**Supporting Information**

**S vacancy modulated ZnxCd1-xS/CoP quantum dots for efficient H2 evolution from water splitting under visible light**

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Table S1 The surface element composition analyzed from the XPS spectra in Figure S4

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Elements | ZCS  (At%) | ZCSv  (At%) | ZCSv/CoP QDs  (At%) | ZCSv/CoP QDs  (At%)\* |
| Cd | 9.4 | 8.73 | 5.77 | 14.18 |
| Zn | 17.08 | 18.58 | 15.79 | 40.80 |
| S | 16.19 | 14.06 | 9.70 | 33.39 |
| P | - | 4.05 | 8.37 | 10.66 |
| Co | - | - | - | 0.47 |

\*Obtained from the EDS mapping analysis.

XPS of S 2p of the as-synthesized ZCS , ZCSv and ZCSv/CoP QDs.

|  |  |  |  |
| --- | --- | --- | --- |
| Smaple | ZCS | ZCSv | ZCSv/CoP QDs |
| 161.11 eV | 19.94% | 46.94% | 33.12% |
| 161.49 eV | 20.80% | 52.00% | 27.20% |
| 162.51 eV | 17.67% | 21.21% | 31.12% |

Table S2 Comparison of H2 evolution rate for ZCSv/CoP QDs with other ZnxCd1-xS/TMPs photocatalysts.

|  |  |  |
| --- | --- | --- |
| Catalyst | H2 evolution rate  （mmol g-1h-1） | Ref. |
| CoP/Zn0.5Cd0.5S | 14.68 | [1] |
| ZCS/10% CoP NWs | 12.17 | [2] |
| Ni2P-Zn0.5Cd0.5S | 9.12 | [3] |
| Ni2P/Zn0.5Cd0.5S | 23.45 | [4] |
| 1.5 wt%Ni2P-Cd0.5Zn0.5S | 7.00 | [5] |
| FeP/Zn0.5Cd0.5S-P | 24.45 | [6] |
| SiO2/Ni2P/rGO/Cd0.5Zn0.5S | 11.65 | [7] |

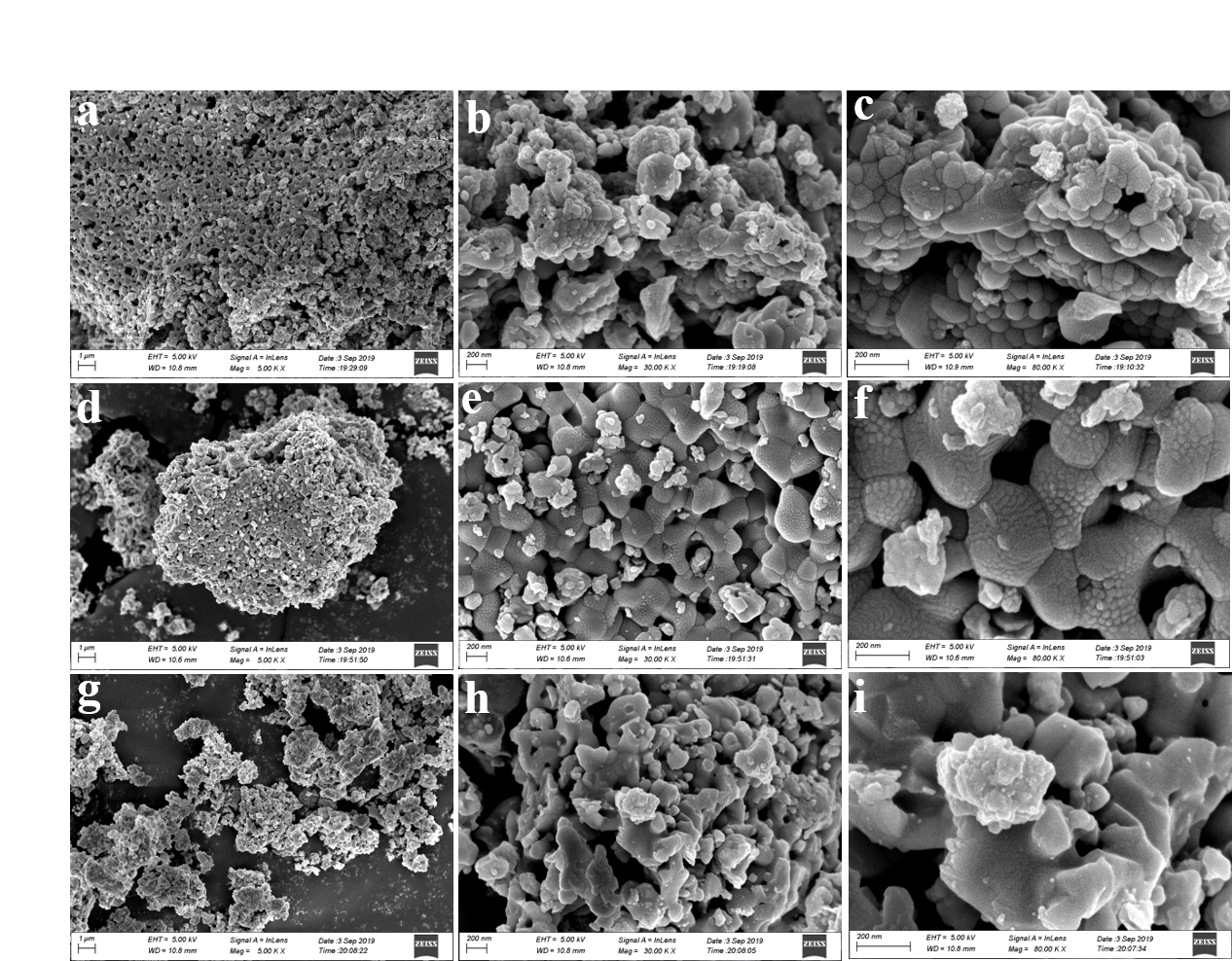


Fig S1 SEM images of ZCS (a, b, c), ZCSv (d, e, f) and ZCSv/CoP QDs (g, h, i)



Fig S2. SEM and elemental mapping images of ZCSv.



Fig S3 SEM and elemental mapping images of ZCSv/CoP QDs.



Fig S4 HRTEM images of ZCSv/CoP QDs.



Fig S5 Survey XPS spectra of ZCS (a), ZCSv (b) and ZCSv/CoP QDs (c).



Fig S6 Co 2p XPS spectrum of ZCSv/CoP QDs.

For the high resolution XPS spectra of Co 2p, two main peaks at 778.52 and 781.51 eV can be assigned to Co-P and oxidized Co species of Co 2p 3/2 in CoP, while one main peak at 793.34 eV corresponds to Co-P of Co 2p 1/2 [8]



Fig S7 Configuration of ZCSv/CoP based on DFT calculations.(a) side view and (b) top view.



Fig S8 TG-DTA (thermo gravimetric and differential thermal analysis) spectra of ZCS under N2 atmosphere.



Fig S9 EPR profiles for ZCS-N2 and ZCSv

Fig S10 The H2 evolution photoactivity of the ZCS, ZCS-N2 and ZCSv.



Fig S11 The H2 evolution photoactivity of the ZCSv-T catalysts prepared at different phosphating temperatures of 350, 500 and 700 °C as indicated in the figure.



Fig S12 EPR profiles for ZCSv-350 and ZCSv-500.



Fig S13 The photoactivity of H2 evolution of the ZCSv/Pt and ZCSv/CoP QDs.



Fig S14 The photoactivity of H2 evolution of the ZCSv/CoP QDs with different CoP QDs loadings and different treatment temperatures.



Fig S15 Cycle runs for the photocatalytic H2 evolution on ZCSv/CoP QDs.

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