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Regulating Band Gap of $Zn_xCd_{1-x}S$ in 3DOM $CaTiO_3$ for High Hydrogen Evolution and Gluconic Acid Selectivity

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Preparation of PS template

PS emulsions are based on previous reports and pass through partially modified[1, 2]. Firstly, the polymerization inhibitor in styrene was removed by mixing 2 mol/L NaOH and styrene in a volume ratio of 3:1 and stirring. 200 mL deionized water and 20 mL styrene were added to the three-neck flask, and access N_2 protection, stirred at 70 ℃ for 30 min, and 0.4 g $K_2S_2O_8$ was added refluxed 5 h to obtain a good dispersion of PS emulsion. The PS emulsion was dripped on the polycarbonate (PC) substrate for 24 h at 60 ℃ to obtain a structural regulatory PS template.

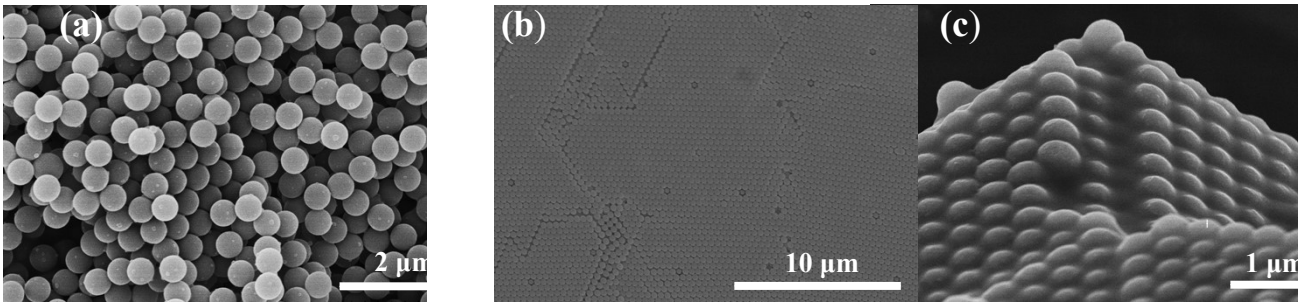

Fig. S1 SEM images of (a) PS, (b) PS template, (c) CTO precursor filling PS Template.

The size of the PS spheres obtained by soap-free emulsion polymerization is uniformly distributed at about 400 nm (Fig. S1 (a)). The PS template structure obtained by the emulsion concentration method has good regulation (Fig. S1 (b)), and after filling CTO precursor, the integrity of PS template is not destroyed (Fig. S1 (c)).

References

1. H. Zhao, C.-F. Li, X. Yong, P. Kumar, B. Palma, Z.-Y. Hu, G. Van Tendeloo, S. Siahrostami, S. Larter, D. Zheng, S. Wang, Z. Chen, M. G. Kibria and J. Hu, Coproduction of hydrogen and lactic acid from glucose photocatalysis on band-engineered $Zn_{1-x}Cd_xS$ homojunction, *iScience*, 2021, **24**, 102-109.

2. F.-Y. Bai, J.-R. Han, J. Chen, Y. Yuan, K. Wei, Y.-S. Shen, Y.-F. Huang, H. Zhao, J. Liu, Z.-Y. Hu, Y. Li and B.-L.Su, The three-dimensionally ordered microporous $CaTiO_3$ coupling $Zn_{0.3}Cd_{0.7}S$ quantum dots for simultaneously enhanced photocatalytic H_2 production and glucose conversion, *Journal of Colloid and Interface Science*, 2023, **638**, 173-183.

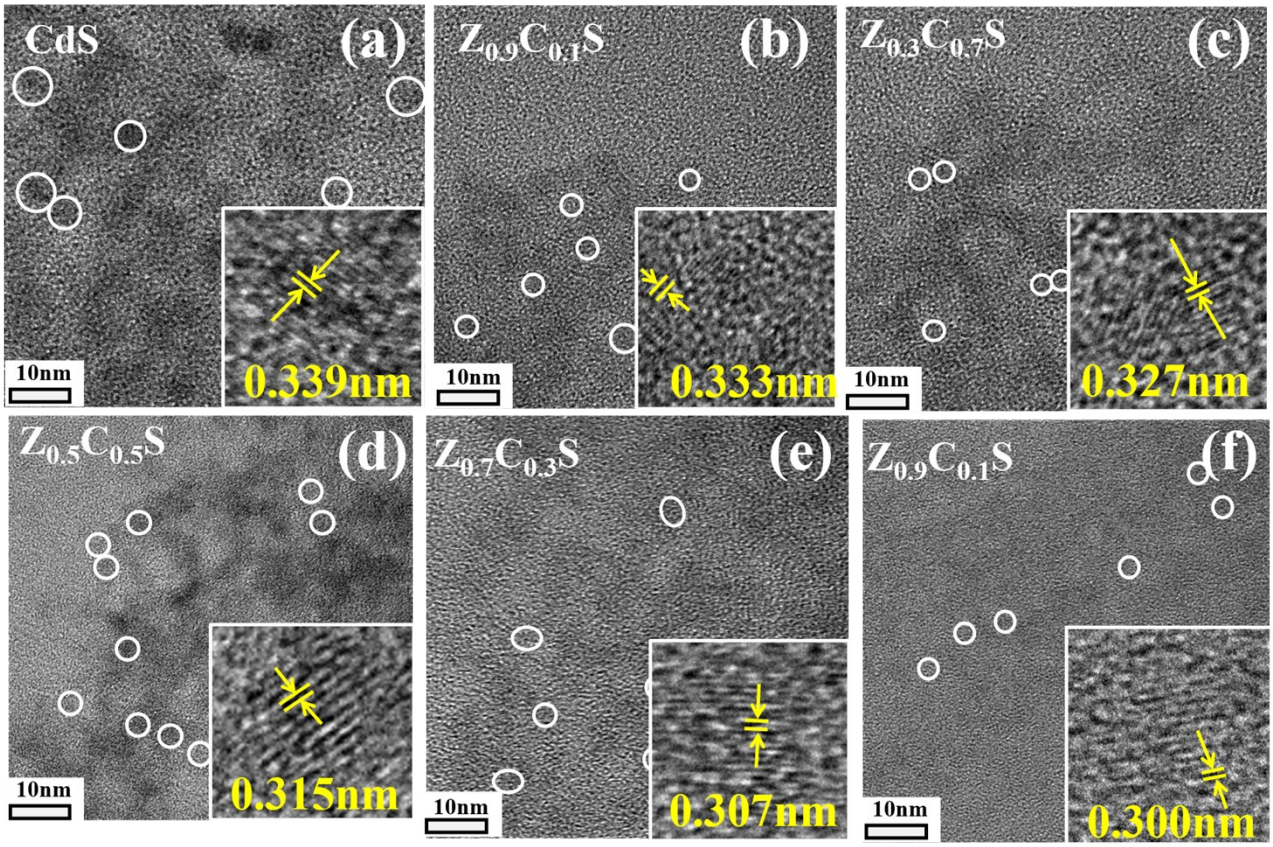

Fig. S2 TEM of $Z_xC_{1-x}S$ QDs with the different chemical composition.

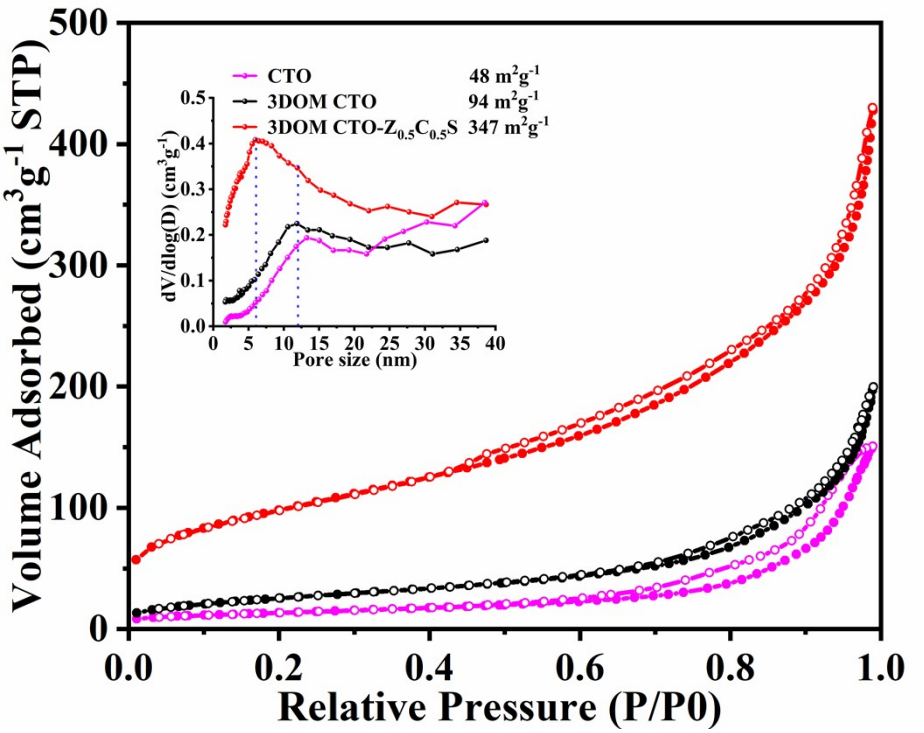

Fig. S3 N_2 absorption-desorption isotherms of CTO、3DOM CTO、3DOM CTO-$Z_{0.5}C_{0.5}S$ QDs (inset is the corresponding pore size distribution).

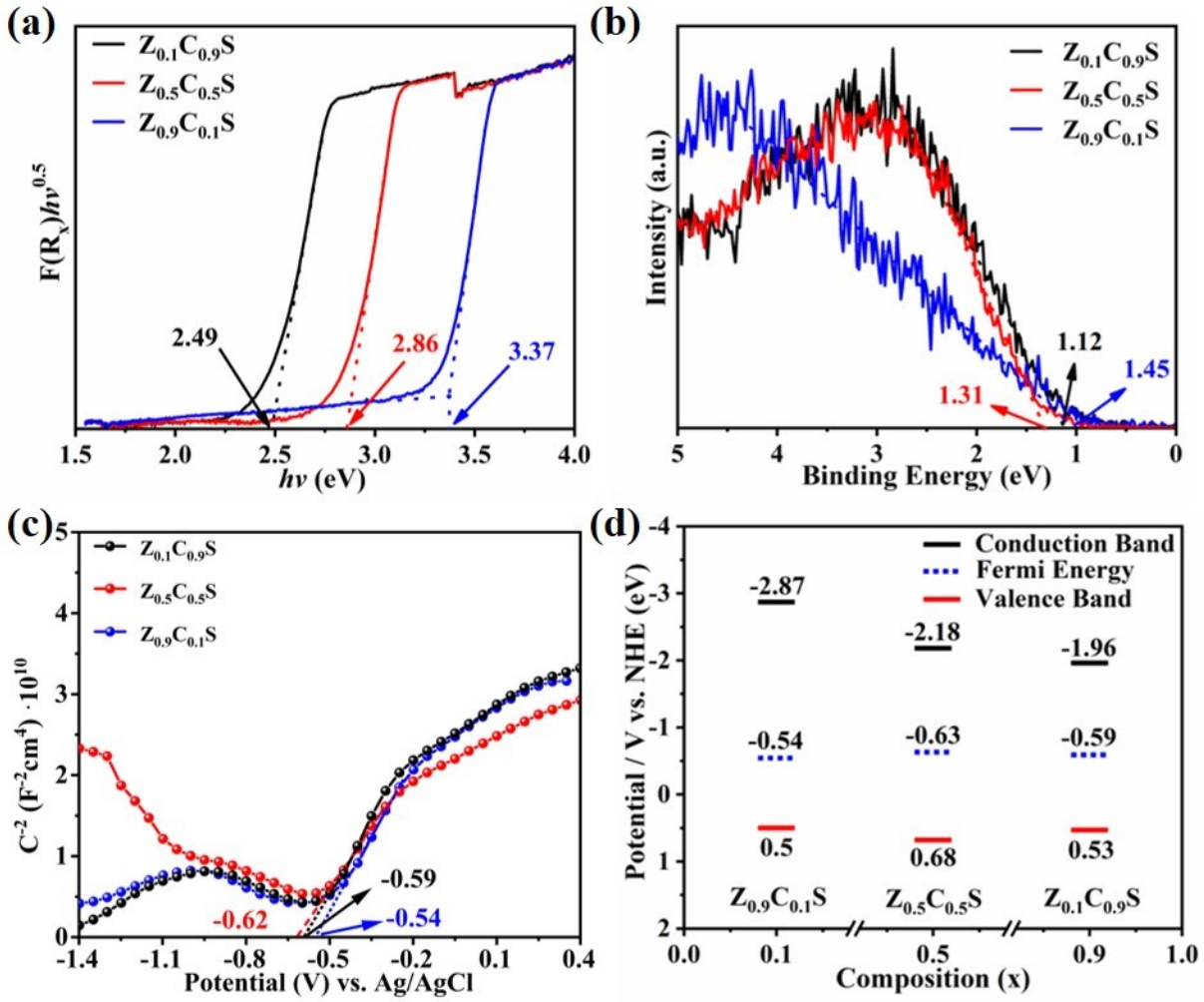

Fig. S4 (a) band gap, (b) XPS-VB spectra, (c) Mott-Schottky plot, (d) position of the conduction band edge and the valence band edge of $Z_{0.1}C_{0.9}S$、$Z_{0.5}C_{0.5}S$ and $Z_{0.9}C_{0.1}S$.

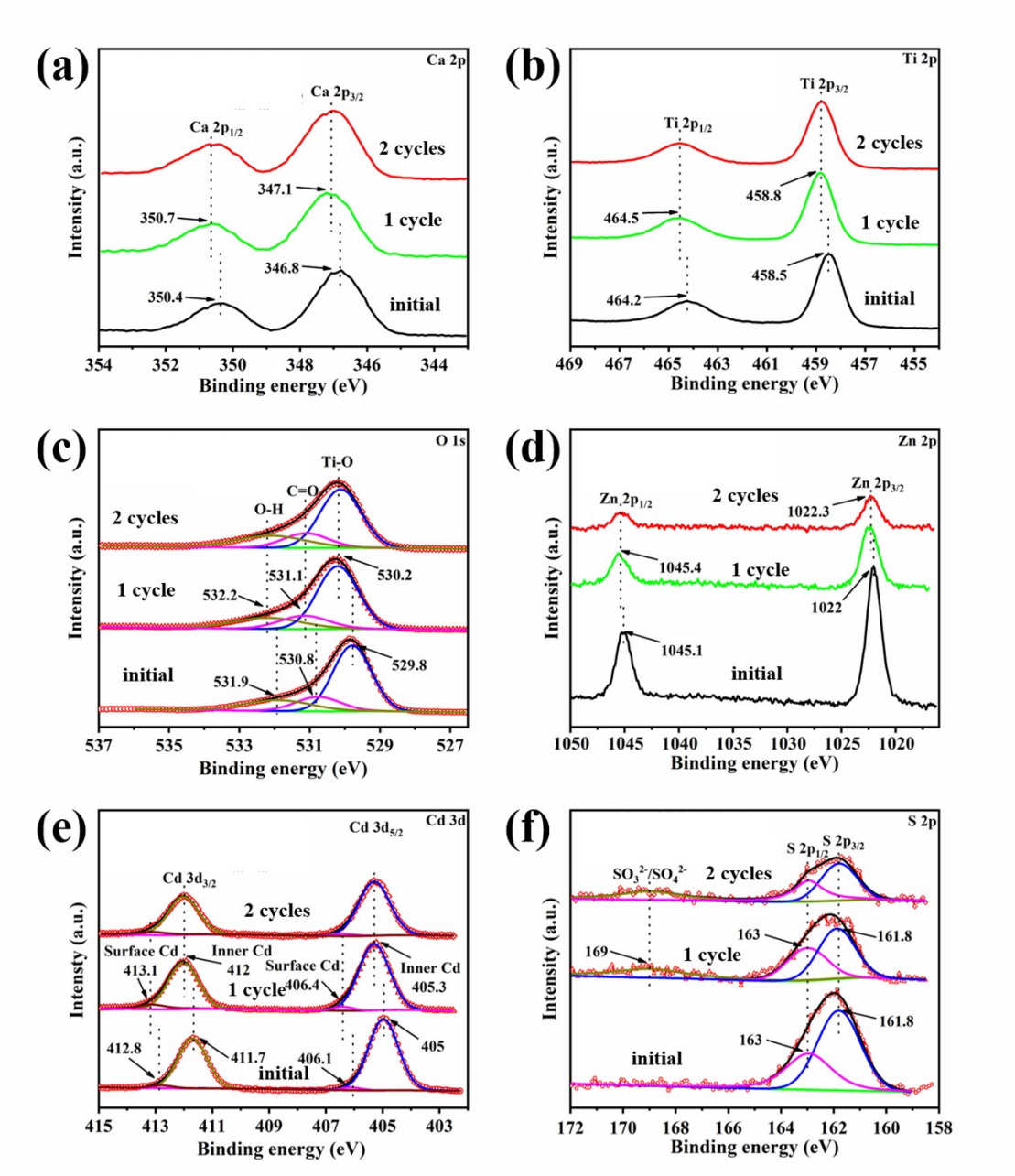

Fig. S5 High-resolution XPS spectra of (a) Ca 2p, (b) Ti 2p, (c) O 1s, (d) Zn 2p, (e) Cd 3d, (f) S 2p of 3DOM CTO-Z0.5C0.5S, 3DOM CTO-$Z_{0.5}C_{0.5}$S-C and 3DOM CTO-$Z_{0.5}C_{0.5}$S-2C.

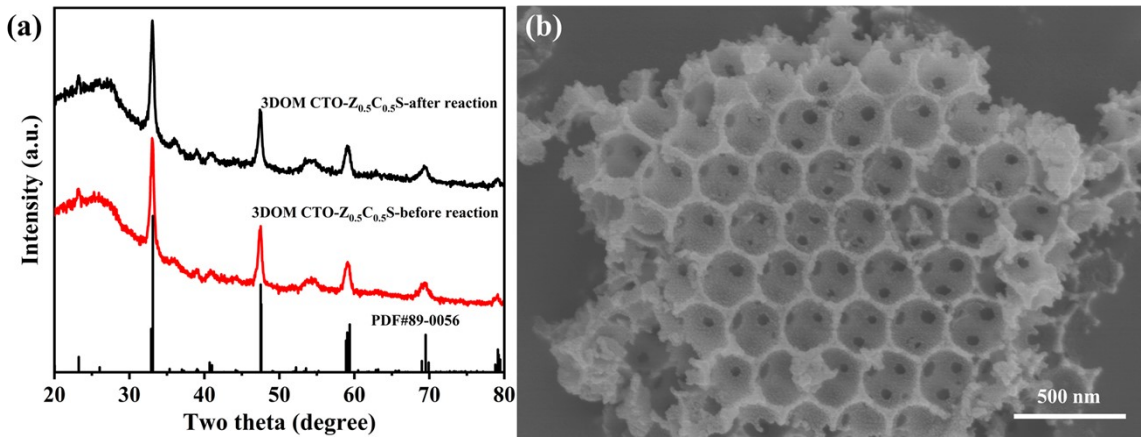

Fig. S6 XRD and SEM spectra before and after the reaction.

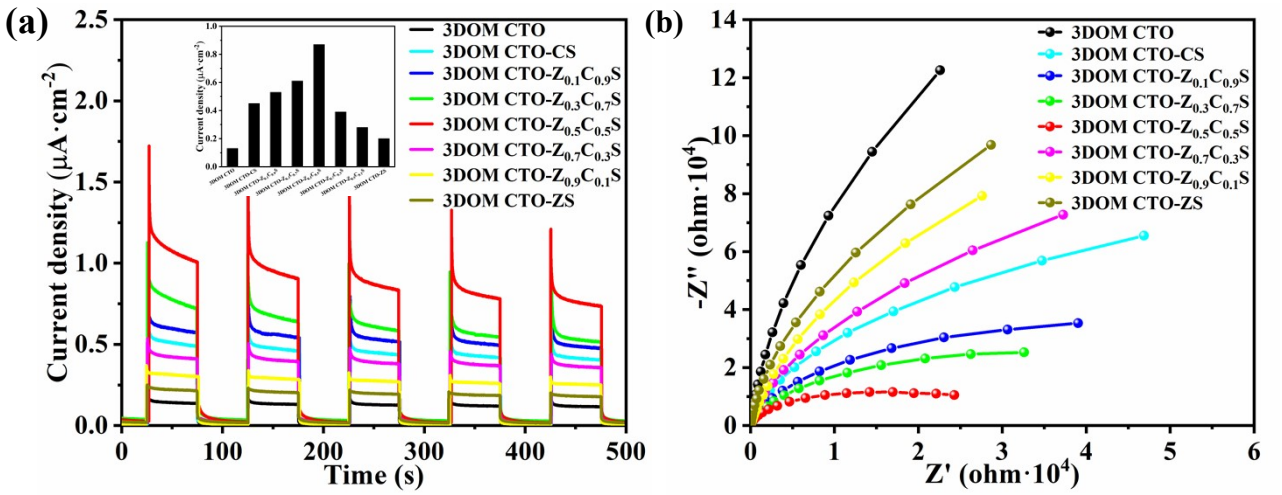

Fig. S7 (a) transient photocurrent (inset is the photocurrent intensity of 250 s), (b) electrochemical impedance spectroscopy of 3DOM CTO-$Z_xC_{1-x}S$ QDs.

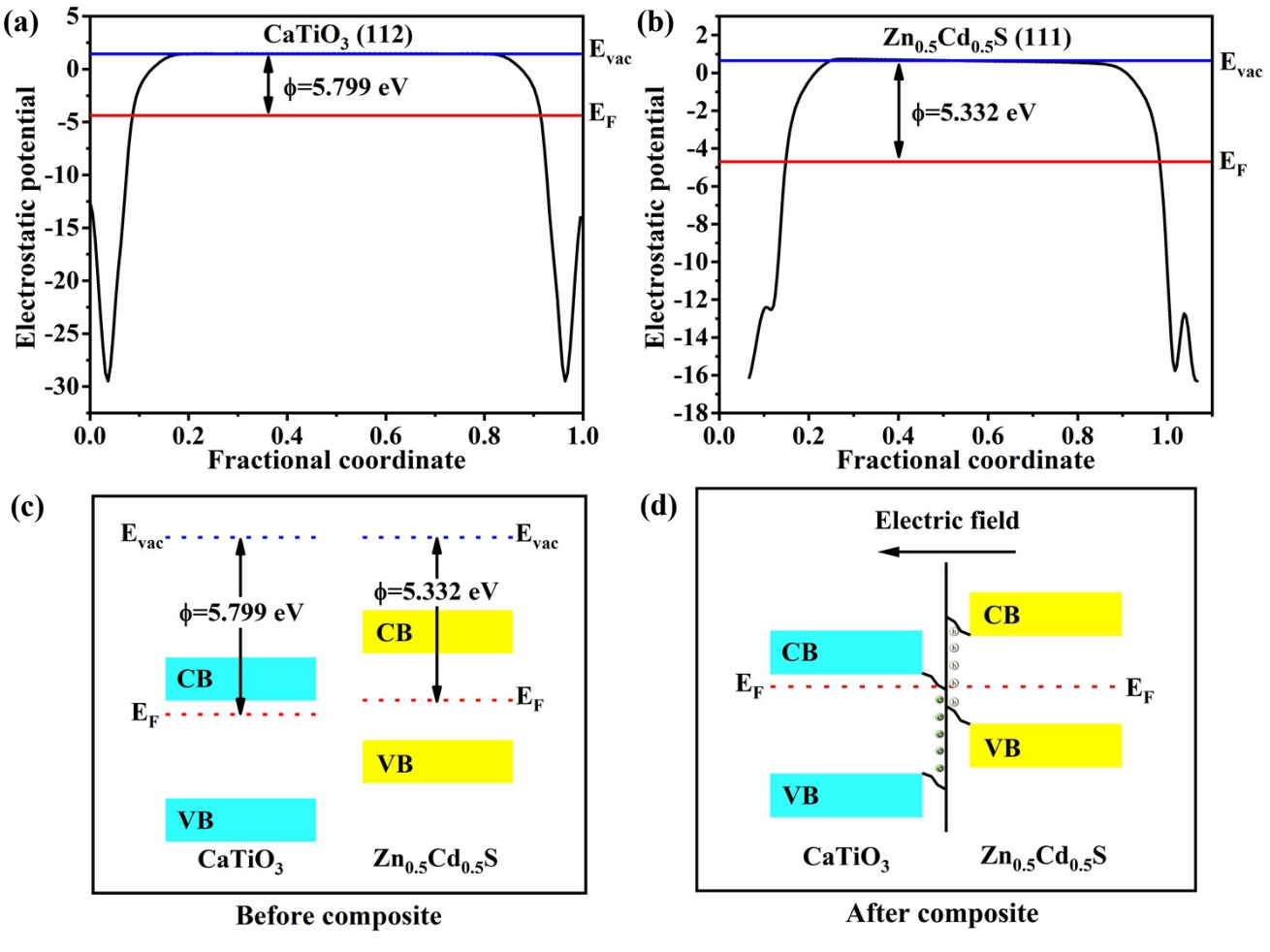

Fig. S8 The work function of (a) CTO (1 1 2), (b) $Z_{0.5}C_{0.5}S$ (1 1 1), band structure of CTO and $Z_{0.5}C_{0.5}S$ (c) before composite, (d) after composite.