Electronic Supplementary Information (ESI)

Hollow Cu-TiO$_2$/C Nanospheres Derived from Encapsulated MOF coating for Efficient Photocatalytic Hydrogen Evolution

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Figure S1. TEM images of SiO$_2$@HKUST-1 and TEM element mapping of Si, C, O and Cu in SiO$_2$@HKUST-1 nanospheres.
Figure S2. TEM EDS of SiO$_2$@HKUST-1 nanospheres (Mo net was used as the support).
Figure S3. The TEM EDS of SiO$_2$@HKUST-1-Ti nanospheres (Mo net was used as the support).
<table>
<thead>
<tr>
<th></th>
<th>Percentage of Ti</th>
<th>Percentage of Cu</th>
<th>Amount of sample for photocatalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$@HKUST-1</td>
<td>0</td>
<td>1.05 %</td>
<td>265 mg</td>
</tr>
<tr>
<td>SiO$_2$@HKUST-1-Ti</td>
<td>1.13 %</td>
<td>1.03 %</td>
<td>265 mg</td>
</tr>
<tr>
<td>SiO$_2$@Cu-TiO$_2$/C</td>
<td>1.19%</td>
<td>1.14%</td>
<td>265 mg</td>
</tr>
<tr>
<td>Hollow Cu-TiO$_2$/C</td>
<td>30.4 %</td>
<td>27.7 %</td>
<td>5 mg</td>
</tr>
<tr>
<td>Cu-TiO$_2$/C</td>
<td>30.4 %</td>
<td>27.7 %</td>
<td>5 mg</td>
</tr>
<tr>
<td>P25</td>
<td>60 %</td>
<td>0</td>
<td>5 mg</td>
</tr>
<tr>
<td>HKUST-1-800</td>
<td>0</td>
<td>58.5%</td>
<td>5 mg</td>
</tr>
<tr>
<td>P25+HKUST-1-800</td>
<td>30.4 %</td>
<td>27.7%</td>
<td>5 mg</td>
</tr>
</tbody>
</table>

**Table S1.** The ICP result of Ti and Cu percentage in sample of SiO$_2$@HKUST-1-Ti, SiO$_2$@Cu-TiO$_2$/C and Hollow Cu-TiO$_2$/C as well as the amount of the sample for photocatalytic experiments.
Figure S4. The XPS spectra of hollow Cu-TiO$_2$/C nanospheres.
**Figure S5.** The XRD of the obtained $\text{SiO}_2@\text{Cu-TiO}_2/C$. 
Figure S6. ESR spectra analyzed in air at room temperature for hollow Cu-TiO$_2$/C nanospheres.
**Figure S7.** The UV-vis absorption spectra band gaps of P25, SiO$_2$@HKUST-1, SiO$_2$@HKUST-1-Ti, SiO$_2$@TiO$_2$-Cu/C and hollow Cu-TiO$_2$/C nanospheres.
Figure S8. The UV-vis absorption comparison of P25+HKUST-1-800 (mixture of P25 and calcinated HKUST-1) and hollow Cu-TiO$_2$/C nanospheres.

In order to demonstrate the existence of p-n junction in the catalysis, the UV-vis absorption spectra of two sample with the same Cu/Ti ratio, one was hollow Cu-TiO$_2$/C nanospheres, another was mixture of P25 and calcinated HKUST-1 (named P25+HKUST-1-800) was studied. The absorption edge of P25+HKUST-1-800 (mixture of P25 and calcinated HKUST-1) and hollow Cu-TiO$_2$/C were ~380 and ~430 nm respectively, indicating an obvious shift from UV region to the visible region. Meanwhile, their related band gaps decreased from 3.3 to 2.89 eV. This phenomenon may be attributed to the p-n hetero-junction formation between Cu$_2$O and TiO$_2$ in hollow Cu-TiO$_2$/C after calcination treatment.
Figure S9. The TEM images with element mapping and EDS of hollow Cu-TiO$_2$/C nanospheres after photocatalytic activity (Mo net was used as the support).
Figure S10. illustration of the band structure and electron transfer process of hollow Cu-TiO$_2$/C nanospheres during the photocatalytic experiment.