Supplementary Information

Composite Catalyst of Rosin Carbon/Fe_3O_4: Highly Efficient Counter Electrode for Dye-Sensitized Solar Cells

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X-ray diffractograms peak assignments of the synthesized rosin carbon (A) and rosin carbon/Fe_3O_4 (B)

In Fig. 1d of the paper, for rosin carbon, the diffraction peaks at 23.62º and 42.96º correspond to amorphous carbon, which is verified by the related literature.[1] For rosin carbon/Fe_3O_4 and pure Fe_3O_4, the diffraction peaks at 18.30, 30.10, 35.45, 43.09, 53.46, 56.98, 62.57 and 70.99 are assigned to the crystal planes (111), (220), (311), (400), (422), (511), (440) and (620), respectively (65–3107, PDF database).

Preparation of CE-A, CE-B and CE-C

The preparation of CE-A, CE-B and CE-C can be described as follows: 100 mg of A, B or C powders and 3 g of zirconium dioxide pearls were dispersed in 5 mL isopropanol and milled for 4 h. The obtained solution was then sprayed on an FTO glass using a spraying method. The FTO glass coated with A, B or C film was then sintered under N_2 atmosphere at 500 °C for 30 min in a tube furnace.

Preparation of dye-sensitized solar cells

The TiO_2 electrodes are commercially available (Ying kou Opvtech New Energy Co., Ltd), which were sintered at 500℃ for 30 min before sensitized by sensitizer. After cooling down to 80℃, the electrodes were dipped into the solutions of cis-bis(isothiocyanato) bis(2, 2'-bipyridyl-4, 4'-dicarboxylato)-ruthenium(II) bis-tetrabuyl -ammonium (N719) for 20 h at 25℃. The dye-sensitized TiO_2 electrodes, CEs were assembled to fabricate DSCs by sandwiching an electrolyte with 0.1 M LiI, 0.03 M I_2, 0.1 M GuSCN and 0.5 M 4-terrbutylpyridine (TBP) in acetonitrile.

Characterization

The surface morphology of A and B were observed using scanning electron microscopy(SEM, FEI QUANTA 450).The X-ray diffraction experiments were carried out with an automatic X-ray powder diffract meter (D/Max 2400, RIGAKU). 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}. The electrochemical impedance spectroscopy (EIS, Zenium Zahner, Germany) was actualized with the symmetric cell in the dark at an open-circuit voltage bias. The measured frequency ranged from 100 mHz to 1MHz, and the AC amplitude was set at 10 mV. The CV curves and Tafel polarization curve were obtained by electrochemical workstation (CHI 660(SHANGHAI, CHEN HUA)).

The effect of milling for morphology of CE-B

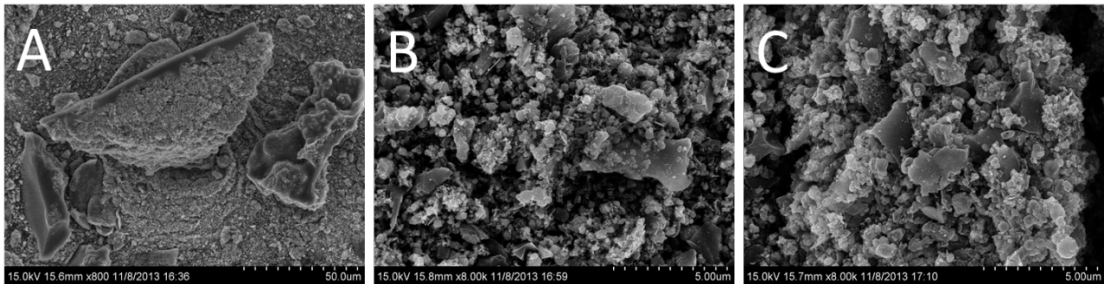

Fig. S1 (A) before milling (B)prepared CE by spraying milling paste (C) as-prepared CE after further sinter

we have carefully observed the morphology change of CE-B, from before milling (A) to prepared CE by spraying milling paste (B), further to sinter to obtain as-prepared CE (C). Compared with A and B, it is clear that the big block rosin carbon was destroyed by milling, which is beneficial to improve the performance of CE. Furthermore, blocky rosin carbon and Fe_3O_4 particles are better mixed together after milling. When the CE was further sintered under N_2 at 500 ℃, a more compact morphology was obtained, which shown that the rosin carbon and Fe_3O_4 particles were better combined again.

Optimization of the best ratio of rosin/$Fe_2SO_4 \cdot 7H_2O$

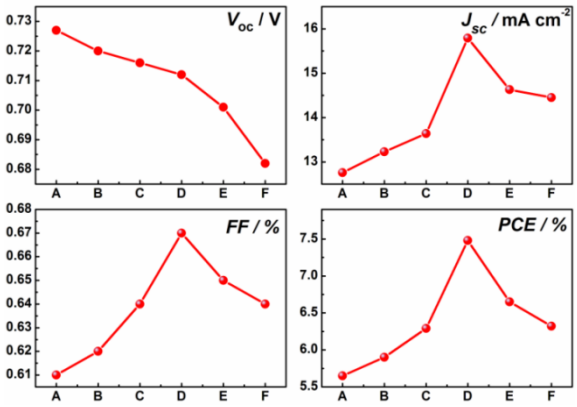

Fig. S2 the change of J-V parameters of DSCs based on six counter electrodes along with change of ration of Rosin/$Fe_2SO_4 \cdot H_2O$

Table S1 J-V parameters of DSCs based on six counter electrodes with different composition ratio at one sun illumination (AM 1.5 G, 100 mW cm^{-2})

	Rosin/$Fe_2SO_4 \cdot 7H_2O$ [Wt./Wt.]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	*FF*	*Eff.* [%]
A	4:1	0.727	12.76	0.61	5.66
B	2:1	0.720	13.23	0.62	5.91
C	1:1	0.716	13.64	0.64	6.25
D	1:2	0.712	15.79	0.67	7.53
E	1:3	0.701	14.63	0.65	6.67
F	1:4	0.682	14.45	0.64	6.31

Equivalent circuit for fitting EIS data

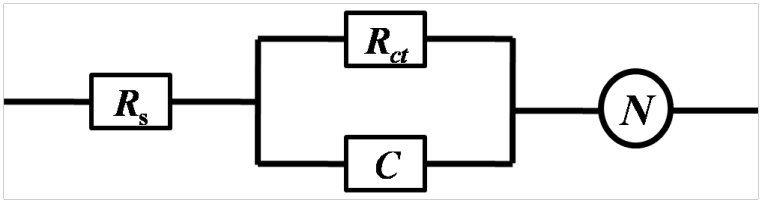

Fig. S3 Equivalent circuit of EIS fitting. R_s: series resistance, R_{ct}: charge-transfer resistance at the CE/electrolyte interface and Z_N: Nernst diffusion impedance of the redox couple in the electrolyte

1. (a) Wang, H.; Wang, A.; Wang, X.; Zhang, T., One-pot synthesized MoC imbedded in ordered mesoporous carbon as a catalyst for N2H4 decomposition. *Chemical Communications* **2008,***0* (22), 2565-2567;(b) Wu, M.; Lin, X.; Wang, T.; Qiu, J.; Ma, T., Low-cost dye-sensitized solar cell based on nine kinds of carbon counter electrodes. *Energy & Environmental Science* **2011,***4* (6), 2308-2315.