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Supporting Information

Iron Oxide Nanostructures as Highly Efficient Heterogeneous Catalyst for Mesoscopic Photovoltaics

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Preparation of heterogeneous flower-like Fe_3O_4

Preparation of Iron oxide precursor was performed according modified literature method.[1] Briefly, 25 mM (1.2g) $FeCl_3\cdot6H_2O$ (99.0%, AR, Aladdin, China), 250 mM (2.7g) urea (99.5%, RP, Sigma-aldrich), and 124 mM (7.2g) tetrabutylammonium bromide (99.0%, AR, Aladdin, China) were added to 180 mL ethylene glycol (99.0%, GC, Aladdin, China) in a 250 mL round flask. The red solution obtained was stirred with a magnetic stirrer bar and heated to 165 °C, a yellow precipitate began to appear and then the mixture turned yellow-green. The reaction was stopped and the mixture was cooled to room temperature immediately. The similar reaction has also been done and stopped at 175 °C, 185 °C and 195 °C, respectively. The dosage of reactants were decreased to 1/2 and 1/10 repeat above react at195 °C. The precipitate was collected by suction filtration and washed with ethanol three times.

Preparation of CE

The paste of CE was prepared by dispersing 50 mg Iron oxide precursor in 3 mL isopropanol (99.5 %, AR, Aladdin, China). The obtained slurry was well-proportioned sprayed on fluorine tin oxide (FTO) glass substrate (Asahi Glass, Japan) using an airbrush (TD-128,Tiandi Co., Ltd) connected to a mini-compressor. By controlling sintered temperature and atmosphere, we can obtain different iron oxide CE listed in below: α-Fe_2O_3 (450 °C, 3h under air), Fe_3O_4(450 °C, 3h under N_2) and γ-Fe_2O_3 (450 °C, 3h under N_2, and then 250 °C, 5h under air).

Fabrication of DSCs

The TiO_2photoanode are commercially available (Yingkou Opvtech New Energy Co., Ltd, China). They were sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO_2 films were immersed in 5 x 10^{-4} M solution of N719 dye (Ruthenizer 535-bis TBA, Solaronix SA, Switzerland) in ethanol (99.5%, anhydrous, Sigma-aldrich) for 20 h. The photoanode and CE sandwich electrolyte to form DSCs. The electrolytes were composed of 0.1MLiI (99.99 %, anhydrous, Sigma-aldrich), 0.03 M I_2 (99.99 %, Sigma-aldrich), 0.1 M GuSCN (99 %, for molecular biology, Sigma-aldrich) and 0.5M 4-tert-butylpyridine(96 %, Sigma-aldrich) in acetonitrile (99.8 %, anhydrous, Sigma-aldrich).

Characterization

The X-ray diffraction experiments were carried out with an automatic X-ray powder diffractometer (D/Msx 2400, RIGAKU). The morphologies of α-Fe_2O_3, Fe_3O_4 and γ-Fe_2O_3 were observed using scanning electron microscopy (SEM, FEI QUANTA 450).Current-voltage curves of the DSCs were measured by a Keithley digital source meter (Keithley 2601, USA). The intensity of the incident light simulates an AM 1.5 solar light through a solar simulator (PEC-L15 Japan). The incident light intensity was calibrated using a silicon photocell (BS-520, Japan) and was set at 100 mW cm^{-2}. Cyclic voltammetry (CV) was carried out in a three-electrode system in an acetonitrile solution of 0.1 M $LiClO_4$, 10 mM LiI and 1 mM I_2 at a scan rate of 10 mV s^{-1} by using a electrochemical work station (CHI 630D). Pt served as a counter electrode and the Ag/Ag^+ couple was used as a reference electrode. Tafel polarization measurements were carried out with a CHI 630D in a symmetric cell with a scan rate of 50 mVs^{-1}. The electrochemical impedance spectroscopy (EIS, Zenium Zahner, Germany) was actualized with above symmetric cell in the dark at an open circuit bias. The measured frequency ranged from 100 mHz to 1MHz, and the AC amplitude was set at 10 mV.

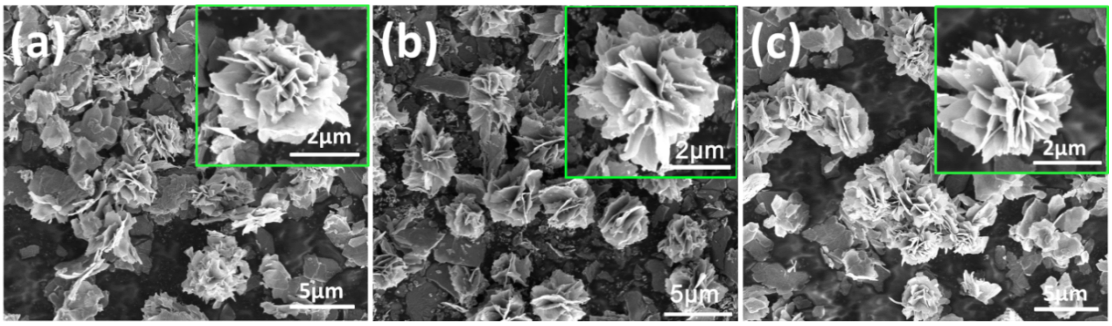

Figure S1. The SEM images of flower-like (a) α-Fe_2O_3, (b) Fe_3O_4 and (c) γ-Fe_2O_3

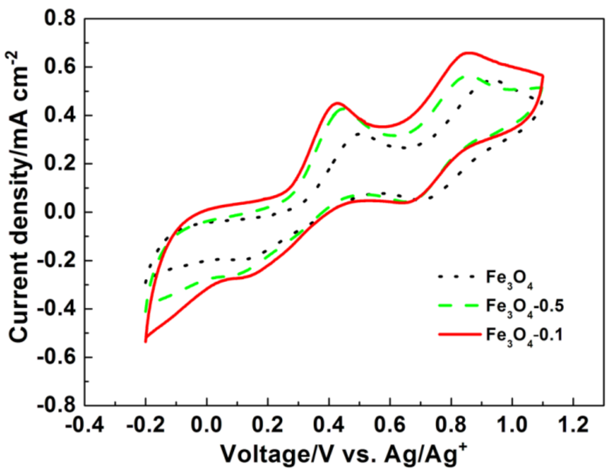

Figure S2. The CV curves of flower-like Fe_3O_4based on different dosage of reactants

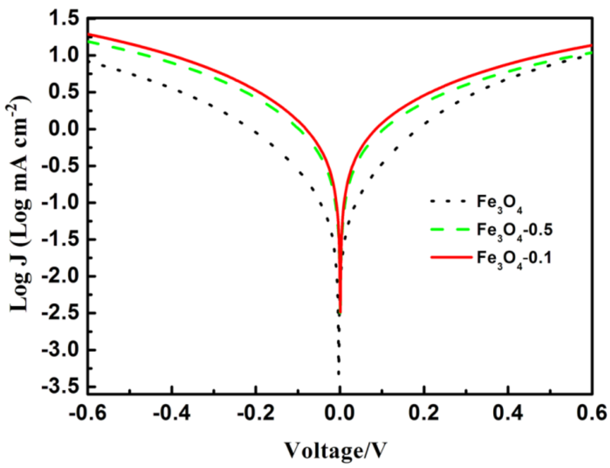

Figure S3. The Tafel curves of flower-like Fe_3O_4 based on different dosage of reactants

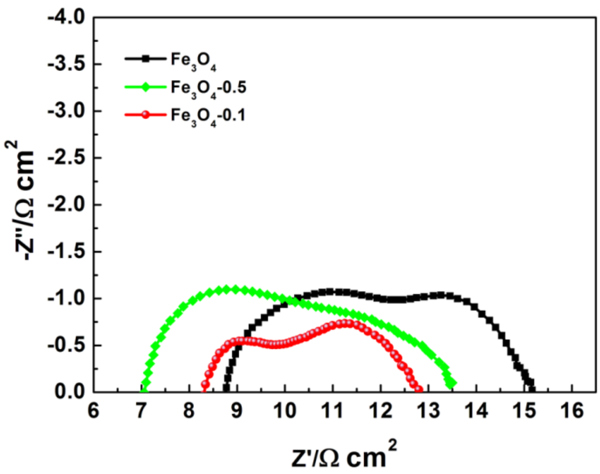

Figure S4. The Nyquist plots of flower-like Fe_3O_4based on different dosage of reactants. Insert: Equivalent circuit

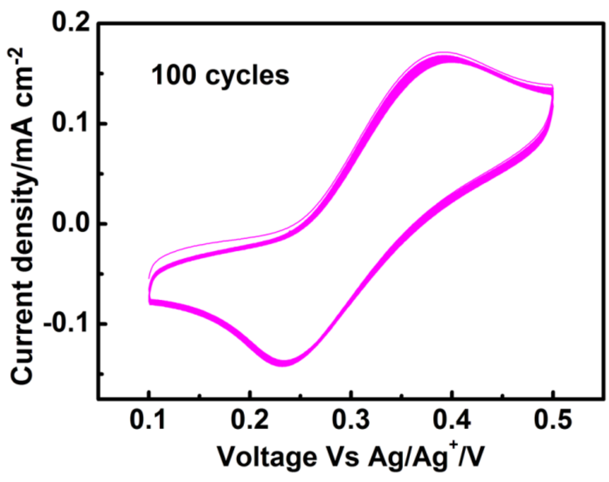

Figure S5. Consecutive cyclic voltammogram of the Fe_3O_4 CE for the I^-/I_3^- redox couple

Table S1.EIS parameters of symmetrical cells using Fe_3O_4 CE prepared with different concentration of reactants.

Sample	$R_s/\Omega\ cm^{-2}$	$R_{ct}/\Omega\ cm^{-2}$	$Z_N/\Omega\ cm^{-2}$
Fe_3O_4	8.75	4.30	4.28
Fe_3O_4-0.5	7.04	3.08	5.52
Fe_3O_4-0.1	8.33	1.67	3.23

The statistical analysis

For religious comparison，the statistical analysis on comparisions of PCEs for solar cells were also conducted. [2]

As shown in eq.1:

$$Z = \frac{\eta_1 - \eta_0}{\sigma_1/\sqrt{N}} \quad (1)$$

Where η_1 is the average PCE based on DSC with Fe_3O_4 CE, η_0 is the average PCE based on DSC with pyrolytic Pt, σ_1 is the standard deviation of PCE derived from DSCs with Fe_3O_4 CE and N is the DSC numbers (Here N=6). Generally, P-value will be will be obtained by using a simple look-up or an online calculator, which is used to evaluate the statistical significance of the results.

Take DSC based on Fe_3O_4 for example, the average PCE is 7.65 % with a standard deviation of 0.12 % and the average PCE of DSC with pyrolytic Pt is 6.88 %. By calculation, the Z-score is more than 3.9. According to Z-score table, when Z is equal or greater than 3.9, the areas are 1.0000 to four decimal places. In other words, P-value is 0. That means the PCE of Fe_3O_4-based DSC is superior to pyrolytic Pt-based DSC.

The result above gives the further proof on our conclusions about the photovoltaic performance of developed Fe_3O_4 and Pt CEs.

1. L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song and L. J. Wan, Advanced Materials, 2006, 18, 2426-2431.
2. E. J. Luber and J. M. Buriak, *ACS nano*, 2013, **7**, 4708.