Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary information

Efficient H_2 evolution on $Co_3S_4/Zn_{0.5}Cd_{0.5}S$ nanocomposite by photocatalytic synergistic reaction

Yang Yang [a, b], Xiuzhen Zheng[b, c], Jiafang Liu [b], Zhulin Qi [b], Tianyue Su[a], Chun Cai [a, *], Xianliang Fu [b], Sugang Meng [b], Shifu Chen [b, *]

[a] School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, P. R. China

[b] Key Lab of Clean Energy and Green Circulation, College of Chemistry and Material Science, Huaibei Normal University, Huaibei, 235000, P. R. China

[c] State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, 350116, P. R. China.

*Corresponding Authors, E-mail: caichunh@njust.edu.cn, chshifu@chnu.edu.cn.

Supplementary experimental section

1. Characterization

A Bruker D8 advance powder X-ray diffractometer (XRD) was used to characterize the crystal structure of the as-prepared samples by Cu Kα radiation operated at 40 kV and 40 mA in the range of 15º to 80º. The prepared samples were performed by Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS, UV-2600, SHIMADZU, Japan) with the background of $BaSO_4$. The surface chemical states were detected on an X-ray photoelectron spectrometer (XPS, ESCALAB 250, America) with mono Al Kα radiation. The microstructure and element mapping of the samples were tested by field emission scanning electron microscopy (FESEM, FEI Nova Nano 230), transmission electron microscopy (TEM, FEI Tecnai G2 F20) and high-resolution transmission electron microscopy (HRTEM). Brunauer-Emmett-Teller (BET) surface areas of the samples were tested on a Micromeritics ASAP 2020. The lifetime of the photogenerated carriers was detected by time-resolved photoluminescence spectrometry (TRPL, RF530, SHIMADZU, Japan). The work functions (WF) of the prepared ZCS, Co_3S_4, and 3% C/ZCS were tested by a commercial scanning Kelvin probe (SKP) test system (SKP 5050, Scotland) at ambient atmosphere. A clean gold surface (WF = 5.1 eV) was used as a reference for the probe potential.

2. Photoelectrochemical measurements

The photoelectrochemical tests were carried out on the electrochemical workstation (CHI660E CH Instruments, China) was used to analyze the photoelectrochemical properties of the obtained samples by amperometric i–t curves, electrochemical impedance spectroscopy (EIS) and Mott–Schottky (M-S) analysis. The tests were carried out with a conventional three-electrode system consisting of Pt wire, Ag/AgCl and conductive glass (FTO, 14 Ω cm^{-2}, Nippon Sheet Glass, Japan) coated with the sample powder, which served as counter electrode, the reference electrode and the working electrode, respectively. Typically, 3.0 mg of sample was dispersed in 0.5 mL of deionized water by sonication to get uniform slurry. And, about 20 μL above slurry was deposited as a film on a FTO (0.5 cm × 0.5 cm) substrate. After drying at room temperature, the working electrode of sample was obtained. Meanwhile, a quartz cell

filled with 0.2 M Na_2SO_4 was used as the electrolyte for i-t and M-S measurement. 0.1 mol L^{-1} KCl and 0.01 mol L^{-1} $K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$ is used as electrolyte for EIS measurement. A 300W Xe lamp (MC-XF300, Beijing Merry Change Technology Co., Ltd) was used as a visible light source, which equipped with an optical filter ($\lambda > 420$ nm). The potential was converted to the reversible hydrogen electrode (RHE) by equation: E(RHE) = E(Ag/AgCl) +0.197 + 0.059 pH.

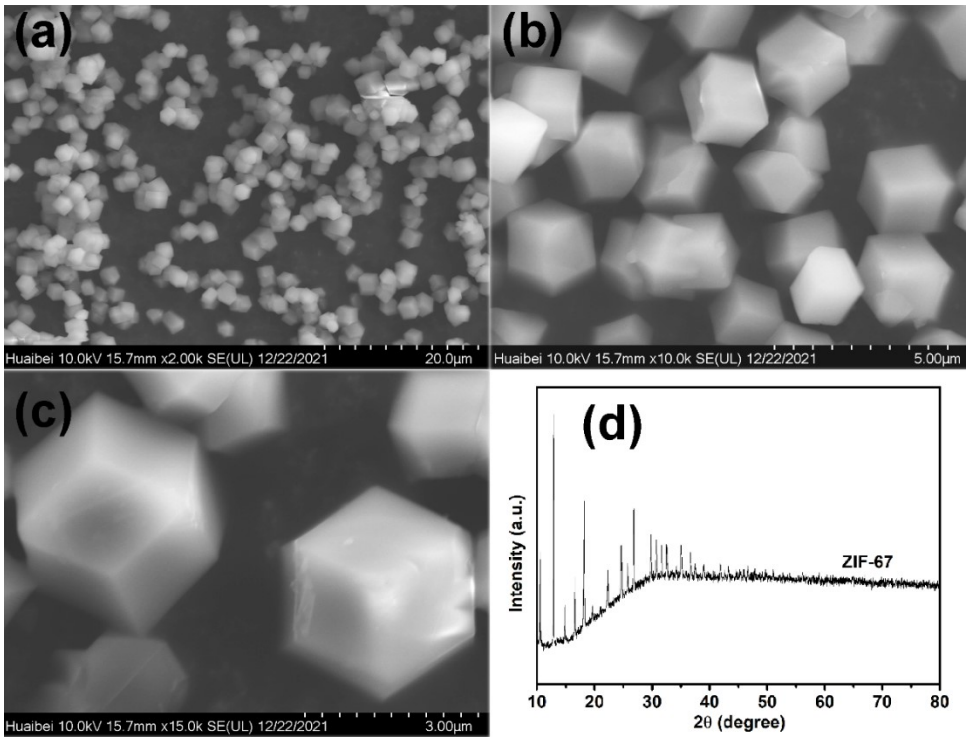

Fig. S1. The SEM images (a-c) and XRD pattern (d) of ZIF.

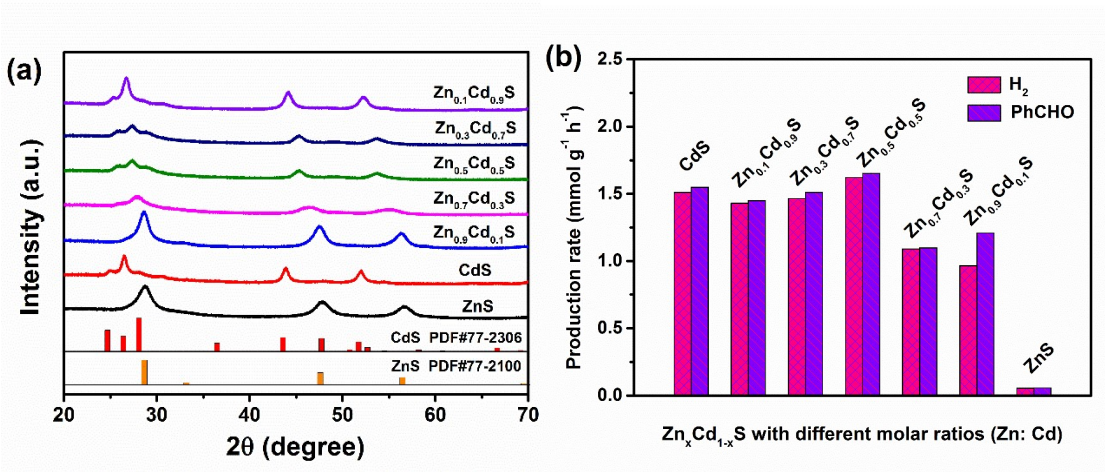

Fig. S2 The XRD (a) and photocatalytic activity (b) of $Zn_xCd_{1-x}S$ with different molar ration of Zn to Cd.

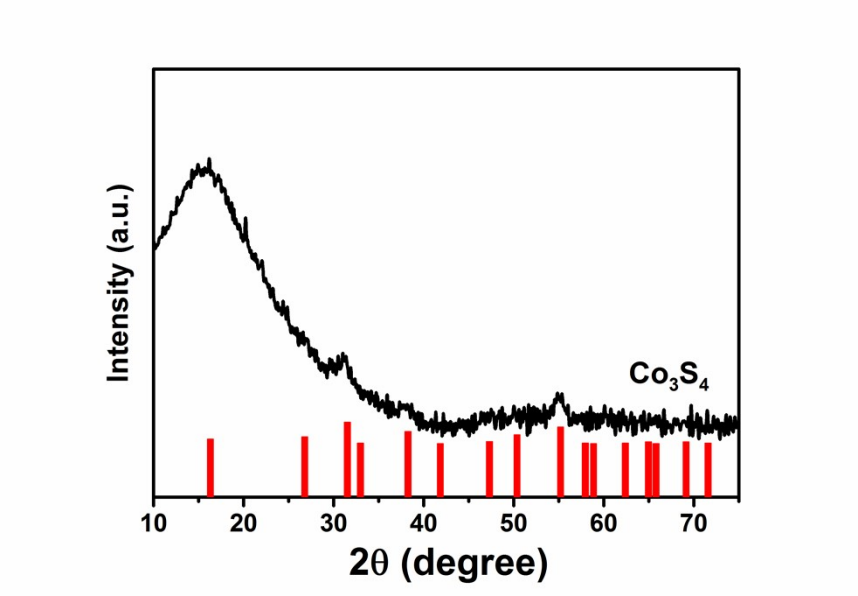

Fig. S3 The XRD pattern of Co_3S_4.

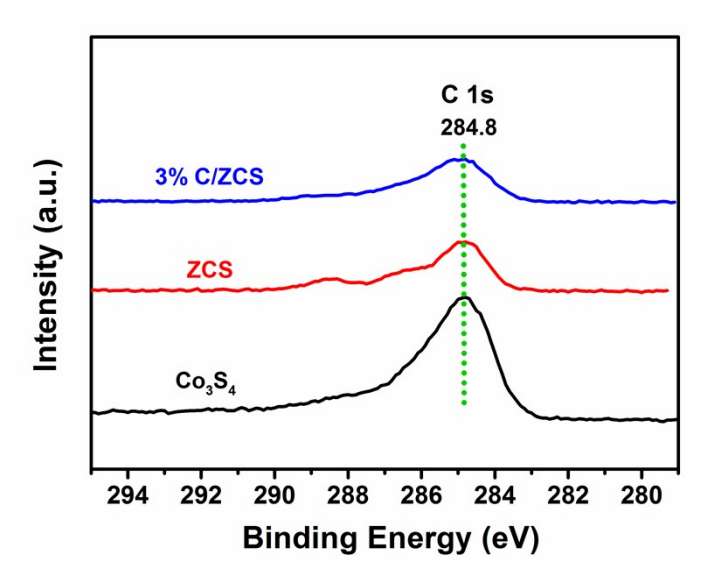

Fig. S4 The XPS of C 1s of Co_3S_4, ZCS and 3% C/ZCS.

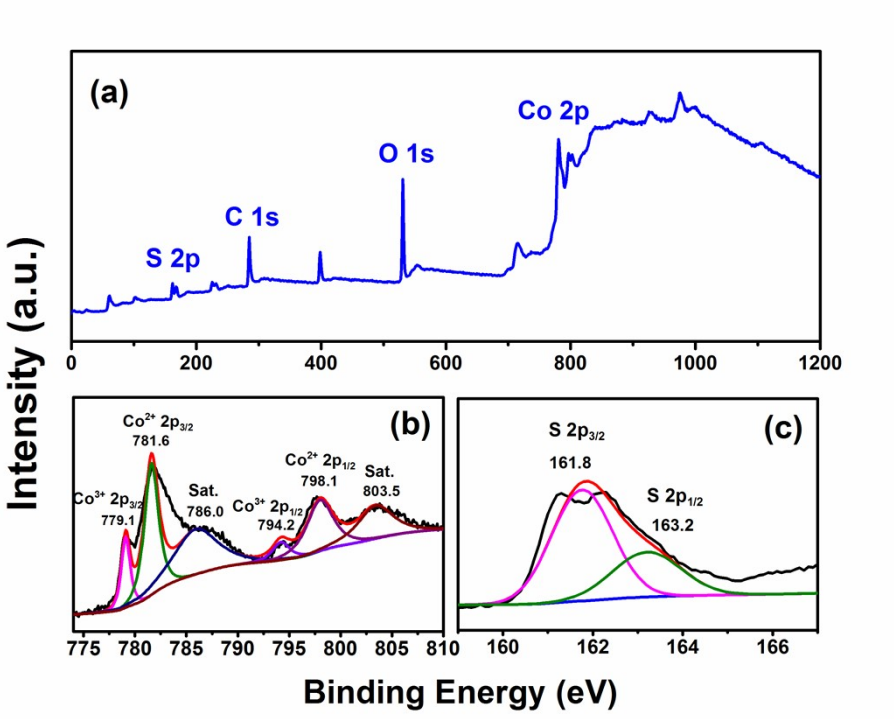

Fig. S5 The survey, high resolution (b) Co 2p and (c) S 2p XPS spectra of Co_3S_4.

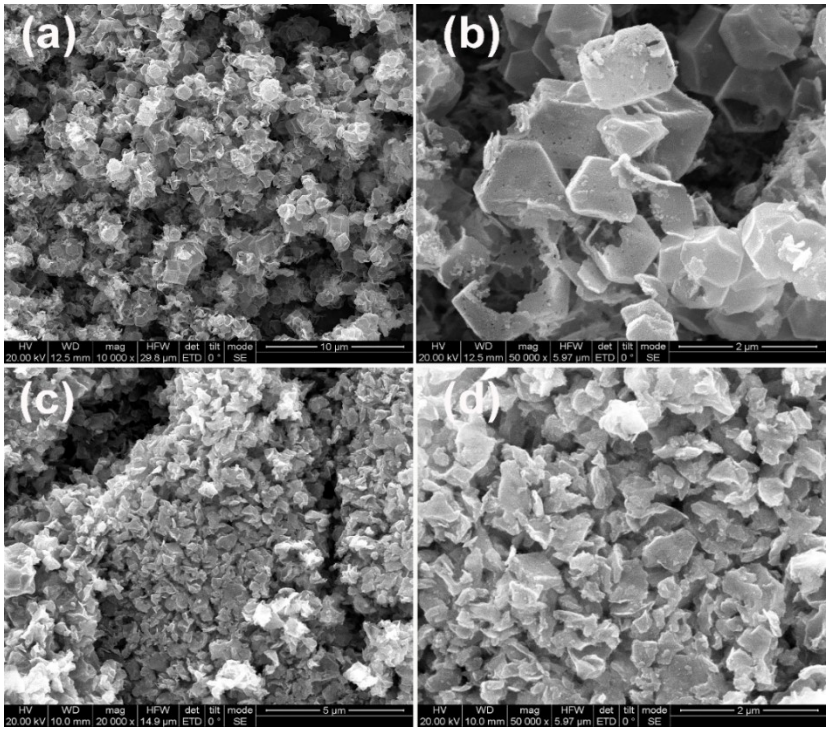

Fig. S6 The SEM of uncalcined (a, b) and calcined (c, d) Co_3S_4.

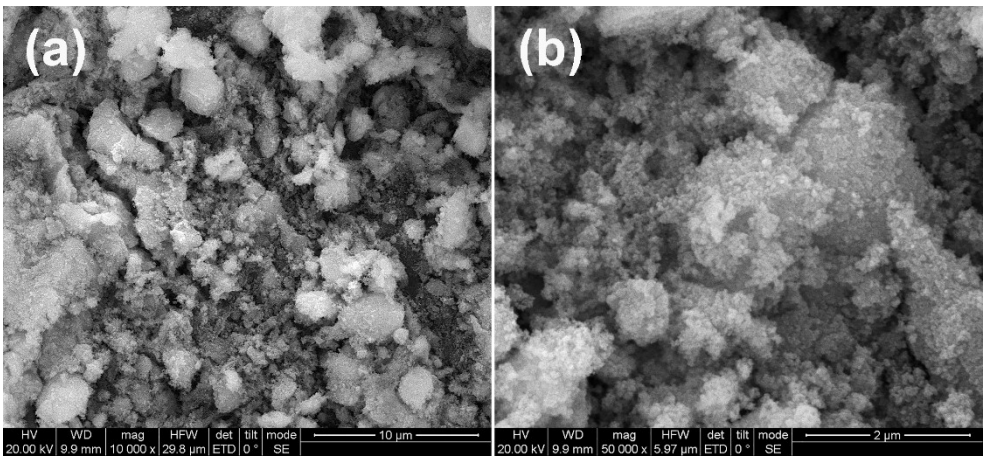

Fig. S7 The SEM images of ZCS (a, b)

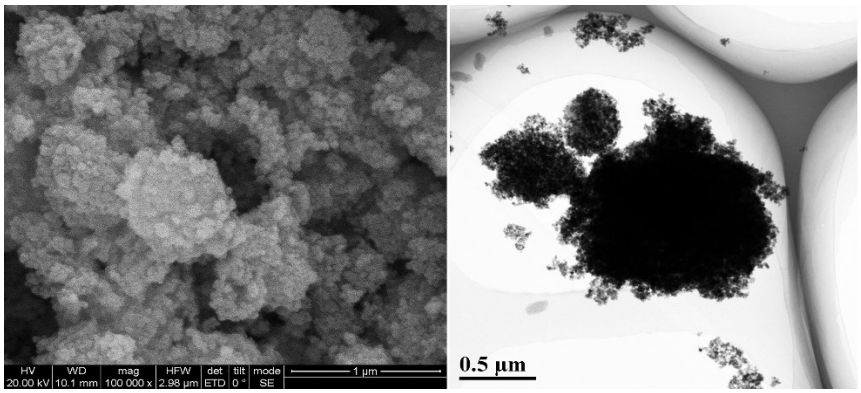

Fig. S8 The SEM images of 10% Co_3S_4/ZCS.

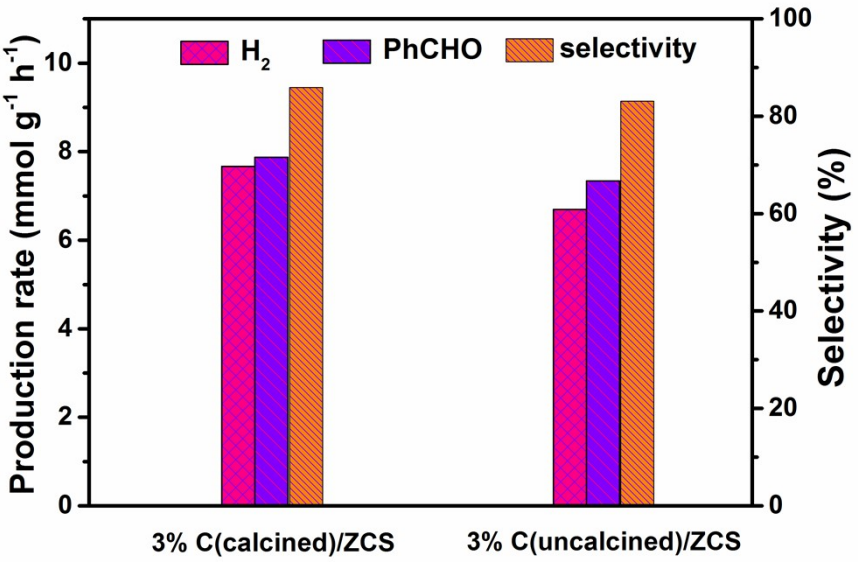

Fig. S9 The photocatalytic activities of 3% C/ZCS with calcined and uncalcined.

Table S1. The AQE results obtained under different monochromic light irradiation (λ = 400, 420, 450, 500 and 550 nm).

Wavelength (nm) / AQE	400	420	450	500	550
H_2	19.79%	19.64%	13.43%	2.70%	1.37%
benzaldehyde)	20.17%	19.73%	13.57%	2.83%	1.08%

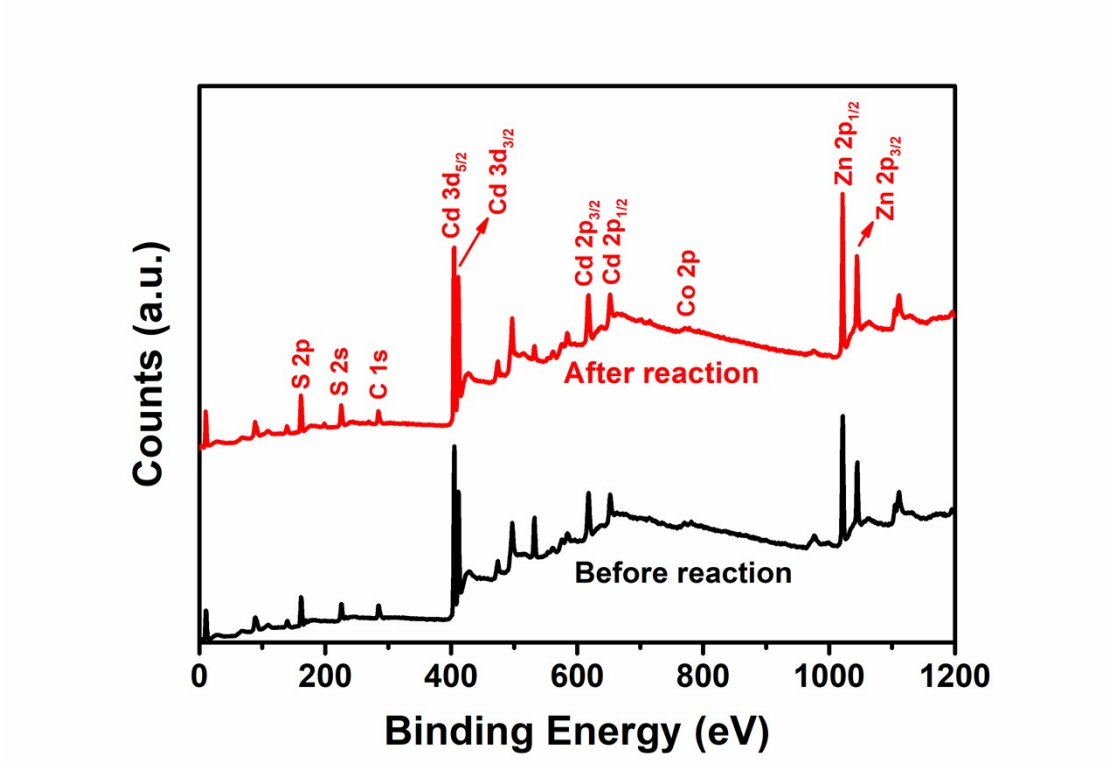

Fig. S10. The XPS of 3% C/ZCS before and after photocatalytic activity

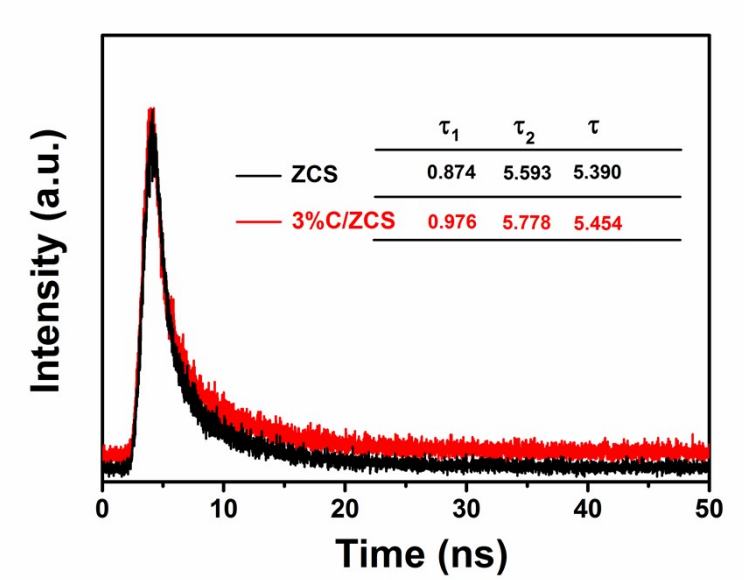

Fig. S11. time-resolved PL spectra of ZCS and 3% C/ZCS

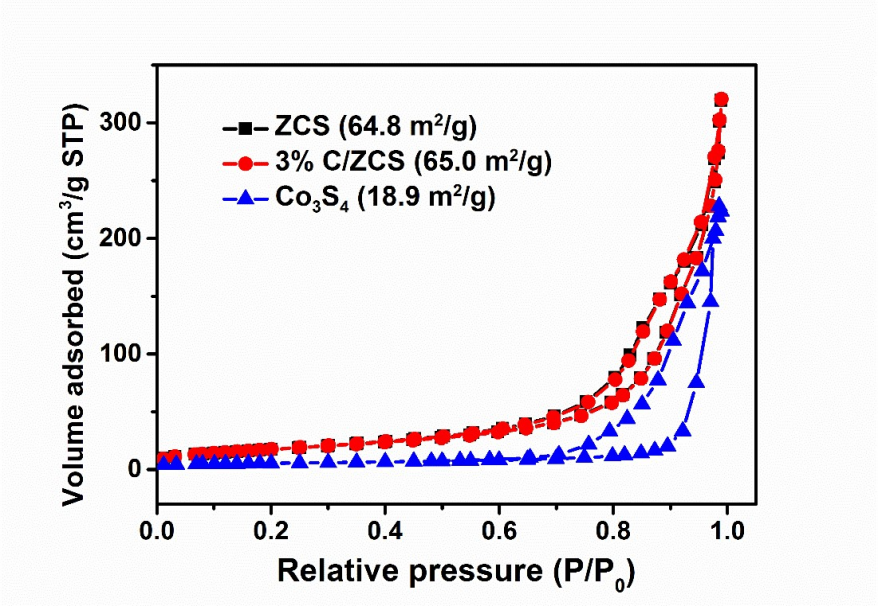

Fig. S12. The BET curses of ZCS, 3% C/ZCS and Co_3S_4.