Electronic Supplementary Material (ESI) for RSC Advances.

The spherical Fe_7S_8@rGO nanoflowers as electrodes with high electrocatalytic performance in dye-sensitized solar cells

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The Synthesis of graphene oxide (GO)

In this experiment, we prepared GO using a modified Hummers' method. First, mix 180 mL of H_2SO_4 and 20 mL of HNO_3 in a 500 mL beaker to which graphite powder (2 g) was added, then the beaker was transferred to a water bath at 50 °C and stirred well. Then, $KMnO_4$ (10 g) was gradually added to the mixed solution. After stirring for 6 h, 200 mL of H_2O_2 solution was added drop by drop to the above liquid and stirred continuously for 3 h. After the mixture was naturally cooled to room temperature, the product (GO) was obtained after 6 centrifugal washes and 12 hours of freeze-drying.

Preparation of Fe_7S_8@rGO-x nanocomposite

First, GO (5 mg, 7.5 mg, 10 mg, 12.5 mg, 15 mg and 20 mg, the weight percentage are 10wt%, 15wt%, 20wt%, 25wt%, 30%, 40% respectively) were taken in four 100 ml beakers, all of which were added with 30 ml of anhydrous ethanol and sonicated for 4 hours. Subsequently, 50 mg of Fe_7S_8 was added to the above four solutions, stirred continuously overnight, and then transferred to a Teflon autoclave and held at 160 ℃ for 8 hours. After the reaction was cooled naturally to room temperature, washed several times using anhydrous ethanol and deionized water, and dried in an oven at 60 ℃ for 12 h to obtain Fe_7S_8@rGO-x. The final samples were expressed as Fe_7S_8@rGO-10wt%, Fe_7S_8@rGO-15wt%, Fe_7S_8@rGO-20wt% Fe_7S_8@rGO-25wt%, Fe_7S_8@rGO-30wt% and Fe_7S_8@rGO-40wt%, respectively.

Preparation of counter electrodes (CE)

The required counter electrodes for the experiments were fabricated by the scalpel coating method. First, the 2×1 cm fluorine-doped tin oxide (FTO) substrates were cleaned with deionized water and anhydrous ethanol and ultrasonicated in anhydrous ethanol. 0.04 g of Fe_7S_8, Fe_7S_8@rGO-10wt%, Fe_7S_8@rGO-15wt%, Fe_7S_8@rGO-20wt%, Fe_7S_8@rGO-25wt%, Fe_7S_8@rGO-30wt%, Fe_7S_8@rGO-40wt% were weighed and mixed with 0.01 g of PEG 20000 in a mortar, and then an appropriate amount of anhydrous ethanol was added dropwise to the mortar and well ground until a colloidal solution was formed. White tape was applied to both ends of the conductive side of the FTO, keeping the exposed area at 0.5×0.5 cm^2. The viscous colloid was transferred to the substrate with an abrasive rod, and then the gel was quickly scraped flat on the surface of the substrate with a sharp knife. After waiting for the substrate to dry naturally, the FTO was transferred to a nitrogen-filled tube furnace and calcined at 400℃ for 1 h at a heating rate of 5 ℃/min to obtain the CE required for the test. for Fe_7S_8 and rGO, the electrodes were prepared by the same procedure as that described above.

Characterization

The crystal structure of the prepared samples was characterized using an X-ray diffractometer (XRD, Rigaku D/Max-2500) with the Cu Kα radiation (λ= 0.15406 nm) source. The presence of graphene was confirmed by an inVia-Reflex laser Raman spectrometer with a laser wavelength of 532 nm. The gas adsorption method was used

for the determination of specific surface area utilizing a fully automated multi-station gas physisorption analyser (Autosorb-iQ). The chemical elemental composition of the samples and the bonding state were determined using an X-ray photoelectron spectrometer (ESCALAB 250Xi) with Al Kα radiation as the radiation source. The microstructure of the samples was characterized by scanning electron microscopy (SEM, Regulus 8230) and transmission electron microscopy (TEM, JEOL, JEM-2010SX). Under the simulated light intensity (AM 1.5 G, 100 $mW \cdot cm^{-2}$), the J-V curve was tested on a digital source meter (Keithley 2410, USA). A three-electrode system was used for cyclic voltammetry testing, with an Ag/AgCl reference electrode, Pt as the auxiliary electrode and the prepared sample as the working electrode. Tafel polarization and EIS tests were carried out using self-assembled symmetrical cells.

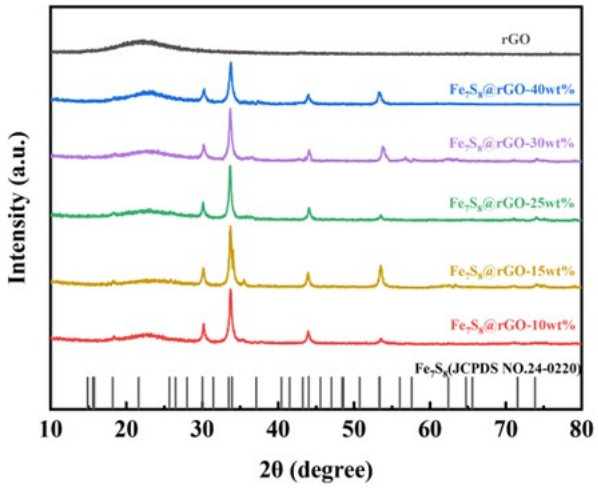

Fig. S1 XRD patterns of rGO, Fe_7S_8@rGO-10wt%, Fe_7S_8@rGO-15wt%, Fe_7S_8@rGO-25wt%, Fe_7S_8@rGO-30wt%, Fe_7S_8@rGO-40wt%

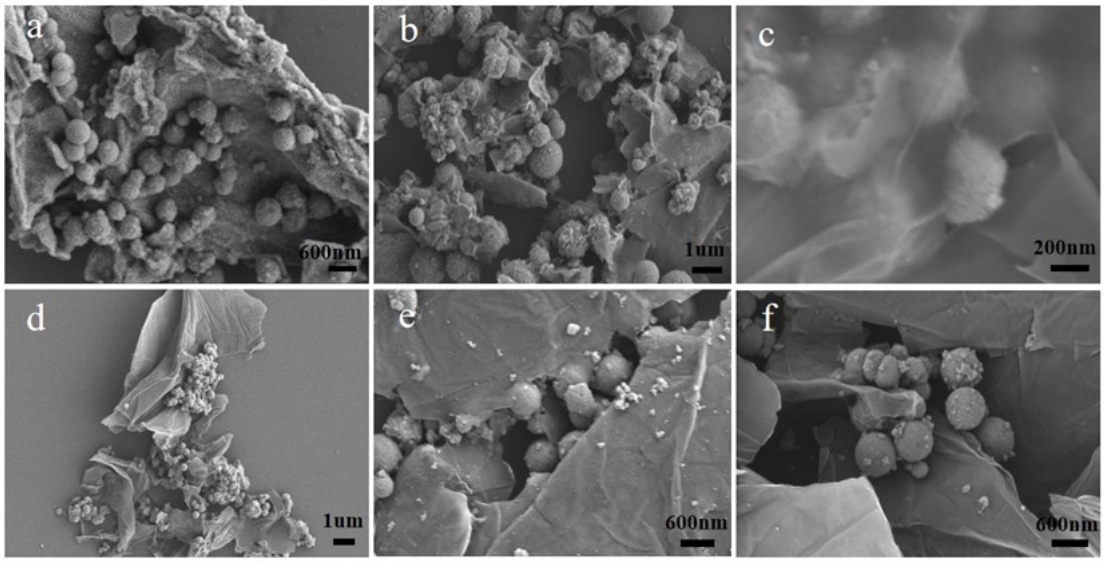

Fig. S2 SEM images of (a) Fe_7S_8@rGO-10wt%, (b) Fe_7S_8@rGO-15wt%, (c) Fe_7S_8@rGO-20wt%, (d)Fe_7S_8@rGO-25wt%, (e) Fe_7S_8@rGO-30wt%, (f) Fe_7S_8@rGO-40wt%

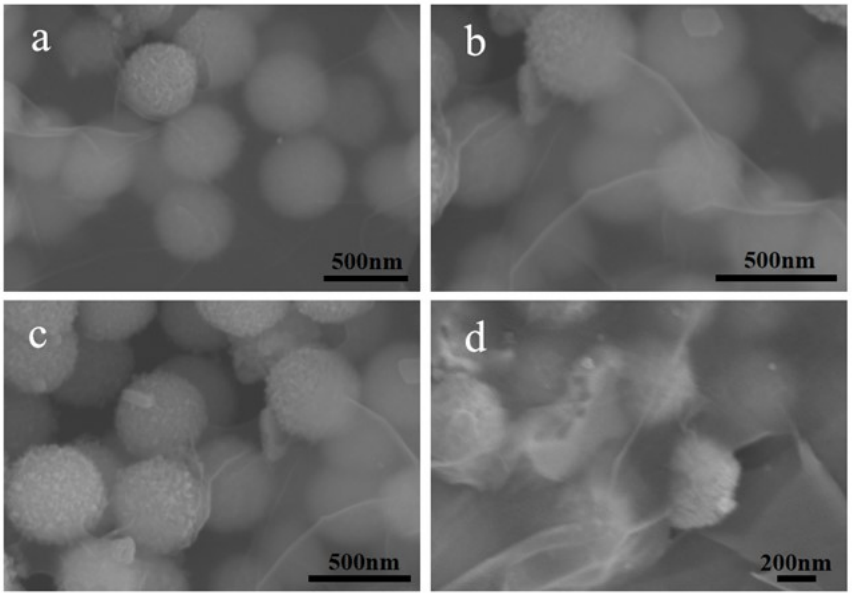

Fig. S3 (a-d) SEM images of Fe_7S_8@rGO-20wt%

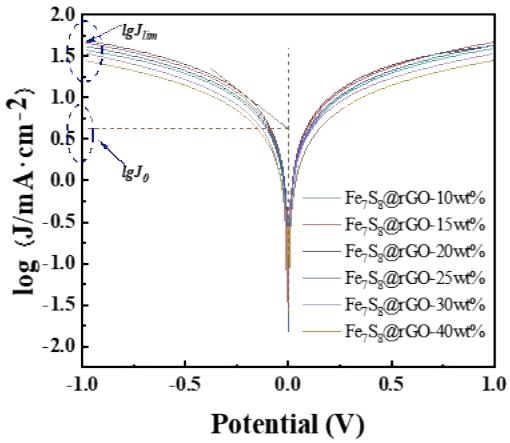

Fig. S4 Tafel curves of Fe_7S_8@rGO electrodes with different rGO contents

Tafel polarization measurements was carried out to study the electrocatalytic activity and diffusion coefficient. As shown in Fig. S4, Fe_7S_8@rGO-20wt% owns the better catalytic activities.

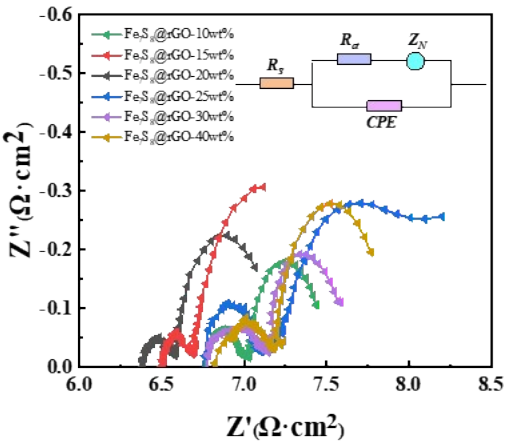

Fig. S5 Nyquist plots of Fe_7S_8@rGO electrodes with different rGO contents

Electrochemical impedance spectroscopy (EIS) was used to evaluate the charge transfer impedance of Fe_7S_8@rGO with different rGO contents, with the best performance for Fe_7S_8@rGO-20wt%. Fig.S5 shows the Nyquist plots of Fe_7S_8@rGO electrodes with different rGO contents.

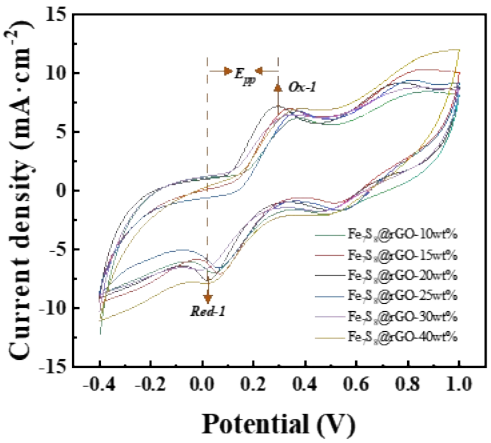

Fig. S6 CV curves of Fe_7S_8@rGO electrodes with different rGO contents

Among the Fe_7S_8@rGO electrodes with different rGO contents, the E_{pp} of the component of Fe_7S_8@rGO-20wt% (0.27 V) is the smallest, and it is obviously smaller than others, as shown in Fig. S6. Fe_7S_8@rGO-20wt% own the better catalytic performance.

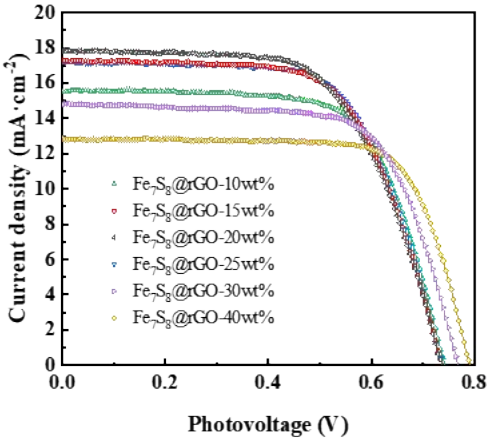

Fig. S7 J-V curves of Fe_7S_8@rGO electrodes with different rGO contents

Photocurrent density-voltage (J-V) curves were tested to estimate photoelectric conversion efficiency of Fe_7S_8@rGO electrodes with different rGO contents directly, which is shown in Fig. S7.

The parameters obtained from the above tests are shown in Table S1 and S2.

Table S1. Electrochemical Parameters for Fe_7S_8@rGO-x CEs

CEs	R_s *(Ω·cm²)*	R_{ct} *(Ω·cm²)*	lgJ_0 *(mA·cm⁻²)*	lgJ_{lim} *(mA·cm⁻²)*
Fe_7S_8@rGO-10wt%	6.77	0.14	0.52	1.57
Fe_7S_8@rGO-15wt%	6.50	0.09	0.59	1.67
Fe_7S_8@rGO-20wt%	6.38	0.08	0.64	1.68
Fe_7S_8@rGO-25wt%	6.74	0.16	0.55	1.61
Fe_7S_8@rGO-30wt%	6.81	0.18	0.46	1.54
Fe_7S_8@rGO-40wt%	6.87	0.19	0.39	1.44

Table S2. Photovoltaic Performance Parameters of Fe_7S_8@rGO-x CEs

CEs	E_{PP} *(V)*	J_{sc} *(mA·cm⁻²)*	V_{oc} *(V)*	*FF (%)*	*PCE (%)*
Fe_7S_8@rGO-10wt%	0.32±0.01	15.53	0.745	67.57	7.82
Fe_7S_8@rGO-15wt%	0.30±0.01	17.29	0.740	64.06	8.20
Fe_7S_8@rGO-20wt%	0.27±0.01	17.83	0.740	63.64	8.40
Fe_7S_8@rGO-25wt%	0.28±0.01	17.24	0.740	64.69	8.25
Fe_7S_8@rGO-30wt%	0.33±0.01	14.80	0.769	68.62	7.81
Fe_7S_8@rGO-40wt%	0.34±0.01	12.83	0.790	73.89	7.49