## Electronic Supplementary Information

## Au nanoparticle-embedded, nitrogen-deficient hollow mesoporous carbon nitride spheres for nitrogen photofixation

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**Fig. S1** Histogram of the diameter distribution of the solid silica spheres. The diameters were measured on the TEM images.



**Fig. S2** HCNS-NV shells with different thicknesses. (a) SEM images of the differently sized solid silica spheres coated with mesostructured silica. (b) TEM images of the solid silica spheres coated with mesostructured silica. The numbers in the images are the average thicknesses of the mesostructured silica shells coated on the solid silica sphere cores. (c) SEM images of the differently sized HCNS-NV samples. (d) TEM images of the HCNS-NV samples. The numbers in the images are the average thicknesses of the HCNS-NV shells.



**Fig. S3** Core@shell nanostructures before and after calcination. In the upper row are the TEM images of the solid silica spheres coated with mesostructured silica. In the bottom row are the TEM images of the corresponding core@shell nanostructures after the removal of CTAC by calcination.



Fig. S4 TGA curves of the Au/HCNS-NV samples with different Au loading amounts.



**Fig. S5** TEM images of the Au/HCNS-NV samples loaded with Au at different amounts. (a) 3.7 wt% Au. (b) 12.9 wt% Au. (c) 19.1 wt% Au.



Fig. S6 Histograms of the size distributions of the Au nanoparticles embedded in the Au/HCNS-NV samples with different Au loading amounts. (a) 3.7 wt% Au. (b) 7.4 wt% Au. (c) 12.9 wt% Au. (d) 19.1 wt% Au.



Fig. S7 HRTEM image of the Au/HCNS-NV sample containing 7.4wt% Au.



**Fig. S8** Characterization of the HCNS sample. (a) SEM image. (b) TEM image. (c) EDX spectra of the HCNS-NV and HCNS samples. The HCNS sample was obtained from the HCNS-NV sample through calcination in air.



**Fig. S9** TEM images of the hybrid Au/HCNS-NV nanostructure samples synthesized by the other methods. (a) Treatment with  $CH_2Cl_2$ . (b) Thermal decomposition. (c) Photoreduction.



**Fig. S10** XRD patterns. (a) XRD patterns of the HCNS-NV, HCNS, Au/HCNS-NV and Au/HCNS samples. (b) Enlarged regions around the (002) peak of polymeric carbon nitride for the HCNS-NV and HCNS samples.



**Fig. S11** N<sub>2</sub> adsorption-desorption isotherms of the four samples. (a) HCNS-NV. The inset shows the corresponding pore size distribution. (b) HCNS. (c) Au/HCNS-NV. (d) Au/HCNS.



**Fig. S12** Tauc plots of the HCNS-NV and HCNS samples derived from their corresponding absorption spectra.



Fig. S13 High-resolution C1s XPS spectra. (a) HCNS-NV. (b) HCNS.



Fig. S14 FTIR spectra of the HCNS-NV, HCNS, Au/HCNS-NV and Au/HCNS samples.



**Fig. S15** Proposed chemical structure of HCNS-NV and the structural evolution upon calcination in air.



**Fig. S16** Dependence of the absorbance on the  $NH_4^+$  determination. (a) Absorption spectra of the standard  $NH_4^+$  solutions at different concentrations. (b) Linear relationship between the absorbance at 425 nm and the  $NH_4^+$  concentration.



**Fig. S17** Characterization of the HCNS*x*-NV samples with different shell thicknesses. (a) XRD patterns. (b) FTIR spectra.



**Fig. S18** Generated ammonia in 1 h under visible light in the presence of methanol in the reaction solution. The ammonia concentration was estimated by ion chromatography.



**Fig. S19** Control experiments for the N<sub>2</sub> photofixation reaction. (a) Concentrations of the ammonia generated under different conditions as functions of the light irradiation time. The light irradiation was turned on at the zero time point. (b) <sup>1</sup>H NMR spectra of the reaction solution upon the photocatalytic N<sub>2</sub> fixation reaction for 2 h using Au/HCNS-NV as the catalyst in Ar, <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> atmosphere, respectively. (c) Photocatalytic production rates of NH<sub>3</sub> and H<sub>2</sub> in a sealed reactor with Au/HCNS-NV and N<sub>2</sub>. (d) Photocatalytic production rates of NH<sub>3</sub> and H<sub>2</sub> in a sealed reactor with Au/HCNS-NV and Ar.



**Fig. S20** DR-FTIR spectra measured on KBr powder. The plot labelled with "sample" is the FTIR spectrum obtained by bubbling the products from the aqueous reaction solution with Au/HCNS-NV into the diffuse reflection cell loaded with KBr powder. The plot labelled with "H<sub>2</sub>O" is the FTIR spectrum obtained by bubbling pure  $H_2O$  into the diffuse reflection cell loaded with KBr.



**Fig. S21** Photocatalytic ammonia production rates over the hybrid Au/HCNS-NV nanostructures prepared by the other methods.



**Fig. S22** N<sub>2</sub> photofixation in different solvents. (a) Ammonia production rates of Au/HCNS-NV in the different solvents under visible light irradiation. (b) Zeta potentials of the aqueous Au/HCNS-NV dispersion solutions at different pH values, which were adjusted by adding aqueous HCl or NaOH solutions. (c) Zeta potentials and ammonia production rates of Au/HCNS-NV as functions of the pH.



Fig. S23 N<sub>2</sub> photofixation reactions performed under AM1.5G light irradiation with methanol as the electron donor. (a) Amounts of ammonia and H<sub>2</sub> formed in a sealed system.
(b) <sup>1</sup>H NMR spectra of the photocatalytic reaction solution in the presence of methanol. (c) Enlarged <sup>1</sup>H NMR spectra in the chemical shift range from 7.6 to 9.8 ppm.



**Fig. S24** Characterization of the stability of the catalysts. (a) FTIR spectra of HCNS-NV and Au/HCNS-NV and those of the samples after the stability test. (b) High-resolution N1s spectra of the fresh and used HCNS-NV sample. (c) High-resolution C1s spectra of the fresh and used HCNS-NV sample.



**Fig. S25** Chemisorption of N<sub>2</sub> molecules on the oxygen vacancies of anatase TiO<sub>2</sub>. (a) Configuration of a N<sub>2</sub> molecule adsorbed at an oxygen vacancy site on the surface of TiO<sub>2</sub>. (b) Corresponding charge density difference of a N<sub>2</sub> molecule adsorbed on the oxygen vacancy. The yellow and light blue isosurfaces represent charge accumulation and depletion in space, respectively. The isovalue is 0.0025 e·Å<sup>-3</sup>.



Fig. S26 Mott-Schottky plots of the samples. (a) HCNS-NV. (b) HCNS.



**Fig. S27** Photoluminescence spectra of the different samples at an excitation wavelength of 380 nm.

HCNS-NV sample	CTAC (mg)	TEOS (mL)	Thickness of the mesostructured silica shell (nm)	Thickness of the mesoporous silica shell (nm)	Thickness of HCNS-NV (nm)
HCNS22-NV	50	0.083	$32.2 \pm 2.6$	$31.8 \pm 2.5$	$21.6 \pm 4.5$
HCNS35-NV	75	0.125	$47.4 \pm 3.6$	39.4 ± 3.7	$34.8 \pm 3.4$
HCNS64-NV	150	0.25	$76.9 \pm 3.4$	$66.6 \pm 3.1$	$64.1 \pm 4.6$
HCNS74-NV	225	0.375	$97.2 \pm 3.4$	89.2 ± 5.8	$73.6 \pm 5.1$
HCNS88-NV	300	0.5	$120.3 \pm 5.2$	$112.5 \pm 3.7$	$88.4 \pm 3.7$

**Table S1**Synthetic variation of the shell thickness of HCNS-NV by changing the amount ofCTAC and TEOS

 Table S2
 Elemental analysis of HCNS-NV calcined in air for different periods of time

Calcination time (h)	0	1	2	4	7	10
N/C ratio	1.383	1.412	1.424	1.439	1.453	1.468

Catalyst	AQY	STA efficiency	Reference
Mo-doped W <sub>18</sub> O <sub>49</sub> nanowires	0.33% at 400 nm	0.028%	S1
$Bi_5O_7Br$ nanotubes with OVs	2.3% at 420 nm		S2
Au/TiO <sub>2</sub> with OVs	0.82% at 550 nm		S3
P-doped g-C <sub>3</sub> N <sub>4</sub> with NVs	1% at 420 nm	0.1%	S4
TiO <sub>2</sub> with OVs	0.7% at $\lambda$ < 350 nm	0.02%	S5
Hybrid CdS:nitrogenase MoFe protein	3.3% at 405 nm		S6
BiOBr with OVs	0.23% at 420 nm		S7
TiO <sub>2</sub> /Au/amorphous TiO <sub>2</sub>	0.005% at 254 nm		S8
Au/(BiO) <sub>2</sub> CO <sub>3</sub>		0.006%	S9
CuCr-LDH nanosheets	0.1% at 500 nm		S10
$Fe^{3+}$ on g-C <sub>3</sub> N <sub>4</sub> nanosheets	0.86% at 420 nm		S11
Amorphous SmOCl nanosheets	0.32% at 420 nm		S12
Au/P25	0.93% at 550 nm		S13
Single-unit-cell Bi <sub>3</sub> O <sub>4</sub> Br nanosheets	1.59% at 400 nm		S14
AuRu core@antenna nanostructures	0.21‰ at 350 nm, 0.17‰ at 550 nm		S15
Cu-doped TiO <sub>2</sub>	0.74% at 380 nm, 0.23% at 420 nm, 0.08% at 600 nm, 0.05% at 700 nm		S16
Au/HCNS-NV	0.64% at 550 nm	0.032%	This work

**Table S3**AQYs and STA efficiencies for  $N_2$  photofixation in recent works

AQY, apparent quantum yield; STA, solar-to-ammonia; OV, oxygen vacancy; LDH, layered-double-hydroxide.

Wavelength	Ammonia generated	Light power density	Light power P	AQY (%)
(nm)	$(\mu mol h^{-1})$	$I (\mathrm{mW} \mathrm{cm}^{-2})$	(mW)	
420	6.86	3.45	132.69	1.23
475	3.21	3.69	141.92	0.48
520	4.14	3.69	141.92	0.56
550	4.96	3.63	139.61	0.64
600	4.52	3.79	145.76	0.52
650	1.77	3.84	147.69	0.18
700	0.14	3.66	140.76	0.014

**Table S4** Calculated AQYs for ammonia generation at different wavelengths

The diameter of the reactor is 7 cm. The irradiation area of the solution is

$$S = \pi \times \left(\frac{d}{2}\right)^2 = 3.14 \times (3.5)^2 = 38.46 \ cm^2 \tag{1}$$

Take the determination of the AQY at 550 nm as an example. The light power is

$$P = I \times S = 3.63 \times 38.46 = 139.61 \, mW \tag{2}$$

The number of the incident photons is

$$N_{incident} = \frac{Pt}{hv} = \frac{Pt\lambda}{hc} = \frac{139.61 \times 10^{-3} \times 3600 \times 550 \times 10^{-9}}{6.63 \times 10^{-34} \times 3 \times 10^8} = 1.39 \times 10^{21}$$
(3)

In the equation above, *P* is the light power, *t* is the irradiation time (1 h = 3600 s), *h* is Planck's constant, *v* is the light frequency, and *c* is the speed of light in free space. The number of reacted electrons is

$$N_{reacted} = 3 \times the number of the generated ammonia molecules$$

$$= 3 \times 4.96 \times 10^{-6} \times 6.02 \times 10^{23} = 8.96 \times 10^{18}$$
(4)

The AQY can be calculated as

$$AQY = \frac{N_{reacted}}{N_{incident}} \times 100\% = \frac{8.96 \times 10^{18}}{1.39 \times 10^{21}} \times 100\% = 0.64\%$$
(5)

For the calculation of the STA efficiency, the diameter of the reactor is 6 cm. The irradiation area is

$$S = \pi \times (\frac{d}{2})^2 = 3.14 \times 3^2 = 28.26 \ cm^2 \tag{6}$$

The total input energy under AM1.5G light irradiation is

$$P = 100 (mW cm^{-2}) \times 28.26 cm^{2} = 2.826 W$$
(7)

The STA efficiency can be calculated as

$$STA \ efficiency = \frac{\left[\Delta G^{\circ} \ for \ NH_{3} \ generation \ (J \ mol^{-1})\right] \times [evolved \ NH_{3} \ (mol)]}{[total \ input \ energy \ (W)] \times [reaction \ time \ (s)]} \times 100_{\%}$$
$$= \frac{339 \times 10^{3} \times 9.51 \times 10^{-6}}{2.826 \times 3600} \times 100\% = 0.032\%$$
(8)

Similarly, the STH efficiency can be calculated as

$$STH \ efficiency = \frac{\left[\Delta G^{\circ} \ for \ H_2 \ generation \ (J \ mol^{-1})\right] \times \left[evolved \ H_2 \ (mol)\right]}{\left[total \ input \ energy \ (W)\right] \times \left[reaction \ time \ (s)\right]} \times 100\%$$
$$= \frac{237 \times 10^3 \times 4.47 \times 10^{-6}}{2.826 \times 3600} \times 100\% = 0.01\%$$
(9)

In the above equations, the  $\Delta G^{\circ}$  values for NH<sub>3</sub> and H<sub>2</sub> generation are 339 and 237 kJ mol<sup>-1</sup>, respectively.

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