

## Figure captions

**Figure S1 Characterization of photocatalytic products and  $\beta$ -O-4 dimer.**

- (a) HPLC pattern of phenol, benzaldehyde, acetophenone, ppe-one and ppe-ol;
- (b) GC pattern of phenol, benzaldehyde, acetophenone, ppe-one and ppe-ol;
- (c) MS pattern of phenol, benzaldehyde, acetophenone, ppe-one and ppe-ol;
- (d)  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectrum phenol, benzaldehyde, acetophenone, ppe-one and ppe-ol.

**Figure S2 The XRD standard card pattern of traditional hexagonal  $\text{ZnIn}_2\text{S}_4$ -based materials.**

**Figure S3 TEM images of ZIS (a-c), ZIS-Sv<sub>0.2</sub> (d-f), ZIS-Sv<sub>0.4</sub> (g-i), ZIS-Sv<sub>0.6</sub> (j-l), ZIS-Sv<sub>0.8</sub> (m-o), ZIS-Sv<sub>1</sub> (a-c).**

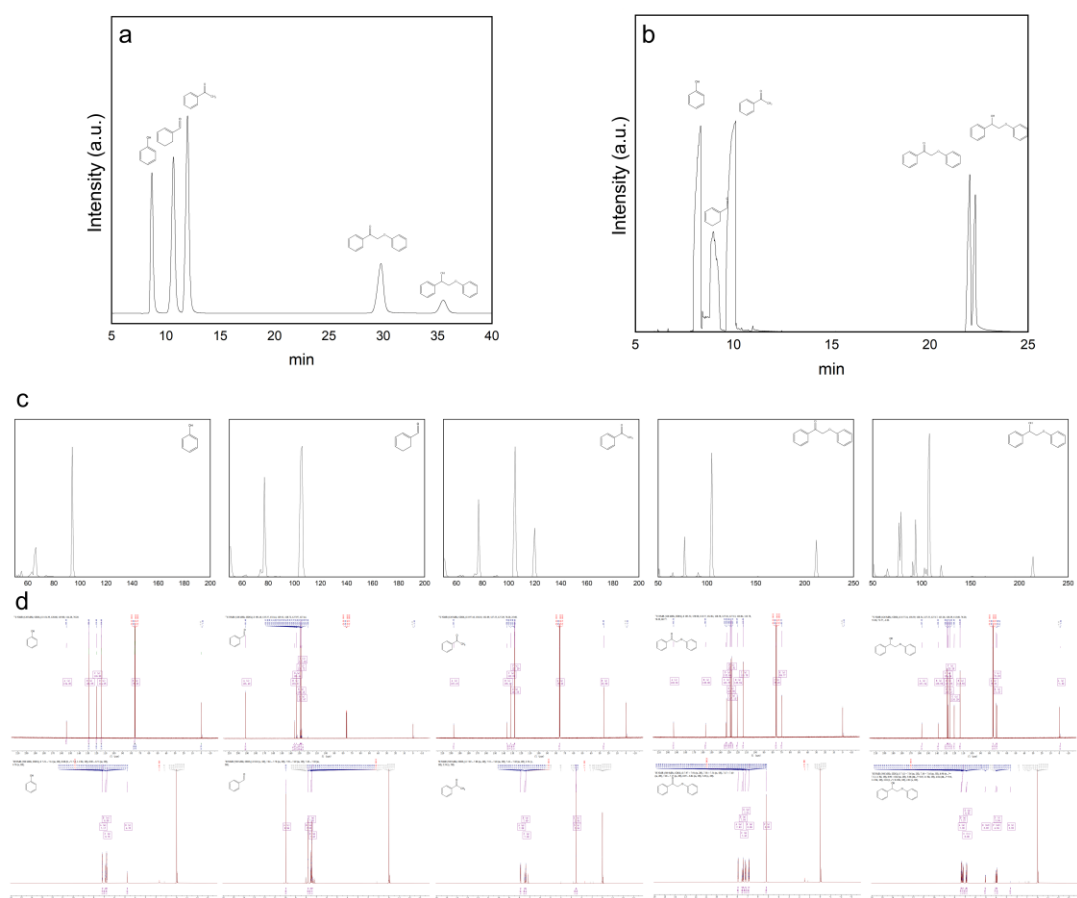
**Figure S4 SEM images of ZIS (a-b), ZIS-Sv<sub>0.2</sub> (c-d), ZIS-Sv<sub>0.4</sub> (e-f), ZIS-Sv<sub>0.6</sub> (g-h), ZIS-Sv<sub>0.8</sub> (i-j), ZIS-Sv<sub>1</sub> (k-l).**

**Figure S5 Characterization of ZIS and ZIS-Sv<sub>0.6</sub>.**

- (a)  $\text{N}_2$  adsorption-desorption isotherms of ZIS and ZIS-Sv<sub>0.6</sub>;
- (b) transient photocurrent responses of ZIS and ZIS-Sv<sub>0.6</sub>;
- (c) CV curves of ZIS and ZIS-Sv<sub>0.6</sub>;
- (d) electrochemical impedance spectroscopy (EIS) of ZIS and ZIS-Sv<sub>0.6</sub>;
- (e) Raman patterns of ZIS and ZIS-Sv<sub>0.6</sub>;
- (f) EPR spectra of ZIS and ZIS-Sv<sub>0.6</sub>;
- (g-h) UV-VIS-IR images of ZIS-Sv<sub>0.6</sub>.

**Figure S6 FTIR spectra of dioxane lignin before and after photocatalytic**

**depolymerization of 12 h by ZIS-Sv<sub>0.6</sub>.**



**Figure S1**

This work involves 5 types of aromatic molecules, including phenol, benzaldehyde, acetophenone, ppe-one, and ppe-ol (order from left to right).

Figure S1a is the HPLC analysis from Agilent 1260 high-performance liquid chromatography (Agilent Technologies, USA). The mobile phase ratio is acetonitrile: water=60:40 (volume ratio), detection temperature is 25 °C, the flow rate is 0.5 mL/min, the detection wavelength is 271 nm, and a single injection of 2.0  $\mu\text{L}$ .

Figure S1b is the GC-MS analysis from Agilent 7890B, which is equipped with an HP-INNOWax chromatography column (column length 30 m, diameter 320  $\mu\text{m}$ , membrane thickness 0.25  $\mu\text{m}$ ), a hydrogen flame ion detector (FID), and a mass spectrometry (MS) model Agilent 5977A. Using  $\text{N}_2$  and He as carrier gases, set the injection volume to 1  $\mu\text{L}$ . During the detection process, the following program was used to raise the temperature: maintain at 150 °C for 5 min, then raise the temperature at a rate of 15 °C /min to 250 °C and maintain it for 20 min. The temperature of both the injector and detector is set to 270 °C.

Figure S1c is MS spectrogram, which represent phenol ( $m/z=94$ ), benzaldehyde ( $m/z=106$ ), acetophenone ( $m/z=120$ ), ppe-one ( $m/z=212$ ) and ppe-ol ( $m/z=214$ ), respectively.

Figure S1d was NMR analysis of phenol, benzaldehyde, acetophenone, ppe-one, and ppe-ol (order from left to right). Meanwhile, the  $^{13}\text{C}$ -NMR spectrums are above and  $^1\text{H}$ -NMR spectrums are below.

**phenol:**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.39, 128.66, 119.80, 114.26, 76.20.

114.26: Two adjacent C atoms connected to substituents on the benzene ring.

119.8: The p-C atom connected to the substituent on the benzene ring.

128.66: Two meta carbon atoms connected to substituents on the benzene ring.

154.39: C atoms connected to substituents on the benzene ring.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 – 7.14 (m, 2H), 6.86 (tt,  $J = 7.5, 1.1$  Hz, 1H), 6.80 – 6.73 (m, 2H), 4.76 (s, 1H).

6.80 – 6.73: H atom connected to adjacent C atom on the benzene ring connected to substituents.

6.86: H atom connected to the p-C atom connected to the substituent on the benzene ring.

7.21 – 7.14: H atom connected to the C atom at the intermediate positions connected to the substituent on the benzene ring.

9.0: H atom on the phenolic hydroxyl group connected to the benzene ring.

**benzaldehyde:**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  191.40, 135.37, 133.44, 129.13, 128.72, 127.97, 127.44.

128.72, 127.97, 127.44: The meta C atom of the substituent on the benzene ring.

129.13: Adjacent C atom of substituent on benzene ring.

133.44: The p-C atom of the substituent on the benzene ring.

135.37: C atoms directly connected by substituents on the benzene ring.

191.40: The C atom on the substituent of the phenyl ring aldehyde group.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.94 (s, 1H), 7.84 – 7.78 (m, 2H), 7.59 – 7.49 (m, 1H), 7.49 – 7.36 (m, 2H).

7.49 – 7.36: H atom connected between aldehyde substituents on the benzene ring.

7.59 – 7.49: H atom connected to the aldehyde substituent on the benzene ring.

7.84 – 7.78: H atom adjacent to aldehyde substituents on the benzene ring.

9.94: H atom connected to aldehyde substituents.

**acetophenone:**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.16, 136.10, 132.09, 127.55, 127.29, 76.20, 25.60.

25.6: Methyl C atom at the  $\beta$  position of benzene ring substituent.

127.55, 127.29: C atom in the ortho and meta positions of the benzene ring.

132.09: P-C atom on benzene ring.

136.10: C atom of the benzene ring connected to the substituent on the benzene ring.

197.16: Ketone C atom at  $\alpha$  position on benzene ring substituent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.86 (m, 4H), 7.53 – 7.46 (m, 2H), 7.43 – 7.36 (m, 4H), 2.54 (s, 1H), 2.54 (s, 5H).

2.54: H atom connected to the  $\text{C}_\beta$  position of the benzene ring.

7.43 – 7.36: H atom connected to two substituents of the benzene ring.

7.53 – 7.46: H atom connected to para substituted groups of benzene ring.

7.92 – 7.86: H atoms connected to two adjacent positions of benzene ring substituents.

**ppe-one:**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.52, 156.98, 133.57, 132.84, 128.56, 127.81, 127.13, 120.64, 113.78, 76.20, 69.77.

193.52: C atom of  $\text{C}_\alpha=\text{O}$  position.

128.56, 127.81, 127.13: all the C atoms of benzene ring.

69.77: C atom of C<sub>β</sub>=H<sub>2</sub> position.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.91 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 7.26 – 7.17 (m, 2H), 6.95 – 6.84 (m, 3H), 5.20 (s, 2H).

8.12 – 7.89: H atom at C<sub>β</sub>-position.

7.97 – 7.91: H atom connected to the adjacent and p-C atom connected to the substituent on the benzene ring A (left, same as above in the following text).

7.26 – 7.17: H atom connected to the C atom at the intermediate positions connected to the substituent on the benzene ring A.

7.58 – 7.51: H atom connected to the p-C atom connected to the substituent on the benzene ring B (right, same as above in the following text).

5.20: H atom connected to the adjacent C atom connected to the substituent on the benzene ring B.

7.47 – 7.40: H atom connected to the C atom at the intermediate positions connected to the substituent on the benzene ring B.

**ppe-ol:**

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.34, 138.59, 128.54, 127.55, 127.17, 125.26, 120.29, 113.60, 76.20, 72.26, 71.57, -1.02.

138.59: the mono substituted C on the benzene ring.

113.60-157.34: C atom on the benzene ring.

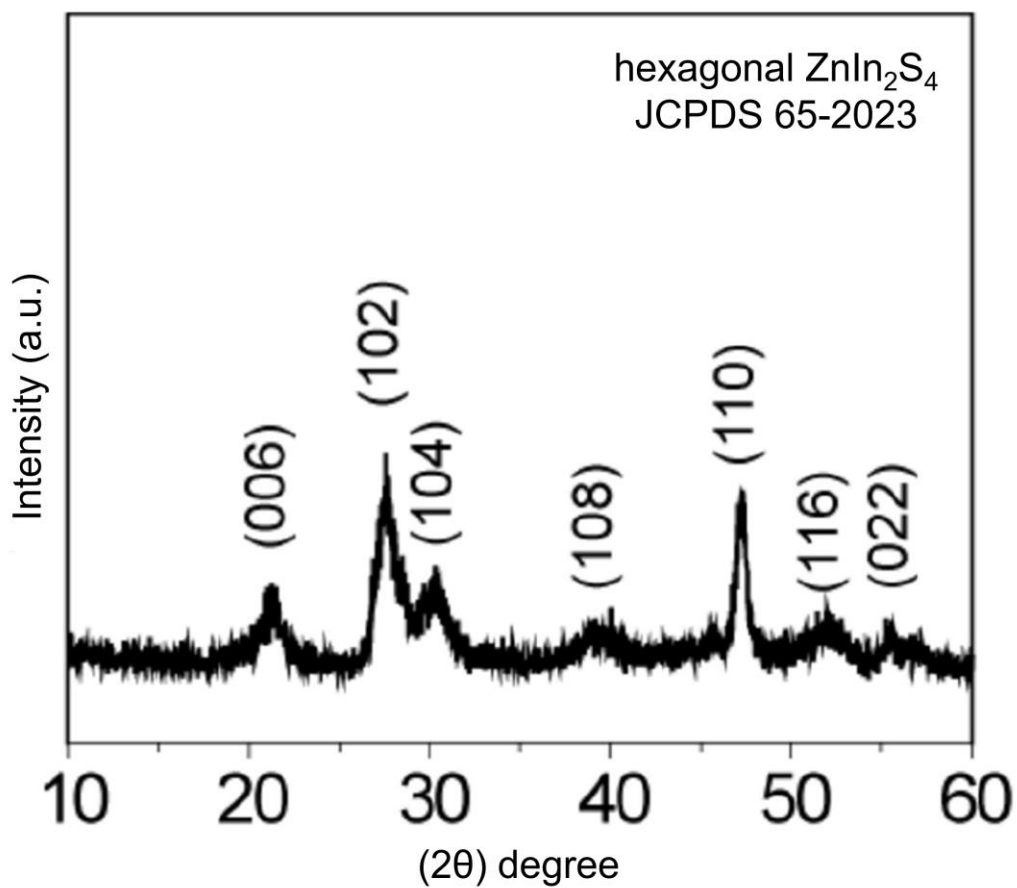
72.26: C atom at C<sub>β</sub>-position.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.36 (m, 2H), 7.36 – 7.16 (m, 5H), 6.90 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.90 – 6.82 (m, 2H), 5.06 (dd, *J* = 8.9, 3.1 Hz, 1H), 4.04 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.94 (t, *J* = 9.2 Hz, 1H), 2.63 (s, 1H).

7.36 – 7.16: H atom on the benzene ring.

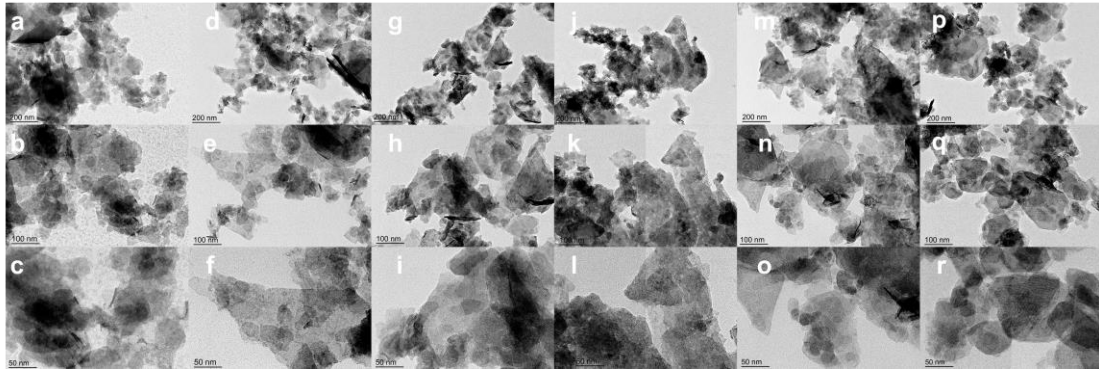
5.06: H atom connected with C atom at C<sub>β</sub>-position.

6.90 – 6.82: H atom on the CH<sub>2</sub>.



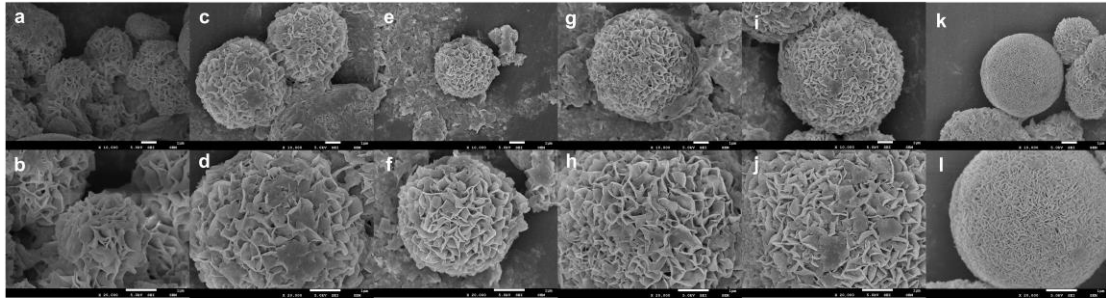
**Figure S2**

Figure S2 was a standard XRD image of hexagonal ZnIn<sub>2</sub>S<sub>4</sub> in “CN 103861620 B”, which was originated from “JCPDS 65-2023”. The peaks were represented by (006), (102), (104), (108), (110), (116), and (220) planes, respectively. And they were same as Figure 1 of ZIS-based materials in our work.



**Figure S3**

Figure S3 has represented by the TEM images of ZIS (Fig. S3a-c), ZIS-Sv<sub>0.2</sub> (Fig. S3d-f), ZIS-Sv<sub>0.4</sub> (Fig. S3g-i), ZIS-Sv<sub>0.6</sub> (Fig. S3j-l), ZIS-Sv<sub>0.8</sub> (Fig. S3m-o) and ZIS-Sv<sub>1</sub> (Fig. S3p-r). Meanwhile, Fig.S3a, Fig.S3d, Fig.S3g, Fig.S3j, Fig.S3m and Fig.S3p were at 5000 times, Fig.S3b, Fig.S3e, Fig.S3h, Fig.S3k, Fig.S3n and Fig.S3q were at 10000 times and, Fig.S3c, Fig.S3f, Fig.S3i, Fig.S3l, Fig.S3o and Fig.S3r were at 20000 times.



**Figure S4**

Figure S4 has represented by the SEM images of ZIS (Fig. S4a-b), ZIS-Sv<sub>0.2</sub> (Fig. S4c-d), ZIS-Sv<sub>0.4</sub> (Fig. S4e-f), ZIS-Sv<sub>0.6</sub> (Fig. S4g-h), ZIS-Sv<sub>0.8</sub> (Fig. S4i-j) and ZIS-Sv<sub>1</sub> (Fig. S4k-l). Meanwhile, Fig.S3a, Fig.S3c, Fig.S3e, Fig.S3g, Fig.S3i and Fig.S3k were at 10000 times, and Fig.S3b, Fig.S3d, Fig.S3f, Fig.S3h, Fig.S3j and Fig.S3l were at 20000 times.



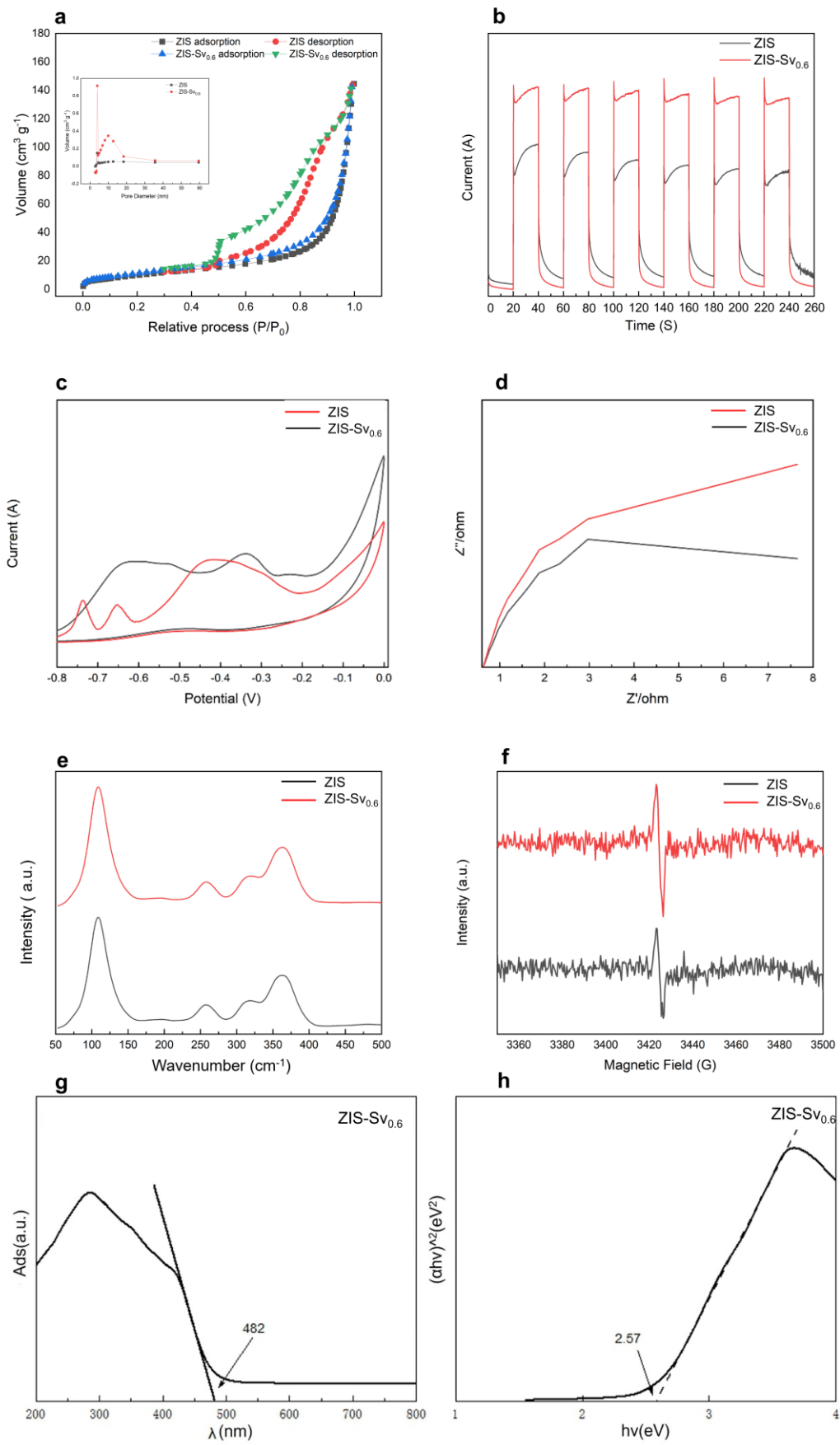


Figure S5

Figure S5a was N<sub>2</sub> adsorption desorption curves of ZIS and ZIS-Sv<sub>0.6</sub>. This BET test was completed at 77k through vacuum treatment at 60°C for 12 hours. Furthermore, there is obvious adsorption in the medium-high pressure region, and the H3 hysteresis loop can indicate that ZIS-based materials were mesoporous type materials. In the small figure, the highest point is called the most accessible pore size, which is the pore size with the highest content. The average pore diameters of **3** and 10 nm, approximately.

Figure S5b was transient photocurrent measurements in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution. Weigh 10 mg of powder sample and disperse it in 1 mL of ultrapure water/ethanol solution. Add 50 uL of Nafion solution and sonicate for 30 minutes to form a uniform suspension. Then, drop 100 uL of suspension onto ITO glass and dry at room temperature for photoelectric testing. Lighting time interval of 20 seconds (turn on for 20 seconds, turn off for 20 seconds), 6 cycles; Light source: Xenon lamp (full wavelength)

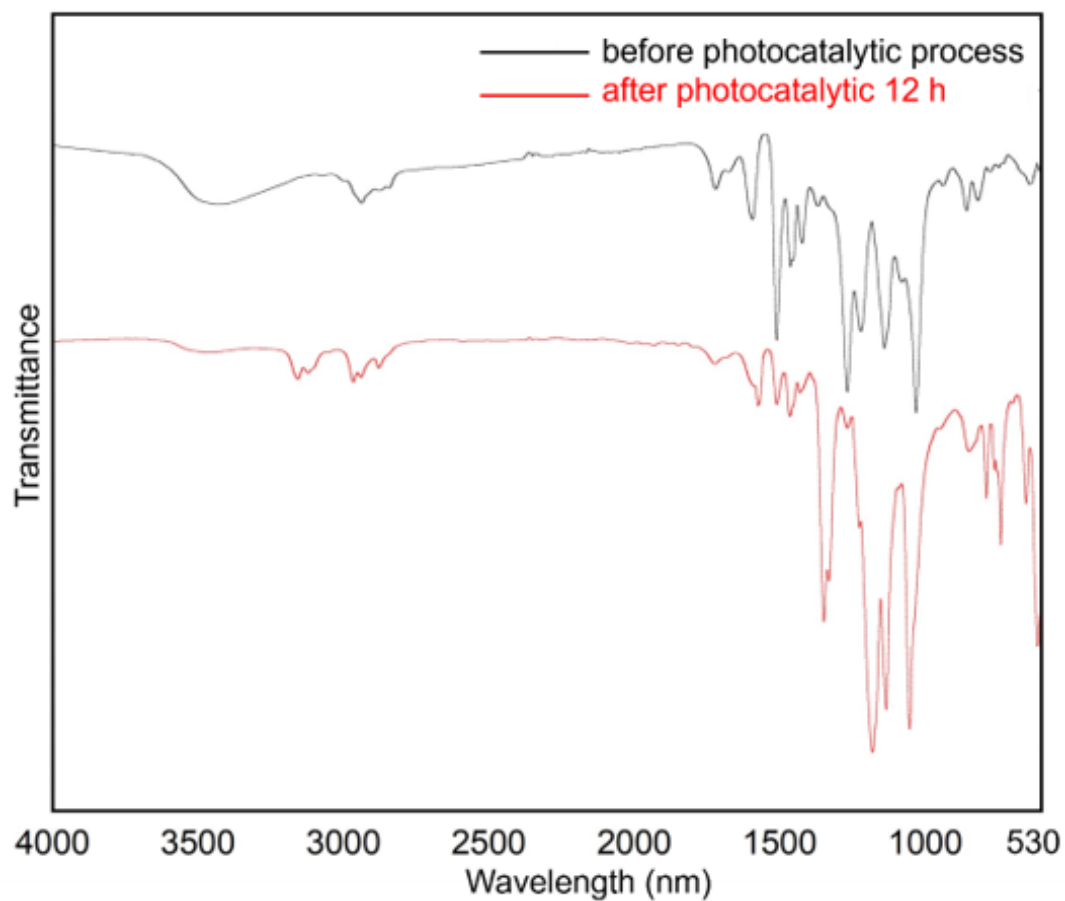
Figure S5c was the CV curves of -0.8 to 0 V by 10 mV/s in KOH (6 mol/L) solution, the integral area of ZIS-Sv<sub>0.6</sub> was the maximum, which indicated the electrochemical window of ZIS-Sv<sub>0.6</sub> was larger than ZIS.

Figure S5d was the EIS curves of ZIS and ZIS-Sv<sub>0.6</sub> in KOH (6 mol/L) solution with an amplitude perturbation of 5 mV and frequency range of 300 Hz to 1 MHz. Through smaller diameter of ZIS-Sv<sub>0.6</sub> was indicated that the electronic transmission obstruction capability of ZIS-Sv<sub>0.6</sub> was lower than that of ZIS. This result has indicated that introducing Sv could increase the interfacial charge-transfer resistance and improve electron-transfer efficiency.

Figure S5e was the Ramen tests of ZIS and ZIS-Sv<sub>0.6</sub>, which was an easy analysis. Through comparing ZIS and ZIS-Sv<sub>0.6</sub>, it could indicate that introducing Sv did not change its structures.

Figure S5f, in the EPR analysis, the photo-excitation intensity of ZIS-Sv<sub>0.6</sub> was higher than ZIS, which indicated that ZIS-Sv<sub>0.6</sub> had greater light absorption ability and could promote separation of photo generated holes and electrons.

Figure S5g-h was UV-Vis-IR spectrum of ZIS-Sv<sub>0.6</sub> in 200-800 nm, which could indicate ZIS-based materials not only absorbed ultraviolet light, but also partial visible light.



**Figure S6**

Figure S6 was FTIR tests of dioxane lignin before photocatalysis and after photocatalysis 12 h. Through 12 hours of photocatalysis process, C-OH (3400 nm) group and C-C bond (2850-2930 nm, R-C-H peaks indirectly judgment) have disappeared. Meanwhile, partial C-O bond of phenol (1200-1300 nm) and C=O (1700-1750 nm). This result has indicated that photocatalysis process was a oxidation/cleavage process.

**Table S1. The pre-experiments of ppe.**

Catalyst	Phenol [ $\mu\text{mol g}^{-1}$ $\text{h}^{-1}$ (%)]	Acetophenone [ $\mu\text{mol g}^{-1}$ $\text{h}^{-1}$ (%)]	Conversion rate of ppe (%)
ZnS	18.33 (29.37)	10.64 (16.02)	7.34
In <sub>2</sub> S <sub>3</sub>	13.38 (42.48)	5.29 (15.93)	3.69
ZIS	58.34 (30.26)	36.67 (19.02)	22.67
ZIS-SV <sub>0.6</sub>	53.69 (23.78)	40.19 (17.83)	26.38

Photocatalysis conditions: optical light density: 600 W cm<sup>-2</sup>; photocatalysis time: 6 h; BMIMNTf<sub>2</sub> concentration: 500 mg/ml; photocatalysts concentration: 1 mg/ml;  $\beta$ -O-4 dimer concentration: 1 mg/ml; ethanol and water mixed solution (volume ratio, 95%:5%)

**Table S2. The pre-experiments of ppe-one.**

Catalyst	Phenol [ $\mu\text{mol g}^{-1}$ $\text{h}^{-1}$ (%)]	Acetophenone [ $\mu\text{mol g}^{-1}$ $\text{h}^{-1}$ (%)]	Conversion rate of ppe-one (%)
ZnS	51.68 (29.89)	41.52 (24.10)	21.99
In <sub>2</sub> S <sub>3</sub>	43.88 (28.09)	35.83 (22.69)	19.62
ZIS	295.61 (55.25)	246.67 (46.11)	68.15
ZIS-SV <sub>0.6</sub>	343.58 (56.34)	291.83 (47.87)	77.51

Photocatalysis conditions: optical light density: 600 W cm<sup>-2</sup>; photocatalysis time: 6 h; BMIMNTf<sub>2</sub> concentration: 500 mg/ml; photocatalysts concentration: 1 mg/ml;  $\beta$ -O-4 dimer concentration: 1 mg/ml; ethanol and water mixed solution (volume ratio, 95%:5%)

**Table S3. The pre-experiments of ppe-ol.**

Catalyst	Phenol [ $\mu\text{mol g}^{-1} \text{h}^{-1}$ <sup>1</sup> (%)]	Acetophenone [ $\mu\text{mol g}^{-1} \text{h}^{-1}$ (%)]	ppe-one [ $\mu\text{mol g}^{-1} \text{h}^{-1}$ <sup>1</sup> (%)]	Conversion rate of ppe-ol (%)
ZnS	50.19 (31.03)	36.68 (22.76)	5.89 (3.10)	20.69
In <sub>2</sub> S <sub>3</sub>	15.31 (10.50)	10.27 (7.01)	6.31 (4.66)	18.35
ZIS	128.33 (23.75)	115.47 (21.29)	50.45 (9.25)	69.37
ZIS-Sv <sub>0.6</sub>	155.56 (30.84)	136.67 (27.19)	26.38 (5.31)	64.53

Photocatalysis conditions: optical light density: 600 W cm<sup>-2</sup>; photocatalysis time: 6 h; BMIMNTf<sub>2</sub> concentration: 500 mg/ml; photocatalysts concentration: 1 mg/ml;  $\beta$ -O-4 dimer concentration: 1 mg/ml; ethanol and water mixed solution (volume ratio, 95%:5%)

**Table S4. The pre-experiments of ppe-one concentration.**

Concentration (mg/ml)	Phenol [ $\mu\text{mol g}^{-1} \text{h}^{-1}$ (%)]	Acetophenone [ $\mu\text{mol g}^{-1} \text{h}^{-1}$ (%)]	Conversion rate of ppe-one (%)
0.5	159.64 (23.36)	151.23 (22.13)	86.91
1	343.58 (56.34)	291.83 (47.87)	77.51
1.5	285.38 (47.43)	222.11 (36.91)	76.54
2	265.85 (45.45)	207.85 (35.54)	74.41
2.5	271.53 (45.61)	225.48 (37.93)	75.72

Photocatalysis conditions: optical light density:  $600 \text{ W cm}^{-2}$ ; photocatalysis time: 6 h; BMIMNTf<sub>2</sub> concentration: 500 mg/ml; ZIS-Sv<sub>0.6</sub> photocatalysts concentration: 1 mg/ml; ethanol and water mixed solution (volume ratio, 95%:5%)