Supporting Information

A Ball-in-Ball g-C₃N₄@SiO₂ Nano-photoreactor for Highly Efficient

H₂ Generation and NO Removal

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Supporting Information

Experimental Section

1. Material synthesis

All reagents for synthesis and analysis were commercially available and used without further treatment.

The mesoporous SiO₂ hollow spheres (MSHS) with an average diameter of around 730 nm (a mesoporous shell of about 105 nm) were prepared by calcining the polystyrene@SiO₂ coreshell composite spheres, where CTAB was used as the porogen agent to generate a mesopores SiO₂ shell.^[1] The g-C₃N₄ microspheres were grown inside the above MSHS to prepare g-C₃N₄@SiO₂ core-shell microspheres. Partially etching technology was used to create the void between the g-C₃N₄ core and MSHS and obtain the ball-in-ball structured g-C₃N₄@SiO₂ composite nano-photoreactor (BSGSCN). Typically, owing to the large volum of 0.1 g of MSHS, 0.1 g of MSHS was immersed in the slightly excess HCl solution (1 M, 10 mL) for 2 h to insure the complete immersion of SiO₂, and then dried in a drying oven at 80 °C. 0.4 g of cyanamide was added into the treated MSHS and heated at 60 °C in a vacuum drying oven for 12 h. 1 mL of deionized water was added the mixture and vigorous stirred at 60 °C for 6 h, and then dried in water bath at 80 °C to obtain white solid. The white solid was annealed at 550 °C for 4 h in a tube furnace with a heating ramp of 2.3 °C min⁻¹ in nitrogen atmosphere. Finally, the BSGSCN with a mesoporous shell of about 35 nm were obtained by using 6 mL of hydrofluoric acid solution (10 wt%, standing for 2 h, 40 °C) to manipulate the thickness of mesoporous SiO₂ shell.

For comparison, the g-C₃N₄ microspheres (CNMs) with an average diameter of about 500 nm were obtained by thoroughly removing mesoporous SiO₂ shell. More specifically, the above g-C₃N₄/SiO₂ core-shell microspheres was vigorous stirred at 40 °C for 12 h in the

solution of hydrofluoric acid (20 wt%, 6 mL) to erode the silica and obtain the $g-C_3N_4$ microspheres.

The pristine g-C₃N₄ (PCN) with the sheet-like structure was prepared as follows: 1 g of cyanamide was directly annealed at 550 °C for 4 h in a tube furnace with a heating ramp of 2.3 °C ·min⁻¹ in nitrogen atmosphere, the resultant canary yellow powder was collected for the further use.

The mixed composite of g-C₃N₄ sheet and mesoporous SiO₂ hollow sphere (MCGS) was prepared as follows: 0.1 g of MSHS was treated with 10 mL of 1 M HCl solution for 2 h and then dried in a drying oven at 80 °C. 0.4 g of cyanamide and 1 mL of deionized water were added into the treated MSHS and stirred at 60 °C for 0.5 h and dried in water bath at 80 °C to obtain white solid. The white solid was annealed at 550 °C for 4 h in a tube furnace with a heating ramp of 2.3 °C·min⁻¹ in nitrogen atmosphere. The final sample was collected for the further use.

2. Characterization

The crystalline structure and phase component of the samples were measured with a powder X-ray diffraction (XRD; SHIMADZU, Lab X XRD-6000). The morphology and microstructures of the samples were obtained by the observation of field-emission scanning electron microscope (JEOL, JSM-6700F), and the energy dispersive X-ray spectroscopy (EDX) was used for elemental analysis. The geometry and surface states of the as-prepared photocatalysts were examined by a transmission electron microscopy (JEOL, JEM-2100). UV-vis diffuse reflectance spectra (DRS) were conducted on a Hitachi U-4100 UV-vis spectrometer. Fourier transform infrared (FT-IR) spectra were conducted on a Nicolet Avatar 360 instrument. Thermogravimetric analysis (TGA) was measured using a Hengjiu HCT-3 type Thermogravimetric Analyzer in N₂ with a ramp rate of 10 °C min⁻¹. The nitrogen adsorption-desorption isotherm curves of samples were collected on a BET analyzer (ASAP 3000), and the samples were degassed at 160 °C for 10 h before the actual measurement. Pore

size distribution and specific surface area of the samples were determined on the basis of Barrett-Joyner-Halenda (BJH) method and Brunauer-Emmett-Teller (BET) equation, respectively. The photoluminescence (PL) emission spectra were obtained on a HORIBA JY Fluorolog-3 type fluorescence spectrophotometer with 340 nm excitation wavelength.

3. Photodegradation test

The photodegradation tests over RhB dye under visible-light illumination ($\lambda \ge 420$ nm) were performed using a 300 W Xenon lamp (HSX-F300, Beijing NBeT) equipped with 420 nm UV filter (HSX-UV300) to assess the ability of contaminated water treatment. Prior to the illumination, 50 mL of RhB aqueous solution (10 mg L⁻¹) containing 0.05 g of the sample were stirred in the dark for 30 min to reach adsorption/desorption equilibrium. During illumination, 3 mL of the solution was withdrawn from the reactor every 30 min to isolate the photocatalysts by centrifugation. Then the concentration of the residual RhB solution was measured by UV-vis spectrophotometer (UV-1900PPC, Shanghai, China).

The repeated experiments were conducted to further study the repeatability and reproducibility of BSGSCN. Specifically, three independent experiments of photodegradation RhB (50 mL, 10 mg L⁻¹) were carried out in the presence of BSGSCN (0.05 g) for 120 min under the same reaction conditions, respectively. As above mentioned, the residual RhB solution was withdrawn and separated every 30 min, then analyzed by the UV-vis spectrophotometer. The mean and standard deviation of the degradation rate at the different irradiation times over BSGSCN in the three independent photodegradation experiments were calculated, respectively.

4. Photocatalytic oxidation test

The photocatalytic oxidation tests over NO (initial concentration of 600 ppb) under visiblelight illumination ($\lambda \ge 420$ nm) were carried out at ppb level in a continuous flow reactor at room temperature. And the flow rates of the air stream and NO were 2.4 L/min and 15 mL/min, respectively. A 150 W tungsten halogen lamp with a 420 nm UV filter (HSX- UV300) was used as the visible light source. The concentration of NO was detected by a NOx analyzer (Thermo Scientific, 42i-TL).

5. Photocatalytic H₂ evolution

Photocatalytic H₂ evolution was performed in a Pyrex reactor (100 mL) under visible light illumination ($\lambda \ge 420$ nm). 0.05 g of the photocatalysts were added to 50 mL of aqueous solution containing 0.25 M of Na₂S and 0.35 M of Na₂SO₃, here the latter two play the role of sacrificial electron donor. Besides, 3 wt% of Pt photodeposits onto the catalysts using H₂PtCl₆ as the Pt-cocatalyst precursor that dissolved in the reactant solution. Prior to irradiation, the reaction system was bubbled with high purity nitrogen for 0.5 h to remove air completely. Then the reactor was exposed to a 300 W Xenon lamp (HSX-F300, Beijing NBeT) equipped with 420 nm UV filter (HSX-UV300). The generated H₂ was determined by a gas chromatograph (Beifen-Ruili, SP-2100A) equipped with 5 **Error!** molecular sieve and a thermal conductivity detector (TCD).

The recycled experiments were performed under the same reaction conditions to further study the stability and durability of the BSGSCN sample. After every 4 h photoreaction, the photocatalyst particles were separated from the reaction system by centrifugation, and rinsed three times with deionized water and ethanol, respectively, then dried in a vacuum drying oven for 6 h at 80 °C. Next, the same volume of aqueous solution (50 mL) and same amount of sacrificial electron donor (0.25 M of Na₂S and 0.35 M of Na₂SO₃) were put into the recovered photocatalyst. Finally, the air in the renewed reaction system was removed by the above bubbling method to perform the next cyclic experiment.

6. Photoelectrochemical measurement

The photocurrent response of all samples was evaluated using an electrochemical station (CHI 660D, Chenhua, Shanghai, China) in a typical three-electrode system, and Na₂SO₄ aqueous solution (1 M) acts as the electrolyte. A platinum wire was selected as the counter electrode, and Ag/AgCl (preserved in 3 M KCl) were used as the reference electrode. The

glassy carbon electrodes (GCE, 0.07065 cm²) containing sample were served as the working electrodes.

7. In situ DRIFTS measurement

The in situ DRIFTS measurements were determined using a FTIR spectrometer (VERTEX 70, Bruker) equipped with an in situ diffuse reflectance cell (Harrick). The DRIFTS spectra were recorded with a scanning range of 4000–600 cm⁻¹ using an average of 100 scans. Prior to each test, the sample was vacuum annealed at 250 °C in He to remove the residual hydrocarbons, CO₂ and H₂O. When the sample was cooled to room temperature, the reactant gas mixture (60 ppm NO and 10% O₂ in He, 25 mL/min) was introduced into the reaction system. All adsorption and photocatalytic reaction spectra of NO were recorded under the same flow (60 ppm NO and 10% O₂ in He, 25 mL/min).



Figure S1. a) SEM image and b) TEM image of MSHS. TEM images of c) $g-C_3N_4@SiO_2$ core-shell microspheres and d) mesoporous silica shell in $g-C_3N_4@SiO_2$ core-shell microspheres. SAED images of (the inset of c) $g-C_3N_4@SiO_2$ core-shell microspheres and (the inset of d) mesoporous silica shell in $g-C_3N_4@SiO_2$ core-shell microspheres.



Figure S2. a) SEM image and b) TEM image of PCN. Inset in (b): SAED image of PCN.



Figure S3. a,b) EDX images of BSGSCN. c,d) EDX images of CNMs. The strong signal peak for Si is due to the uniform dispersion of samples on the silicon substrate in the SEM test.



Figure S4. FT-IR spectra of PCN, CNMs, BSGSCN and MSHS.

In the FT-IR spectra of PCN, CNMs and BSGSCN (Figure S4), the bands at 789 cm⁻¹, 1200-1700 cm⁻¹ and 3100-3700 cm⁻¹ correspond to s-triazine ring, CN heterocycles, the coeffect of N-H components and the absorbed H₂O molecules, respectively.^[2] In the case of MSHS, the bands at 498 cm⁻¹, 789 cm⁻¹, 1100 cm⁻¹ and 1590 cm⁻¹ coincide with the bending of Si-O bond, the bending of Si-OH bond, the stretching of Si-O bond and the hydroxyl groups, respectively.^[3] However, the bands of SiO₂ could not found in BSGSCN due to the cover up of g-C₃N₄ peaks.



Figure S5. Thermogravimetric analysis (TGA) of BSGSCN, CNMs and PCN.



Figure S6. Values of RhB (10 mg L⁻¹) degradation rate over different irradiation time in the presence of BSGSCN under visible light irradiation ($\lambda \ge 420$ nm). Each point was the average of three independent experiments. Error bars show standard deviations.

Irradiation time (min)	Mean (%)	Standard deviation (%)
30	51.67	2.81
60	77.65	3.88
90	93.52	1.63
120	100	0

Table S1 The mean and standard deviation of the degradation rate at the different irradiation times over

 BSGSCN in the three independent photodegradation experiments.



Figure S7. Schematic illustration of photocatalytic mechanism of RhB degradation (10 mg L⁻¹) in the presence of BSGSCN under visible light irradiation ($\lambda \ge 420$ nm).

To make clear the effects of structural advantages of the ball-in-ball nano-photoreactor on RhB photodegradation, a possible visible-light-driven photodegradation RhB mechanism of BSGSCN was proposed ($\lambda \ge 420$ nm). As shown in in Figure S7, the RhB molecules can reach the inside space of BSGSCN due to the presence of numerous pore channels on the MSHS. Owing to the presence of multiple scattering and reflecting effects in the nanophotoreactor, massive photogenerated electron-hole pairs were generated under the visiblelight illumination ($\lambda \ge 420$ nm). The photogenerated electrons rapidly leaped to the conduction band (CB) of g-C₃N₄ core, and then interacted with O₂ molecules dissolved in aqueous solution to create the superoxide radical (\cdot O₂⁻) and the hydrogen peroxide (H₂O₂), the two active species could further react and generate the hydroxyl radical (\cdot OH). The active species of \cdot O₂⁻ and \cdot OH could fully contact with RhB molecules in the homogeneous confined environment of nano-photoreactor, thus effectively mineralized RhB into CO₂ and H₂O. Furthermore, the photoexcited holes remained on the valence band (VB) of g-C₃N₄ core also could directly oxidize RhB molecules into CO₂ and H₂O.



Figure S8. a) SEM image and b) TEM image of the mixed composite of g-C₃N₄ sheet and MSHS (MCGS).



Figure S9. a,b) TEM images of BSGSCN after four photoreactions. c,d) TEM images of CNMs after similar treatment.



Figure S10. X-ray diffraction patterns of BSGSCN before and after four photoreactions.



Figure S11. In situ IR spectra of NO adsorbed on a) CNMs and b) BSGSCN in a flow of 60 ppm NO + $10\% O_2$ in He at room temperature.

Wavenumbers (cm ⁻¹)	Assignment	References
1060-1010	NO_3^- (bidentate)	[4]
1285-1085	NO^{-}, NO_{2}^{-} (bidentate),	[4-6]
	NO ₃ ⁻ (bidentate)	
1128	NO ⁻	[7]
1307	Nitro species	[5, 6]
1470-1410	Nitro species	[5, 7]
1533	NO ₃ ⁻ (monodentate)	[4, 8]
1611	NO_3^- (bridged)	[6, 7]
1789	N_2O_4	[5]

Table S2 Assignments of the IR bands observed upon NO adsorption and removal over CNMs andBSGSCN.



Figure S12. Nitrogen adsorption/desorption isotherms of BSGSCN, CNMs and PCN. The table of textural properties of the corresponding samples are embedded in the figure.

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