

**Supporting Information**

**for**

**Enhanced photocatalytic hydrogen evolution by  
combining water soluble graphene with cobalt salts**

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## Experimental

### Instruments

The TEM images were taken on a JEOL JEM 2100F transmission electron microscope with an accelerating voltage of 200 kV. The Raman spectrum was recorded on a Via-Reflex Raman system using a 532 nm excitation wavelength. The XPS measurements were performed on an ESCALAB 250 spectrophotometer with Al-K $\alpha$  radiation. FTIR spectra were taken on Excalibur 3100 system (Varian, USA). Powder XRD was performed on a Bruker D8-Advance X-ray diffractometer with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The composition of material was determined by inductively coupled plasma mass spectroscopy (ICP-MS, Varian 710-ES, USA). A three-electrode system, a 3 mm glass carbon working electrode, a platinum wire counter electrode, and a SCE reference electrode, was used to measure the cyclic voltammograms with 0.2 M K<sub>2</sub>SO<sub>4</sub> as electrolyte.

### Experimental details

#### Synthesis of GO and water-dispersible sulfonated-graphene G-SO<sub>3</sub>

GO is synthesized by the modified Hummers' method from graphite. The graphite powder was pretreated with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/P<sub>2</sub>O<sub>5</sub>/concentrated H<sub>2</sub>SO<sub>4</sub>, and then oxidized by H<sub>2</sub>SO<sub>4</sub>/KMnO<sub>4</sub> consistent with our previous work [1].

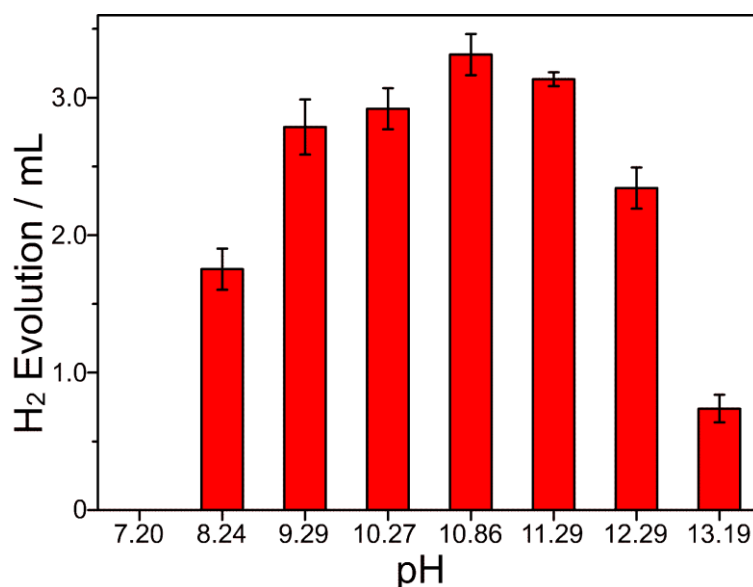
G-SO<sub>3</sub> is obtained as follows. In brief, 40 mL 0.5 mg/mL GO suspension was first reduced with 160 mg NaBH<sub>4</sub> (4.22 mmol) at 80 °C for 1 h. 0.7 g (4 mmol) sulfanilic acid was dissolved in 50 mL water in a 100 mL round-bottom flask, then 9.2 mL 1M



HCl was added. 0.3 g  $\text{NaNO}_2$  (4.35 mmol) dissolved in 5 mL water was dropped slowly to the above flask in ice bath. After reacting for 1 h, the obtained RGO suspension was added to the flask, and the mixture was maintained at 0 °C for 4 h, and then kept stirring overnight at room temperature.

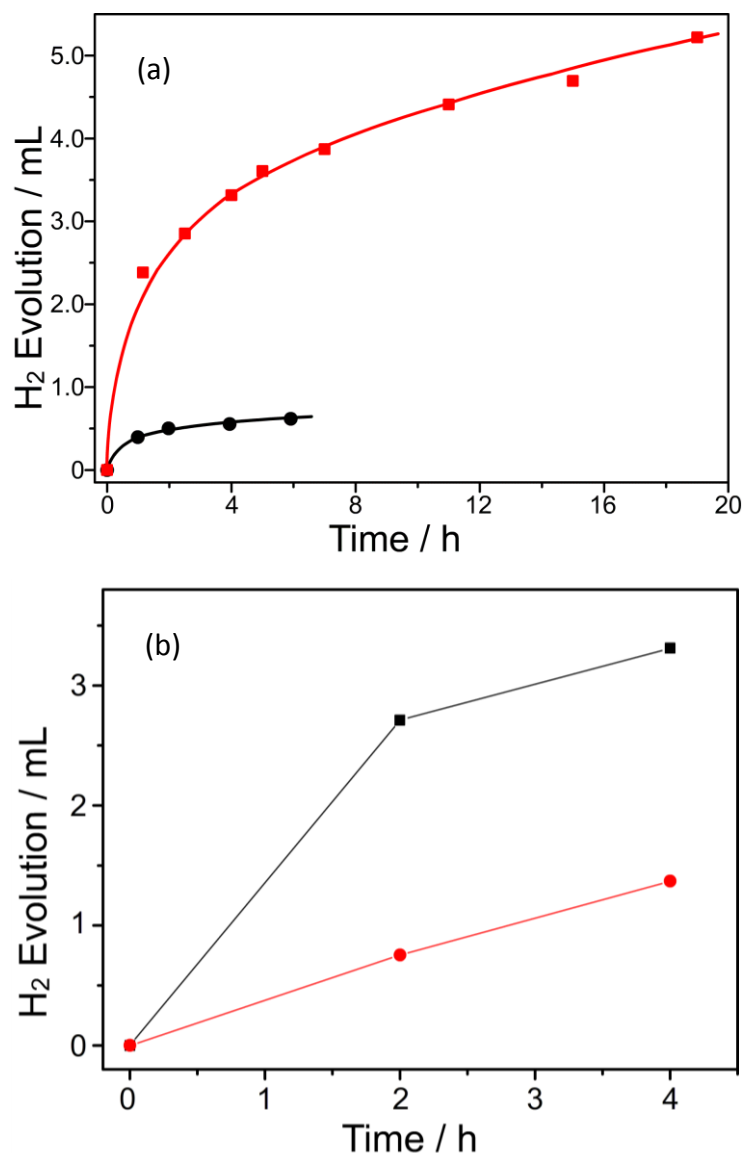
### Photocatalytic hydrogen evolution measurements

A typical procedure for hydrogen production is as follows. Aqueous suspension of  $\text{G-SO}_3$ ,  $\text{CoSO}_4$ , EY (Eosin Y) and TEOA (triethanolamine) were added to a Pyrex tube. The amount of each component is according to the determined condition experiments. The total volume is adjusted to 10 mL. The pH value of the mixed solution was determined by a pH meter and was adjusted by the addition of aqueous NaOH or HCl solution. The sample was irradiated under 525 nm LEDs. The generated photoproduct of  $\text{H}_2$  was characterized by GC analysis (Shimadzu 14B).



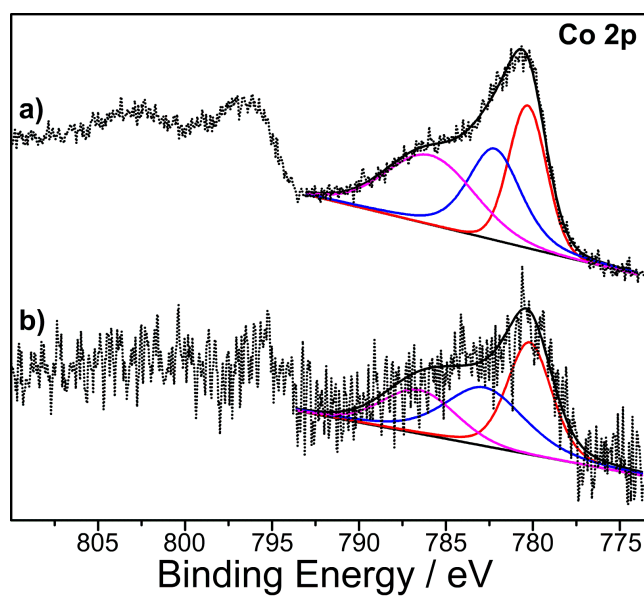
**Figure S1:** Photocatalytic hydrogen evolution at different pH in  $\text{H}_2\text{O}$  in 4 h; sample concentration:  $\text{CoSO}_4$  ( $2.0 \times 10^{-4}$  mol/L),  $\text{G-SO}_3$  (0.04 mg/mL), EY ( $4.0 \times 10^{-4}$  mol/L) and TEOA (0.2 mol/L).





**Figure S2:** (a) Kinetic curves of the photocatalytic hydrogen evolution with the optimized condition (the concentration of CoSO<sub>4</sub>, G-SO<sub>3</sub>, EY and TEOA are  $2.0 \times 10^{-4}$  mol/L, 0.04 mg/mL,  $4.0 \times 10^{-4}$  mol/L and 0.2 mol/L, respectively, the pH value 10.86) with (red) and without (black) G-SO<sub>3</sub>. (b) Photocatalytic hydrogen evolution with different photosensitizer under the optimal condition (the concentration of CoSO<sub>4</sub>, G-SO<sub>3</sub>, EY (or fluorescein), and TEOA are  $2.0 \times 10^{-4}$  mol/L, 0.04 mg/mL,  $4.0 \times 10^{-4}$  mol/L and 0.2 mol/L, respectively, at pH 10.86): EY (black) and fluorescein (red) as the photosensitizer, respectively.





**Figure S3:** XPS spectra of Co 2p after irradiation: (a) without and (b) with G-SO<sub>3</sub>.

## References

1. Zhang, H.-H.; Liu, Q.; Feng, K.; Chen, B.; Tung, C.-H.; Wu, L.-Z.  
*Langmuir* **2012**, 28, 8224–8229. doi:[10.1021/la301429g](https://doi.org/10.1021/la301429g)