Electronic supporting information

Symmetry-Breaking Synthesis of Janus Au/CeO$_2$ Nanostructures for Visible-Light Nitrogen Photofixation

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Supporting Experimental Section

**Chemicals.** Sodium borohydride (NaBH₄, 99%), silver nitrate (AgNO₃, ≥ 99.0%), L-ascorbic acid (AA, ≥ 99%), 4-mercaptophenylacetic acid (4-MPAA, 97%), tetraethyl orthosilicate (TEOS, 98%), cerium (III) acetate hydrate (Ce(AC)₃·xH₂O, 99.9%) were purchased from Sigma-Aldrich. Tetrachloroauric (III) acid tetrahydrate (HAuCl₄·4H₂O), ammonia solution (NH₃·H₂O, ~25.0–28.0 wt%), hydrochloric acid (HCl, ~36.0–38.0 wt%), isopropanol (≥ 99.7%), and sodium hydroxide (NaOH, ≥ 96.0%) were obtained from Sinopharm Chemical Reagent. Hexadecyltrimethylammonium chloride (CTAC, 97%), salicylic acid (C₆H₄(OH)COOH, ≥ 99.0%) and sodium hypochlorite solution (NaClO, available chlorine ≥ 5.0%) were obtained from Aladdin Reagent. Cetyltrimethylammonium bromide (CTAB, > 98%) was purchased from Alfa Aesar. Sodium nitroferricyanide (III) dihydrate (Na₂[Fe(CN)₅NO]·2H₂O) was purchased from Macklin. Poly (acrylic acid) (PAA, MW = 6200, Mₘ/Mₙ = 1.09) was purchased from Polymer Source INC. Dimethyl sulfoxide-d₆ (DMSO-d₆, (D, 99.9%) + 0.03% V/V TMS) was obtained from Cambridge Isotope Laboratories, Inc. Nitrogen (¹⁴N₂, 99.999%), nitrogen (¹⁵N₂, 98 atom% ¹⁵N), and argon (Ar, 99.999%) were use as received. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was used in all experiments.

**Growth of the Au NSs.** The monodisperse Au NSs were prepared using a seeded growth method as described in previous work.¹ The whole process can be divided into three steps: (1) growth of the small Au NSs; (2) growth of the large Au nanopolyhedrons; and (3) growth of the large Au NSs.

- **Growth of the small Au NSs:** The small Au NSs were prepared using a seeded growth method. Specifically, the seed solution was made by injecting a freshly prepared, ice-cold NaBH₄ solution (10 mM, 600 μL) into an mixture solution composed of CTAB (0.1 M, 9.75 mL) and HAuCl₄ (10 mM, 250 μL) under vigorous stirring. The resultant seed solution was kept under gentle stirring for 3 h before use. The growth solution was made by the sequential addition of CTAB (0.1 M, 9.75 mL), HAuCl₄ (10 mM, 4 mL), and AA (0.1 M, 15 mL) into DI water (190 mL), followed by the injection of the as-prepared seed solution (0.12 mL). The resultant solution was mixed by gently inversion and kept undisturbed overnight at room temperature. The obtained small Au NSs were concentrated by centrifugation and redispersion into DI water (55 mL) for further use.
Growth of the large Au nanopolyhedrons: The small Au NSs were employed as seeds for the growth of the large Au nanopolyhedrons. Typically, the small Au NSs (4 mL) was first added into a CTAC solution (25 mM, 30 mL), followed by the sequential addition of AA (0.1 M, 0.75 mL) and HAuCl₄ (10 mM, 1.5 mL). The resultant solution was placed in an air-bath shaken (45 °C, 160 rpm/min) for 3 h. The as-prepared large Au nanopolyhedron sample was centrifuged and redispersed into CTAB (20 mM, 30 mL) for further use.

Growth of the large Au NSs: The large Au NS sample was obtained by etching the large Au nanopolyhedron sample with HAuCl₄. Typically, HAuCl₄ solution (10 mM, 0.2 mL) was added into the large Au nanopolyhedron sample (30 mL) and the mixture solution was placed in an air-bath shaker (45 °C, 160 rpm/min) for 2 h. Large Au NSs were obtained through the mild oxidation of the large Au nanopolyhedrons.

Growth of the Janus Au NS/SiO₂ Nanostructures. The Janus Au NS/SiO₂ nanostructures were prepared through competitive ligand coordination as described in previous work.² Typically, 4-MPAA (5 mM in C₂H₅OH, 400 μL) and PPA (0.645 mM in DI water, 400 μL) were added in 2-propanol (50 mL) under vigorous stirring. Then the large Au NS solution with optical density (OD) at the plasmon peak pre-adjusted to 2.0 was added dropwise to the mixture solution. After stirring for 30 min, concentrated ammonia solution (30 wt%, 12 mL) was added, followed by the added dropwise of TEOS solution (8.9 mM in DI water, 1.8 mL). The resultant solution was kept stirring for 12 h to obtain the Janus Au NS/SiO₂ nanostructures.

Growth of the Janus Au NS/CeO₂ Nanostructures. The as-prepared Janus Au NS/SiO₂ sample (10 mL) was centrifuged once and redispersed into DI water (1.8 mL). To trigger the autoredox reaction, AgNO₃ (0.1 mM, 100 μL) was added and the resultant solution was kept at room temperature for 1 min to allow for the adsorption of Ag⁺ on the Au NSs. Then Ce(AC)₃ solution (1 mM, 100 μL) was added. The resultant solution was placed in an oven set at 90 °C for 1 h to produce the Janus Au NS/CeO₂ nanostructures.

Growth of the ternary Janus Ag/Au NS/CeO₂ Nanostructures. The as-prepared Janus Au NS/CeO₂ sample was centrifuged once and redispersed in PVP solution (0.1 M in repeating unit, MW = 40000). Then AA (0.1
M, 20 μL) and AgNO₃ (10 mM, 20 μL) were added under vigorous stirring. The ternary Janus Ag/Au NS/CeO₂ nanostructures were obtained after 5 min reaction.

**Growth of the ternary Janus Pd/Au NS/CeO₂ Nanostructures.** The as-prepared Janus Au NS/CeO₂ sample was centrifuged once and redispersed in CTAC solution containing CTAC (150 μL, 25 wt%) and DI water (10 mL). The mixture solution was stirred for 1 min, followed by the addition of H₂PdCl₄ (30 μL, 0.01 M) and AA (15 μL, 0.1 M) solution. The resultant solution was stirred for 1 min, followed by placing in an oven (30 °C) overnight to obtain the ternary Janus Pd/Au NS/CeO₂ nanostructures.

**Growth of the Au NS@CeO₂ core@shell nanostructures.** Typically, the large Au NSs (OD = 2.0, 5 mL) was centrifuged at 5500 rpm for 10 min and redispersed in DI water (8.95 mL). CTAB (1 mM, 50 μL), AgNO₃ (0.1 mM, 0.5 mL), and Ce(AC)₃ (10 mM, 0.5 mL) were subsequently added the Au NS solution under gentle shaking. The overall volume was 10 mL with a final CTAB concentration of 5 μM. The resultant solution was placed in an oven set at 90 °C for 1 h to produce the core@shell nanostructures.

**Growth of the CeO₂ nanocrystals.** The preparation of CeO₂ nanocrystals was similar to that of the core@shell nanostructures except that the Au NS solution was replaced by DI water and the volumes of DI water (9.55 mL), AgNO₃ (0.2 mL) and Ce(AC)₃ (0.2 mL) were changed to keep the overall volume to 10 mL.

**Photocatalytic N₂ fixation under the visible-light irradiation.** The photocatalytic N₂ fixation reaction was carried out in a customized reactor (diameter = 3 cm) with three ends. Two side ends were used as inlet and outlet for gas flow, while the middle end was equipped with a quartz window on the top for light illumination. Typically, the photocatalyst (0.7 mg) was dispersed into DI water (8 mL). CH₃OH (2 mL) was added as the hole scavenger. High-purity N₂ was bubbled in the mixture solution at a speed of 20 mL·min⁻¹ for 10 min before each photocatalytic reaction. A continuous Xe lamp (CEL-HXF 300 W) equipped with an AM 1.5 G and a 420–780 nm filters was employed as the visible light source. The optical power density was 300
mW-cm⁻². A circulation cooling system was used to keep the reaction solution temperature at 25 °C. The N₂ photofixation reaction was performed under visible-light illumination for 2 h. N₂ was bubbled in the reaction solution at a speed of 20 mL·min⁻¹ for the entire photocatalytic process. The produced NH₃ in the supernatant was determined using indophenol-blue method.³,⁴ Each photocatalytic experiment was repeated three times.

The ¹⁵N₂ isotope labelling experiments were conducted in a customized gastight reactor (diameter = 3 cm) with three ends. Two side ends were used as inlet and outlet for gas flow, while the middle end was equipped with a quartz window on the top for light illumination. The two side ends were closed with glass stopcocks during photocatalytic reaction. Before the light illumination, high-purity Ar was firstly bubbled in the reaction solution at a speed of 100 mL·min⁻¹ for 30 min, followed by the ¹⁵N₂ at a speed of 20 mL·min⁻¹ for 15 min. After 2-h illumination, the reaction solution was centrifuged to remove the catalyst. The supernatant (500 µL) was acidified with HCl (1M, 200 µL), followed by the addition of DMSO-d₆ (300 µL) for ¹H NMR measurements.

Characterization. TEM imaging was conducted on an HT7700 electron microscope operated at 100 kV. The sizes and thicknesses were measured from the TEM images, with more than 300 particles being counted. HRTEM, HAADF-STEM imaging and EDX elemental mapping were performed on an FEI Talos F200S microscopy. The extinction spectra were measured with a Hitachi U-3900 ultraviolet/visible/NIR spectrophotometer. XPS spectra were obtained on a Thermo Scientific ESCALAB 250Xi spectrometer. XRD patterns were performed on a Smart Lab Se diffractometer equipped with Cu Kα radiation. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carrier out on a PerkinElmer Optima 7300 DV system. ¹H NMR spectra were measured on a Bruker Avance II 400 NMR spectrometer.
Supplementary Figures

**Fig. S1** HRTEM images of a single ternary Janus Au NS/SiO$_2$/CeO$_2$ nanostructure and three selected areas.

**Fig. S2** HAADF-STEM image (a) and corresponding elemental maps (b–g) of a representative ternary Janus Au NS/SiO$_2$/CeO$_2$ nanostructure.
Fig. S3 Representative product TEM images of the Janus Au NS/SiO$_2$/CeO$_2$ nanostructures obtained at 10 min (a), 20 min (b), and 40 min (c) of the etching, respectively. The positions marked by white arrows in (b) indicate that the SiO$_2$ semi-shells are separating from the ternary Janus Au NS/SiO$_2$/CeO$_2$ nanostructures.

Fig. S4 Effect of the precursor amount upon the CeO$_2$ semi-shell thickness. TEM images of the Janus Au NS/CeO$_2$ nanostructures prepared with 50 μL (a), 80 μL (b), and 200 μL (c) Ce(AC)$_3$ solutions, respectively. The thicknesses of the CeO$_2$ semi-shell are 6.9 ± 1.2 nm (a), 7.4 ± 1.0 nm, and 21.8 ± 2.0 nm (c), respectively.
Fig. S5 Extinction spectra of the Au NSs (blue), Janus Au NS/SiO$_2$ nanostructures (green), and Janus Au NS/CeO$_2$ nanostructures (red), respectively.

Fig. S6 Elemental profiles of a single Janus Au NS/CeO$_2$ nanostructure. (a) HAADF-STEM image. (b) Elemental profiles of Au (blue) and Ce (red) acquired along the green line indicated in (a).
**Fig. S7** XRD patterns of the Janus Au NS/CeO$_2$ nanostructures (red). The blue and green curves are the standard powder diffraction patterns of the face-centered-cubic structure of Au (space group, Fm-3m; lattice constant, 0.40796 nm) and the face-centered-cubic structure of CeO$_2$ (space group, Fm-3m; lattice constant, 0.541134 nm).

**Fig. S8** XPS spectra of the Janus Au NS/CeO$_2$ nanostructures. (a) Survey spectrum. (b, c) High-resolution Au 4f (b) and Ag 3d (c) XPS spectra.
**Fig. S9** Extinction spectra of the Janus Au NS/CeO$_2$ nanostructures before (green) and after (red) the overgrowth of Ag nanocrystals.

**Fig. S10** (a) HAADF-STEM image and (b) corresponding elemental profiles of Au, Ag, O, and Ce acquired along the green line in (a) of a ternary Janus Ag/Au NS/CeO$_2$ nanostructure.
Fig. S11 XPS spectra of the ternary Janus Ag/Au NS/CeO$_2$ nanostructures. (a) XPS survey spectrum. (b–e) High resolution Au 4f (b), Ag 3d (c), Ce 3d (d), and O 1s (e) XPS spectra, respectively.

Fig. S12 Ternary Janus Pd/Au NS/CeO$_2$ nanostructures. (a) TEM image. (b) HAADF-STEM image and the corresponding elemental maps.
**Fig. S13** TEM images of the CeO$_2$ nanocrystals (a) and the Au NS@CeO$_2$ core@shell nanostructures (b) used for the N$_2$ photofixation.

**Fig. S14** (a) Absorption spectra of the NH$_4$Cl solutions with different concentrations. (b) Linear relationship between the absorbance values and the NH$_4$Cl solution concentrations. The coefficient of determination for the linear fitting is $R^2 = 0.99985$. 
**Fig. S15** Comparison of the N$_2$ photofixation activity of the binary (Janus Au NS/CeO$_2$) with that of the ternary (Janus Ag/Au NS/CeO$_2$) Janus nanostructures.

**Fig. S16** Extinction (red, left axis) and AQE action (purple, right axis) spectra of the Janus Au NS/CeO$_2$ nanostructures.
Fig. S17 Control experiments of the N\textsubscript{2} photofixation under different conditions.

Fig. S18 TEM image of the Janus Au NS/CeO\textsubscript{2} nanostructures after the photocatalytic N\textsubscript{2} fixation.
**Fig. S19** XPS spectra of the Janus Au NS/CeO$_2$ nanostructures after the photocatalytic N$_2$ fixation. (a) XPS survey spectrum. (b–e) High-resolution Au 4f (b), Ag 3d (c), Ce 3d (d), and O 1s (e) XPS spectra.

**Fig. S20** NH$_3$ generation rates during three successive cycles with the Janus Au NS/CeO$_2$ nanostructures as the catalyst.
**Fig. S21** \( N_2 \) TPD profile of the Janus Au NS/CeO\(_2\) nanostructures.

**References**

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