Supporting Information for the manuscript

Integrating $Co(OH)_2$ nanosheet arrays on graphene for efficient noble-metal-free EY-sensitized photocatalytic H_2 evolution

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Synthetic procedures and characterization of products

1. Preparation of graphene oxide

Synthesis of graphene oxide: GO was synthesized by a modified Hummers' method. In detail, 10 g graphite powder (provided from Qingdao Zhong tian Company, China) was put into 230 mL concentrated H_2SO_4 under moderate stirring. Then, 30 g $KMnO_4$ was added gradually under stirring and the solution was cold below 5 °C in an ice bath. After that, the solution was heated to 35 °C in a water-bath and kept stirring for 2 h. Then, the mixture was diluted with 500 mL DI water in an ice bath to keep the temperature below 5 °C. Shortly after the further diluted with 1.5 L of DI water, 80 mL 30% H_2O_2 was then added into the mixture. The mixture was centrifuged and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. After that, the mixture was dialyzed for one week and the final GO sample was obtained after full sonication.

2. Characterizations

The morphological characteristics were tested through scanning electron microscopy SEM (ZEISS Sigma 500 instrument) and transmission electron microscopy TEM (Jeol JEM-2100F instrument). The determination of crystal structures was determined by X-ray diffraction (XRD) with Cu Kα (λ = 0.15406 nm, Bruker D8). The surface composition of the samples was determined by X-ray photoelectron spectrometer (XPS, Thermo Fisher K-Alpha). The nitrogen adsorption-desorption isotherm of samples was analyzed using ASAP 2020 automatic analyzer. Raman spectra were recorded on a Renishaw in Via Raman System 1000 with a 532 nm Nd:YAG excitation source. The photoluminescence of the samples was analyzed by using FLS980 fluorescence spectrometer at the excitation wavelength λ=490 nm. The above PL measurements were performed in H_2O/TEOA (5:1, 6mL) mixed solution containing 15 mg EY and 1 mg as-prepared cocatalysts. Contact angle measurements were carried out using the static drop method using a Fangrui Instrument Company JCY contact angle meter. Likewise, gas-solid phosphating was performed on the samples using a tube furnace (OTF-1200X). Furthermore, all the electrochemical measurements of the photocurrent, the electrochemical impedance spectra (EIS), the Mott–Schottky (MS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves were carried out in the three-electrode cell, in which Ag/AgCl was used as reference electrode, a Pt wire was used as a counter electrode and an indium in oxide (ITO) conductive glass was used with the samples as a working electrode in 0.1 M Na_2SO_4 electrolyte (pH=7.56), all measurements were carried out on CH Instruments CHI-660E electrochemical workstation. The values relative to Ag/AgCl could be directly converted to the values *vs* NHE to facilitate comparison.

$$E_{NHE} = E_{Ag/AgCl} + 0.059 \times pH + E^{\theta}_{Ag/AgCl}$$

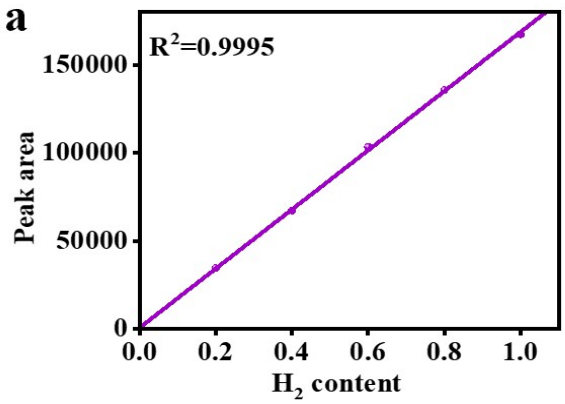

Fig. S1 Gas chromatography curves for H_2 standard under different contents.

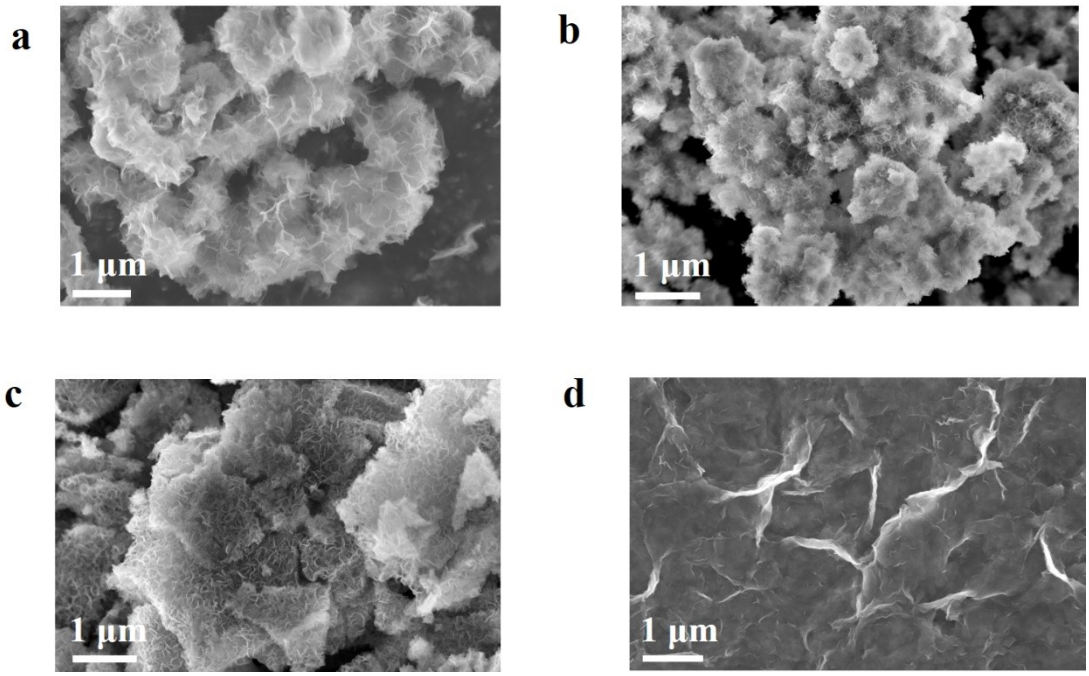

Fig. S2 Morphology information of $Co(OH)_2$-GR FESEM images of (a) $Co(OH)_2$, (b) $Co(OH)_2$-1%GR, (c) $Co(OH)_2$-5%GR and (d) $Co(OH)_2$-30%GR.

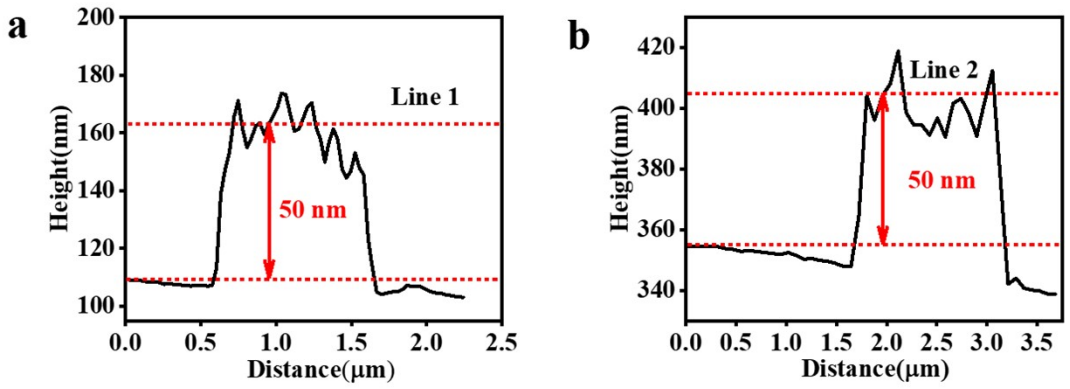

Fig. S3 Thickness information of $Co(OH)_2$ -10%GR The corresponding height profiles along the (a) white line 1 and (b) white line 2 drawn in **Fig. 1g**.

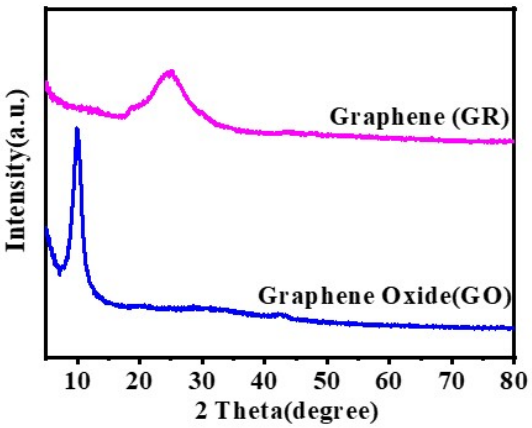

Fig. S4 XRD patterns of graphene oxide (GO) and graphene (GR).

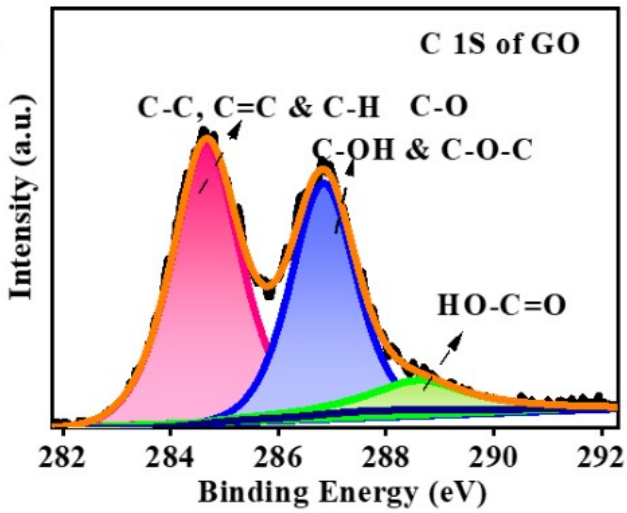

Fig. S5 High-resolution C 1s XPS spectrum of GO.

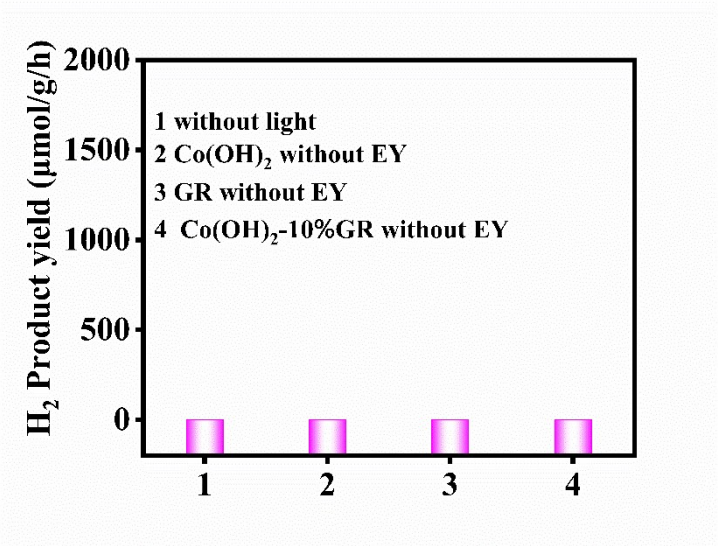

Fig. S6 Control experiments for photocatalytic measurements.

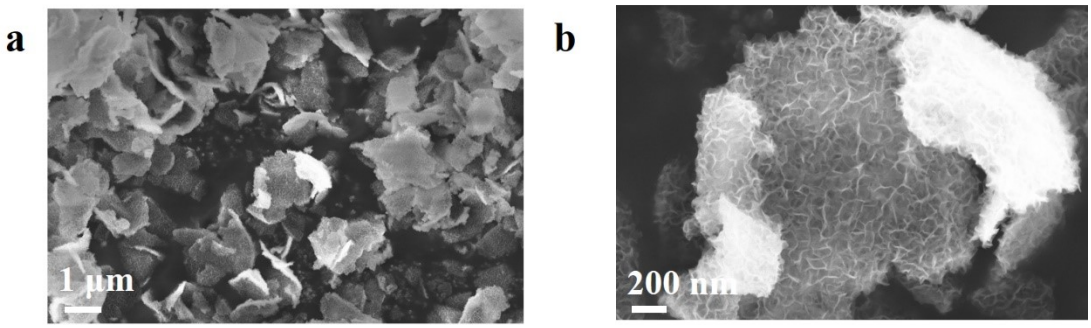

Fig. S7 SEM images of used $Co(OH)_2$-10%GR composite.

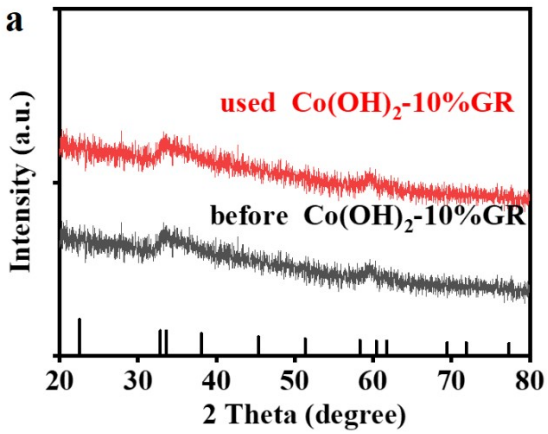

Fig. S8 XRD patterns of used $Co(OH)_2$-10%GR composite.

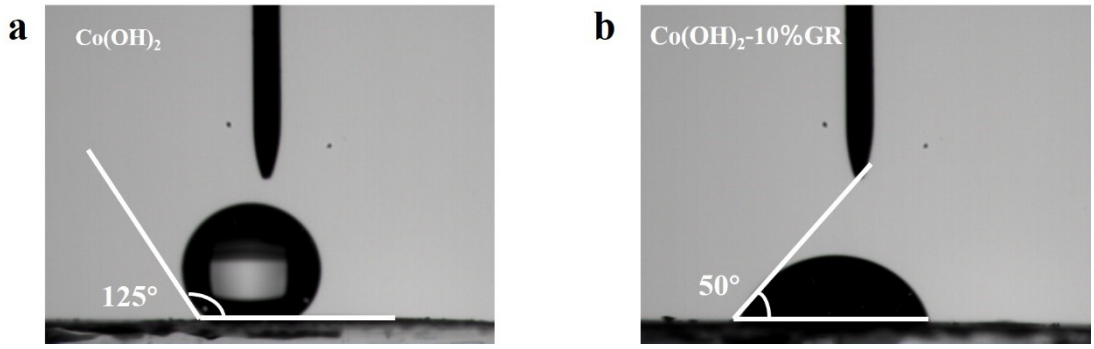

Fig. S9 Contact angle tests of (a) pure $Co(OH)_2$, (b) $Co(OH)_2$-10%GR composites.

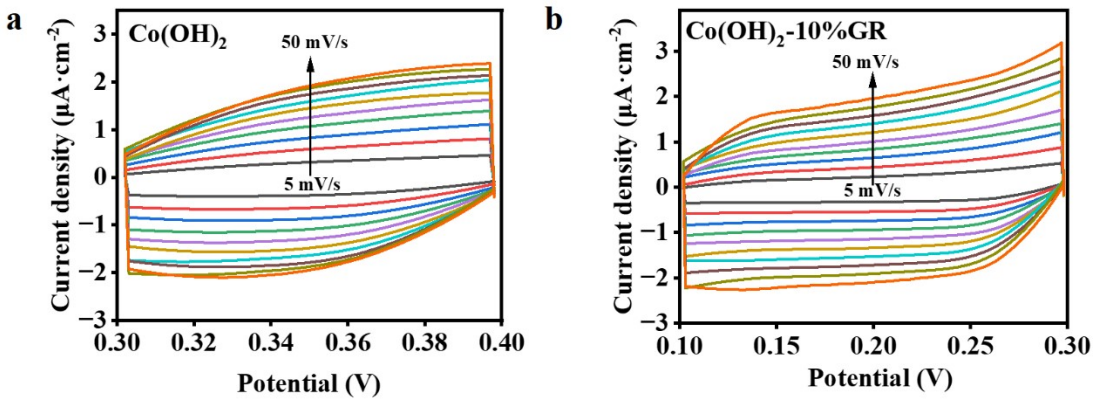

Fig. S10 The CV curves of (a) pure $Co(OH)_2$ and (b) $Co(OH)_2$-10%GR.

Table S1. Comparison of this work and other photocatalysts for photocatalytic hydrogen evolution.

Photocatalysts	photosensitizer	Light sources	Sacrificial agents	H_2 ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Ref
$Co(OH)_2$-GR	EY	300 W Xe lamp; λ> 420 nm	TEOA	17539	this work
UiO-66-NH_2	EY	300 W Xe lamp; λ> 380 nm	TEOA	2760	1
MoS_2	EY	300 W Xe lamp; λ> 400 nm	TEOA	18	2
$Co(OH)_2$/CdS	EY	300 W Xe lamp; λ> 420 nm	TEOA	14430	3
RGO/NiS_x	EY	300 W Xe lamp; λ> 420 nm	TEOA	109.9	4
$Co(OH)_2$/g-C_3N_4	EY	300 W Xe lamp; λ> 400 nm	TEOA	431.9	5
Sb/SnO_2	EY	300 W Xe lamp; λ> 420 nm	TEOA	49.94	6
$Zn_{0.3}Co_{2.7}S_4$	EY	300 W Xe lamp; λ> 400 nm	TEOA	155.2	7
$Co(OH)_2$/TiO_2	EY	300 W Xe lamp; λ> 420 nm	TEOA	746.93	8
$Co_2(OH)_3Cl$/GO	EY	300 W Xe lamp; λ> 420 nm	TEOA	97.4	9
ZnO/$SrTiO_3$	EY	300 W Xe lamp; λ> 420 nm	TEOA	16006.12	10
ZnO/BiOCl	EY	300 W Xe lamp; λ> 420 nm	TEOA	4146.77	11
2DCo-MOF/p-g-C_3N_4/ 5% Sm doped	EY	300 W Xe lamp; λ> 420 nm	TEOA	73.42	12

Table S2. Surface areas of samples.

Samples	BET surface area ($m^2 \cdot g^{-1}$)
$Co(OH)_2$	35.85
$Co(OH)_2$-10%GR	76.34

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