

空心 NiCo_2S_4 纳米球助催化剂负载 ZnIn_2S_4 纳米片用于可见光催化制氢

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Hollow NiCo_2S_4 Nanospheres as a Cocatalyst to Support ZnIn_2S_4 Nanosheets for Visible-Light-Driven Hydrogen Production

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1 AQY measurement

The determination of apparent quantum efficiency (AQY) for H₂ generation was performed using same closed circulating system under illumination of a 300 W Xe lamp with optical band pass filter (400 nm). The AQY of the sample was calculated using the following Eq. (1):

$$\text{AQY} = \frac{2 \times \text{the number of evolved H}_2 \text{ molecules}}{\text{the number of incident photos}} \times 100\% \quad (1)$$

2 The calculation process of the value of valence band maximum (E_{VB}) from UPS spectrum

The detailed calculation process of the value of valence band maximum (E_{VB}) obtained from UPS spectrum is as follows:

The work function (ϕ) can be calculated using Eq. (1): $\phi = h\nu - E_{\text{SEO}}$. Here, $h\nu = 21.22$ eV, represents the energy of the monochromatic ionizing light, while E_{SEO} is the secondary electron onset, obtained from the linear extrapolation of the UPS spectrum. The Fermi level (E_{f}) is obtained from the work function using Eq. (2): $E_{\text{f}} = -\phi$. Then, the position of the valence band (E_{VB}) is obtained from Eq. (3): $E_{\text{VB}} = E_{\text{f}} - X$, in which X is obtained from the extrapolation of the onsets in the UPS spectrum. All the calculated potentials mentioned above refer to the vacuum energy (eV vs. vacuum level). The vacuum energy (E_{vac}) in electronvolt can be converted to E (V vs. RHE) according to the relationship between the potential of the reversible hydrogen electrode (RHE) and E_{vac} (i.e., $E_{\text{RHE}} = -E_{\text{vac}} - 4.44$). The value of the potential of RHE equals to the normal hydrogen electrode (NHE) at pH = 0. Based on the relationship between the potential of the reversible hydrogen electrode (RHE) and the normal hydrogen electrode (NHE) (i.e., $E_{\text{NHE}} = E_{\text{RHE}} + 0.0591\text{pH}$), the value of the potential can be converted to E (V vs. NHE, pH = 7).

According to the detailed calculation process mentioned above, the work function of NiCo₂S₄ was estimated to be 4.65 eV (vs. vacuum level), applying the method of linear approximation to the UPS spectrum to obtain the secondary electron onset (i.e., 16.57 eV vs. vacuum level for NiCo₂S₄). The Fermi level of NiCo₂S₄ was estimated to be -4.65 eV (vs. vacuum level). Simultaneously, the valence band maximum was calculated to be -5.48 eV (vs. vacuum level). according to the formula $E_{\text{RHE}} = -E_{\text{vac}} - 4.44$, the valence band maximum of NiCo₂S₄ is determined to be 1.04 V vs. RHE. According to the relationship between the potential of RHE and NHE. The valence band maximum of NiCo₂S₄ is located at 0.63 V (vs. NHE, pH = 7). Similarly, the valence band maximum of ZnIn₂S₄ is located at 1.42 V (vs. NHE, pH = 7).

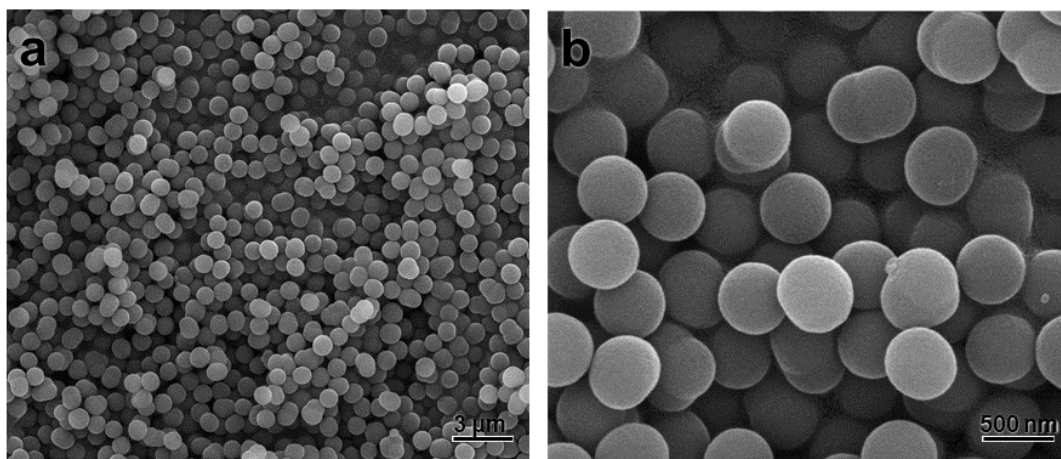


Fig. S1 FESEM images of NiCo-glycerate solid spheres.

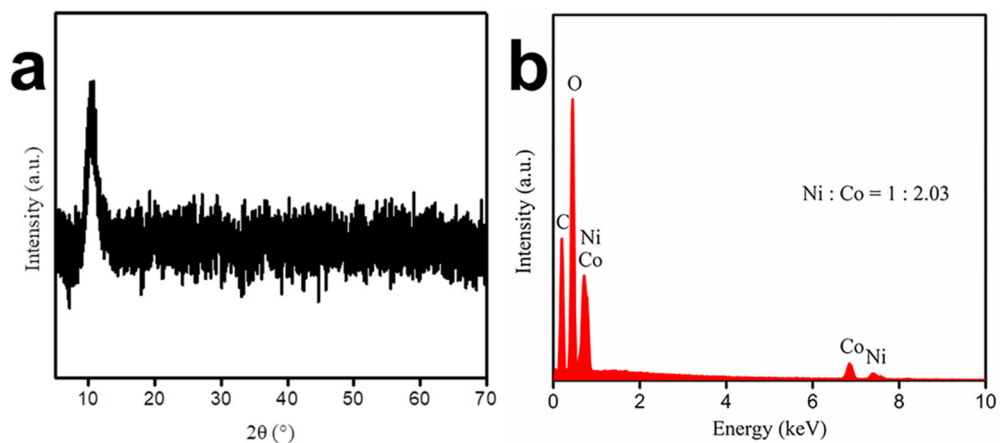


Fig. S2 (a) XRD pattern and (b) EDX spectrum of NiCo-glycerate solid spheres.

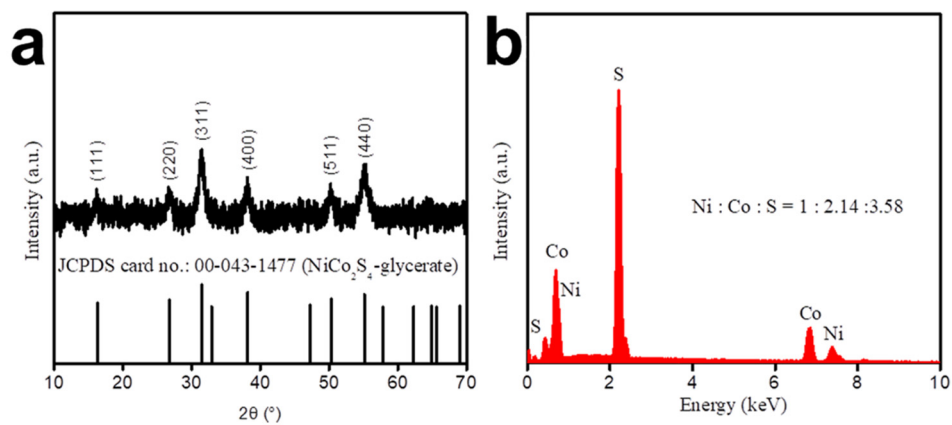


Fig. S3 (a) XRD pattern and (b) EDX spectrum of NiCo₂S₄ hollow spheres.

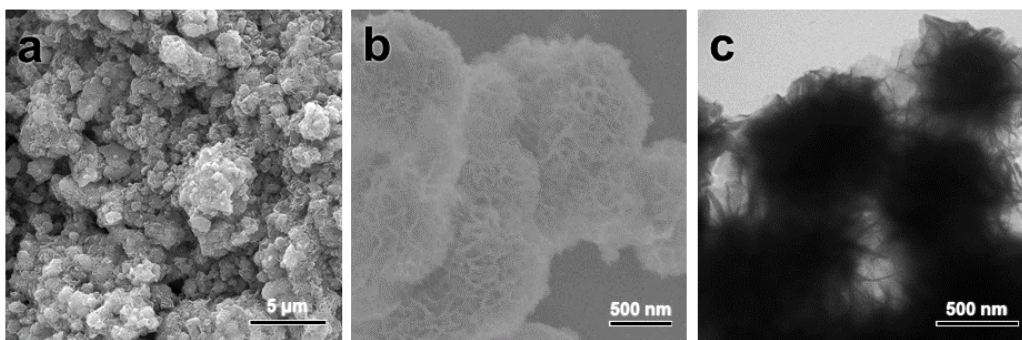


Fig. S4 (a, b) FESEM images and (c) TEM images of NiCo₂S₄@ZnIn₂S₄ NPs.

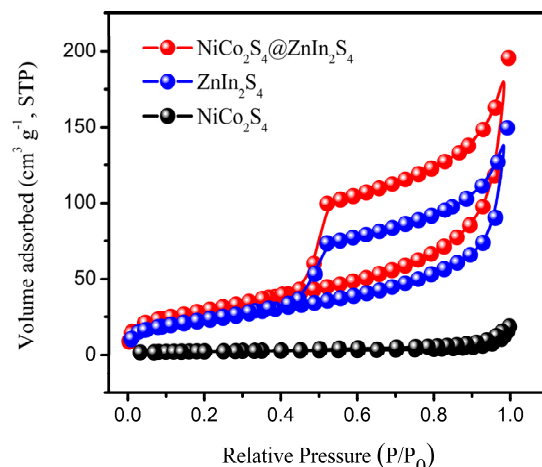


Fig. S5 N₂ sorption isotherms of different samples.

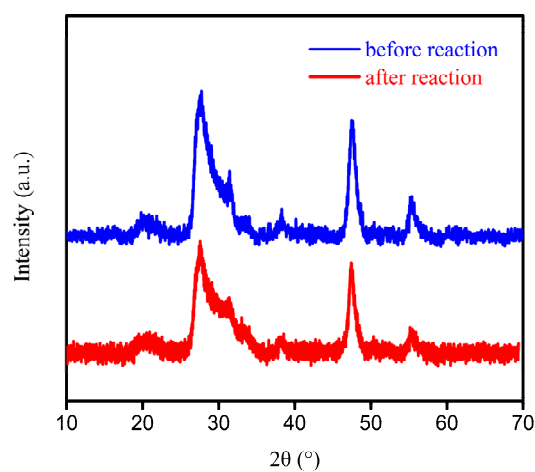


Fig. S6 XRD patterns of the NiCo₂S₄@ZnIn₂S₄ materials before and after reaction.

Table S1 Comparison of photocatalytic H₂ generation performance.

Catalyst	Mass/mg	Light source	Hole scavenger Cocatalyst	H ₂ evolution rate (μmol·h ⁻¹ ·g ⁻¹)	Refs.
NiCo ₂ S ₄ @ZnIn ₂ S ₄	20	(λ > 420 nm)	TEOA	3900	this work
LaNiO ₃ /CdS	20	(λ > 420 nm)	Na ₂ S-Na ₂ SO ₃	3700	1
CdS/Co ₉ S ₈	20	AM 1.5	Na ₂ S-Na ₂ SO ₃	1061	2
O-doped ZnIn ₂ S ₄	20	(λ > 420 nm)	Na ₂ S-Na ₂ SO ₃	2120	3
TiO ₂	50	(λ > 420 nm)	methanol Pt	1441	4
Ta ₃ N ₅ /BaTaO ₂ N	150	(λ > 420 nm)	methanol Pt	182	5
LaNiO ₃ /ZnIn ₂ S ₄	20	(λ > 420 nm)	TEOA	1600	6
Co ₉ S ₈ @ZnIn ₂ S ₄	4	(λ > 400 nm)	TEOA	6250	7
ZnIn ₂ S ₄	5	(λ > 400 nm)	Lactic acid Pt	1748	8

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