

## Electronic Supporting Information

# **Synthesis of 3D N-doped graphene/carbon nanotubes hybrid with encapsulated Ni NPs and its catalytic application in hydrogenation of nitroarenes**

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## **1. Experimental Section**

### **1.1. Catalysts preparation**

First of all, Ni(en)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> was prepared via direct mixing the aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> and ethylenediamine. The mixed powder of agar (5 g) and melamine (10 g) were ground in a ceramic mortar, followed by dropping 20 mL of above prepared Ni(en)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> solution (containing 0.5 g Ni totally) in it and further ground to form a slurry. And then, the slurry was dried at 80 °C in vacuum overnight. The dried powder was transferred to a tube furnace and underwent thermal treatment at 600 °C for 1 h, then further pyrolyzed at 700 °C for 6 h with a heating rate of 2.5 °C/min under nitrogen flow of 50 mL/min. The product was collected when the reactor was cooled to room temperature. After that, the pyrolyzed sample was treated in 100 mL HCl (10 wt%) for 6 h to remove soluble species. The acid-treated sample was denoted as Ni@N-CNTs-GS.

For comparison, other reference catalysts were prepared in the same procedures except the composition of solid raw precursors to be pyrolyzed. The melamine-free Ni/C was obtained via the pyrolysis of mixed agar (15 g) and Ni(en)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> (containing 0.5 g Ni totally). The agar-free Ni@N-CNTs was prepared via the pyrolysis of mixed melamine (15 g) and Ni(en)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> (containing 0.5 g Ni totally). All the products were also treated by 10 wt% HCl solution.

Ni contents in prepared Ni-based catalysts were measured in the following procedures. Sample (0.1 g) was pretreated in air from 25 to 900 °C (with a heating rate of 5 °C/min), and then the residual solids were dissolved with 50 mL aqua regia solution. Metal ion (Ni<sup>2+</sup>) in above solution was detected via inductively coupled plasma-atomic emission spectroscopy (ICP, Plasma-Spec-II spectrometer), and the results were also listed in Table S1.

## 1.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (RIGAKUD/MAX 2550/PC) at 40 kV and 100mA with Cu *K*α radiation ( $\lambda=1.5406$  Å). Raman spectra were collected on a Rhenishaw 2000 Confocal Raman Microprobe (Rhenishaw, Instruments, England) using a 514.5 nm argon laser. X-ray photoelectron spectra (XPS) were recorded on a PerkinElmer PHI ESCA System. X-ray source was Mg standard anode (1253.6 eV) at 12 kV and 300 W. The scanning electron microscope (SEM) images were obtained with Zeiss Sigma field emission SEM (MERLIN). Transmission electron microscopy (TEM) images were obtained with JEOL JEM-2100F operating at an accelerating voltage of 200 kV. N<sub>2</sub>-adsorption and desorption of the samples were measured at its boiling point (-197 °C) after pretreated at 200 °C for 4 h in high vacuum using micromeritics ASAP 2020 HD88. Specific surface area was calculated using Brunner-Emmet-Teller (BET) method in the range of  $P/P_0 = 0.05-0.30$ , and pore size distribution were calculated from the desorption data using the Barrett-Joyner-Halenda (BJH) method.

### 1.3. Catalytic reactions

The selective hydrogenation of NB was examined in a 50 mL custom designed stainless autoclave with a Teflon inner layer. In a typical procedure, a certain amount of catalyst was dispersed in NB solution which contained 1.5 mmol substrate in 12 mL ethanol. After the reactor was sealed, air was purged by flushing three times with 2.0 MPa H<sub>2</sub>, the autoclave was pressurized with H<sub>2</sub> to 2.0 MPa and stirred at the desired temperature. After the reaction, the reactor was cooled to room temperature and depressurized carefully. Then, the products were analyzed by GC (HP 5890, USA) with a 30 m capillary column (HP-5) using a flame ionization detector. Leaching experiment of Ni@N-CNTs-GS was performed in the following procedure: after the reaction proceeded for 1 h, catalyst was removed and the supernatant was sealed in the autoclave for further reaction. Hydrogenation reactions of a series of nitroarenes were conducted in the same reactor using similar procedures. For each successive run of recycle usage, the catalyst was separated by an external magnetic field and washed with ethanol twice prior to the next run.

## 2. Results and discussion

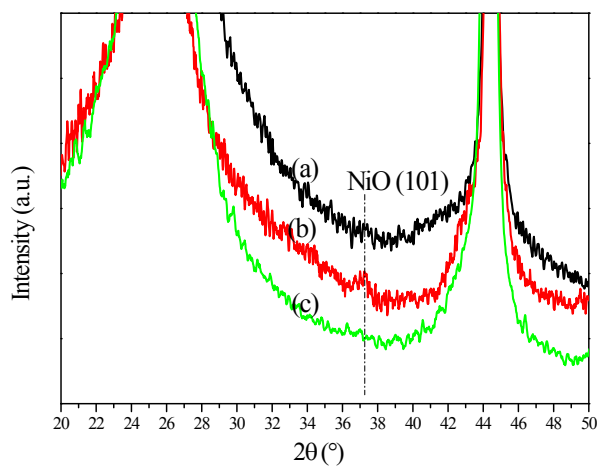
**Table S1** The textural properties and particle size of Ni in various catalysts.

| Sample                            | Ni<br>(wt%) <sup>a</sup> | S <sub>BET</sub><br>(m <sup>2</sup> /g) | V <sub>total</sub><br>(cm <sup>3</sup> /g) | Ni size<br>(nm)  |                  |
|-----------------------------------|--------------------------|---|--|------------------|------------------|
|                                   |                          |   |  | XRD <sup>b</sup> | TEM <sup>c</sup> |
| Ni/C                              | 10.83                    | 2                                       | 0.006                                      | 8.2              | 10.5             |
| Ni@N-CNTs                         | 25.42                    | 252                                     | 0.675                                      | 28.6             | 29.5             |
| Ni@N-CNTs-GS-fresh                | 18.74                    | 363                                     | 0.483                                      | 14.4             | 15.1             |
| <b>Ni@N-CNTs-GS-<br/>recycled</b> | <b>18.56</b>             | -                                       | -  | -                | <b>15.5</b>      |

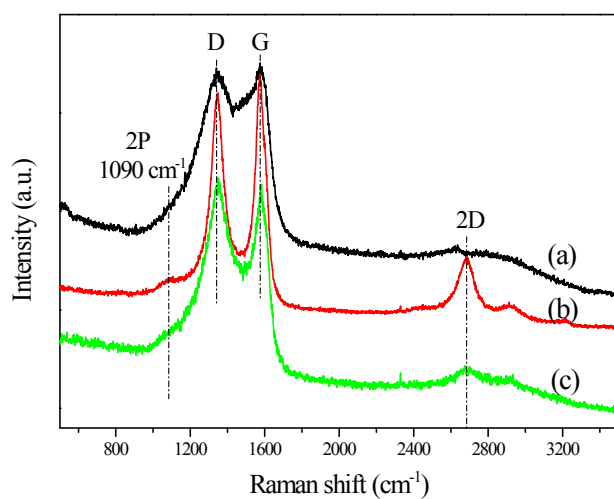
<sup>a</sup> Detected via TG and ICP-AES.

<sup>b</sup> Calculated from the Scherrer formula according to the Ni(111) (2θ=44.5°) diffraction plane.

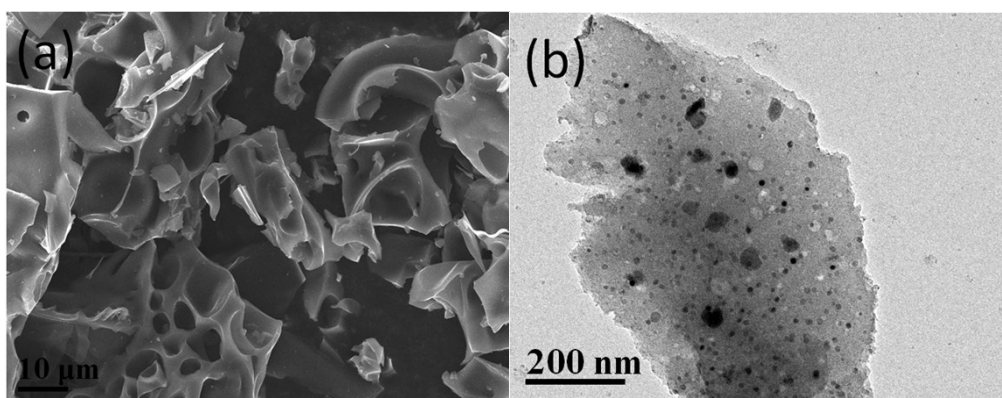
<sup>c</sup> Derived from the TEM images.

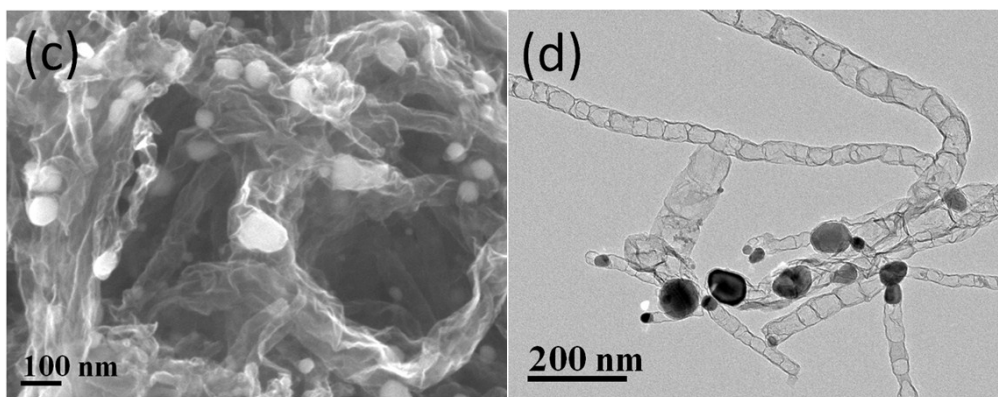


**Fig. S1** Enlarged XRD patterns of (a) Ni/C, (b) Ni@N-CNTs and (c) Ni@N-CNTs-GS.

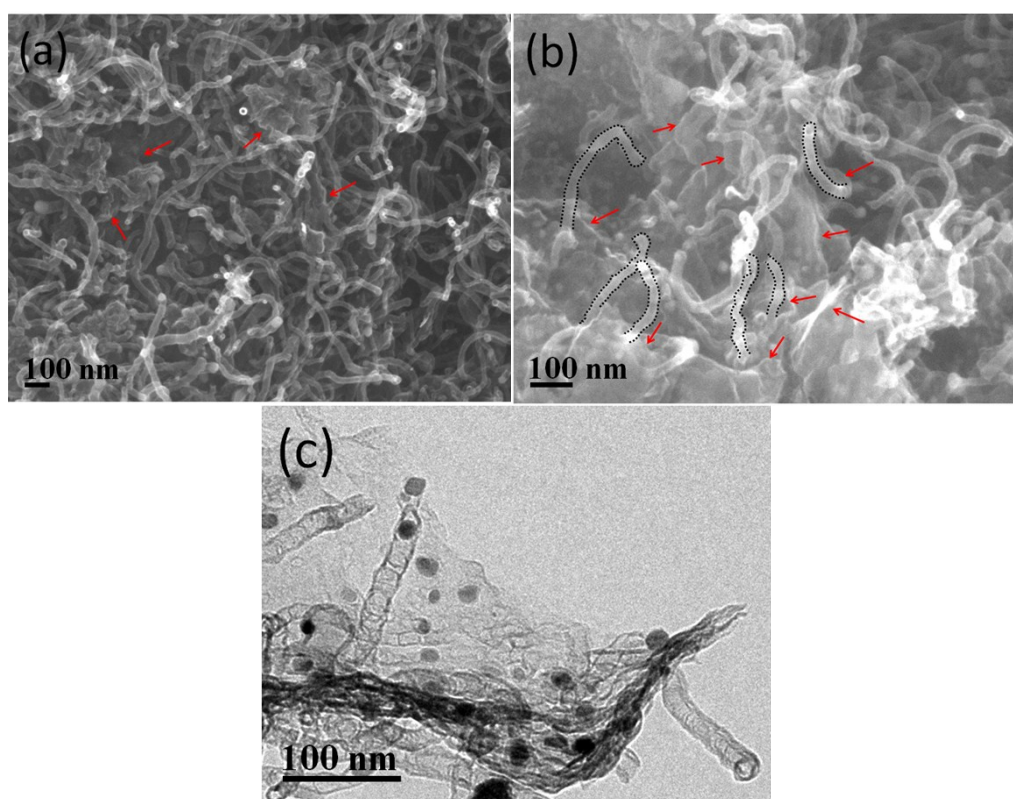


**Fig. S2** Raman spectra of (a) Ni/C, (b) Ni@N-CNTs and (c) Ni@N-CNTs-GS.

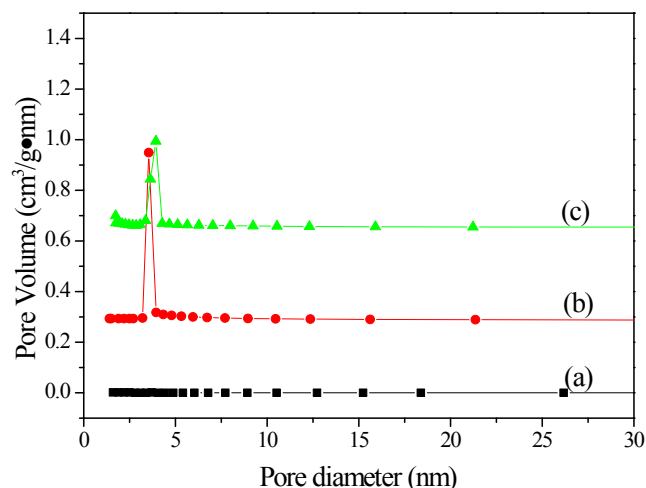




**Fig. S3** (a, c) SEM and (b, d) TEM images of (a, b) Ni/C and (c, d) Ni@N-CNTs.



**Fig. S4** (a, b) SEM, (c) TEM images of Ni@N-CNTs-GS. CNTs were lined out with black dotted line, and the graphene sheets were pointed out with red arrows.

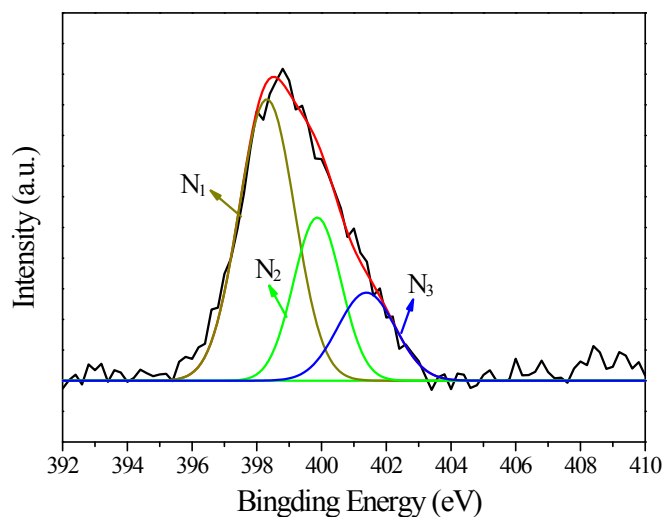


**Fig. S5** Pore-size distribution of (a) Ni/C, (b) Ni@N-CNTs and (c) Ni@N-CNTs-GS.

**Table S2** Surface composition of different Ni-based catalysts. <sup>a</sup>

| Sample                | Relative atomic percentage (%) |       |      |      |
|-----------------------|--------------------------------|-------|------|------|
|                       | C                              | O     | N    | Ni   |
| Ni/C                  | 69.42                          | 26.09 | 0.13 | 4.36 |
| Ni@N-CNTs             | 92.24                          | 6.38  | 0.71 | 0.66 |
| Ni@N-CNTs-GS-fresh    | 83.25                          | 9.68  | 4.90 | 2.17 |
| Ni@N-CNTs-GS-recycled | 83.37                          | 8.70  | 5.31 | 2.62 |

<sup>a</sup> Surface composition determined from XPS.



**Fig. S6** High-resolution deconvoluted N 1s spectra of Ni@N-CNTs-GS (N<sub>1</sub>: pyridinic-N, N<sub>2</sub>: pyrrolic-N, N<sub>3</sub>: quaternary-N).

**Table S3** Hydrogenation of NB over Ni@N-CNTs-GS catalysts prepared under different conditions.<sup>a</sup>

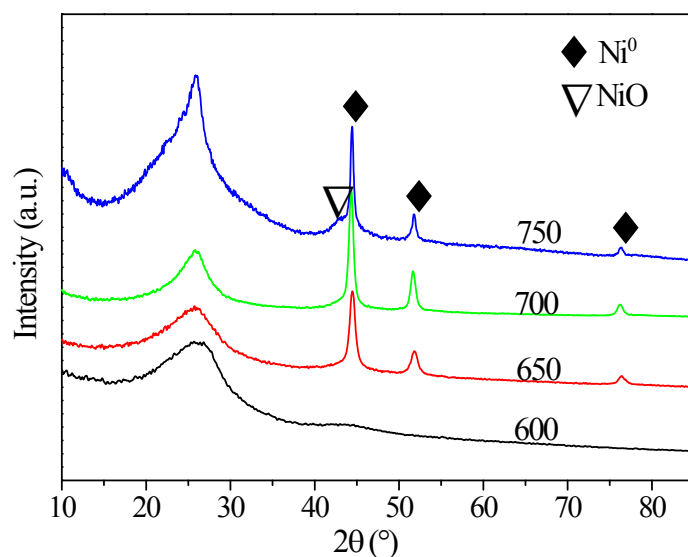
| Entry | Ni precursor  | Mass of Ni in precursor (g) | Pyrolysis temp. (°C) | Pyrolysis time (h) | Ni size <sup>b</sup> (nm) | Conv. (%) |
|-------|---|-----------------------------|----------------------|--------------------|---------------------------|-----------|
| 1     | Ni(NO <sub>3</sub> ) <sub>2</sub>                   | 0.5                         | 700                  | 6                  | 25.1                      | 16.4      |
| 2     | Ni(en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> | 0.3                         | 700                  | 6                  | 13.6                      | 60.7      |
| 3     | Ni(en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> | 0.5                         | 700                  | 2                  | 11.9                      | 63.4      |
| 4     | Ni(en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> | 0.5                         | 600                  | 6                  | -                         | 1.6       |
| 5     | Ni(en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> | 0.5                         | 650                  | 6                  | 9.9                       | 32.5      |
| 6     | Ni(en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> | 0.5                         | 700                  | 6                  | 14.4                      | 100       |
| 7     | Ni(en) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> | 0.5                         | 750                  | 6                  | 22.1                      | 13.0      |

<sup>a</sup> Reaction conditions: 1.5 mmol nitrobenzene in 12.0 mL ethanol, Ni 6.0 mol% of NB, 2.0 MPa H<sub>2</sub>, 120 °C, 3 h.

<sup>b</sup> Calculated from the Scherrer formula according to the Ni(111) (2θ=44.5°) diffraction plane.

The properties and catalytic performance of Ni@N-CNTs-GS catalysts prepared under varied conditions were summarized in Table S3. When Ni(NO<sub>3</sub>)<sub>2</sub> was used as Ni precursor (Entry 1), the prepared composite contained larger Ni NPs (25.1 nm), exhibiting a very poor catalytic activity compared to the catalyst derived from Ni(en)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> (Entry 6, similar preparation conditions). Decreasing the amount of Ni (Entry 2, 0.3 g) in the mixed precursors or shortening the pyrolysis time to 2 h (Entry 3) led to smaller Ni NPs (13.6 and 11.9 nm, respectively) but lower activity (60.7, 63.4%) compared with Entry 6. It was deduced that enough amount of Ni and pyrolysis time were both indispensable for the growth of 3D CNTs-GS composites. In addition, the pyrolysis temperature was increased from 600 to 750 °C, and the XRD patterns of the prepared catalysts (denoted as Ni@N-CNTs-GS-T) were shown in Fig. S7. No metallic Ni was observed in Ni@N-CNTs-GS-600, suggesting that Ni(en)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> precursor cannot be reduced to metallic Ni at 600 °C. Subsequently, it was found that the mean size of Ni NPs increased continuously as the pyrolysis temperature increased from 650 to 750 °C, while the activity of prepared catalysts

first increased and then decreased. The particle size of Ni NPs was the smallest in Ni@N-CNTs-GS-650 (Entry 5, 9.9 nm), but its activity was lower than that of Ni@N-CNTs-GS-700, which may be attributed to the lower surface area of Ni@N-CNTs-GS-650. Further increasing the pyrolysis temperature to 750 °C would not only result in the agglomeration of Ni NPs (22.1 nm), but also in the oxidation of metallic Ni, so the 3D composite prepared at 700 °C exhibited the best performance for the hydrogenation of nitrobenzene (denoted as Ni@N-CNTs-GS).



**Fig. S7** XRD patterns of a series of Ni@N-CNTs-GS-T synthesized at varied pyrolysis temperatures.

**Table S4** Hydrogenation of NB over Ni@N-CNTs-GS under varied conditions.<sup>a</sup>

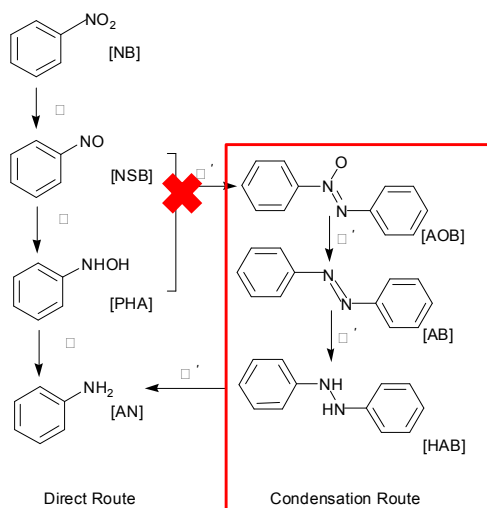
| Entry | Temp.<br>(°C) | H <sub>2</sub> Pressure<br>(MPa) | Time<br>(h) | Conv.<br>(%) | Sel. (%) |     |
|-------|---------------|----------------------------------|-------------|--------------|----------|-----|
|       |               |                                  |             |              | AN       | NSB |
| 1     | <b>100</b>    | 2                                | 3           | 34.0         | 98.8     | 1.2 |
| 2     | <b>120</b>    | 2                                | 3           | 100          | 100      | 0   |
| 3     | <b>140</b>    | 2                                | 3           | 100          | 100      | 0   |
| 4     | 120           | <b>1</b>                         | 3           | 44.9         | 98.4     | 1.6 |
| 5     | 120           | 4                                | 3           | 100          | 100      | 0   |

<sup>a</sup> Reaction conditions: 1.5 mmol nitrobenzene in 12.0 mL ethanol, Ni 6.0 mol% of NB.

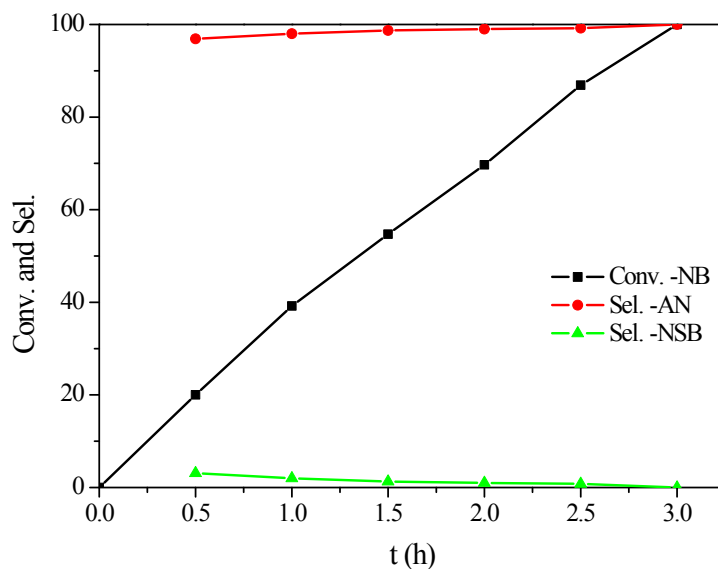
Hydrogenation of nitrobenzene at varied H<sub>2</sub> pressure, reaction temperature was carried out to optimize the reaction conditions. Table S4 showed that the



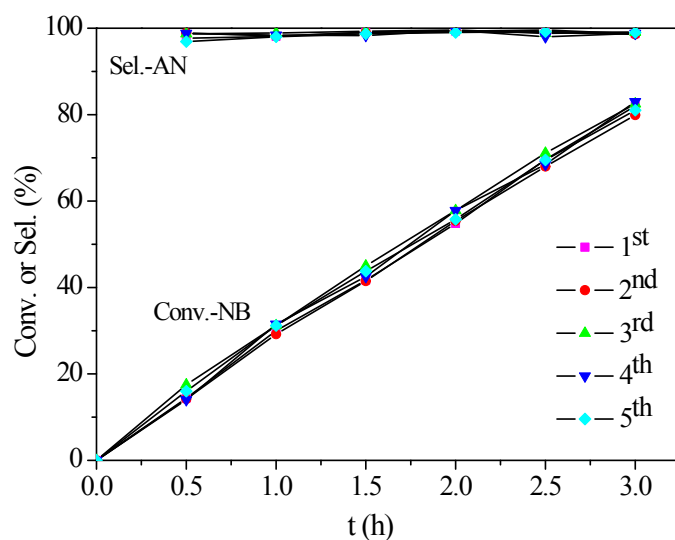
hydrogenation of nitrobenzene proceeded relatively slowly at lower temperature (100 °C). At the same time, lower H<sub>2</sub> pressure (Entry 4, 1 MPa) also led to much slower reaction rate, demonstrating that H<sub>2</sub> pressure was key to the hydrogenation of nitrobenzene. 120 °C and 2 MPa of H<sub>2</sub> were proved to be more favorable for the reaction.



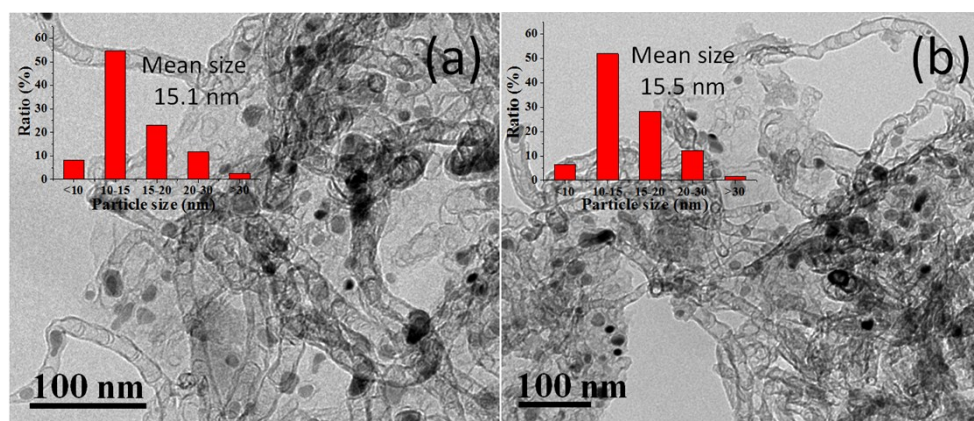
**Fig. S8** Reaction pathways for the hydrogenation of nitrobenzene.



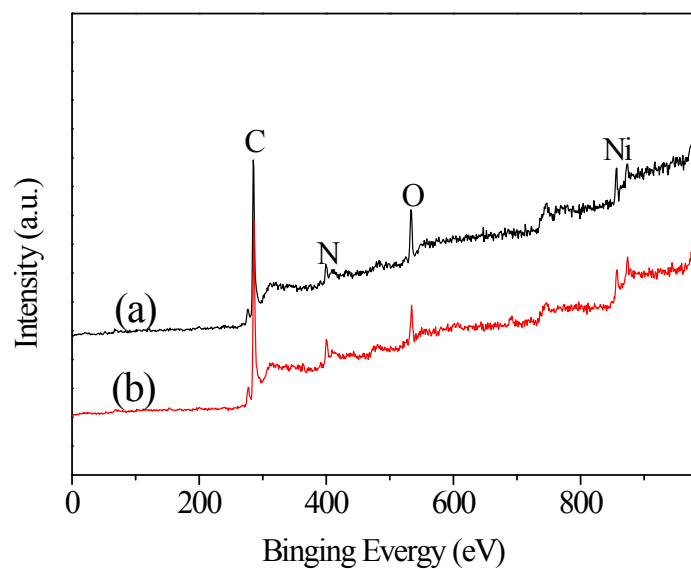
**Fig. S9** Time course of NB hydrogenation over Ni@N-CNTs-GS catalyst. Reaction conditions: 1.5 mmol nitrobenzene in 12.0 mL ethanol, Ni 6.0 mol% of NB, 2.0 MPa H<sub>2</sub>, 120 °C.



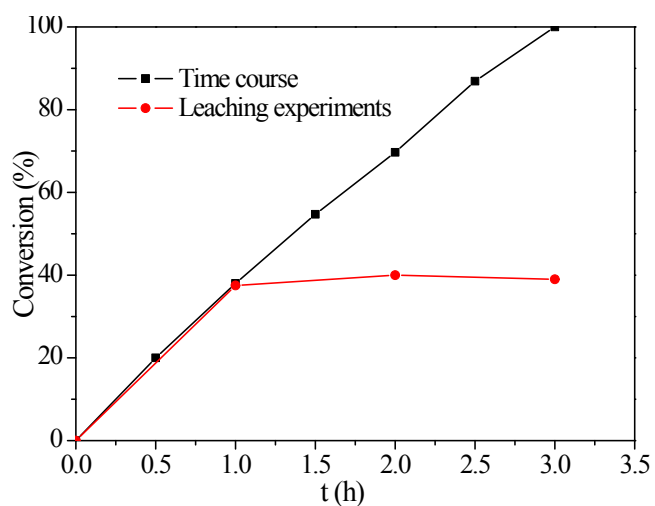
**Fig. S10** Time course of the five recycles over Ni@N-CNTs-GS catalyst. Reaction conditions: 1.5 mmol nitrobenzene in 12.0 mL ethanol, Ni 5.0 mol% of NB, 2.0 MPa H<sub>2</sub>, 120 °C.



**Fig. S11** TEM images and the corresponding Ni particle size distribution of (a) fresh and (b) **five times recycled** Ni@N-CNTs-GS.



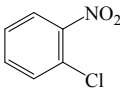
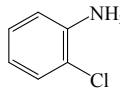
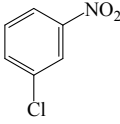
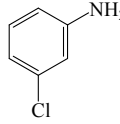
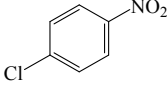
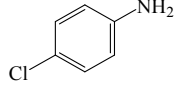
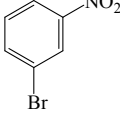
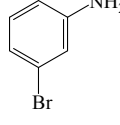
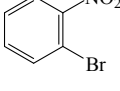
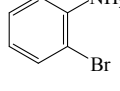
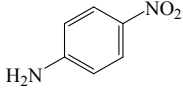
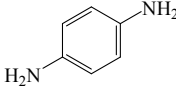
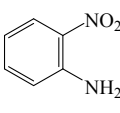
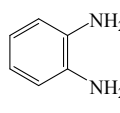
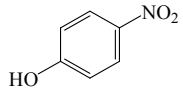
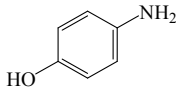
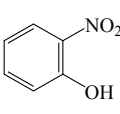
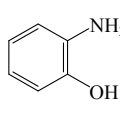
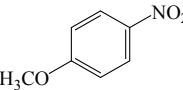
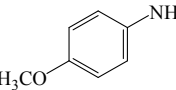
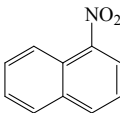
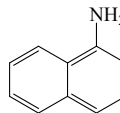
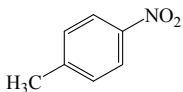
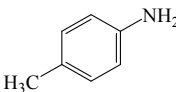
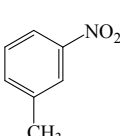
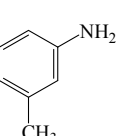
**Fig. S12** XPS spectra of (a) fresh and (b) **five times recycled** Ni@N-CNTs-GS.

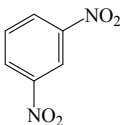
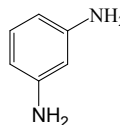
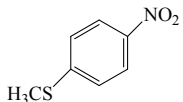
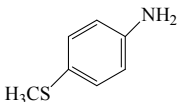
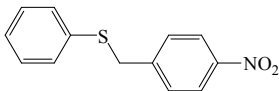
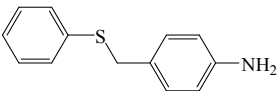
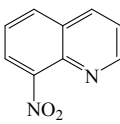
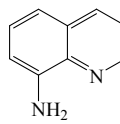
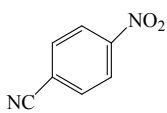
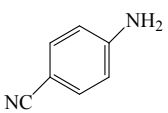
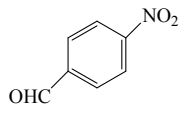
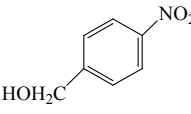
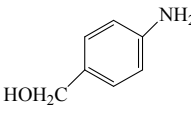


**Fig. S13** Leaching experiment of Ni@N-CNTs-GS.

Reaction conditions: 1.5 mmol nitrobenzene in 12.0 mL ethanol, Ni 6.0 mol% of NB, 2.0 MPa H<sub>2</sub>, 120 °C.

**Table S5** Hydrogenation of various substrates over Ni@N-CNTs-GS<sup>a</sup>.

| Entry | Substrate   | Temp<br>(°C) | Time<br>(h) | Conv.<br>(%) | Product   | Yield<br>(%) |
|-------|---|--------------|-------------|--------------|---|--------------|
| 1     |    | 120          | 3           | 100          |    | 97.0         |
| 2     |    | 120          | 3           | 100          |    | 100          |
| 3     |    | 120          | 3           | 100          |    | 100          |
| 4     |    | 120          | 3           | 100          |    | 96.6         |
| 5     |    | 120          | 3           | 100          |    | 93.6         |
| 6     |  | 120          | 2           | 100          |  | 100          |
| 7     |  | 120          | 3           | 97.6         |  | 97.6         |
| 8     |  | 120          | 2           | 97.9         |  | 97.9         |
| 9     |  | 120          | 2           | 100          |  | 100          |
| 10    |  | 120          | 2           | 98.0         |  | 98.0         |
| 11    |  | 120          | 3           | 99.3         |  | 99.3         |
| 12    |  | 120          | 3           | 100          |  | 100          |
| 13    |  | 120          | 3           | 99.1         |  | 99.1         |

| Entry | Substrate   | Temp<br>(°C) | Time<br>(h) | Conv.<br>(%) | Product   | Yield<br>(%) |
|-------|---|--------------|-------------|--------------|---|--------------|
| 14    |    | 120          | 6           | 100          |    | 99.0         |
| 15    |    | 120          | 1.7         | 100          |    | 100          |
| 16    |    | 120          | 2.5         | 100          |     | 100          |
| 17    |    | 120          | 3           | 100          |    | 100          |
| 18    |   | 120          | 2           | 100          |   | 100          |
| 19    |  | 110          | 3           | 100          |  | 74.2         |
|       |   |              |             |              |  | 25.8         |

<sup>a</sup> Reaction conditions: 0.5 mmol nitroarenes in 5.0 mL ethanol, Ni 9.0 mol% of NB, 2 MPa H<sub>2</sub>.