Supporting Information

for

Controlled growth of ZnS/ZnO heterojunctions on porous biomass carbons via one–step carbothermal reduction enables visible–light–driven photocatalytic H_2 production

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Table Caption

Table S1 Elemental analysis and ICP results of the PBCs and ZnS/ZnO@C800–n (n = 0.5/1/2/3).

Table S2 Band gap energy (E_g), specific surface area (S_{BET}) and H_2 production rate activity of ZnS/ZnO@C800–n (n = 0.5/1/2/3).

Table S3 Time–resolved fluorescence decay parameters of ZnS/ZnO@C800–n (n = 0.5/1/2/3).

Figure Caption

Fig. S1. (a) Thermogravimetric analysis (TGA) of $ZnSO_4 \cdot 7H_2O$ precursor; and (b) powder X–ray diffraction (PXRD) patterns of ZnS/ZnO@CT–1 (T = 600/700/900) composite materials.

Fig. S2. (a) N_2 adsorption/desorption isotherms; and (b) pore–size distribution of the PBCs support and ZnS/ZnO@C800–n (n = 0.5/2/3).

Fig. S3. High–resolution XPS spectra of ZnS/ZnO@C800–n (n = 0.5/2/3) for (a) C 1s; (b) Zn 2p; (c) O 1s; and (d) S 2p.

Fig. S4. Photoluminescence (PL) spectra (Excitation spectrum) of ZnS/ZnO@C800–n (n = 0.5/1/2/3).

Fig. S5. (a) PXRD patterns; (b) UV–vis DRS spectra (Inset: the K–M plots); (c) Mott–Schottky plots; and (d) room–temperature ESR spectra of ZnO and ZnO–Ov.

Fig. S6. (a) UV–vis DRS spectra (Inset: the K–M plots); (b) Mott–Schottky plots of ZnS.

Characterizations

Powder X–ray diffraction (PXRD) patterns were collected by using a Rigaku Miniflex 600 X–ray diffractometer with Cu Kα radiation (λ = 0.154 nm). Scanning electron microscopy (SEM) images were photographed by using a JSM6700–F with a working voltage of 10 kV. Transmission electron microscopy (TEM) and high resolution TEM (HR–TEM) images were recorded by using an FEIT 20 working at 200 kV. The inter–planer distances and the inverse Fast Fourier Transform (FFT) were calculated using the Digital Micrograph software. X–ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi spectrometer with Al Kα X–ray source (15 kV, 10 mA). In order to compensate effects related to charge shifts C 1s peak at 284.6 eV was used as internal standard. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV–vis spectrophotometer (UV–2550) with $BaSO_4$ as the background. The photoluminescence (PL) spectra and time–resolved fluorescence emission spectrum were collected on a FLS 980 fluorescence spectrometer at room temperature. Elemental analyses (C, H, O and S) were performed on a CE–440 elemental analyzer. Zn was determined using a Jobin Yvon Ultima2 inductively coupled plasma (ICP) atomic emission spectrometer. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere with a heating rate of 10 °C min^{-1} by using a SDT Q600 thermogravimetric analyzer. N_2 adsorption–desorption isotherms were obtained on a Micromeritics ASAP 2460 instrument and used for Brunauer–Emmett–Teller (BET) surface area and pore size distribution (PSD) calculations. Electron spin resonance (ESR) spectra were recorded on a Bruker E500 spectrometer.

Table S1

Composite photocatalyst	C (%)	O (%)	S (%)	Zn (%)	ZnS:ZnO

PBCs	67.7	N.A.	N.A.	N.A.	N.A.
ZnS/ZnO@C800–0.5	53.4	8.33	1.85	7.55	1:1
ZnS/ZnO@C800–1	39.2	10.2	2.75	16.9	1:2
ZnS/ZnO@C800–2	26.3	12.6	3.85	31.3	1:3
ZnS/ZnO@C800–3	18.2	14.1	4.40	44.3	1:4.7

Table S2

Composite photocatalyst	E_g (eV)	S_{BET} (m^2 g^{-1})	H_2 production activity (μmol h^{-1} g^{-1})
ZnS/ZnO@C800–0.5	3.01	1779	3.12
ZnS/ZnO@C800–1	2.94	1331	37.1
ZnS/ZnO@C800–2	2.98	874.6	18.6
ZnS/ZnO@C800–3	3.01	533.1	4.68

Table S3

Composite photocatalyst	Lifetime <τ> (ns)	Pre–exponential factor A%	<τ_{ave}> (ns)*
ZnS/ZnO@C800–0.5	τ_1=3.3 τ_2=29.0 τ_3=220.6	A_1 = 25.63 A_2 = 35.14 A_3= 39.23	198.7
ZnS/ZnO@C800–1	τ_1=1.6 τ_2=15.8 τ_3=138.1	A_1 = 38.37 A_2 = 28.20 A_3= 33.43	125.8
ZnS/ZnO@C800–2	τ_1=1.5 τ_2=17.6 τ_3=156.2	A_1 = 12.33 A_2 = 25.19 A_3= 62.48	140.8
ZnS/ZnO@C800–3	τ_1=2.4 τ_2=19.4 τ_3=168.2	A_1 = 31.97 A_2 = 32.06 A_3= 35.97	149.9

***** Time–resolved fluorescence decay curves were fitted by using the three–expontial fitting method. Average lifetime <τ_{ave}> was determined by using the following equation: $<\tau_{ave}>=\sum_{i=1}^{i=n} A_i\tau_i^2 \Big/ \sum_{i=1}^{i=n} A_i\tau_i$ according to the literature [S1].

References

(S1) M. Zhou, S. B. Wang, P. J. Yang, C. J. Huang and X. C. Wang, *ACS Catal.*, 2018, **8 (6)**, 4928-4936.

Fig. S1.

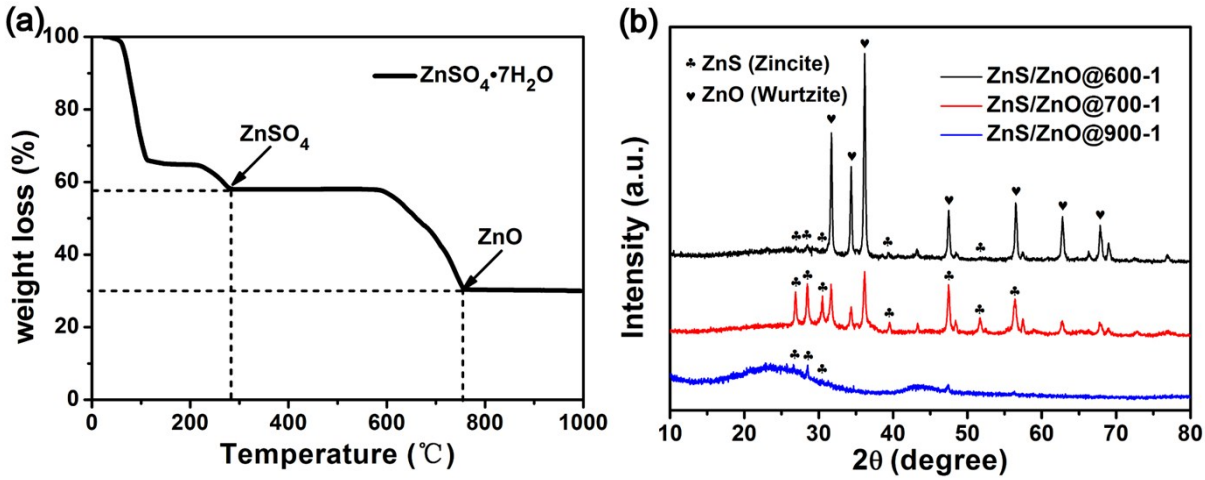

(a)
ZnSO4•7H2O
ZnSO4
ZnO
weight loss (%)
Temperature (℃)
(b)
♣ ZnS (Zincite)
♥ ZnO (Wurtzite)
ZnS/ZnO@600-1
ZnS/ZnO@700-1
ZnS/ZnO@900-1
Intensity (a.u.)
2θ (degree)

Fig. S2.

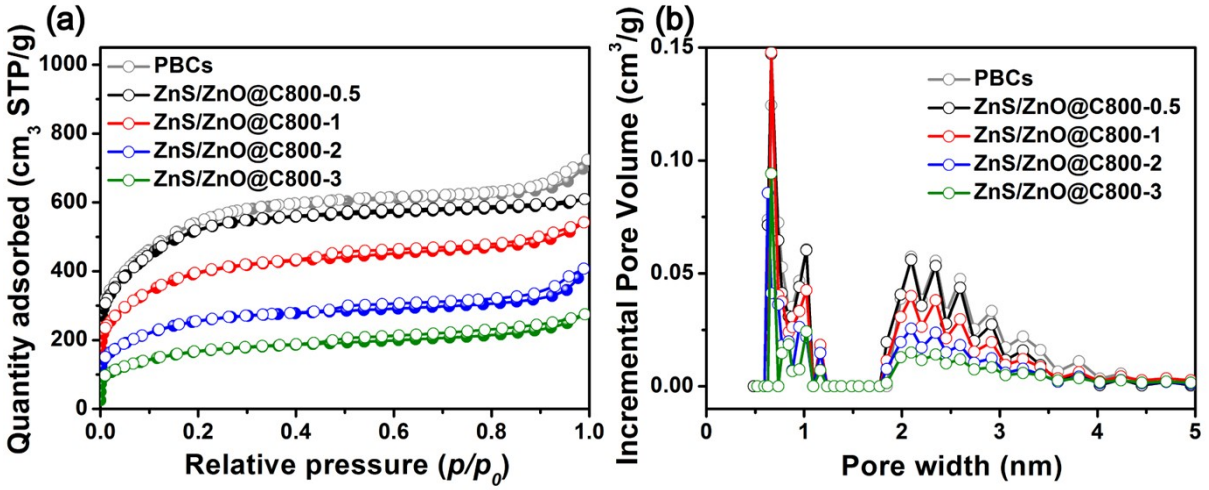

(a)
PBCs
ZnS/ZnO@C800-0.5
ZnS/ZnO@C800-1
ZnS/ZnO@C800-2
ZnS/ZnO@C800-3
Quantity adsorbed (cm3 STP/g)
Relative pressure (p/p0)
(b)
Incremental Pore Volume (cm3/g)
Pore width (nm)

Fig. S3.

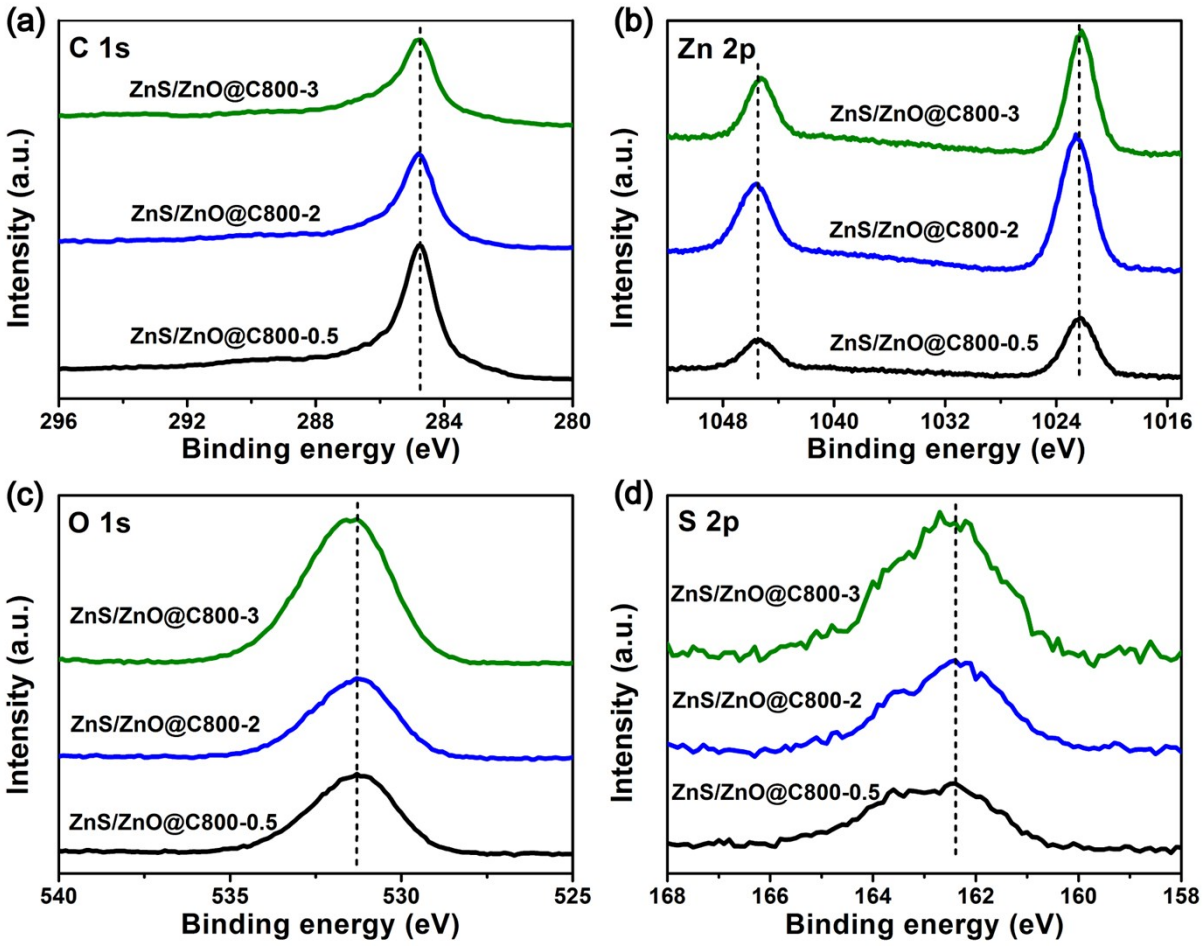

(a)
C 1s
ZnS/ZnO@C800-3
ZnS/ZnO@C800-2
ZnS/ZnO@C800-0.5
Intensity (a.u.)
296
292
288
284
280
Binding energy (eV)
(b)
Zn 2p
ZnS/ZnO@C800-3
ZnS/ZnO@C800-2
ZnS/ZnO@C800-0.5
Intensity (a.u.)
1048
1040
1032
1024
1016
Binding energy (eV)
(c)
O 1s
ZnS/ZnO@C800-3
ZnS/ZnO@C800-2
ZnS/ZnO@C800-0.5
Intensity (a.u.)
540
535
530
525
Binding energy (eV)
(d)
S 2p
ZnS/ZnO@C800-3
ZnS/ZnO@C800-2
ZnS/ZnO@C800-0.5
Intensity (a.u.)
168
166
164
162
160
158
Binding energy (eV)

Fig. S4.

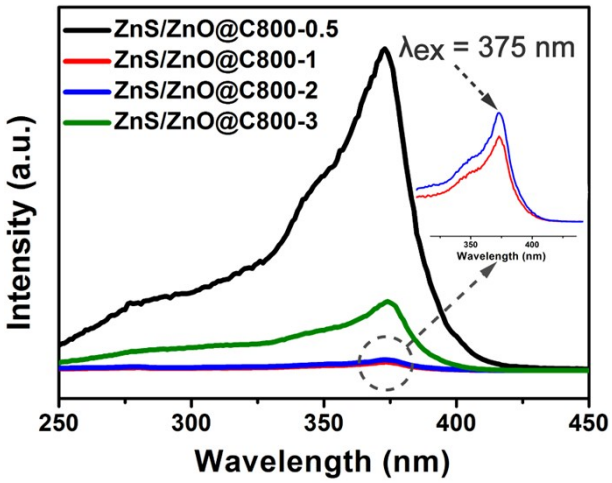

ZnS/ZnO@C800-0.5
ZnS/ZnO@C800-1
ZnS/ZnO@C800-2
ZnS/ZnO@C800-3
λex = 375 nm
Intensity (a.u.)
Wavelength (nm)
250
300
350
400
450
350
400
Wavelength (nm)

Fig. S5.

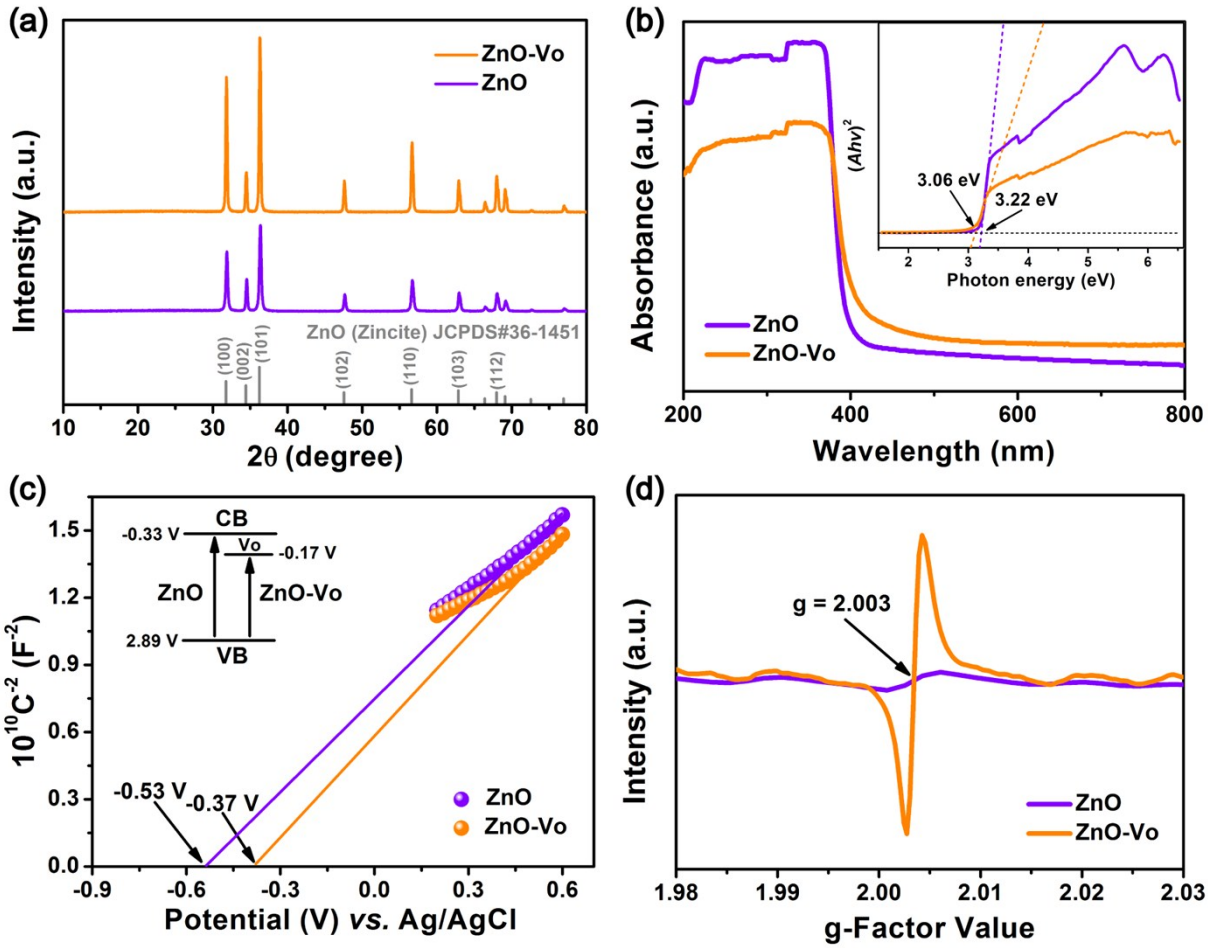
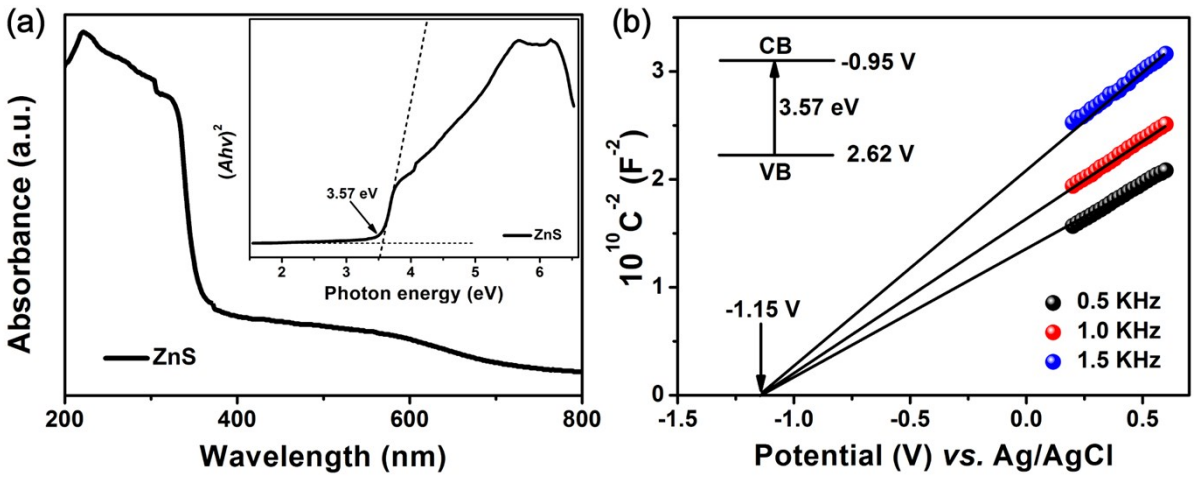

(a)
ZnO-Vo
ZnO
Intensity (a.u.)
ZnO (Zincite) JCPDS#36-1451
(100)
(002)
(101)
(102)
(110)
(103)
(112)
10
20
30
40
50
60
70
80
2θ (degree)
(b)
Absorbance (a.u.)
(Ahν)²
3.06 eV
3.22 eV
2
3
4
5
6
Photon energy (eV)
ZnO
ZnO-Vo
200
400
600
800
Wavelength (nm)
(c)
CB
-0.33 V
Vo
-0.17 V
ZnO
ZnO-Vo
2.89 V
VB
10¹⁰C⁻² (F⁻²)
1.5
1.2
0.9
0.6
0.3
0.0
-0.53 V
-0.37 V
ZnO
ZnO-Vo
-0.9
-0.6
-0.3
0.0
0.3
0.6
Potential (V) vs. Ag/AgCl
(d)
g = 2.003
Intensity (a.u.)
ZnO
ZnO-Vo
1.98
1.99
2.00
2.01
2.02
2.03
g-Factor Value

Fig. S6.


(a)
Absorbance (a.u.)
Wavelength (nm)
ZnS
(Ahν)²
3.57 eV
Photon energy (eV)
ZnS
(b)
CB
-0.95 V
3.57 eV
2.62 V
VB
-1.15 V
0.5 KHz
1.0 KHz
1.5 KHz
10¹⁰ C⁻² (F⁻²)
Potential (V) vs. Ag/AgCl