Supporting Information

Ni-promoted synthesis of graphitic carbon nanotubes from \textit{in situ} produced graphitic carbon for dehydrogenation of ethylbenzene

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Experimental Section

Characterization

SEM images were obtained on a SU-70 microscope. High-resolution TEM (HRTEM) was performed on Tecnai G2 F30 S-Twin at an acceleration voltage of 300 KV. Powder X-ray diffraction (XRD) patterns were measured on a D/tx-Ultima TV wide angle X-ray diffractometer equipped with Cu Kα radiation (1.54 Å). The X-ray photoelectron spectra (XPS) were obtained with an ESCALAB MARK II spherical analyzer using an aluminum anode (Al 1486.6 eV) X-ray source. The Raman spectra were collected on a Raman spectrometer (JY, HR 800) using 514-nm laser. N₂ adsorption analysis was performed at 77 K using a Micromeritics ASAP 2020 to access the surface areas and pore distributions. All the samples were outgassed at 150 °C for 8 h. The specific surface area was calculated by the conventional Brunauere-Emmette-Teller (BET) method. The pore size distribution (PSD) plot was recorded by the BJH method. The Ni content was determined by ICP-AES (Perkin Elmer Optima OES 8000) and aqua regia was used to dissolve the sample. CO₂ temperature-programmed desorption (CO₂-TPD) was conducted with a FINESORB-3010 apparatus equipped with a thermal conductivity detector (TCD). Before a TPD run, catalysts were pretreated in Ar at 873 K for 30 min, then cooled down to room temperature. Afterwards CO₂ was adsorbed at 50 °C for 30 min. The physically adsorbed CO₂ was removed by a flushing procedure with Ar until the signal baseline detected by TCD went steadily stable. Then TPD-CO₂ was carried out in the stream of Ar at heating rate of 15 °C min⁻¹ up to 550 °C, and the effluent was detected by a TCD detector.

Materials

D-glucosamine hydrochloride (GAH), melamine, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, cellulose, sucrose, glucose and chitin were purchased from Aladdin. All the chemicals were used as delivered without further treatment. Commercial CNTs were used as received from Shenzhen Nanotech Port Co., Ltd.

Methods

GCNTs were prepared by annealing the mixture of GAH-melamine-Ni, and the tubular morphology was formed during the pyrolysis process. Briefly, mixture solid of GAH, melamine and Ni(NO₃)₂·6H₂O was grinded into powder, then directly calcined by flowing N₂ of 400 ml min⁻¹. After that, the samples were cooled to room temperature under N₂ ambient. Finally, the hybrid materials were collected from the crucible. Then treated with HCl, GCNTs were obtained. The morphology can be easily controlled by tailoring the mass ratio between GAH, melamine and Ni(NO₃)₂·6H₂O or the pyrolysis temperature. Cellulose, sucrose, glucose and chitin were served as carbon sources for testifying the flexibility of this
method. They were prepared under the same conditions that the mass ratio of carbon source/melamine/Ni was 1:20:1.1 at 1000 °C for 1 h. All the products were treated by 2 M HCl.

Taking the synthesis of GCNTs (mass ratio GAH:melamine:Ni=1:20:1.1, at 1000 °C for 1 h) as an example: Firstly, melamine (20 g), GAH (1 g) and Ni(NO$_3$)$_2$·6H$_2$O (1.1 g) were mixed together adequately. The mixture was then transferred into a 30 ml-crucible. Then, the solid mixture was calcined to 1000 °C (calcination process is as shown in Scheme S1) followed by an isothermal hold period of 1 h in a Muffle furnace in N$_2$ flow (400 mL/min). After it cooled down to room temperature, loose black solid (NiO$_x$@GCNTs) was gained. Then the black solid was ground into black powder and transferred into a plastic bottle, 2 M HCl was also added into the bottle. The mixtures were stirred for 48 hours at room temperature. After filtering the solution, the black solid residue was dried at 70 °C in an oven overnight.

Fe-GCNTs and Co-GCNTs were prepared with the pyrolysis of solid mixture of melamine (20 g), GAH (1 g), and nickel nitrate (0.7 g, without crystal water). The furnace was heated to the reaction temperature of 1000 °C in N$_2$ atmosphere. After carbonization for 1 h, products were collected when the reactor was cooled to room temperature. All the products were treated by 2 M HCl.

GCNs was prepared by pyrolysis of GAH/melamine (mass ratio GAH:melamine=1:20, 1000 °C, 1 h).

![Scheme S1. calcination process for samples.](image)

**Catalytic performance measurement:**

Direct dehydrogenation of ethylbenzene was carried out at 550 °C for 165 h in a continuous flow fixed-bed quartz tube using 98 mg NiO$_x$@GCNTs and appropriate amount of quartz sand. The system was heated to 600 °C and kept for 15 min in Ar. After the system was cooled down to 550 °C, the reactant (ethylbenzene feed flow rate 100 μL h$^{-1}$, total flow rate 10 mL min$^{-1}$, Ar as balance) was then fed to the reactor. Quantitative analysis of the collected reaction products (ethylbenzene, styrene, toluene, and benzene) was analyzed on GC (Shimadzu, GC-2014) equipped with a Rtx-1071 column. The resulting carbon balance was above 100 ± 4% in all reactions.
Table S1. Textural properties of the catalysts

<table>
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<tr>
<th>entry</th>
<th>catalyst</th>
<th>BET surface area (m²/g)</th>
<th>pore volume (cm³/g)</th>
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</thead>
<tbody>
<tr>
<td>1ᵃ</td>
<td>GCNTs</td>
<td>166</td>
<td>0.35</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>NiO₅@GCNTs</td>
<td>156</td>
<td>0.33</td>
</tr>
</tbody>
</table>

[a] GCNTs was prepared by thermal condensation of GAH, melamine, and Ni(NO₃)₂·6H₂O (mass ratio GAH:melamine:Ni=1:20:1.1) at 1000 °C for 1 h, and was treated by 2 M HCl.
[b] NiO₅@GCNTs was prepared by thermal condensation of GAH, melamine, and Ni(NO₃)₂·6H₂O (mass ratio GAH:melamine:Ni=1:20:1.1) at 1000 °C for 1 h.

Table S2. Electronic conductivity

<table>
<thead>
<tr>
<th>entry</th>
<th>Sample</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵃ</td>
<td>GCNTs</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>Commercial CNTs</td>
<td>92</td>
</tr>
</tbody>
</table>

[a] GCNTs was prepared by thermal condensation of GAH, melamine, and Ni(NO₃)₂·6H₂O (mass ratio GAH:melamine:Ni=1:20:1.1) at 1000 °C for 1 h, and was treated by 2 M HCl.

Scheme S2. The devices applied to evaluate electronic conductivity.

The conductivity of GCNTs was evaluated by a mould filled with samples (as diagramed in Scheme S2).¹ For comparison, the conductivity of commercial CNTs was also measured and summarized in Table S2. The conductivity of GCNTs is poorer than CNTs, since the carbonization temperature is low.
**Fig. S1.** a, b) TEM images of commercial CNTs with different magnifications.

**Fig. S2.** a) N 1s XPS peak of GCNTs. b) Raman spectra of GCNTs and GCNs. c) XRD patterns of GCNTs and GCNs. GCNTs was prepared by thermal condensation of GAH, melamine, and Ni(NO$_3$)$_2$·6H$_2$O (mass ratio GAH:melamine:Ni=1:20:1.1) at 1000 °C for 1 h, and then treated by HCl. GCNs was prepared by thermal condensation of GAH and melamine (mass ratio GAH:melamine=1:20) at 1000 °C for 1 h.
Fig. S3. a) Adsorption/desorption isotherms of GCNTs (mass ratio GAH:melamine:Ni=1:20:1.1, treatment with HCl) at 1000 °C for 1 h. The inset shows the pore size distribution of GCNTs. b) Adsorption/desorption isotherms of NiO₅₋@GCNTs (mass ratio GAH:melamine:Ni=1:20:1.1) at 1000 °C for 1 h. The inset shows the pore size distribution of NiO₅₋@GCNTs.

As evidenced by N₂ adsorption-desorption isotherms (Fig. S3), the as-synthesized GCNTs and NiO₅₋@GCNTs exhibited the similar pore size distribution. The specific surface area of GCNTs slightly increased to 166 m² g⁻¹ (Table S1) after acid treatment, owing to the dissolution of metal particles.

Fig. S4. Blank control experiments. a) SEM image of GAH/Ni (mass ratio=1:1.1). c) SEM image of GCNs (mass ratio GAH:melamine=1:20). e) SEM image of Ni/melamine (mass ratio=1.1:20). b, d, f) TEM images of a, c, e. All the products were prepared at 1000 °C for 1 h. The red circles highlight the carbon spheres stack into lines, and the red arrows indicate carbon tubes.
Fig. S5. SEM images for control experiments. a) GCNs (mass ratio melamine:GAH=5:1). b) GCNs (mass ratio melamine:GAH=10:1). c) GCNs (mass ratio melamine:GAH=20:1). d, e, f) Products from the pyrolysis of GAH/melamine/Ni corresponding to a, b, c with 1.1 g Ni(NO$_3$)$_2$·6H$_2$O. All the products were calcinated at 1000 °C for 1 h.

Fig. S6. SEM images of products. a) mass ratio GAH:melamine:Ni=1:20:0.48. b)
mass ratio GAH:melamine:Ni=1:20:0.95. c) mass ratio GAH:melamine:Ni=1:20:1.1. d) mass ratio GAH:melamine:Ni=1:20:1.6. All the products were calcinated at 1000 °C for 1 h. The yellow arrow indicated the baby nanotubes.

Fig. S7. SEM images of products (mass ratio GAH:melamine:Ni=1:20:1.1), 1 h. a) 600 °C, b) 800 °C, c) 900 °C, d) 1000 °C. The yellow arrow indicated the baby nanotubes.

Fig. S8. a) XRD patterns of products (mass ratio GAH:melamine:Ni=1:20:1.1) at different calcination temperature for 1 h. b) XRD patterns of products (mass ratio GAH:melamine:Ni=1:20:1.1, 800 °C) with different holding time. All the samples were not treated with HCl.
Fig. S9. SEM images of products (mass ratio GAH:melamine:Ni=1:20:1.1) with different holding time at 1000 °C. a) 10 min, b) 60 min. The yellow arrow indicated the baby nanotubes.

In order to further confirm our conclusion, the as-synthesized GCNTs (mass ratio GAH:melamine:Ni=1:20:1.1, 1000 °C) maintained with different holding time purposefully as well. Just as we expected, the growth of GCNTs has experienced the same process. Namely, within 10 minutes, large range plates were observed with baby nanotubes (Fig. S9a). Increasing the holding time to 60 minutes, they finally grew up to typical carbon nanotubes (Fig. S9b). We have reason to believe that GCNTs were in situ formed during the growth of graphitic carbon.
Fig. S10. SEM images of different biomass as carbon sources. a) cellulose. b) sucrose. c) glucose. d) chitin.
Fig. S11. SEM images of graphitic carbon nanomaterials with different catalyst precursors. a, b) Fe(NO$_3$)$_3$·9H$_2$O. c, d) Co(NO$_3$)$_2$·6H$_2$O.
Fig. S12. Direct ethylbenzene dehydrogenation activity of GCNTs (mass ratio GAH:melamine:Ni=1:20:1.1, 1000 °C, treated by HCl). Reaction condition: GCNTs 80 mg, 550 °C, ethylbenzene feed flow rate 100 μL h⁻¹, total flow rate 10 mL min⁻¹, Ar as balance. The yield and selectivity of GCNTs are 7.5% and 97.0%, respectively. The specific reaction rate is 4.6 μmol m⁻² h⁻¹.
The chemical status of O is investigated by X-ray photoelectron spectroscopy (XPS). The high resolution O 1s spectra of NiO\textsubscript{x}@GCNTs (Fig. S13) display three oxygen species, corresponding to O1 (C=O, ~531.53 eV), O2 (O=O=C-O, ~532.76 eV), and O3 (C-O-C/C-OH, ~533.45 eV), respectively. Remarkably, the energy peak O1 (C=O) phase reaches up to ~61.4% (Fig. S13a), which has been reported as active species for direct dehydrogenation of ethylbenzene.
Fig. S14. CO$_2$-TPD of NiO$_x$@GCNTs and GCNTs (mass ratio GAH:melamine:Ni=1:20:1.1, 1000 °C).

References