Supporting Information

Copper Nanoparticles Modified Silicon Nanowires with Enhanced Cross-coupling Catalytic Ability

SiNWs were fabricated by oxide-assisted growth via thermal evaporation of silicon monoxide power and the detailed preparation process can be found elsewhere. The oxide layer of the as-grown SiNWs was removed by 2% HF etching for 10 min, under N₂ protection. Then rinsed with distilled water and immersed into 5 mL 1×10⁻³ M CuSO₄ aqueous solution. When the yellow SiNWs turned ashy gradually, they were modified with Cu nanoparticles. The product (Cu@SiNWs) was then rinsed lightly by distilled water.

The EDX of CuNPs@SiNWs (Fig. S1, inset) show no peaks of other element except Si, Cu and O, indicating the high purity of the product. The peaks of Si is much higher than that of Cu, and the atomic ratio of silicon to copper is close to 7:1 calculated from the spectrum, which clearly reveals the content of Cu in CuNPs@SiNWs.

![EDX of CuNPs@SiNWs](image)

**Fig. S1** EDX of CuNPs@SiNWs.
The coupling reaction of aniline and benzene halides using the as-prepared CuNPs@SiNWs as the catalyst, DMSO as the solvent, was performed under N₂ protection. The reaction was shown as follows:

\[
\begin{align*}
\text{Ar-X} + \text{H}_{2}\text{N} & \xrightarrow{\text{CuNPs@SiNWs, DMSO, N₂, KOH, 110°C}} \text{Ar-NAr} \\
\text{X} & = \text{I, Br, Cl}
\end{align*}
\]

The mixed solution was heated at 110°C for 18 h and the progress of the reaction was monitored by thin-layer chromatography. After the reaction, the mixture was treated with 5 mL ethyl acetate and 2 mL water, and the aqueous layer was separated and extracted with ethyl acetate. The combined organic solution was dried with Na₂SO₄ and purified on silica gel column chromatography using ethyl acetate and hexane as eluent. The conversion yields of product were calculated.

**Table S1** Test of catalytic activity of CuNPs@SiNWs for coupling reaction

<table>
<thead>
<tr>
<th>entry</th>
<th>Aryl halides</th>
<th>Aniline</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{Ar-I})</td>
<td>(\text{H}_{2}\text{NH})</td>
<td>CuNPs@SiNWs</td>
<td>18</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>(\text{Ar-Br})</td>
<td>(\text{H}_{2}\text{NH})</td>
<td>CuNPs@SiNWs</td>
<td>18</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>(\text{Ar-Cl})</td>
<td>(\text{H}_{2}\text{NH})</td>
<td>CuNPs@SiNWs</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>(\text{Ar-Cl})</td>
<td>(\text{H}_{2}\text{NH})</td>
<td>SiNWs</td>
<td>24</td>
<td>nr</td>
</tr>
</tbody>
</table>