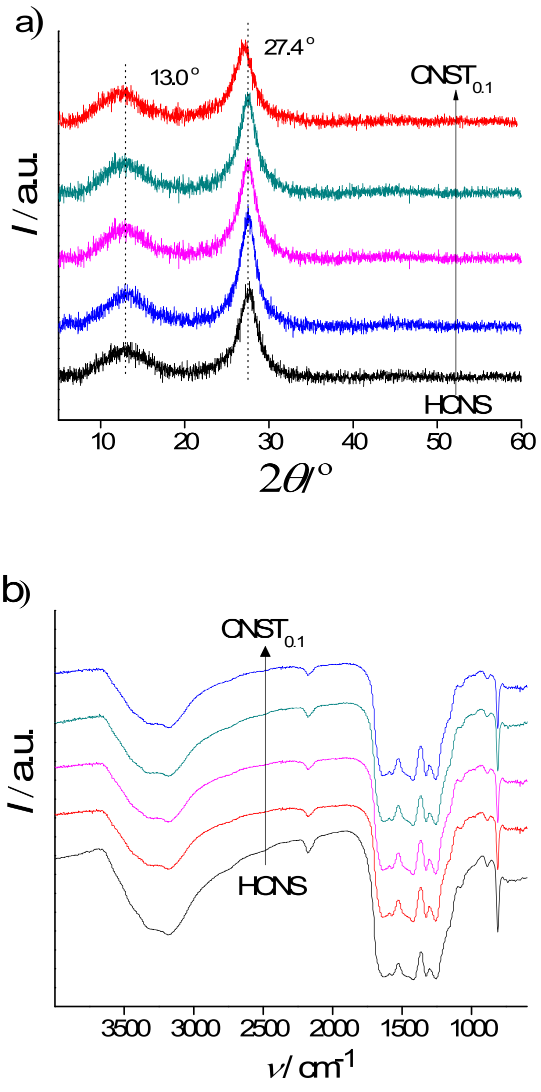

Figure S3. (a) XRD pattern of CNST; (b) FTIR spectra of CNST.

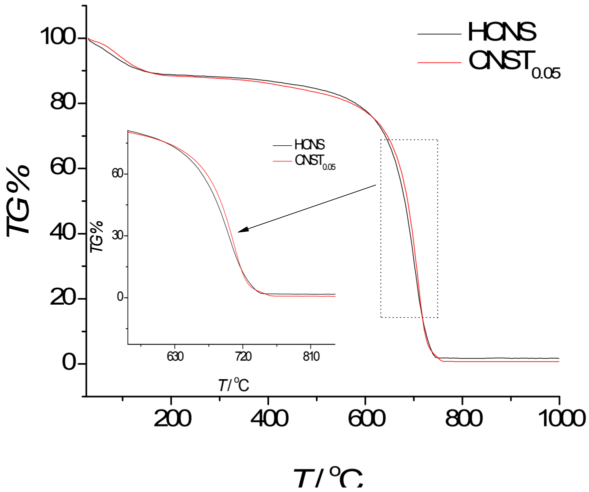

Figure S4. TGA curves of HCNS and CNST0.05 in air. As shown in the figure, the ATCN modification slightly increases the thermal stability of HCNS, potentially due to the fact that the extended delocalization by ATCN doping stabilizes the π-conjugated system.

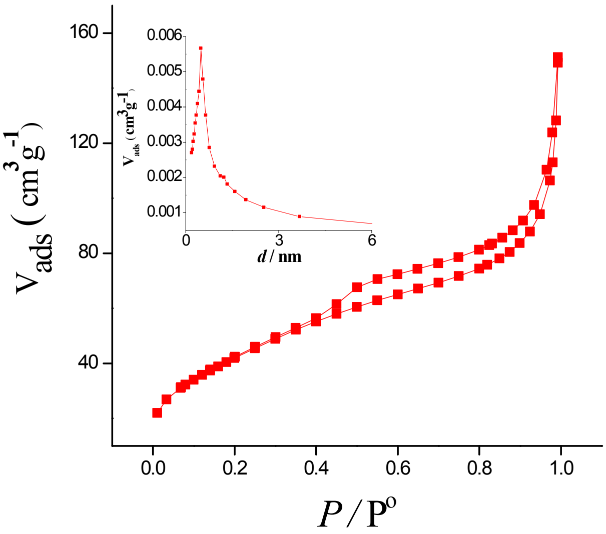

Figure S5. N_2 adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda pore-size distribution (inset) of $CNST_{0.05}$.

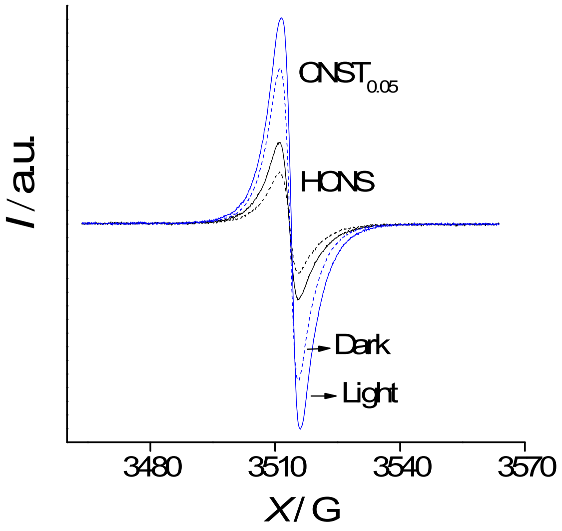

Figure S6. EPR spectrum of $CNST_{0.05}$ under visible light (λ > 420 nm).

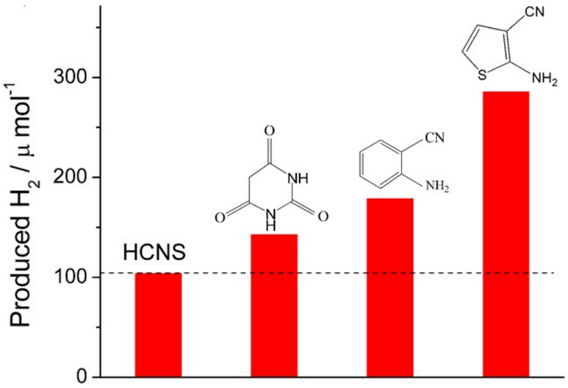

Figure S7. Photocatalytic H_2 evolution rate (λ >455 nm, 20 mg cat.).

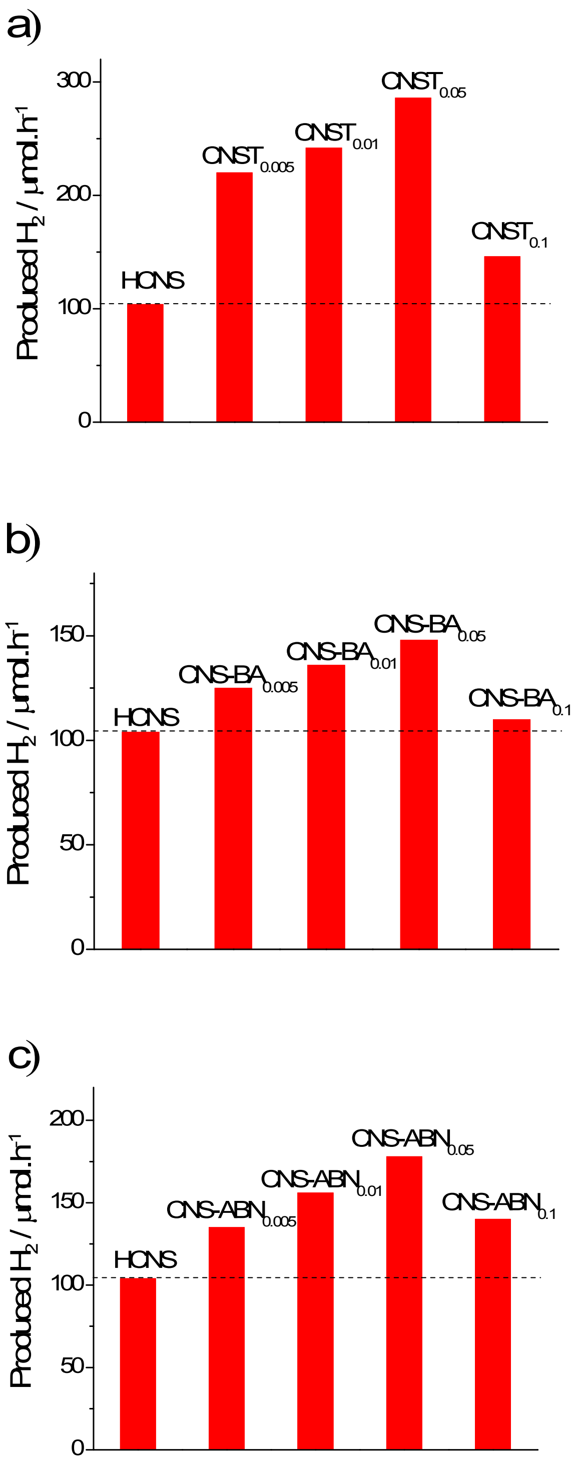

Figure S8. a), b), c) Photocatalytic hydrogen evolution by CNST, CNS-BA, CNS-ABN photocatalysts under visible-light irradiation (λ > 455 nm), respectively.

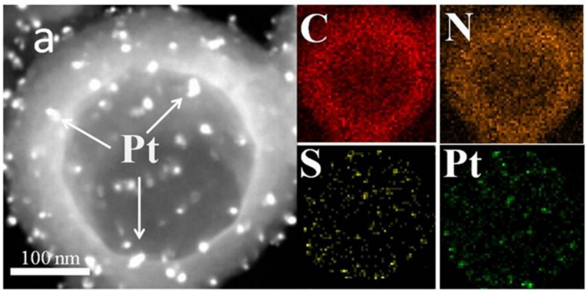

Figure S9. Elemental mapping a) and TEM b) of $CNST_{0.05}$ after photocatalytic activity test.

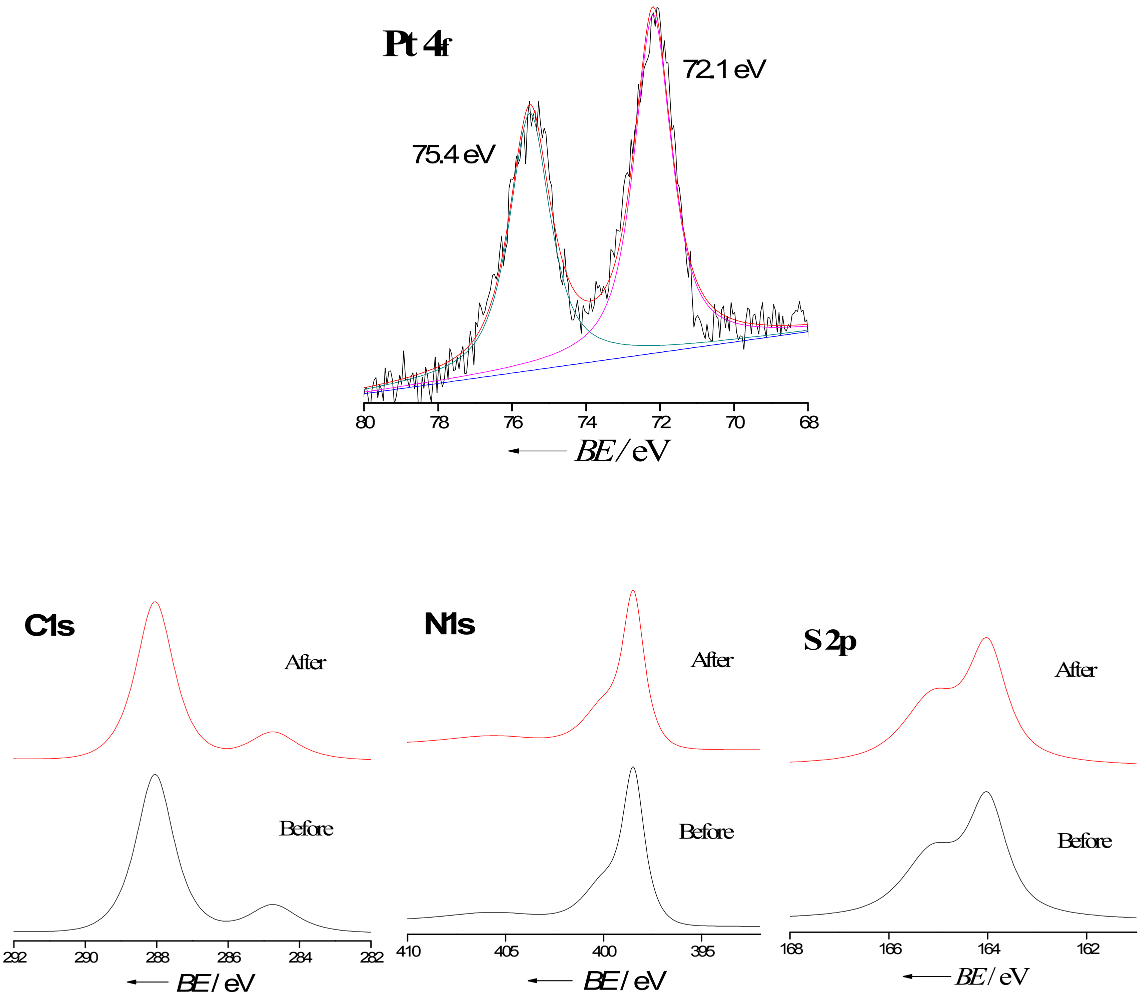

Figure S10. XPS specra of CNST$_{0.05}$ after the photochemical reaction.

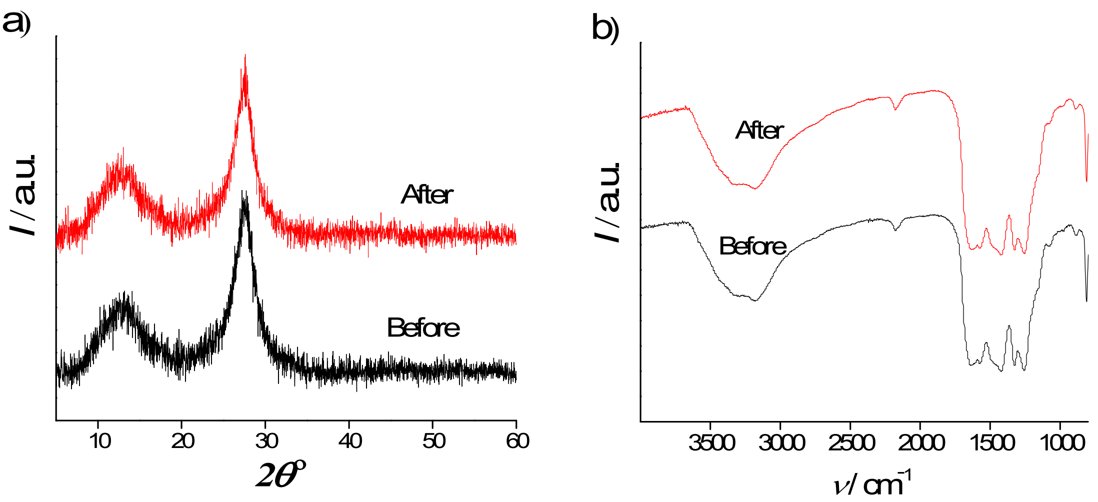

Figure S11. Structure of CNST$_{0.05}$ after the photochemical reaction. a) XRD pattern; b) FTIR spectra.