Supporting Information

Scalable synthesis of copper submicron/nanoplates with high stability and their recyclable superior catalytic activity towards 4-nitrophenol reduction

Yang Sun  Li Xu  Zhilei Yin  Xinyu Song*

Fig.S1 The size distribution of copper submicroplates as-prepared (pH=4.5) in a typical synthesis

Fig.S2 (a-b) HR-TEM images of a triangular copper submicroplate.
Fig. S3 TEM images of Cu$_2$O sampled at different pH of the initial reaction solution:

(a) pH~7.0, (b) pH~8.0, (c) pH~9.0, (d) pH~10.0.

\[
\begin{array}{c}
\text{H-O-P-O} \\
\text{H} \\
\end{array} \xrightarrow{k_1} \frac{1}{k_2} \begin{array}{c}
\text{H-O-P-O} \\
\text{H} \\
\end{array}
\]

Normal state metastable state

Fig. S4 The structure changes of NaH$_2$PO$_2$ with variation of the pH in aqueous solution

Fig. S5 XRD pattern of the obtained copper nanoplates at pH~9.0 reacting with 28 hours
Section 1:

The secondary reaction can be expressed by:

$$2H_2PO_2^- + H^+ = P + HPO_3^- + H_2O + 1/2H_2$$

With the large amount of $H^+$ ions in solution and the continuous generated $H^+$ ions from the $H_2PO_2^-$, part of sodium hypophosphate would react with $H^+$ and finally convert into $HPO_3^-$ and $P$. Therefore $NaH_2PO_2$ as reductant in the solution (pH=4.0) can’t reduce copper ion completely and the products obtained were the compound of Cu and $Cu_2O$. If the amount of $NaH_2PO_2$ was increased twice at pH~4.0, the copper product was obtained that proved in Fig. S6.

![XRD pattern of the obtained copper nanoplates at pH~4.0, adding twice amount of NaH$_2$PO$_2$ to solution](image1)

**Fig. S6** XRD pattern of the obtained copper nanoplates at pH~4.0, adding twice amount of NaH$_2$PO$_2$ to solution

![Size distribution of copper nanoplates and percentage of circular and triangular nanoplates & small nanoparticles](image2)

**Fig. S7** (a) The size distribution of copper nanoplates as-prepared with 0.35g KNaC$_4$H$_6$O$_6$

(b) Percentage of circular and triangular nanoplates & small nanoparticles
Fig. S8  TEM images of the Cu plates synthesized with different concentration of sodium potassium tartrate: (a) ~ (b) 1.75 g, (c) ~ (d) 2.10 g

Section 2:

The interaction energies (U) were calculated, expressed by:

$$U = E_{\text{total}} - (E_{\text{surface}} + E_{\text{polymer}})$$

where $E_{\text{total}}$ is the total energy of the Cu-surfactant system, $E_{\text{surface}}$ is the surface energy without the surfactant, $E_{\text{polymer}}$ is the energy of PVP molecules.
Fig. S9  The MD simulation shows PVP adsorbed on each of the copper surfaces

(a) (100), (b) (110) and (c) (111)
Fig. S10 TEM images of the synthesized copper submicroscale products at different stages: (a) 2h, (b) 4h, (c) 6h and (d) 8h

Fig. S11 Successive UV–Vis spectra of the different copper samples: (a) fresh Cu-1, Cu-1 after stored several months (b) fresh Cu-1, Cu-2 after stored several months
Table S1 Results of the reduction rate of 4-NP at room temperature catalyzed by the different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>k (min⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>Cu-1 (obtained with 1.05g KNaC₄H₄O₆)</td>
<td>0.340</td>
</tr>
<tr>
<td>Cu-2 (obtained with 0.35g KNaC₄H₄O₆)</td>
<td>0.373</td>
</tr>
<tr>
<td>Cu-3 (obtained with Na-citrate)</td>
<td>0.202</td>
</tr>
<tr>
<td>Cu-4 (commercial Cu powder)</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Fig. S12 Successive UV–Vis spectra of solutions of 4-NP sampled converted into 4-AP at different time with catalyst Cu-1.

Conditions: [4-NP] =5.0×10⁻⁴ M; Cu=0.07mg; [NaBH₄] =3.0×10⁻² M; with T=25℃
Fig. S13  Absorbance ln(A) vs. time plot for the reduction of 4-NP with Cu-1

Fig. S14  Successive UV–Vis spectra of the reduction reaction after several months
(a) the copper catalyst in size 180~280 nm, (b) the copper nanocatalyst within 25~45 nm
**Fig. S15** Absorbance ln(A) vs. time plot for the reduction of 4-NP in the presence of solid catalyst: (a) the fresh Cu-1, (b) the fresh Cu-2, (c) the Cu-1 storing for 2 months, (d) Cu-2 storing for 2 months,

**Fig. S16** TEM image of the used Cu as catalyst