

Electronic supplementary information

Facile synthesis of $\text{Co}_2(\text{OH})_3\text{Cl}$ /cobalt carbide/reduced graphene oxide composite for enhanced dye-sensitized photocatalytic H_2 evolution

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1. Experimental section

1.1 Characterization

X-ray photoelectron spectra (XPS) were conducted on an ESCALAB250xi XPS spectrometer (ThermoFisher Scientific, America) equipped with an Al $K\alpha$ X-ray source. The C1s peak set at 284.6 eV was used as an internal reference for absolute binding energy. X-ray diffraction (XRD) patterns were recorded with an XD-2/3 diffractometer employing nickel-filtered Cu $K\alpha$ radiation. Scan electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken on a JEOL JSM-6701F and JEOL JEM-2100, respectively. Raman spectra were recorded on InVia Plus Raman spectroscopy (excited by 532 nm laser). TG and DSC curves were performed on TG/DSC (Labsys Evo, France) in N_2 (95%) + H_2 (5%) atmosphere from room temperature to 600 °C at heating rate of 10 °C min^{-1} . UV-DRS spectra of CG-350 before and after dye sensitization were conducted on a Hitachi U-3310 spectrophotometer.

The fluorescence spectra of Eosin Y (EY) before and after addition of RGO, or CG-T were measured on a Hitachi F-7000 fluorescence spectrophotometer. 200 mL of EY solution (1.0×10^{-5} mol L⁻¹), and 2.5 mg of CG-T composite was treated with ultrasound for 1 h at room temperature.

Transient absorption decay measurements for ³EY* were performed on a LP-920 laser flash photolysis spectrometer (Edinburgh). The excitation pulses were obtained from the unfocused second harmonic (532 nm) output of a Nd:YAG laser (Brilliant b), the probe light was provided by a Xenon short arc lamp (450 W). 200 mL of EY solution (1.0×10^{-5} mol L⁻¹), and 2.5 mg of CG-T composite was treated with ultrasound for 1 h at room temperature. The dispersion was transferred to a cuvette with a cover, and then deaerated for 10 min with nitrogen gas before measurements.

1.2 Photocatalytic performance

Photocatalytic H₂ production reaction was carried out under visible light irradiation in a closed 190 mL Pyrex cell with an efficient irradiation area of ca. 16.9 cm². 400 W high pressure Hg lamp was used as the light source. Its ultraviolet and infrared light were eliminated by a cut-off glass filter ($\lambda \geq 420$ nm) and a water cooling jacket to ensure visible light irradiation only (the incident light intensity of 5.2 mw m⁻²). Typically, 10.0 mg of CG-T, 98 mL of the trimethylamine (TMA) solution (pH 10.0), and 4 ml of Eosin Y solution (EY 10.0×10^{-3} mol L⁻¹) were added together in the cell. Before irradiation, the mixture was treated with ultrasound for 5 min, and then aerated with N₂ for 25 min. The product H₂ amount was determined on a gas chromatograph. In the stability test, the recovery of the catalyst was similarly conducted as described in Ref 2.

AQY as a comparison standard for photocatalytic H₂ evolution activity, was calculated according to the following formula.

$$\text{AQY} [\%] = 2 \times \frac{\text{mole of hydrogen evolved}}{\text{mole of incident photon}} \times 100$$

The effect of incident wavelength on AQYs was investigated using LED lamps (UVEC-4) as the irradiation resources. The other photocatalytic reaction conditions were the same as above.

1.3 Electrochemical test

1.3.1 Linear sweep voltammetry (LSV)

The Linear sweep voltammetry (LSV) curves of RGO, $\text{Co}_2(\text{OH})_3\text{Cl}$, and CG-350 composite were performed on LK2100 electrochemical workstation in the three-electrode system. A saturated calomel electrode and a Pt wire electrode were used as the reference and the counter electrode, respectively. The working electrode was prepared as following: 10.0 mg of the above samples and 10 μL of 5.0 wt% Nafion solution (Dupont, America) were dispersed in 2.0 mL of distilled water by at least 2 h sonication to form a homogeneous ink. Then 10 μL of the ink (containing 50 μg of catalyst) was loaded onto a clean glassy carbon electrode of 3 mm in diameter (loading content $\sim 0.70 \text{ mg cm}^{-2}$). The test was conducted in a 1.0 M KOH solution with the scan rate of 10.0 mV s^{-1} .

1.3.2 Mott-Schottky (M-S) curve

M-S test was performed on an IVIUMSTAT (Netherlands) electrochemical workstation. The conditions were as follows: Pt wire and Ag/AgCl electrode as the counter and reference electrode, respectively, and 1.0 M KOH as the electrolyte solution.

1.3.3 Photocurrent curve

The photocurrent test was conducted on a LK 2100 electrochemical workstation in a three electrode cell. A Pt and saturated calomel electrode were used as the counter and reference electrode, respectively. The working electrode was prepared as follows. First, an ITO conducting glass ($1.0 \text{ cm} \times 3.0 \text{ cm}$) was ultrasonically cleaned using acetone, ethanol and water in turn. Next, 5 mg of CG-T, and 10 μL of Nafion solution were dispersed in 2 mL of distilled

water via ultrasound. Then, 15 μL of the dispersion was loaded on the cleaned glass (the covering area: $1.0\text{ cm}\times 1.0\text{ cm}$). Finally, the dispersion was dried at room temperature to obtain the working electrode. The electrolyte was TMA solution of pH 10.0 containing $0.20\text{ mol L}^{-1}\text{ Na}_2\text{SO}_4$ and $2\times 10^{-4}\text{ mol L}^{-1}\text{ EY}$. A 350 W Xe lamp was used as the light source with a cut-off filter glass to remove irradiation below 420 nm.

2. Results

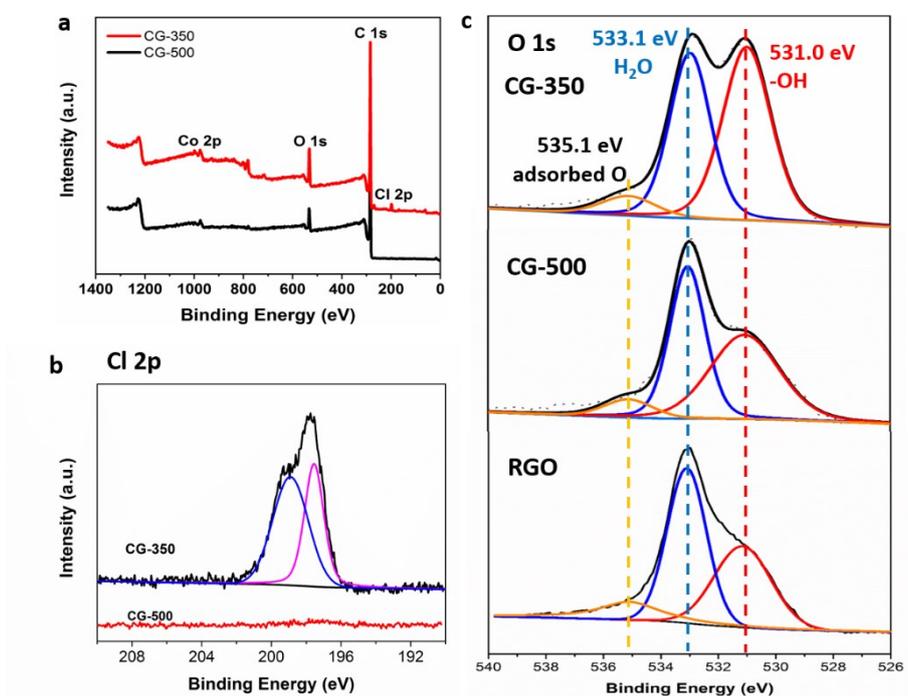


Fig. S1 The XPS survey for CG-350 and CG-500 (a), high resolution XPS spectra of Cl 2p for CG-350, and CG-500 (b), and O 1s for CG-350, CG-500 and RGO (c).

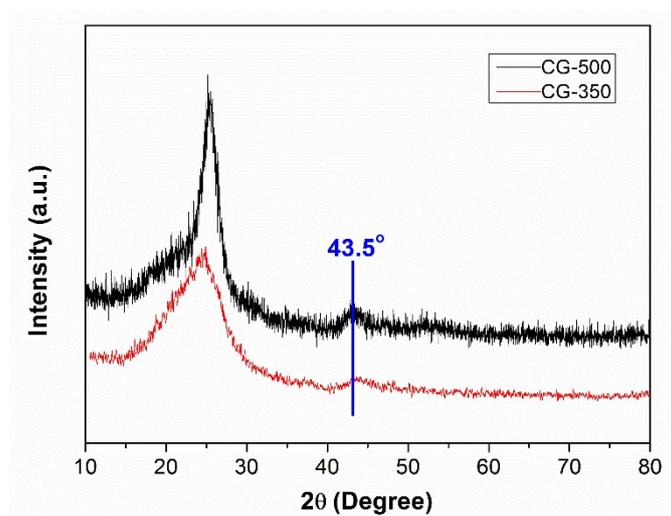


Fig.S2 XRD patterns of CG-350 and CG-500 composites after soaking in acidic solution (1.0 mol L^{-1})

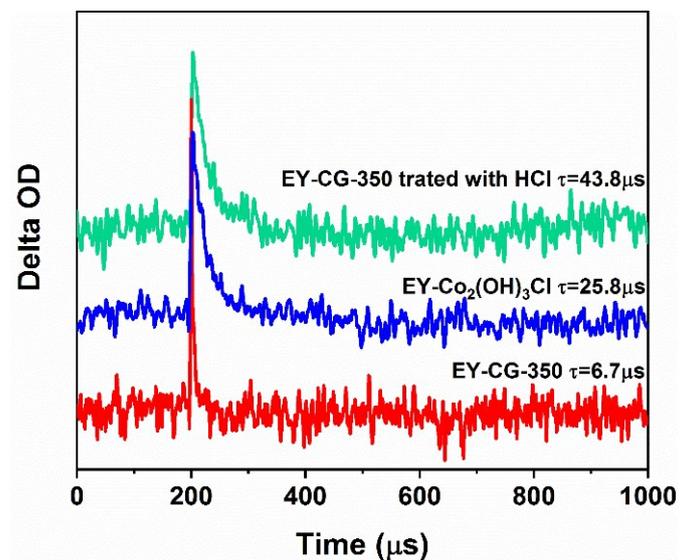


Fig. S3 Transient absorption decay of $^3\text{EY}^*$ followed at 580 nm under pulse irradiation of 532 nm. Conditions: $12.5 \mu\text{g mL}^{-1}$ sample; $1.0 \times 10^{-5} \text{ mol L}^{-1}$ EY.

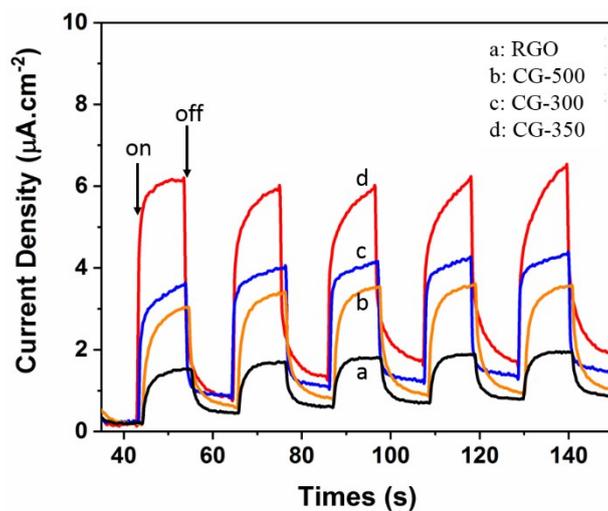


Fig. S4 Transient photocurrent-time curves of RGO, and CG-T.

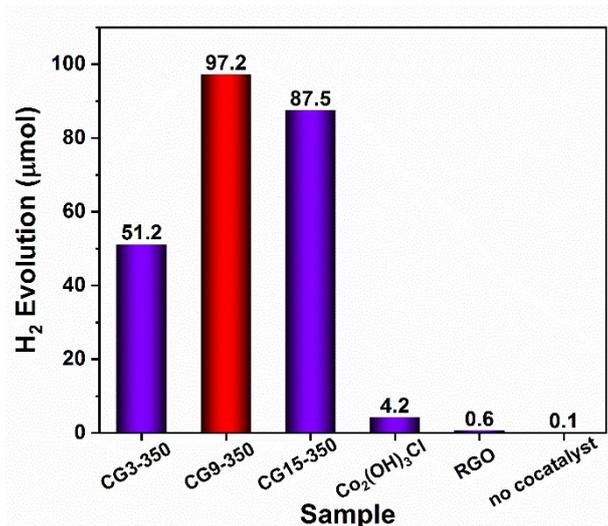


Fig. S5 The comparison of the dye-sensitization photocatalytic H₂ evolution activity for CG-350 composites, Co₂(OH)₃Cl, and RGO. Conditions: 10 mg of sample, 4×10⁻⁴ mol L⁻¹ EY, TMA solution (1.0% v/v) of pH 10.0, 2h.

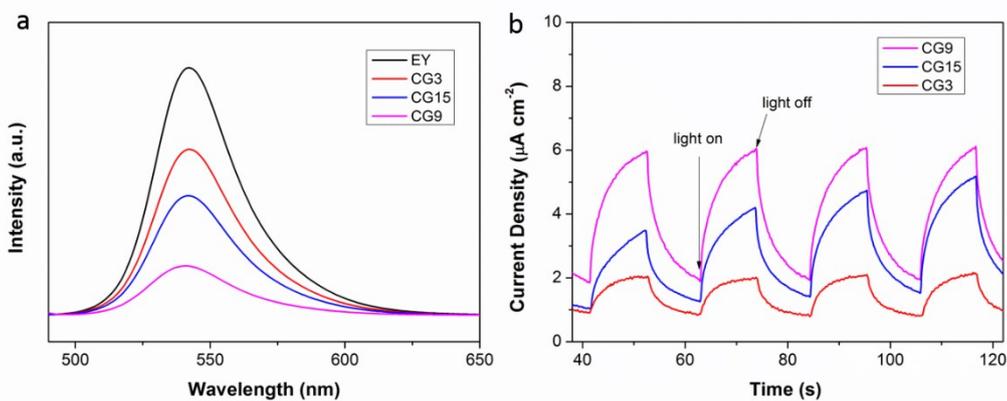


Fig.S6 Fluorescence spectra of EY before and after addition of CG-350 with different Co loading amount (a) and photocurrent density (b) of CG-350 with different Co loading amount in the presence of EY in TMA solution.

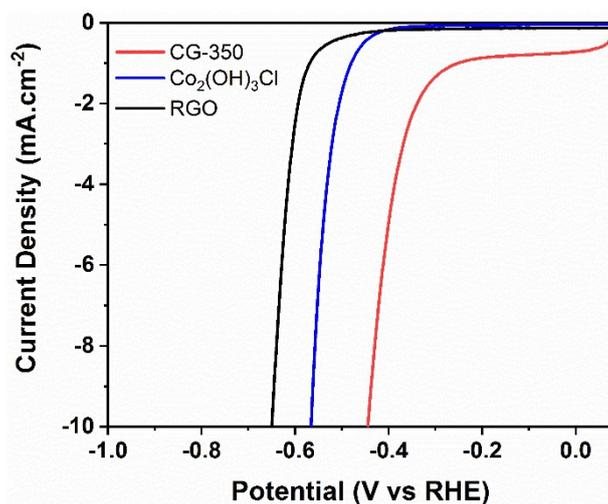


Fig. S7 The LSV curves of RGO, Co₂(OH)₃Cl, and CG-350 sample in 1.0 M KOH solution.

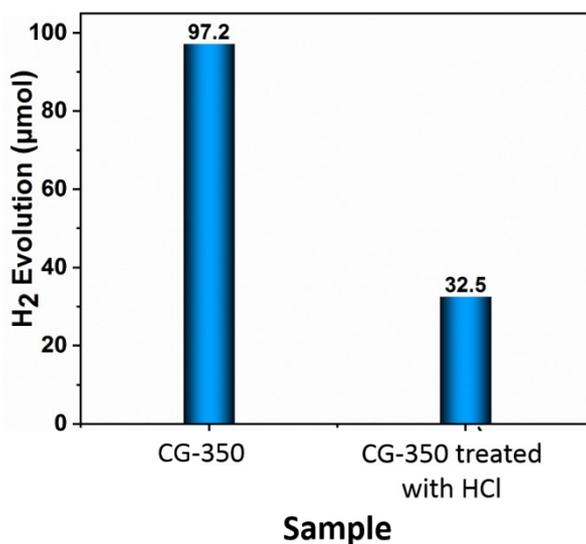


Fig. S8 The comparison of dye-sensitized photocatalytic H₂ evolution activities for CG-350 composite before and after treatment with HCl. Conditions: 10 mg of sample, 4×10⁻⁴ mol L⁻¹ EY, TMA solution (1.0% v/v) of pH 10.0, 2h.

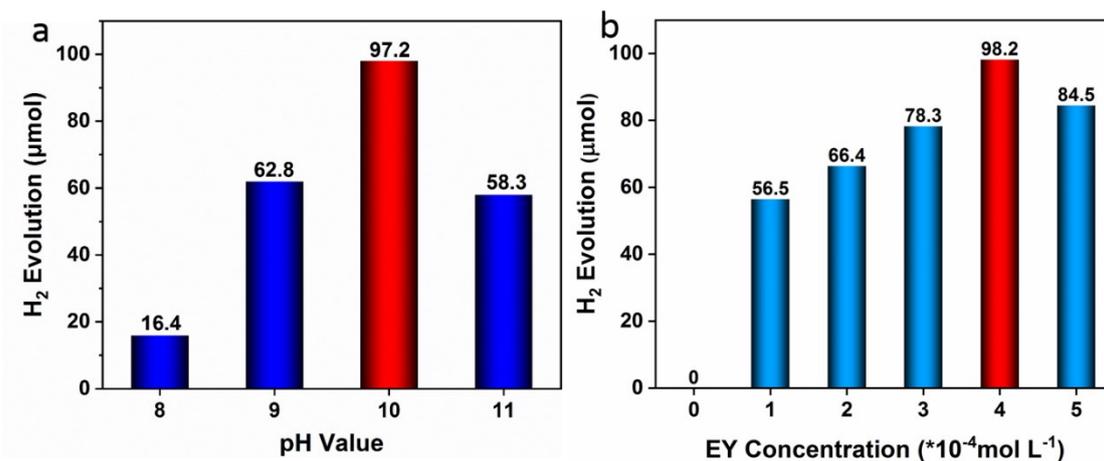


Fig. S9 The effect of pH value (a) and EY concentration (b) on photocatalytic H₂ evolution activity over EY-CG-350. Conditions: (a) 10 mg CG-350, 4×10^{-4} mol L⁻¹ EY, TMA solution (1.0 % v/v), 2h. (b) 10 mg CG-350, TMA solution (1.0 % v/v) of pH 10.0, 2 h.

As shown in Fig.S9b, the activity increases with the increasing the dye concentration from 0 to 0.4 mM, then decreases at the dye concentration of 0.5 mM. Excess EY molecules in solution produce the severe self-quenching, which decreases greatly utilization efficiency of the incident light. Hence, the activity decreases when the dye concentration increasing from 0.4 to 0.5 mM.

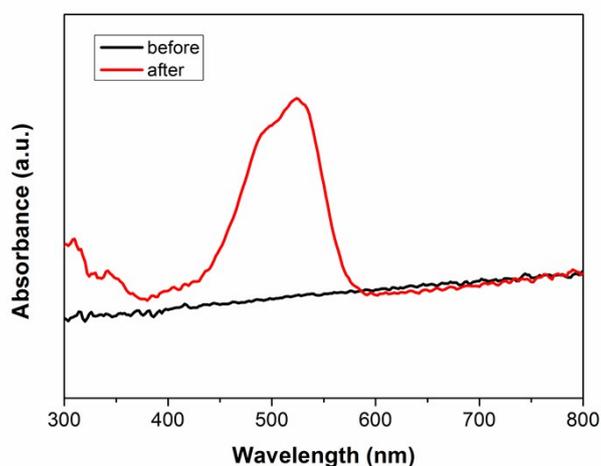


Fig.S10 UV-DRS spectra of CG-350 before and after dye sensitization.

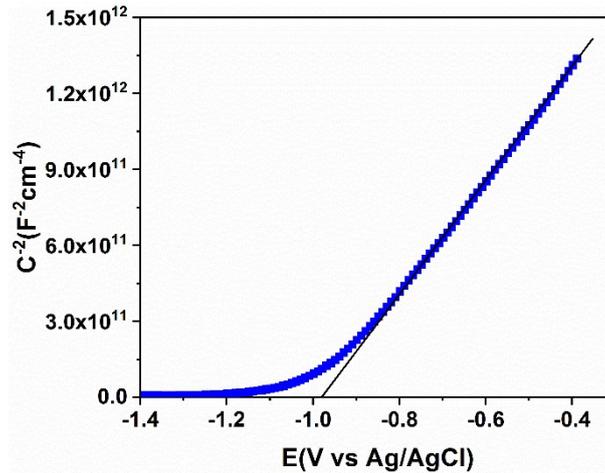


Fig. S11 Mott-Schottky plots of $\text{Co}_2(\text{OH})_3\text{Cl}$ in 1.0 M KOH at frequency of 1000 Hz.

The intercept of X axis is -0.98 V vs Ag/AgCl, the E_{NHE} is -0.78 V. According to the equation $E(\text{eV}) = -4.5 - E_{\text{NHE}}(\text{V})$, the flat band potential of $\text{Co}_2(\text{OH})_3\text{Cl}$ is -3.72 eV.

References:

(1) Zhang, W. Y.; Li, W. T.; Li, Y. X.; Peng, S. Q.; Xu, Z. D. One-step synthesis of nickel oxide/nickel carbide/graphene composite for efficient dye-sensitized photocatalytic H_2 evolution. *Catal. Today*. **2019**, 335, 326-33