Electronic Supplementary Information

Bioinspired Noble-Metal-Free Reduction of Nitroarenes over NiS_{2+x}/g-C_3N_4

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Chemicals: Cyanamide (Aldrich, 50 wt% in H_2O, contains 0.1 % formic acid as stabilizer), Ludox
HS40 solution (Alfa Aesar, Silicon(IV) oxide, 40 % in H_2O, colloidal dispersion), Hydrofluoric
acid (HF, Sinopharm Chemical Reagent Co., Ltd., ≥40.0%), Ethanol (CH_3CH_2OH, 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(NO_3)_2•6H_2O Sinopharm Chemical
Reagent Co., Ltd., ≥98.0%), Thioacetamide (TAA, Sinopharm Chemical Reagent Co., Ltd., ≥
99.0%), Dichloromethane (CH_2Cl_2, 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 SiO_2 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 N_2. 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(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.

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(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.

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 N$_2$ flow. 200 mg of the as-formed N-LC was dispersed into 20 mL of distilled water with 0.2 mmol Ni(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.
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 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.

2. Catalytic reduction of aromatic nitro compounds

2.1. Testing of NiS₂ 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 NaBH₄ (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 CH₂Cl₂ 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. % NiS₂ₓ/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 NaBH₄ (1 mmol) aqueous solution was added into the mixture while stirring at room temperature for 1 hour. The product was extracted by CH₂Cl₂ 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 Kα1 radiation. The PXRD measurements were performed on a Rigaku D/Max 2550 X-ray diffractometer operating at the Cu Kα1 radiation. The XPS measurements were performed on a Kratos AXIS ULTRA DLD X-ray photoelectron spectrometer with a monochromatized X-ray source (Al KR hυ = 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 triglycerine 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. % NiS$_{2+x}$/CN and (b) the regenerated 9 wt. % NiS$_{2+x}$/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-C$_3$N$_4$. 
Figure S7. Conversion of 4-nitrophnol 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 NaBH$_4$ (No. 4)
Table S1. Testing of different amount of NiS$_2$ loaded on CN. Reaction condition: 0.5 mmol nitrobenzene, 50 mL of water, 10 mg of catalyst, 0.5 mmol NaBH$_4$, room temperature, 1 h.

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<th>Entry</th>
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<th>Conv.[%]</th>
<th>Sel.[%]</th>
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<td>1wt.% NiS$_2$/CN</td>
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<td>0</td>
</tr>
<tr>
<td>2$^a$</td>
<td>3wt.% NiS$_2$/CN</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>3$^a$</td>
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<td>16</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
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<td>$&gt;$99</td>
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<tr>
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<td>$&gt;$99</td>
<td>95</td>
</tr>
<tr>
<td>6$^a$</td>
<td>15wt.% NiS$_2$/CN</td>
<td>$&gt;$99</td>
<td>86</td>
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</table>

$^a$The 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.

<table>
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Scheme S1. Proposed reaction mechanism. The unique heterocyclic macrocycle structure of g-C3N4 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 NiS2+X in the catalyst was not optimized (Table S1). This is to say that the support effect of g-C3N4 dominated the activity of NiS2+X nanoparticles. Under optimized conditions with a suitable loading amount of NiS2+X on g-C3N4 (9 wt. %), aniline was the only reaction product observed (on the basis of GC analysis) with a selectivity of > 99%.