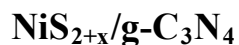


Electronic Supplementary Information

Bioinspired Noble-Metal-Free Reduction of Nitroarenes over



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Chemicals: Cyanamide (Aldrich, 50 wt% in H₂O, contains 0.1 % formic acid as stabilizer), Ludox HS40 solution (Alfa Aesar, Silicon(IV) oxide, 40 % in H₂O, colloidal dispersion), Hydrofluoric acid (HF, Sinopharm Chemical Reagent Co., Ltd., ≥40.0%), Ethanol (CH₃CH₂OH, Sinopharm Chemical Reagent Co., Ltd., ≥99.7%) Dicyandiamide (DCDA, Acros Organics, 99.5%), Monohydrate glucose (AppliChem, pure Ph. Eur.). Acetylene black (C, carbon black, commercially available), Nickel nitrate hexahydrate (Ni(NO₃)₂•6H₂O Sinopharm Chemical Reagent Co., Ltd., ≥98.0%), Thioacetamide (TAA, Sinopharm Chemical Reagent Co., Ltd., ≥99.0%), Dichloromethane (CH₂Cl₂, Sinopharm Chemical Reagent Co., Ltd., ≥99.5%).

1. Procedure for catalyst preparation

1.1. Synthesis of 9 wt. % NiS_{2+x}/CN

Mesoporous carbon nitride was obtained according to Ref. 18. Briefly, 5 g of cyanamide was dissolved in 7.5 g of Ludox HS40 solution (dispersion of 12-nm SiO₂ particles with 40 wt% in water) and heated at 65 °C overnight to remove water. The as-formed white powder was heated at a temperature of 600 °C for 4 h (ramp: 2.3 °C min⁻¹) under the protection of N₂. The resulting brown-yellow powder was treated with a 4 M HF solution for 24 h to remove the silica template.

The powders were then centrifuged and washed three times with distilled water and twice with ethanol. Finally the powders were dried at 60 °C in vacuum overnight.

200 mg of the as-prepared mpg-CN was dispersed into 20 mL of distilled water with 0.2 mmol Ni(NO₃)₂ via sonication and vigorous stir for about two days. Then 0.153 g of TAA was added while stirring at room temperature for about two hours. And then the mixture were treated at 80 °C stirring for three days. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

1.2. Synthesis of 9 wt. % NiS_{2+x}/C

200 mg of carbon black was dispersed into 20 mL of distilled water with 0.2 mmol Ni(NO₃)₂ via sonication and vigorous stir for about two days. Then 0.153 g of TAA was added while stirring at room temperature for about two hours. And then the mixture were treated at 80 °C stirring for three days. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

1.3. Synthesis of 9 wt. % NiS_{2+x}/N-LC

Nitrogen-doped layered carbon was obtained according to Ref. 39 In summary, a mixture of dicyandiamide (5 g) and glucose (1 g) was heated at a temperature of 900 °C for 1 hour (ramp: 2.3 °C min⁻¹ under protecting N₂ flow. 200 mg of the as-formed N-LC was dispersed into 20 mL of distilled water with 0.2 mmol Ni(NO₃)₂ via sonication and vigorous stir for about two days. Then 0.153 g of TAA was added while stirring at room temperature for about two hours. And then the mixture were treated at 80 °C stirring for three days. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

1.4. Activation of the used catalyst

200 mg of the used catalyst was dispersed into 20 mL of distilled water with 0.2 mmol $\text{Ni}(\text{NO}_3)_2$ via sonication and vigorous stir for about two days. Then 0.153 g of TAA was added while stirring at room temperature for about two hours. And then the mixture were treated at 80 °C stirring for three days. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and ethanol and finally dried in vacuum at 60 °C overnight.

2. Catalytic reduction of aromatic nitro compounds

2.1. Testing of NiS_2 loaded g-CN catalyst

0.5 mmol substrate and 10 mg of catalyst was dispersed into 2 mL distilled water via sonication and vigorous stir for about 3 minutes. Then 50 mL of fresh NaBH_4 (0.5 mmol) aqueous solution was added into the mixture while stirring at room temperature for 1 hour. Afterwards, the catalyst was separated via filter. The sample obtained by extraction in CH_2Cl_2 was used for GC analysis. Conversions and selectivity were determined by GC-FID (HP6890 with FID detector, column HP530 m x 250 mm x 0.25 μm).

2.2 Recycle test of the reduction of 4-nitrophenol with 9 wt. % $\text{NiS}_{2+x}/\text{CN}$

1 mmol 4-nitrophenol and 20 mg catalyst was dispersed into 4 mL distilled water via sonication and vigorous stir for about 3 minutes. Then 100 mL fresh NaBH_4 (1 mmol) aqueous solution was added into the mixture while stirring at room temperature for 1 hour. The product was extracted by CH_2Cl_2 every one hour. And the catalyst was separated via filter for recycling. Then the catalyst was reused again in the same condition.

3. Catalyst characterization

The **TEM** and **HRTEM** measurements were taken with a JEM-2100F microscope operated at an acceleration voltage of 200 kV measurements. **Nitrogen sorption** experiments were performed

with a Quadrasorb at 77 K, and data analysis was performed with Quantachrome software. Samples were degassed at 150 °C for 20 h before measurements. The **PXRD** measurements were performed on a Rigaku D/Max 2550 X-ray diffractometer operating at the Cu K α 1 radiation. The **XPS** measurements were performed on a Kratos AXIS ULTRA DLD X-ray photoelectron spectrometer with a monochromatized X-ray source (Al KR $h\nu = 1486.6$ eV). The photoluminescent (**PL**) emission spectra were recorded on a QM-4-CW (Photo technology international, Int.USA/CAN). The **FTIR** spectra were recorded using a Bruker IFS 66v/S FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The **UV-vis** spectrophotometer (UV-3600) was employed to obtain the diffuse reflectance spectra of the samples. The **GC** analysis was performed on Shimadzu GC-2014 gas chromatograph.

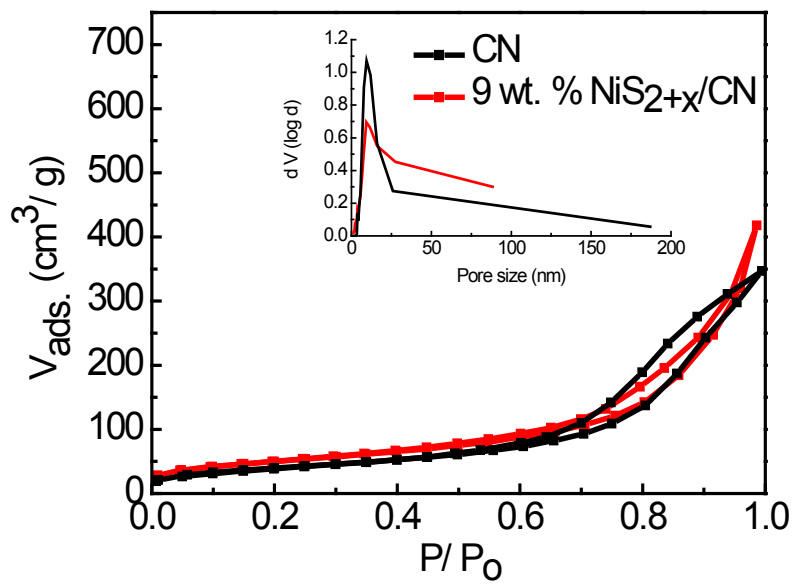


Figure S1. Nitrogen sorption of pure CN and 9 wt. % NiS_{2+x}/CN catalyst. Inset: pore-size distributions.

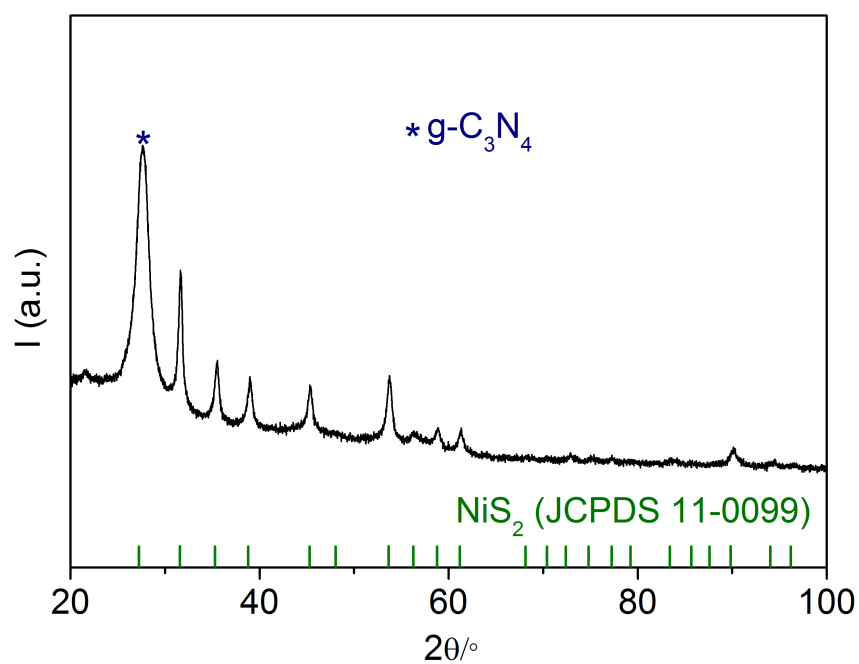


Figure S2. XRD profile for 9 wt. % NiS_{2+x}/CN catalyst.

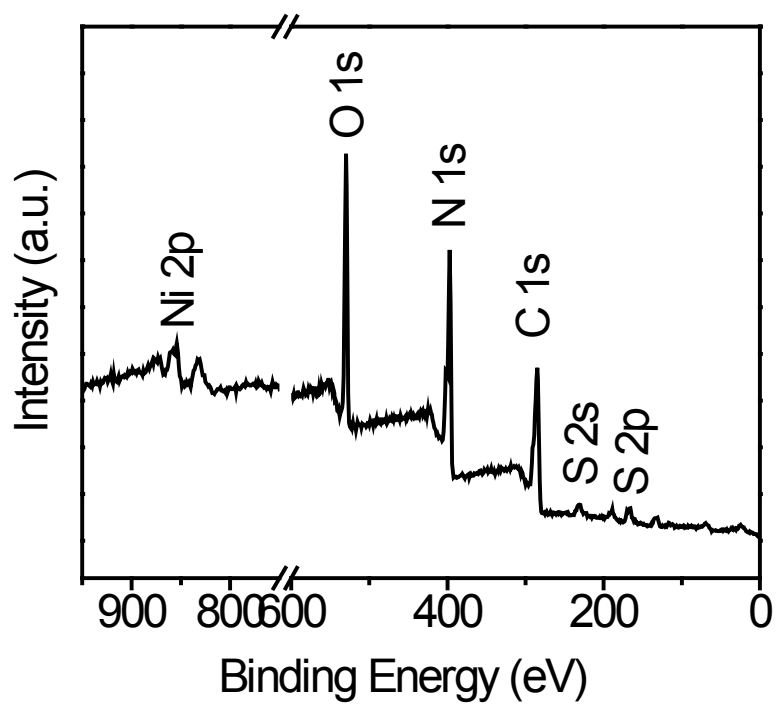


Figure S3. XPS spectra of 9 wt. % NiS_{2+x}/CN catalyst.

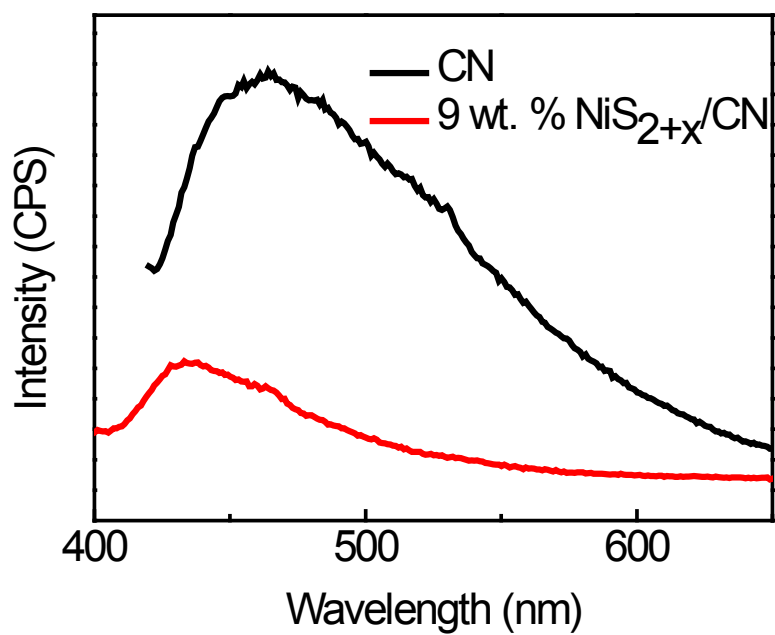


Figure S4. Photoluminescence (PL) spectra of bare mesoporous carbon nitride (CN) and 9 wt. % NiS_{2+x}/CN catalyst. The decreased photoluminescence intensity (red line) of carbon nitride after the introduction of NiS_{2+x} NPs rather speaks for an electron transfer from carbon nitride to NiS_{2+x} NPs.

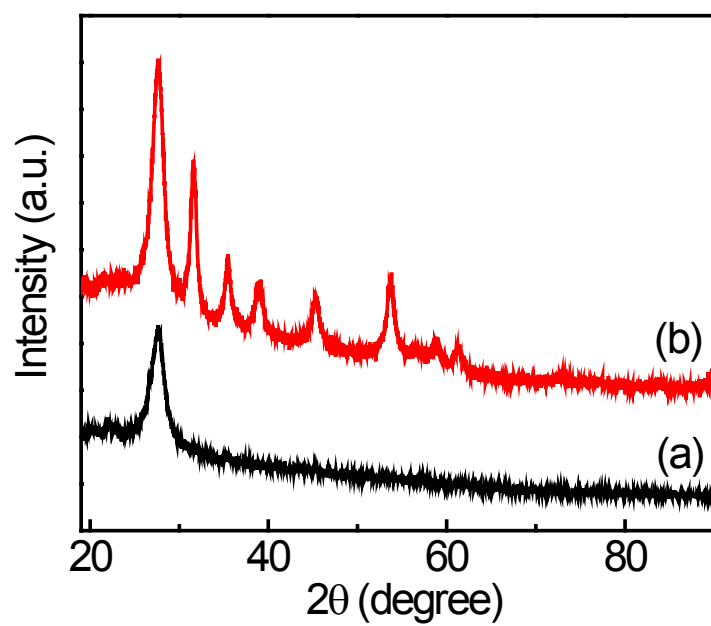


Figure S5. XRD profiles for (a) used 9 wt. % $\text{NiS}_{2+x}/\text{CN}$ and (b) the regenerated 9 wt. % $\text{NiS}_{2+x}/\text{CN}$ catalyst.

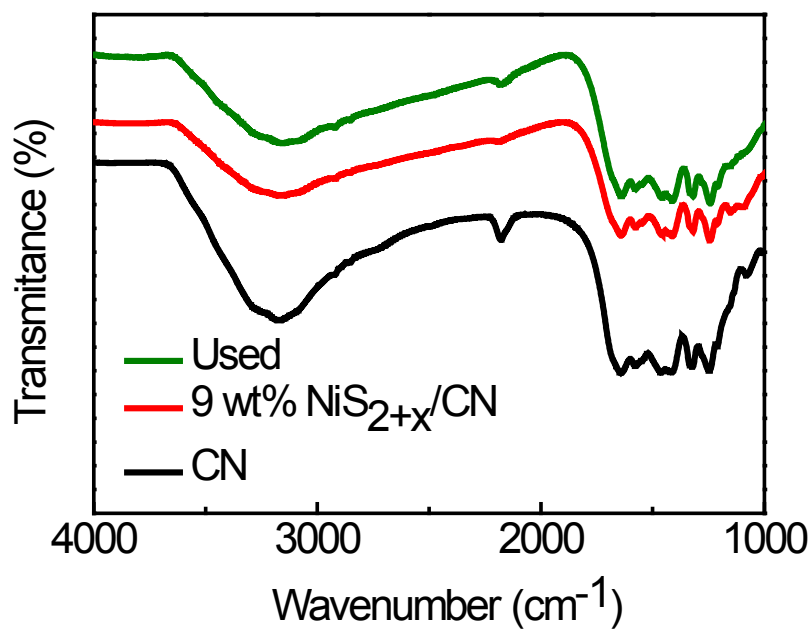


Figure S6. FTIR profiles for bare mesoporous carbon nitride (CN), 9 wt. % NiS_{2+x}/CN catalyst and the used 9 wt. % NiS_{2+x}/CN catalyst. The infrared absorption around 3200 cm⁻¹ is indicative of secondary and primary amines. The peaks of C–N heterocycle stretches of the extended network connection in the 1100–1600 cm⁻¹ region are also very strong and sharp, again speaking for the well development of polymeric melon network in g-C₃N₄.

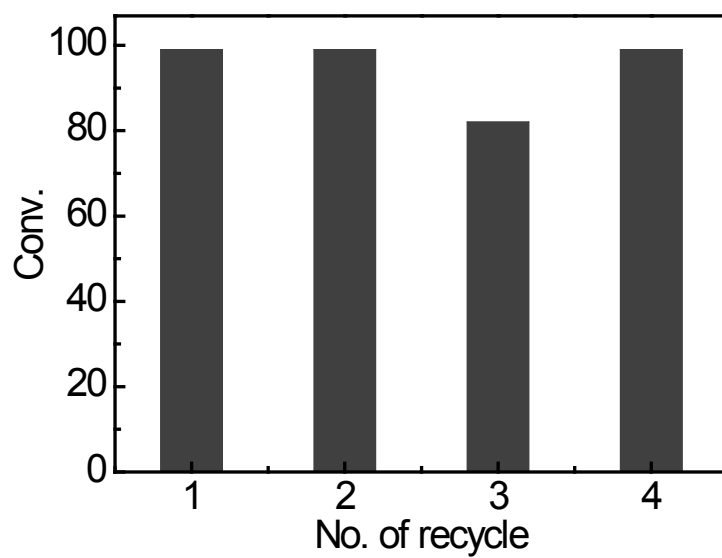


Figure S7. Conversion of 4-nitrophenol over used 9 wt. % NiS_{2+x}/CN (No. 1-3) and the regenerated 9 wt. % NiS_{2+x}/CN catalyst in the presence of NaBH₄ (No. 4)

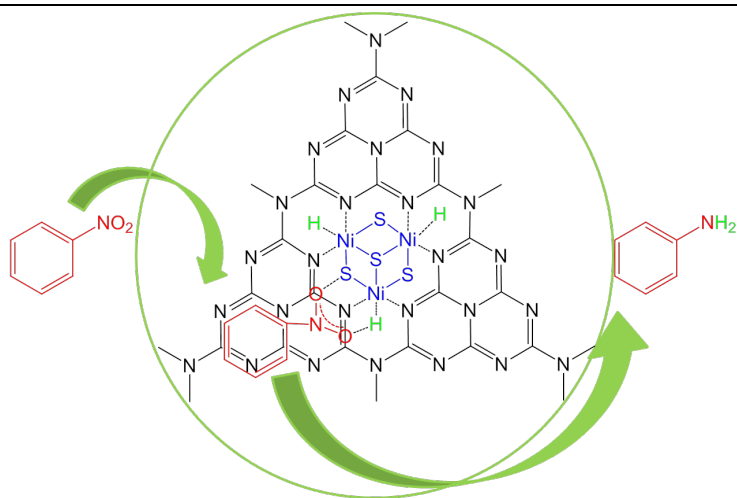
Table S1. Testing of different amount of NiS₂ loaded on CN. Reaction condition: 0.5 mmol nitrobenzene, 50 mL of water, 10 mg of catalyst, 0.5 mmol NaBH₄, room temperature, 1 h.

Entry	Catalyst	Conv.[%]	Sel.[%]
1	1wt.% NiS ₂ /CN	8	0
2 ^a	3wt.% NiS ₂ /CN	15	14
3 ^a	6wt.% NiS ₂ /CN	16	31
4	9wt.% NiS ₂ /CN	>99	>99
5 ^a	12wt.% NiS ₂ /CN	>99	95
6 ^a	15wt.% NiS ₂ /CN	>99	86

^aThe byproduct is nitrosobenzene

Table S2. Testing of catalysts (9 wt. %) prepared at different temperatures. Reaction condition: 0.5 mmol nitrobenzene, 50 mL of water, 10 mg of catalyst, 0.5 mmol NaBH₄, room temperature, 1 h.

Entry	T/ (°C)	Conv.[%]	Sel.[%]
1	30	-	-
2	80	>99	>99
3	160	99	77



Scheme S1. Proposed reaction mechanism. The unique heterocyclic macrocycle structure of $g\text{-C}_3\text{N}_4$ with an N–C–N– bonding pattern makes it easily contact with the aromatic ring. The hydrogen atoms were activated by the ([Ni-S] or [Ni-N]) centers and then transferred to the nitrobenzene. Indeed, a certain amount of nitrosobenzene can be detected as the byproduct when the content of the NiS_{2+X} in the catalyst was not optimized (Table S1). This is to say that the support effect of $g\text{-C}_3\text{N}_4$ dominated the activity of NiS_{2+X} nanoparticles. Under optimized conditions with a suitable loading amount of NiS_{2+X} on $g\text{-C}_3\text{N}_4$ (9 wt. %), aniline was the only reaction product observed (on the basis of GC analysis) with a selectivity of > 99%.