Visible light-driven selective carbon-carbon bond formation for
production of vicinal diol

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Supporting Information

1. Experimental section

1.1 Materials and instruments

ZnSO$_4$·7H$_2$O, cetyltrimethylammonium bromide (CTAB), polyethylene glycol 6000 (PEG-6000) and benzyl alcohol were commercially available from Tianjin Guangfu Fine Chemical Research Institute. InCl$_3$·4H$_2$O and thioacetamide (TAA) were purchased from Aladdin Chemistry Co., Ltd.. All chemicals were of analytical grade and used without further treatment. All the solvents were extra-dry solvents, and purchased from Saen Chemical Technology (Shanghai) Co., Ltd..

Quantitative analyses of the products were performed on a GC device with a FID detector and the capillary column is HP-5MS, 30 m×0.25 mm×0.25 μm. The structures of main products were determined by Agilent 6890/5973 Gas Chromatography-Mass Spectrometer (GC-MS) instrument and NMR analysis. The light source is a CEL-LED100, which is a blue LED lamp with a single wavelength of $\lambda = 455$ nm, purchased from Beijing China Education Au-light Co., Ltd..

1.2 Preparation of catalyst

1.2.1 Synthesis of ZnIn$_2$S$_4$ photocatalyst

Typically, 0.2940 g of ZnSO$_4$·7H$_2$O and 0.6242 g of InCl$_3$·4H$_2$O were dissolved in 20 mL of deionized water under magnetic stirring. After 10 min, 0.6048 g of TAA was added under stirring until it was dissolved completely. Subsequently, the resulting mixture was transferred into a 50 mL Teflon-sealed autoclave and maintained at 160 °C for 16 h. After being cooled down to room
temperature naturally, the yellow precipitates were collected and washed several times with deionized water and ethanol by the centrifugation. Finally, the obtained sample was dried under a vacuum at 60 °C for 4 h.

1.2.2 Synthesis of ZnIn$_2$S$_4$-C and ZnIn$_2$S$_4$-P photocatalyst

The ZnIn$_2$S$_4$ catalyst is further modified through using different reagents in order to obtain the catalyst with more balanced electron and holes effect [S1], where the ionic surfactant CTAB and the nonionic surfactant PEG-6000 were employed to regulate the photocatalytic abilities of ZnIn$_2$S$_4$ semiconductor, respectively.

The modified ZnIn$_2$S$_4$ photocatalyst were prepared using a similar procedure as the synthesis of usual ZnIn$_2$S$_4$ except that the ionic surfactant CTAB and the nonionic surfactant PEG-6000 was added as modifier, respectively. Particularly, 0.2940 g of ZnSO$_4$·7H$_2$O and 0.6242 g of InCl$_3$·4H$_2$O were dissolved in 20 mL of deionized water under magnetic stirring. After 10 min, 0.6048 g of TAA was added under stirring until it was dissolved completely. Next, 0.2606 g of CTAB or 0.4418 g of PEG-6000 was added into the solution under magnetic stirring, respectively, and the sample obtained was named as ZnIn$_2$S$_4$-C or ZnIn$_2$S$_4$-P, respectively. Subsequently, the resulting mixture was transferred into a 50 mL Teflon-sealed autoclave and maintained at 160 °C for 16 h. After being cooled down to room temperature naturally, the yellow precipitates were collected and washed several times with deionized water and ethanol by the centrifugation. Finally, the obtained sample was dried under a vacuum at 60 °C for 4 h.

1.3 The characterization of catalyst

The X-ray powder diffraction (XRD) patterns of samples were measured on a Rigaku D/max-III A diffractometer, using Cu Kα as the radiation source with $\lambda = 1.54056$ Å, in the range from 5° to 80° (20). The morphology of catalyst is determined by the scanning electron microscope (SEM: JSM-6301F, JEOL) equipped with a JED-2300 (JEOL) EDXS spectrometer for chemical element analysis. X-ray photoelectron spectra (XPS) is recorded on a KRATOS AXIS 165 with a dual X-ray anode (Mg and Al) and the obtained XPS results are provided using the Mg Kα line. BET surface areas, pore volumes, and average pore diameters of the samples are obtained from N$_2$ adsorption measurement using a Micro-meritics ASAP2020M system. UV-Vis spectra are detected on the Hitachi-3900 UV-Vis Spectrophotometer in the range of 200-800 nm. Electron paramagnetic resonance (EPR) spectra are obtained on an EPR Spectrometer (EMXplus-6/1, Bruker, Germany)
using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trap reagent. Time-resolved fluorescence (TRF) emission decay spectrum is performed on a Microtime 200 spectrometer.

The photoelectrochemical measurements were performed on a CHI-760E electrochemical workstation (Shanghai Chenhua Instruments Company, China) using a conventional three-electrode. The used photoelectrodes were prepared as follows. 50 mg of the as-prepared photocatalyst powder was dispersed into 600 μL of ethanol and 400 μL Nafion under ultrasonication. Then, the mixture was coated onto a 1.5 × 2.0 cm² FTO glass electrode and dried at 60 °C. Meanwhile, Pt electrode and Ag/AgCl electrode were respectively employed as the electrode and reference electrode. The electrochemical impedance spectroscopy (EIS) was tested in a 0.5 M Na₂SO₄ aqueous solution in the range from 100,000 to 0.01 Hz. Photoelectrochemical response test was carried out on an electrochemical workstation in a three-electrode cell with 0.5 M Na₂SO₄ as electrolyte at room temperature under the visible light.

1.4 Photocatalytic selective coupling of benzylic alcohols

All photocatalytic selective coupling processes are conducted with a 120 mL autoclave equipped with a glass window under the magnetic stirring. A typical procedure for the selective coupling of benzyl alcohol is as follows: 0.1 g of benzyl alcohol, 0.05 g of photocatalyst and 10 mL of extra-dry solvent are added into the reactor, and the atmosphere inside is replaced three times by argon gas after being sealed. Then, pure argon is charged to 0.1 MPa at room temperature. Subsequently, the mixed solution is irradiated through the window of autoclave by a blue LED lamp with light intensity of 33 mW under stirring, and then is kept for 6 h. After reaction, the excess gas is purged, and the mixture is transferred into a 100 mL volumetric flask, in which the reactor is washed using the solvent for 3-5 times in order to transfer the mixture completely. The obtained products are analyzed with internal standard technique by GC with a flame ionization detector (all products are determined on GC-MS with an Agilent 6890N GC/5973 MS detector).

2. The characterization of catalysts

2.1 XRD patterns

As exemplified in Figure S1, the crystalline structure of the ZnIn₂S₄, ZnIn₂S₄-C and ZnIn₂S₄-P samples were systemically characterized by means of XRD. It can be seen from the XRD pattern...
that the peak of the ZnIn$_2$S$_4$ sample is in good agreement with the standard pattern of the hexagonal ZnIn$_2$S$_4$ (ICDD-JCPDS card No. 72-0773), indicating that the sample is high pure without other impurities. The diffraction peaks at the 2θ values of 21.5°, 27.6°, 40.9°, 47.1°, 52.4°, 55.5° and 76.4° can be indexed to the (006), (102), (108), (110), (116), (202) and (213) plane of ZnIn$_2$S$_4$, respectively, which is consistent with the literature reported [S2]. However, when ZnIn$_2$S$_4$ was modified by the surfactant CTAB or PEG-6000, the diffraction peak of the (006) plane was significantly shifted from 21.5° to 20.9°. In addition, a new diffraction peak was produced at 24.3° for the ZnIn$_2$S$_4$-P sample. These results indicate that the addition of the surfactant does modify the structure of ZnIn$_2$S$_4$ which can increase the photocatalytic activity at some extent.

2.2 XPS detection

X-ray photoelectron spectroscopy (XPS) analyses were carried out to elucidate the chemical composition and identify the chemical status of the element in different samples, and the data are shown in Figure S2. It can be seen that the anticipated elements of C, S, In and Zn were detected in the XPS survey spectra of ZnIn$_2$S$_4$ samples, which is consistent with the literature reported [S3], proving the ZnIn$_2$S$_4$ samples are of high purity. Moreover, three main peaks at 161.7, 162.8 and 169.4 eV were observed on the spectrum of S 2p in the ZnIn$_2$S$_4$ sample where the peaks at 161.7 and 162.8 eV can be assigned to divalent sulfide (S$^{2-}$) [S4] and the peak located at 169.4 eV can be attributed to hexavalent sulfur (S$^{6+}$), respectively. Compared with ZnIn$_2$S$_4$ sample, the peak of S 2p$_{3/2}$ at 169.4 eV on the spectrum of ZnIn$_2$S$_4$-C sample became weak, and that on the spectrum of
ZnIn$_2$S$_4$-P samples completely disappeared, suggesting that the structure of ZnIn$_2$S$_4$-C and ZnIn$_2$S$_4$-P samples changed after the introduction of surfactant to modify ZnIn$_2$S$_4$ sample. As for In 3d$_{5/2}$ and In 3d$_{3/2}$ spectra of prepared ZnIn$_2$S$_4$ samples, the peaks at 445.0 and 452.6 eV can be ascribed to In$^{3+}$ species on the samples. In addition, compared with the ZnIn$_2$S$_4$ sample, the In 3d binding energy of the ZnIn$_2$S$_4$-C material became slightly larger, and that of the ZnIn$_2$S$_4$-P material became slightly smaller. Furthermore, the binding energy on Zn 2p spectra of the ZnIn$_2$S$_4$ and ZnIn$_2$S$_4$-C samples is the same, among of them the peaks located at 1022.1 and 1045.1 eV are assigned to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ of the Zn$^{2+}$ component, respectively. However, for Zn 2p of the ZnIn$_2$S$_4$-P sample, located at 1021.7 and 1044.8 eV, two peaks respectively shifted down 0.4 eV and 0.3 eV compared with ZnIn$_2$S$_4$ sample, indicating that ZnIn$_2$S$_4$-P sample can display a better photochemical property. Therefore, all these results showed that the structural and photochemical properties of the ZnIn$_2$S$_4$ sample could be significantly regulated after being modified by the CATB or PEG-6000 surfactant.

Figure S2. XPS spectra of ZnIn$_2$S$_4$ samples [(a) survey scan, (b) S 2p core, (c) In 3d core, (d) Zn 2p core]
2.3 The UV-vis measurements of catalysts

The obtained ZnIn$_2$S$_4$ samples were respectively examined by the UV-Vis technique and the corresponding spectra from 200-800 nm and band gap energy are presented in Figure S3. It can be seen that all the ZnIn$_2$S$_4$ samples have a steep absorption edge located from 400 nm to 500 nm, indicating the photo response may be achieved during the blue light regions. Compared with the ZnIn$_2$S$_4$ catalyst, the ZnIn$_2$S$_4$-C and ZnIn$_2$S$_4$-P samples exhibit a slight blue shift absorption due to the modification of the surfactant during preparation. Meanwhile, it is found that the band gap energy of the ZnIn$_2$S$_4$ catalyst is 2.34 eV, while the value is significantly reduced when it is modified by the surfactant and the band gap energy of ZnIn$_2$S$_4$-P and ZnIn$_2$S$_4$-C sample is 2.09 eV and 2.28 eV, respectively, exhibiting that the catalytic activity of tZnIn$_2$S$_4$-C and ZnIn$_2$S$_4$-P samples can be greatly improved.

![Figure S3](attachment:image.png)

**Figure S3.** The UV-vis spectra (a) and band gap energy (b) of ZnIn$_2$S$_4$ photocatalysts

2.4 The SEM images and BET data of catalysts

In order to investigate the effect of surfactant modification on the morphology and microstructure of ZnIn$_2$S$_4$ sample, the obtained ZnIn$_2$S$_4$ catalysts were characterized by SEM analysis. The corresponding results are displayed in Figure S4. From the images of magnification, it can be seen that the morphology of the ZnIn$_2$S$_4$ sample appears as a large number of adherent flower clusters; however, when the ZnIn$_2$S$_4$ sample was modified with the surfactant PEG-6000, the morphology of the ZnIn$_2$S$_4$-P sample became more dispersed than that of the ZnIn$_2$S$_4$ sample, so its specific surface area was significantly reduced. The flower-like more dispersed sample
ZnIn$_2$S$_4$-P is more conducive to the absorption of blue light and can be beneficial to the adsorption of benzyl alcohol, which explains the decrease of the band gap energy and the increase on catalytic activity of the ZnIn$_2$S$_4$-P sample. In addition, when the ZnIn$_2$S$_4$ sample was modified with the surfactant CTAB, the morphology of the ZnIn$_2$S$_4$-C sample changed to the most dispersed flower sphere, which resulted in the smallest surface area among all the samples. These also caused its photocatalytic activity to be somewhat inhibited. Furthermore, the results of EDX analysis of the ZnIn$_2$S$_4$-P sample indicated that only the S, In and Zn exist on the catalyst surface, which confirms that the material is of high purity.

![Figure S4. SEM images of (a) ZnIn$_2$S$_4$, (b) ZnIn$_2$S$_4$-P and (c) ZnIn$_2$S$_4$-C and (d) EDX spectrum of ZnIn$_2$S$_4$-P](image)

Moreover, the BET data of Table S1 showed that the specific surface area, pore volume and pore size of ZnIn$_2$S$_4$ sample are 73.9 $\text{m}^2/\text{g}$, 0.13 $\text{cm}^3/\text{g}$ and 69.8 Å, respectively. After the ZnIn$_2$S$_4$ sample was modified by different surfactant, the specific surface area and pore volume of the samples were greatly reduced while the size of pore was increased. Among of them, the specific surface area and the pore volume of the ZnIn$_2$S$_4$-P sample were respectively reduced to 27.5 $\text{m}^2/\text{g}$ and 0.068 $\text{cm}^3/\text{g}$; meanwhile, the specific surface area and the pore volume of the ZnIn$_2$S$_4$-C sample was further decreased to 13.9 $\text{m}^2/\text{g}$ and 0.060 $\text{cm}^3/\text{g}$, respectively. Also, it can be clearly seen that the pore size of the ZnIn$_2$S$_4$-P sample was slightly increased to 98.4 Å, whereas the ZnIn$_2$S$_4$-C sample was greatly increased to 171.8 Å. These results indicate that their structures and
catalytic performances of the ZnIn$_2$S$_4$ samples were greatly regulated after being modified.

**Table S1.** The N$_2$ physisorption results of different ZnIn$_2$S$_4$ samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnIn$_2$S$_4$-P</td>
<td>27.5</td>
<td>0.068</td>
<td>98.4</td>
</tr>
<tr>
<td>ZnIn$_2$S$_4$-C</td>
<td>13.9</td>
<td>0.060</td>
<td>171.8</td>
</tr>
<tr>
<td>ZnIn$_2$S$_4$</td>
<td>73.9</td>
<td>0.13</td>
<td>69.8</td>
</tr>
</tbody>
</table>

3. Catalytic test

3.1 The effect of reaction medium on the selective coupling of benzyl alcohol

In order to reveal the influence of solvent on the photocatalytic selective coupling of benzyl alcohol, five kinds of extra-dry solvents, including dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile (ACN), dichloromethane (DCM) and N, N-dimethylformamide (DMF), were investigated as reaction medium, and the results are presented in Figure S5. When the DMSO was employed as the solvent, the conversion of 1 was only 34.5% in which the main product was compound 3. Then, THF, ACN and DCM were also used as the solvent; as a result, all the obtained main products were compound 2, where the conversion of 1 were respectively 38.4%, 49.7% and 79.0%, and the selectivity of 2 were 87.5%, 72.6% and 54.8%, respectively. Finally, when the photocatalytic selective coupling of benzyl alcohol reaction was carried out in DMF, the conversion of 1 was as high as 92.2% and the selectivity of 2 was 92.9%, indicating that DMF is the best reaction medium for the selective coupling of benzyl alcohol under blue light irradiation.
Figure S5. The effect of reaction medium for the coupling of benzyl alcohol (Reaction conditions: 0.1 g of benzyl alcohol, 50 mg of catalyst, in 10 mL extra-dry solvent, under 0.1 MPa of Ar, using LED lamp with a wavelength of 455 nm and light intensity of 33 mW, 6 h, 25 °C)

3.2 The effects of light intensity and reaction time on the selective coupling of benzyl alcohol

The effects of light intensity and reaction time on the conversion of benzyl alcohol were further studied, and the results are summarized in the Figure S6. It can be seen that the conversion of 1 and the selectivity of 2 increased as the light intensity was gradually increased, demonstrating that enhancing the light intensity is advantageous for the selective coupling of benzyl alcohol with the ZnIn$_2$S$_4$-P photocatalyst. Moreover, seen from the effect of the illumination time of blue light on the selective coupling reaction, the conversion of 1 and the selectivity of 2 were respectively 18.2% and 77.2% when the reaction time was 2 h. Then, when the reaction time was extended to 4 h and 6 h, the conversion of 1 gradually increased to 68.7% and 92.2%; also, the selectivity of 2 was further increased to 87.1% and 92.9%, respectively. It is worth noting that when the reaction time was extended to 8 h, the compound 1 was fully converted, but the selectivity of 2 was slightly reduced to 86.5%. When the reaction time was further prolonged to 12 h, the conversion of 1 was 92.0% and the selectivity of 2 was about 88.0%. Herein, this phenomenon illustrates that the selective coupling of benzyl alcohol should be reversible and the compound 2 is probably decomposed if the
overlong time light irradiation was performed. Thus, the best reaction time for the production of compound 2 is 6 h in the selective coupling of benzyl alcohol under the argon gas.

![Figure S6](image)

Figure S6. The effects of light intensity (a) and reaction time (b) on the selective coupling of benzyl alcohol (Reaction conditions: 0.1 g of benzyl alcohol, 50 mg of catalyst, in 10 mL extra-dry DMF, under 0.1 MPa of Ar, using LED lamp with a wavelength of 455 nm and light intensity of 33 mW (b), 6 h (a), 25 °C)

3.3 The effect of the amount of PEG-6000 on the photocatalytic activity of ZnIn$_2$S$_4$-P sample

Table S2 shows the effect of the amount of PEG-6000 on the photocatalytic activity of ZnIn$_2$S$_4$-P sample. As a result, the catalytic activity is first elevated and then declined along with the increase of the amount of PEG-6000, and the best value was 0.4418 g for the preparation of the ZnIn$_2$S$_4$-P catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of PEG-6000 (g)</th>
<th>Conversion (%)$^b$</th>
<th>Selectivity (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2209</td>
<td>70.6</td>
<td>91.1</td>
</tr>
<tr>
<td>2</td>
<td>0.3314</td>
<td>74.1</td>
<td>90.3</td>
</tr>
<tr>
<td>3</td>
<td>0.4418</td>
<td>92.2</td>
<td>92.9</td>
</tr>
<tr>
<td>4</td>
<td>0.5523</td>
<td>58.6</td>
<td>88.5</td>
</tr>
<tr>
<td>5</td>
<td>0.6627</td>
<td>36.7</td>
<td>91.4</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 0.1 g of benzyl alcohol, 50 mg of catalyst, in 10 mL extra-dry DMF, under 0.1 MPa of Ar, using LED lamp with a wavelength of 455 nm and light intensity of 33 mW, 6 h, 25 °C. $^b$The data are obtained by GC with internal standard technique.
4. The separation of reaction product of selective coupling of benzyl alcohol

After the selective coupling of benzyl alcohol was finished, the reaction mixture was centrifuged 3-5 times to filter off the ZnIn$_2$S$_4$-P catalyst and the resulting relatively clear liquids were collected. Then, the collected reaction liquid was filtered using a syringe with a filter membrane until a fully clear liquid was obtained for the next purification. Then, the obtained liquid mixture was poured into vacuum-rotary evaporation and further treated at 100 °C until all the reaction solvents were put off. At last, the remaining white crude products were collected and further dried under a vacuum oven at 150 °C overnight to obtain the purified hydrobenzoin product. The pictures of purified reaction product hydrobenzoin and the hydrobenzoin from commercial were presented in Figure S7.

![Figure S7](image.png)

Figure S7. The purified reaction product hydrobenzoin (a) and purchased hydrobenzoin from commercial (b)

5. The GC-MS and NMR spectra of products
Figure S8. The GC-MS result for the selective coupling of benzyl alcohol
Figure S9. The $^1$HNMR spectrum for the main product from selective coupling of benzyl alcohol (400 MHz, DMSO-$d_6$) δ 7.30-7.25 (m, 10H) 7.22-7.12 (m, 10H) 5.46 (d, $J$ = 3.9 Hz, 2H) 5.31 (d, $J$ = 4.3 Hz, 2H) 4.64 (d, $J$ = 2.6 Hz, 4H)

Figure S10. $^1$HNMR spectrum for the product from selective coupling of 4-methyl benzyl alcohol (400 MHz, DMSO-$d_6$) δ 7.89 (d, $J$ = 8.2 Hz, 4H) 7.30-7.24 (m, 8H) 7.10 (d, $J$ = 7.9 Hz, 4H) 6.03 (d, $J$ = 5.9 Hz, 2H) 5.88 (d, $J$ = 5.9 Hz, 2H) 2.89 (s, 2H) 2.73 (s, 2H) 2.31 (s, 6H) 2.22 (s, 6H)
Figure S11. $^1$HNMR spectrum for the product from selective coupling of 3-methoxy benzyl alcohol (400 MHz, DMSO-$d_6$) δ 7.18-7.08 (m, 4H) 6.83-6.67 (m, 12H) 5.38-5.33 (m, 2H) 5.23-5.20 (m, 2H) 4.57-4.52 (m, 4H) 3.69 (s, 6H) 3.64 (s, 6H)

Figure S12. $^1$HNMR spectrum for the product from selective coupling of 4-chloro benzyl alcohol (400 MHz, DMSO-$d_6$) δ 7.32-7.29 (m, 4H) 7.26-7.20 (m, 8H) 7.15-7.09 (m, 4H) 5.58-5.52 (m, 2H) 5.46-5.42 (m, 2H) 4.64-4.62 (m, 2H) 4.57-4.55 (m, 2H)
Figure S13. $^1$HNMR spectrum for the main product from the selective coupling of 1-phenylthanol (400 MHz, DMSO-d$_6$) $\delta$ 7.98-7.95 (m, 2H) 7.65-7.62 (m, 1H) 7.54-7.50 (m, 2H) 2.58 (s, 2H)

References