Supporting Information

One-Step Preparation of Hollow ZnO Core/ZnS Shell Structures with Enhanced Photocatalytic Properties

Wei Chen, Hong Ruan, Yin Hu, Danzhen Li*, Zhixin Chen, Jiangjun Xian, Jing Chen, Xianzhi Fu, Yu Shao and Yi Zheng

Research Institute of Photocatalysis, National Research Center of Environmental Photocatalysis, Fujian Provincial Key Laboratory of Photocatalysis-State Key Laboratory Breeding Base, Fuzhou University, Fuzhou 350002, P. R. China

Fig. S1 XPS spectra of ZnOS15, pZnO and pZnS: (a) O1s spectrum of ZnOS15, (b) S2p spectrum of ZnOS15 and (c) Zn2p spectra of ZnOS15, pZnO and pZnS.
**Experimental details of the reactions conducted at low temperatures**

All of the nutrient solution used below was prepared as described in experimental section within the main text: 0.1854 g (1 mmol) dodecylamine (DDA) was added into 60 ml deionized water followed by vigorous stir for two hours of above. When it became suspension, 60 ml deionized water solution contained 5.9476 g (20 mmol) Zn(NO$_3$)$_2$·6H$_2$O was added. Then 40 ml of 0.75 M thiourea solution was added into the mixture above. Three samples were synthesized at 80 °C for 1, 3 and 5 min, respectively. And other samples were prepared at 85 °C (90 °C, 100 °C) for 20 s, 1 and 5 min, respectively.

![Fig. S2](image_url) The morphological evolution of bifid structures varies with time under different reaction temperatures. (a$_1$ ~ a$_3$) The samples obtained at 80 °C for 1, 3 and 5 min, respectively. (b$_1$ ~ b$_3$) The samples obtained at 85 °C for 20 s, 1 and 5 min, respectively. (c$_1$ ~ c$_3$) The samples obtained at 90 °C for 20 s, 1 and 5 min, respectively. (d$_1$ ~ d$_3$) The samples obtained at 100 °C for 20 s, 1 and 5 min, respectively.
Experimental details of the preparation of ZnOS NS

All of the reagents are analytical-grade and used without further purification. In a typical procedure, 5.95 g Zn(NO$_3$)$_2$$\cdot$6H$_2$O was mixed with 0.76 g CH$_4$N$_2$S in 50 mL deionized water to form a clear solution. After that, 5 mL aqueous ammonia (NH$_3$·H$_2$O) was added to adjust the pH value of the solution to about 7.5. Then, the mixture was finally loaded into a 100 mL Teflon-lined autoclave and maintained at 120 °C for 4 h. After cooling to room temperature naturally, the product was collected, washed with deionized water and absolute ethyl alcohol several times, and finally dried in air at 80 °C.

Fig. S3 XRD patterns of ZnOS15 and ZnOS NS (a) and FE-SEM image of ZnOS NS (b).
Experimental details of the photocatalytic degradation of MO

The photocatalytic degradations of MO (30 µmol L⁻¹) aqueous solution were conducted in a quartz tube with 4.6 cm inner diameter and 17 cm length. Four 4 W UV lamps with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5) were used as the irradiation source. A photocatalyst (40 mg) was suspended in 80 mL of MO solution and stirred for 30 min to ensure the establishment of adsorption-desorption equilibrium. An aliquot (3 mL) was taken at a certain time interval during the experiment and centrifuged (TDL-5-A) to remove the powders. The filtrates were analyzed on a Varian UV-vis spectrophotometer (Cary 50, Varian Co.). The percentage of degradation is reported as C/C₀. C is the absorption of pollutants at each irradiated time interval of the main peak of the absorption spectrum. C₀ is the absorption of the initial concentration when adsorption-desorption equilibrium was achieved.

![Photocatalytic activities of the representative photocatalysts for the degradation of MO solution under 254 nm UV light irradiation.](image_url)

**Fig. S4** Photocatalytic activities of the representative photocatalysts for the degradation of MO solution under 254 nm UV light irradiation.
**Fig. S5** XRD patterns of ZnOS15 before and after photocatalytic reaction.

**Fig. S6** FE-SEM images of ZnOS15 before (a) and after (b) photocatalytic reaction.
Table S1  The concentrations of Zn$^{2+}$ in some reaction systems before and after different times of irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before irradiation (μg·mL$^{-1}$)</th>
<th>After 30 min irradiation (μg·mL$^{-1}$)</th>
<th>After 90 min irradiation (μg·mL$^{-1}$)</th>
<th>After 120 min irradiation (μg·mL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CP solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnOS15</td>
<td>9.700</td>
<td>108.900</td>
<td>110.325</td>
<td>112.400</td>
</tr>
<tr>
<td>ZnO</td>
<td>9.000</td>
<td>147.000</td>
<td>179.950</td>
<td>191.050</td>
</tr>
<tr>
<td>Aqueous solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnOS15</td>
<td>15.700</td>
<td>81.600</td>
<td>99.500</td>
<td>114.850</td>
</tr>
</tbody>
</table>