

**Co(dmgh)<sub>2</sub>pyCl as a Noble-Metal-Free Co-catalyst for Highly  
Efficient Photocatalytic Hydrogen Evolution over Hexagonal ZnIn<sub>2</sub>S<sub>4</sub>**

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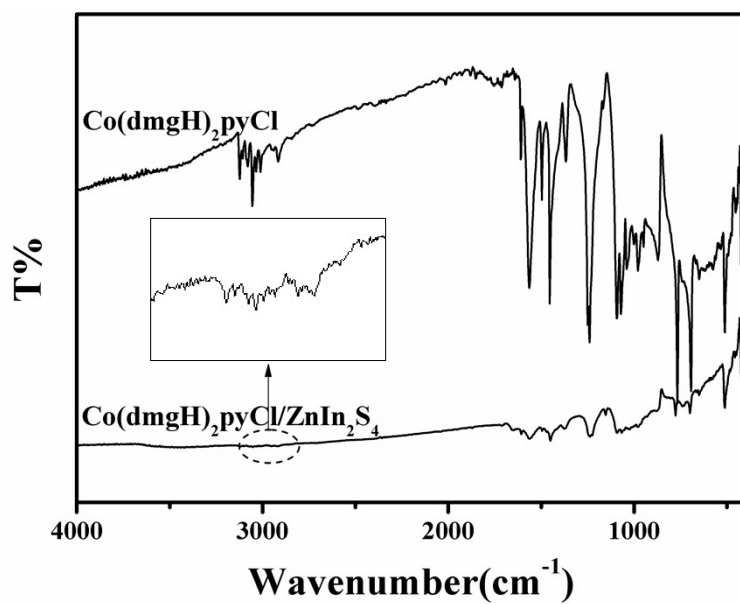
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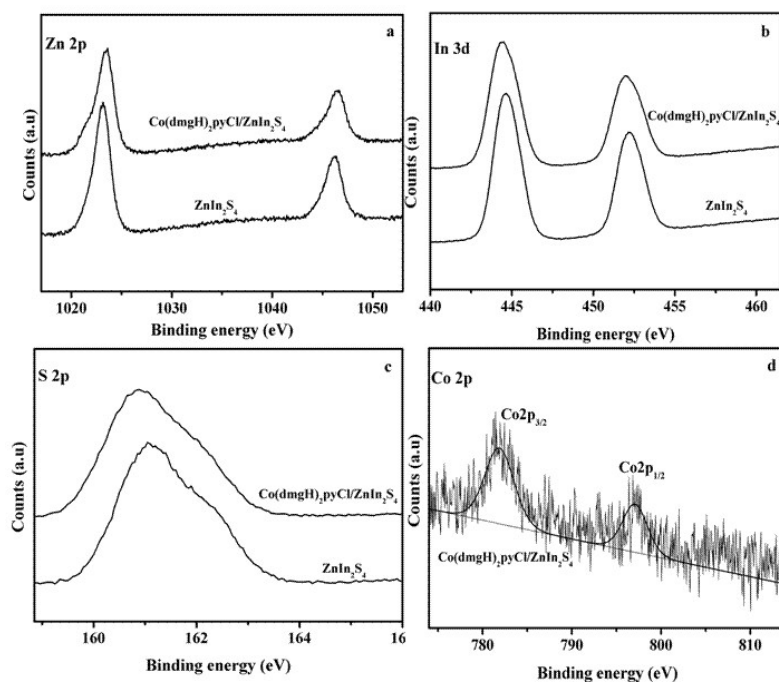
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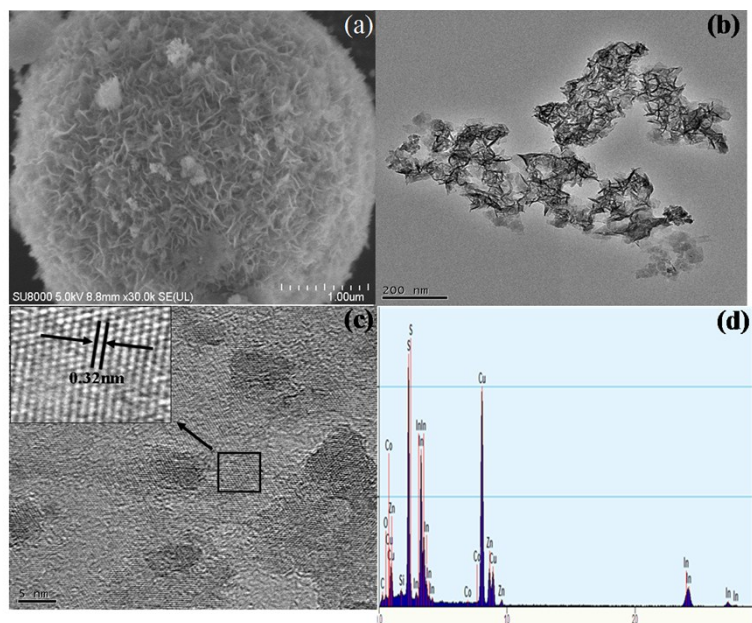
**Fig. S1** IR spectrum of prepared  $\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}$  and 3.0 wt%  $\text{Co}(\text{dmgH})_2\text{pyCl}/\text{ZnIn}_2\text{S}_4$  composite.



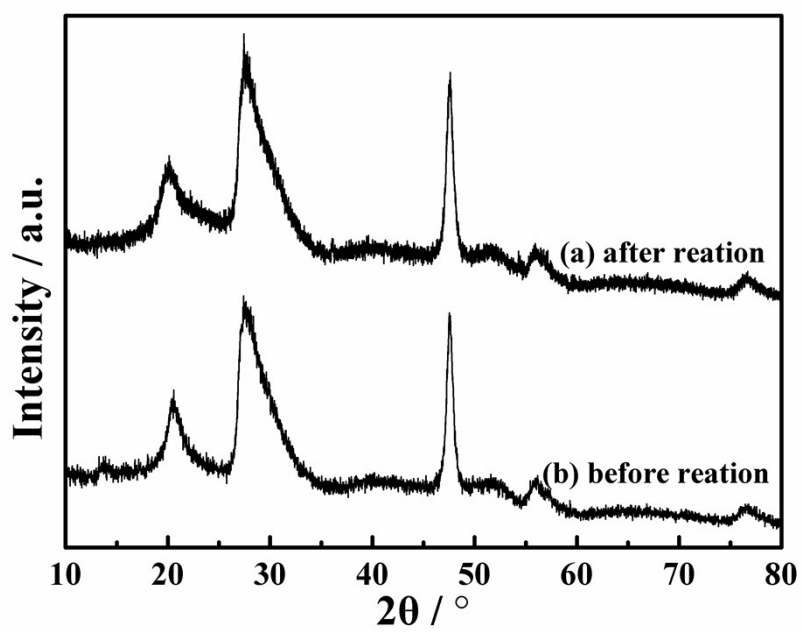
**Fig. S2** XPS spectra of (a) Zn 2p, (b) In 3d, and (c) S 2p in ZnIn<sub>2</sub>S<sub>4</sub> and 3.0-wt%-Co(dmgh)<sub>2</sub>pyCl/ZnIn<sub>2</sub>S<sub>4</sub> composite. (d) XPS spectra of Co 2p in 3.0-wt%-Co(dmgh)<sub>2</sub>pyCl/ZnIn<sub>2</sub>S<sub>4</sub> composite.



**Fig. S3** 3.0 wt%-Co(dmgh)<sub>2</sub>pyCl/ZnIn<sub>2</sub>S<sub>4</sub> composite (a) SEM image, (b) low magnification TEM image, (c) HRTEM image, and (d) EDS.



**Fig. S4** XRD patterns of 3.0 wt %-Co(dmgh)<sub>2</sub>pyCl/ZnIn<sub>2</sub>S<sub>4</sub> (a) after and (b) before photocatalytic hydrogen production reaction.



**Table S1**  $^1\text{H}$ NMR and MS (ESI $^+$ ) data for  $\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}$ .

Compound	$^1\text{H}$ NMR ( $\delta$ )	MS (ESI $^+$ )
$\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}$	$^1\text{H}$ NMR in DMSO- $d_6$ : 8.04 [d, 2H, J = 5.6 Hz], 7.90 [t, 1H, J = 7.2 Hz], 7.48, [t, 2H, J = 7.2 Hz], 2.32 [s, 12H].	m/z $\text{C}_{13}\text{H}_{19}\text{N}_5\text{O}_4\text{ClCo}$ , calcd. 403.5, found: 403.8