Electronic Supplementary Information

A Freestanding SiO$_2$ Ultrathin Membrane with NiCu Nanoparticles Embedding on Its Double-faces for Catalyzing Nitro-amination

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1. The Supplement of Experimental Section

1.1 Chemicals
Nickel chloride hexahydrate (NiCl₂·6H₂O, 98%), copper chloride dihydrate (CuCl₂·2H₂O, 99%), ethanol (C₂H₅OH, 99%), ethanol (C₂H₅OH, 75%) and acetone (C₃H₆O, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). Sodium borohydride (NaBH₄, 98%), urea (CH₄N₂O, 99%) and 4-nitrophenol (4-NP), 4-aminophenol (4-AP), 4-nitroanisole, 4-anisidine, 4-nitrobenzyl alcohol, 4-aminobenzyl alcohol, 4-nitrobenzaldehyde, 4-aminobenzaldehyde, 4-nitrotoluene and 4-toluidine were purchased from Aladdin Reagents, Shanghai. All reagents were used without further purification. The silicon wafers were purchased from Zhejiang Lijing Silicon Material Co., Ltd. and they were used after pretreatment.

1.2 Pretreatment of silicon wafers
The silicon wafers were cut into small pieces of 5mm*5mm. Then the small pieces of silicon wafers were alternately washed by ethanol and acetone until the solution is no longer turbid. After that, they were washed by deionized water for three times and kept in deionized water for further experiments.
2. Results and Discussion

Figure S1. SEM (A), TEM (B) images, XRD pattern (C) and EDS analysis (D) of NiCu-SiO$_2$ nanocomposite precursor.

Figure S1 shows the morphology characterization and structure analysis of NiCu-SiO$_2$ nanocomposite precursor. By SEM and TEM images (Figure 1A, B), a freestanding ultrathin membrane can be observed. The XRD pattern (Figure S1C) shows six peaks and all the diffraction peaks (12.0° (002), 19.5° (110) and 24.4° (004), 34.1° (200), 36.7° (202) and 60.5° (060)) match well with the standard pattern of Ni$_3$Si$_2$O$_6$(OH)$_4$, whereas EDS analysis of the nanocomposite in Figure 1D shows it contains Cu element, therefore NiCu-SiO$_2$ nanocomposite precursor could be named as NiCuSiO$_3$-hydroxide.
Figure S2. SEM images (a) and TEM images (b) of NiCu-SiO$_2$ nanocomposite obtained by different reducing conditions: 500°C for 2 h (A), 600°C for 2 h (B), 700°C for 2 h (C), 500°C for 5 h (D), 500°C for 8 h (E), 600°C for 5 h (F) and 600°C for 8 h (G).

In order to obtain 2D structured NiCu-SiO$_2$ nanocomposite with uniform distribution of NiCu alloy NPs, different reducing conditions have been studied in detail. Firstly, 500 °C for 2 h, 600 °C for 2 h and 700 °C for 2 h reducing conditions have been designed and performed. From Figure S2A~2C, we can clearly see that the high temperature (700 °C) make the size of NiCu alloy NPs increased quickly. And then the different reducing time for 500 °C and 600 °C have been further performed, as shown in Figure S2D~2G, we can observe that the size of NiCu alloy NPs increased with the reducing time such as 500°C for 8 h and 600°C for 8 h, meanwhile, the precursor can’t be completely reduced at 500°C. From the above, 600°C for 5 h can be the optimum reducing conditions.
Figure S3. SEM images of the precursor of NiCu-SiO$_2$ nanocomposite (A), Ni-SiO$_2$ nanocomposite (B), NiCu (C) and Ni (D) before (a) and after (b) H$_2$ reduction at 600℃ for 5 h.

As shown in Figure S3A, NiCuSiO$_3$-hydroxide precursor could be reduced under high temperature to obtain 2D structured NiCu-SiO$_2$ nanocomposite with NiCu NPs evenly embedding on SiO$_2$ nanosheets. Additionally, Figure S3B presents NiSiO$_3$-hydroxide precursor can also be reduced to Ni-SiO$_2$ nanocomposite and maintained the original 2D structure, proving the morphology thermal stability may be ascribed to the presence of SiO$_2$. From Figure S3C and Figure S3D, we can clearly see that the reduced products without the protection of SiO$_2$ have obvious aggregation, further confirming the above conclusion.
Figure S4. AFM image of SiO$_2$ membrane prepared by etching the NiCu of NiCu-SiO$_2$ nanocomposite (A) and height profile of SiO$_2$ nanosheets (B).

To further confirm the thickness of SiO$_2$ membrane, AFM and corresponding height profile were performed, as shown in Figure S4B, the SiO$_2$ membrane have a height of 1.76 nm, which is consistent with the thickness presented in the high-magnification TEM image (Figure 1H).
Figure S5. (a) TEM images, (b) EDS analysis and (c) UV-Vis spectra of different catalysts: (A) NiCu-SiO$_2$ nanocomposite; (B) Ni-SiO$_2$ nanocomposite; (C) NiCu NPs and (D) Ni NPs.

The morphology characterization and element analysis of Ni-SiO$_2$ nanocomposite, NiCu NPs and Ni NPs are also presented in Figure S5. In the TEM image of Ni-SiO$_2$ nanocomposite we can clearly observe that Ni NPs evenly distribute on the double-surfaces of SiO$_2$ support. And both of the obtained NiCu NPs and Ni NPs by etching SiO$_2$ support of NiCu-SiO$_2$ and Ni-SiO$_2$ nanocomposite have an average diameter of 7 nm in a narrow distribution. The EDS analysis of NiCu-SiO$_2$ and Ni-SiO$_2$ nanocomposites present Ni, Cu, Si, O and Ni, Si, O elements, respectively; and reveal the molar ratio of Si/Ni/Cu at 20:10:1, which can be confirmed by ICP data. Meanwhile, no Si element can be observed in NiCu NPs and Ni NPs, indicating the complete removement of SiO$_2$ support.

The UV-Vis adsorption spectra for the nitro-amination reaction of 4-NP catalyzed by NiCu-SiO$_2$ nanocomposite, Ni-SiO$_2$ nanocomposite, NiCu NPs and Ni NPs are shown in Figure S5Ac, S5Bc, S5Cc and S5Dc, respectively. It can be clearly seen that the peak of 4-NP for NiCu-SiO$_2$ nanocomposite decreases much more quickly than others, especially Ni NPs, demonstrating the obvious advantages of the nanocomposite structure and the synergetic effect of alloys.
Figure S6. Detailed XPS analysis for Cu 2p.

Figure S6 presents the detailed XPS analysis of Cu 2p, and the peaks located at the binding energies of 931.2 eV and 951.4 eV are corresponding to the Cu (0), as the nanocomposite only contained a small amount of Cu, the unsmooth spectrum was resulting from great influence of external environment.
Figure S7. UV-vis spectra for nitro-amination reaction of 4-NP without catalyst.

Figure S7 presents the spectra of blank experiment, which performed the reduction of 4-NP at room temperature and ambient atmosphere by employing excess NaBH₄ without any catalysts in the reaction. The absorption peak at 400 nm represents 4-NP, and the peak intensity remains unchanged over time and shows a series of overlapped spectra, indicating the reaction can’t take place without catalyst involving in the reaction.
Figure S8. Plots of $\ln(C_t/C_0)$ versus time for the amination reaction of 4-NP catalyzed by NiCu-SiO$_2$ nanocomposite obtained by different reducing conditions.

Table S1. Comparison of the catalytic performance of NiCu-SiO$_2$ nanocomposite obtained by different reducing conditions.

<table>
<thead>
<tr>
<th>Reducing conditions</th>
<th>$k$</th>
<th>No. of cycle</th>
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<tbody>
<tr>
<td>700°C 2h</td>
<td>0.0905</td>
<td>12</td>
</tr>
<tr>
<td>600°C 8h</td>
<td>0.0996</td>
<td>13</td>
</tr>
<tr>
<td>600°C 5h</td>
<td>0.1138</td>
<td>23</td>
</tr>
<tr>
<td>600°C 2h</td>
<td>0.0653</td>
<td>20</td>
</tr>
<tr>
<td>500°C 8h</td>
<td>0.0803</td>
<td>15</td>
</tr>
<tr>
<td>500°C 5h</td>
<td>0.0680</td>
<td>20</td>
</tr>
<tr>
<td>500°C 2h</td>
<td>0.0296</td>
<td>18</td>
</tr>
</tbody>
</table>

Figure S8 and Table S1 present the catalytic performance of NiCu-SiO$_2$ nanocomposite obtained by different reducing conditions. We found that NiCu-SiO$_2$ nanocomposite obtained by reducing at 600°C for 5h possesses the best catalytic activity and stability. When reducing condition were 700°C 2h, 600°C 8h and 500°C 8h, NiCu NPs size of NiCu-SiO$_2$ nanocomposite was bigger than others (Figure S2), which eventually leads to easier aggregation of NiCu NPs and shows worse catalytic stability. In addition, when reduced at 600°C for 2h, 500°C for 5h and 500°C for 2h, especially 500°C for 2h, the rate constants $k$ was only 0.0296 which is much lower than others, because only a fraction of NiCu alloy NPs can be obtained, as shown in Figure S2A.
The morphology of NiCu-SiO$_2$ nanocomposite after long-term recycling tests was also monitored and shown in Figure S9. From the SEM image (Figure S9A) we can clearly see that after long-term recyclability tests, the NiCu-SiO$_2$ nanocomposite still remained 2D structure. However, the TEM image in Figure S9B shows that NiCu NPs were coated by a layer of nanosheets, which explains the slight deactivation of NiCu-SiO$_2$ nanocomposite after 20 times successive catalytic tests.
Figure S10. Comparison of XPS analysis of NiCu-SiO$_2$ nanocomposite before (top line) and after (bottom line) long-term recycling tests.

Table S2. Comparison of atom percentages of NiCu-SiO$_2$ nanocomposite before and after long-term recycling tests.

<table>
<thead>
<tr>
<th>catalysts</th>
<th>Atom Percentages (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>Before catalytic</td>
<td>43.37</td>
</tr>
<tr>
<td>After catalytic</td>
<td>34.13</td>
</tr>
</tbody>
</table>

As the TEM image in Figure S9B shows that after 20 times successive catalytic tests NiCu NPs of NiCu-SiO$_2$ nanocomposite were coated by a layer of nanosheets. To confirm the composition of surface-covered nanosheets, the XPS analysis of NiCu-SiO$_2$ nanocomposite after tests was also measured. As shown in Figure S10 and Table S2, we can observed that Si content of the nanocomposite surface increased after long-cycling tests, meanwhile, Ni and Cu content decreased. Thus we conclude the nanosheets covered on NiCu NPs is SiO$_2$. 
The morphology of NiCu alloy NPs after 5 times successive catalytic tests was also monitored and shown in Figure S11. The SEM and TEM images show a quite easy agglomeration compared with NiCu-SiO$_2$ nanocomposite, which eventually leads to the catalyst invalid, indicating the catalytic stability can be efficiently promoted by embedding NiCu alloy NPs in SiO$_2$ membrane.
For more comprehensively evaluating the catalytic performance of 2D structured NiCu-SiO$_2$ nanocatalyst, different nitroarenes have been designated as the catalytic substrates and the UV-Vis adsorption spectra were presented in Figure S12. It can be observed that most substrates can be converted completely, and the rate constants $k$ of all these reactions reached a favorable level. In addition, as shown in Table 1 the selectivity are all above 90%. It revealed the excellent universality of the as-prepared 2D structured NiCu-SiO$_2$ nanocatalyst for the nitro-amination reaction.