Supporting information

Cu$_2$O mesoporous spheres with high internal diffusion capacity and improved catalytic ability for aza-Henry reaction driven by visible light

Jun Wang, Jingwen Ma, Xiaojie Li, Yang Li, Guoliang Zhang, Fengbao Zhang, and Xiaobin Fan*

State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China, E-mail: xiaobinfan@tju.edu.cn
1. EXPERIMENTAL SECTION

1.1 Materials and instruments

Unless otherwise stated, all chemical materials were purchased from commercial sources and used without further purification. X-ray power diffraction (XRD) analysis was conducted on a Bruker advance-D8 power diffractometer with Cu Kα radiation (λ=0.154178 nm). Field-emission scanning electron microscopic (FESEM) images were performed on a Hitachi S-4800 microscope operating at 5 kV. Transmission electron microscopic (TEM) images and high-resolution transmission electron microscopic (HRTEM) images were obtained on a JEM-2011F microscope with accelerating voltage of 200 kV and a JEOL JEM-3010 microscope operated at 200 kV, respectively. The nitrogen adsorption-desorption isotherms were collected on an ASAP2010 apparatus at 77 K. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore-size distributions was derived from the adsorption using the Barrett-Joyner-Halenda (BJH) theory.

1.2 Synthesis of Cu₂O spheres

The porous Cu₂O nanospheres with small pore size (SP-Cu₂O) were prepared according to template synthetic process with some modification. Typically, 0.5 g triblock copolymer pluronic P123 (MW 5800) was firstly dissolved in 40 ml deionized water at 293 K under constant stirring for at least 5 h. Then, 3 mL of 0.2 M Cu(NH₃)₄²⁺ solution (10:1, NH₃:Cu²⁺) was poured into the solution of P123 solution under constant stirring. After 40 min, 6 mL of 0.6 M ascobic acid solution was added dropwise into the above mixture, during this procedure, the reaction underwent a series of color changes from deepblue, lightblue, limpid, white turbid, and finally to yellow turbid. After stirring for 40 min, the resulting precipitate was collected by centrifuging,
washed with ethanol at 333 K overnight to remove the P123 and finally dried in vacuum at 333 K for 4 h.

The porous Cu$_2$O nanospheres with large pore size (LP-Cu$_2$O) were prepared using the etching method. Typically, 5 mg of the as prepared SP-Cu$_2$O was added into 10 mL of the ethanol solution containing 1.2 mg/mL of L-proline under constant stirring. After 8 h, the precipitate was collected by centrifuging, washed several times with distilled water and ethanol, and finally dried in vacuum at 333 K for 4 h.

1.3 Representative procedure for aza-Henry reaction.

Table. S1 Parameters of products.

<table>
<thead>
<tr>
<th>Product</th>
<th>R$_f$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Product Image]</td>
<td>0.5</td>
<td>Yellow solid</td>
</tr>
<tr>
<td>![Product Image]</td>
<td>0.6</td>
<td>Yellow oil</td>
</tr>
<tr>
<td>![Product Image]</td>
<td>0.6</td>
<td>Yellow oil</td>
</tr>
<tr>
<td>![Product Image]</td>
<td>0.4</td>
<td>Yellow solid</td>
</tr>
</tbody>
</table>
Fig. S1 SEM image of LP-Cu_2O with longer etching time.

Fig. S2 XRD patterns of the as prepared SP-Cu_2O and LP-Cu_2O.
Fig. S3 The apparatus of photocatalytic aza-Henry reaction.

Fig. S4 SEM image of LP-Cu$_2$O after 5 cycles.
