## **Electronic supplementary information**

#### **Template-Free Synthesis of Hollow Ni/Reduced Graphene Oxide**

## **Composite for Efficient H<sub>2</sub> Evolution**

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### **Experimental section**

X-ray photoelectron spectrum (XPS) of graphene oxide (GO) was conducted on an ESCALAB250xi XPS spectrometer equipped with an Al Kα X-ray source.

Adsorption amounts of Eosin Y (EY) onto hollow Ni/reduced graphene oxide composites (named as HNG) were carried out as follows. 5 mg of above catalyst was added into 100 mL of EY solution ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>). The mixture was treated with sonication for 2 h, and then centrifugated twice to remove the catalyst. The EY concentration of the supernatant was measured on a spectrophotometer (Hitachi U3310). The adsorption amount of EY onto catalyst was calculated based on the concentration difference ( $\Delta$ C) before and after the mixing.

The photoluminescence (PL) spectra of EY before and after adding HNG were performed on a fluorospectrophotometer (Hitachi F-7000). 5.0 mg of above catalyst was mixed with 100 mL of aqueous EY ( $2.0 \times 10^{-5}$  mol L<sup>-1</sup>) solution. The sample was treated with 2 h sonication and then 2-fold dilution for PL measurement.

Electrochemical impedance spectra (EIS) were performed on an IVIUMSTAT (Netherlands) electrochemical workstation. The working electrode was prepared similarly as LSV test using 0.5 mg mL<sup>-1</sup> HNG or RGO dispersion. Pt wire and Ag/AgCl electrode were employed as the counter and reference electrode, respectively. The electrolyte was phosphate buffer solution (0.1 mol L<sup>-1</sup>, pH=7.0) containing 0.1 mol L<sup>-1</sup> KCl, 0.01 mol L<sup>-1</sup> K<sub>3</sub>Fe(CN)<sub>6</sub> and 0.01 mol L<sup>-1</sup> K<sub>4</sub>Fe(CN)<sub>6</sub>.

# Results

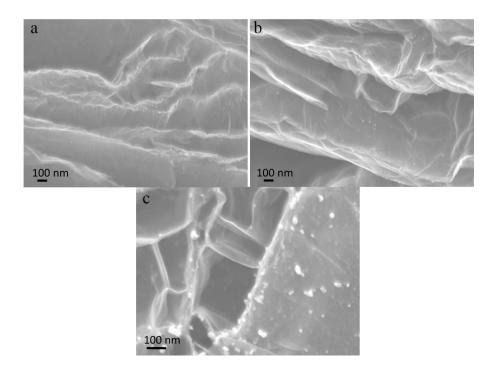


Fig.S1 SEM images of HNG3 (a), HNG6 (b) and HNG9 (c).

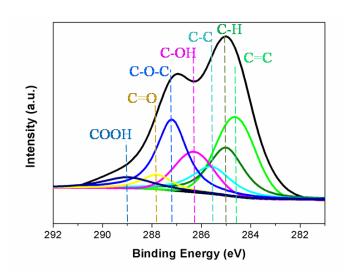


Fig.S2 High resolution XPS spectrum of C 1s for GO (the black line is the raw spectrum, whereas the coloured lines are fitting spectra).

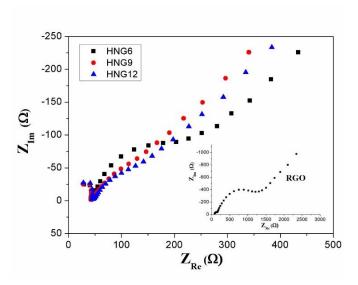


Fig.S3 Nyquist diagram of HNG6, HNG9 and HNG12. The inset shows the diagram of RGO.

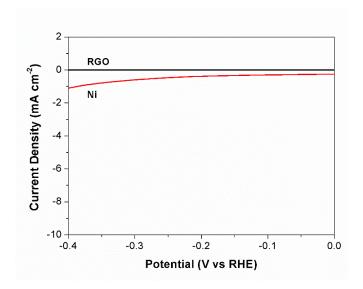


Fig.S4 LSV curves of Ni and RGO in 1.0 mol L<sup>-1</sup> KOH solution.

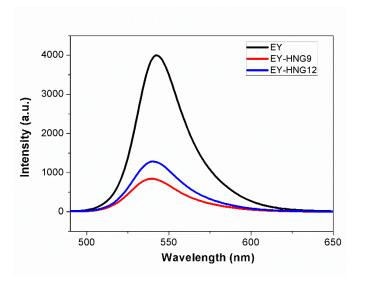


Fig.S5 The PL spectra of aqueous EY solution before and after adding HNG9 and HNG12. Conditions:  $1.0 \times 10^{-5}$  mol L<sup>-1</sup> EY; 25.0 µg mL<sup>-1</sup> catalyst; excited wavelength 480 nm.

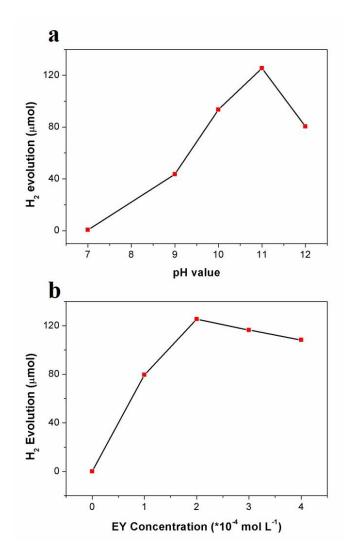


Fig.S6 The effects of pH (a) and EY concentration (b) on photocatalytic H<sub>2</sub> evolution activity in EY-HNG9 system. Conditions: (a) 5 mg of HNG9; 2.0×10<sup>-4</sup> mol L<sup>-1</sup> EY;
7.7×10<sup>-2</sup> mol L<sup>-1</sup> TMA; 1 h irradiation. (b) 5 mg of HNG9; 7.7×10<sup>-2</sup> mol L<sup>-1</sup> TMA, pH 11.0; 1 h irradiation.

Table S1 The adsorption amounts of EY on HNG composites.

Sample	Adsorption amount of EY (µmol g <sup>-1</sup> )
HNG3	218.5
HNG6	193.8
HNG9	178.6
HNG12	150.1