Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

ZnO-nitrogen doped carbon derived from zeolitic imidazolate framework as an efficient counter electrode in dye-sensitized solar cells

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1 Materials and reagents

All used reagents and solvents were obtained from commercial sources. Both of PEDOT:PSS (1.3 wt % dispersed in H_2O), lithium iodide (LiI, 99%), Iodine (I_2, 99.8%), 4-tert-butylpyridine (4-TBP, $C_9H_{13}N$, 96%), titanium di-isopropoxide bis (acetylacetonate) (TAA) $[(CH_3)_2CHO]_2Ti$ $(C_5H_7O_2)_2$, 75 wt. % in isopropanol, bis (tri-fluoromethane) sulfonamide lithium salt (LiTFSI), hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 37.50% Pt basis) , 2-methylimidazole (98.0%) and MK2 dye were purchased from Sigma-Aldrich, while Anhydrous acetonitrile (CH_3CN, 99.80%) , tert-butyl alcohol were from Alfa Aesar and Ru dye, cis-di (thiocyanato) bis (2, 2-bipyridyl-4, 4-dicarboxylate) ruthenium (II) (N719) from Dyesol. Titanium dioxide paste (average particle size: 18, 30 nm and 400 nm) and FTO conductive glass (2 mm thickness, square resistance 10–15 Ω sq^{-1}) from OPV Tech Co. $Zn(NO_3)_2.6H_2O$ (~99.99%), were obtained and ethylene glycol (EG) from Sinopharm Chemical Reagent Beijing Co., Ltd. All used reagents were of analytical purity and used as received. De-ionized (DI) water was obtained from an ultra-pure purifier (Ulupure, China, resistivity ≥ 18.2 MΩ).

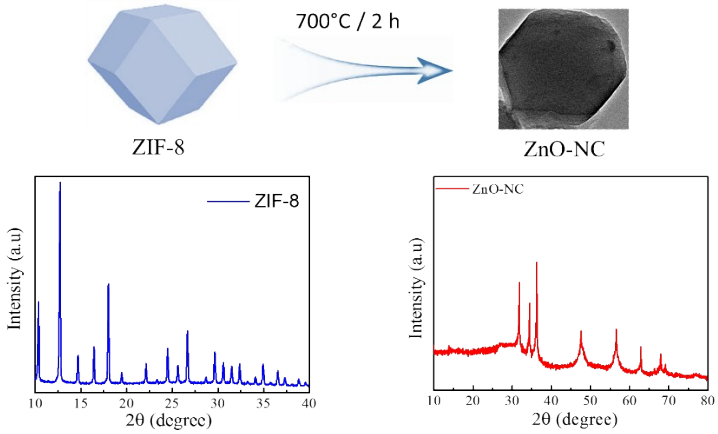
2 Fabrication of Mesoporous TiO_2 photoanode

The iodine electrolyte-based DSSCs were prepared as follows; TiO_2 photoanodes was prepared by using clean fluorine-doped SnO_2 (FTO) conducting glass substrates washed with a detergent solution, rinsed with de ionized (DI) water and finally ethanol in ultrasonic bath for 30 min. A thin blocking layer of TiO_2 was prepared on a clean FTO glass via spray pyrolysis of a 10% (v/v) solution of titanium isopropoxide bisacetyl acetonate in ethanol at 450°C. A commercial TiO_2 Paste (18 nm-sized) was printed onto the treated FTO-titanium isopropoxide to form the transparent layer (4×4 mm). The printing process was repeated for five times followed by annealing at 120 °C for 10 min. A scattering layer was printed on top of the transparent layer. The screen printed TiO_2 films with 0.16 cm^2 active area were sintered at 500 °C for 30 min in programmable system followed by treated in 20 mM $TiCl_4$ (aq) bath at 70 °C for 30 min, and fired at 500°C in air for 30 min. Once cooled, the electrodes were bathed into a 0.3 mM solution of N-719 dye in absolute ethanol for 18 h at room temperature.

In case of cobalt electrolyte-based DSSCs, TiO_2 photoanode was fabricated by printing technique as mentioned in iodine DSSCs, except TiO_2 paste (20 nm) was used in transparent layer with little thickness, the obtained TiO_2 films were immersed on 0.3 mM MK-2 dye solution (1:1 acetonitrile and tert-butanol) at room temperature for 5 h.

The symmetrical dummy cells were prepared by two identical CEs and the redox electrolytes are similar to that used in assembling complete DSSCs.

3 Mechanism of ZnO-NC derived ZIF-8.



Schem 1. Mechanism of ZnO-NC derived ZIF-8.

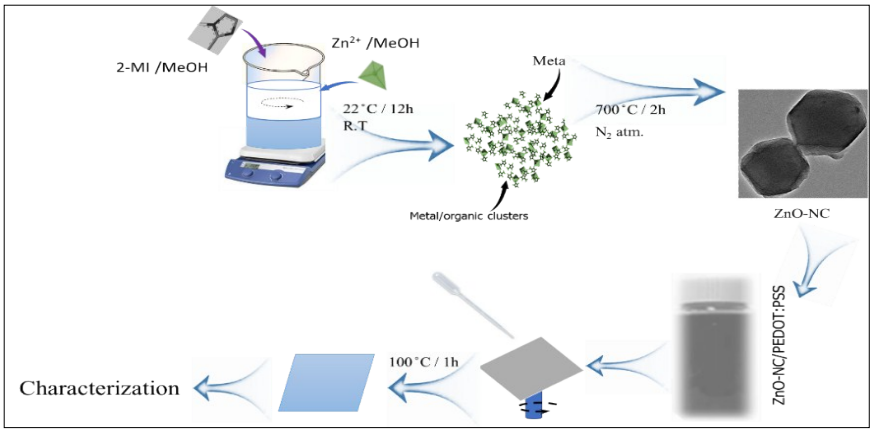


Fig. S1: Schematics for the prepare of ZnO-NC/PEDOT: PSS CEs

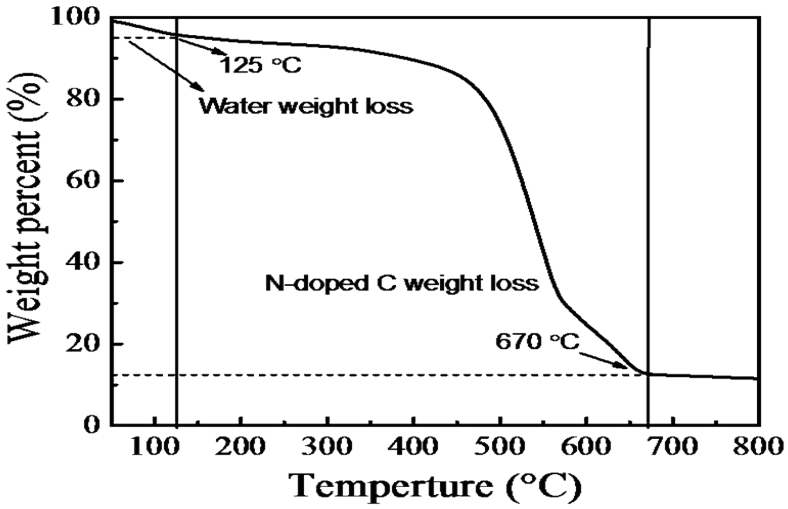


Fig. S2: TGA thermograms of ZnO-NC composite.

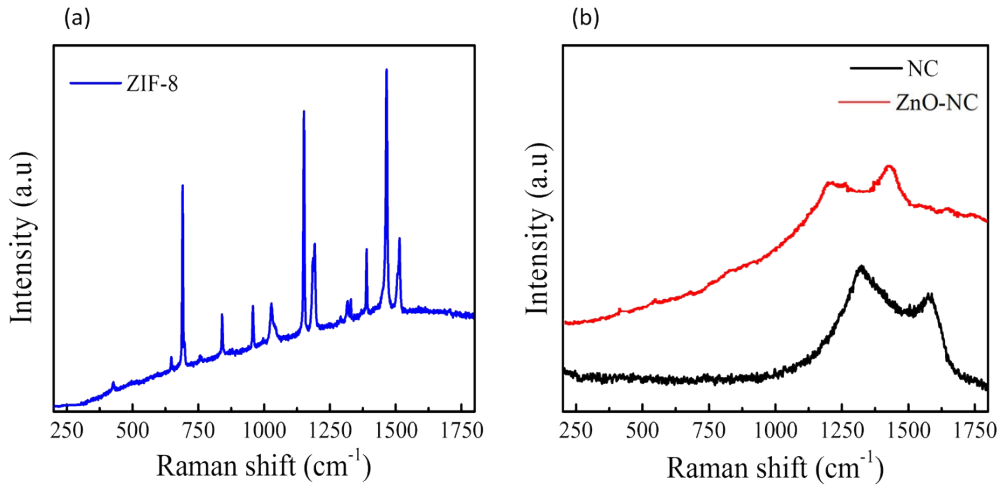


Fig. S3 Raman spectra of (a) ZIF-8 and (b) NC and ZnO-NC.

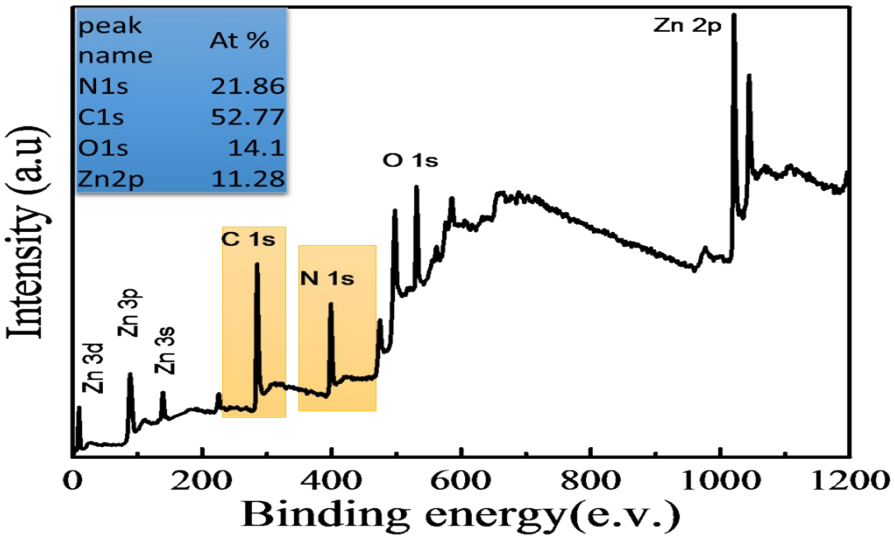


Fig. S4 XPS full-spectrum of ZnO-NC nanocomposite derived ZIF-8.

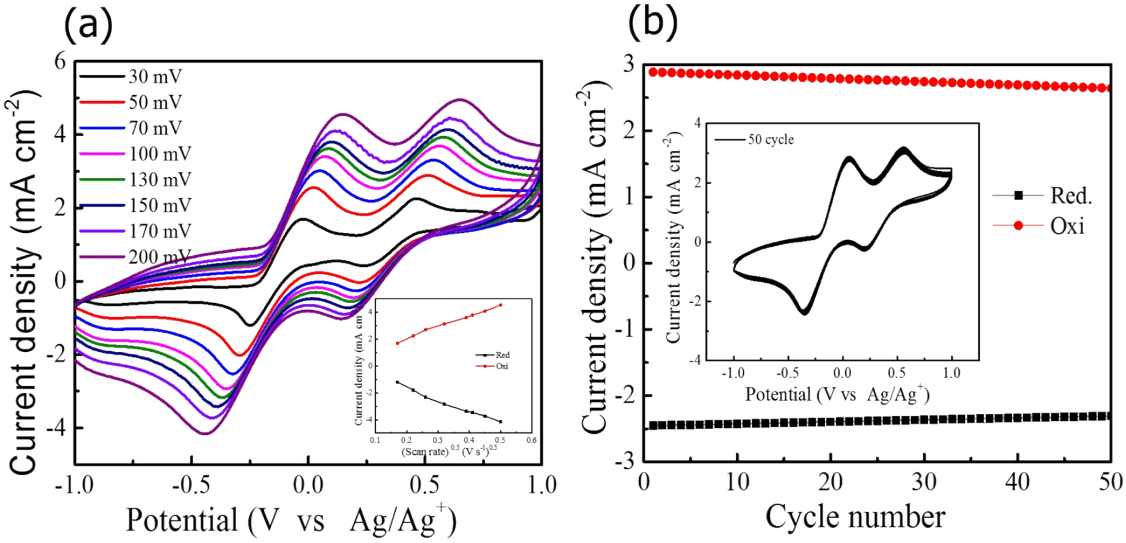


Fig.S4 (a) CV curves at different scan rates; inside the relationship between peak current density and the square root of scan rates, and **(b)** 50 times continuous cycle scans CVs of the 7% ZnO-NC/PEDOT: PSS CE with the scan rate of 50 mV s^{-1}.

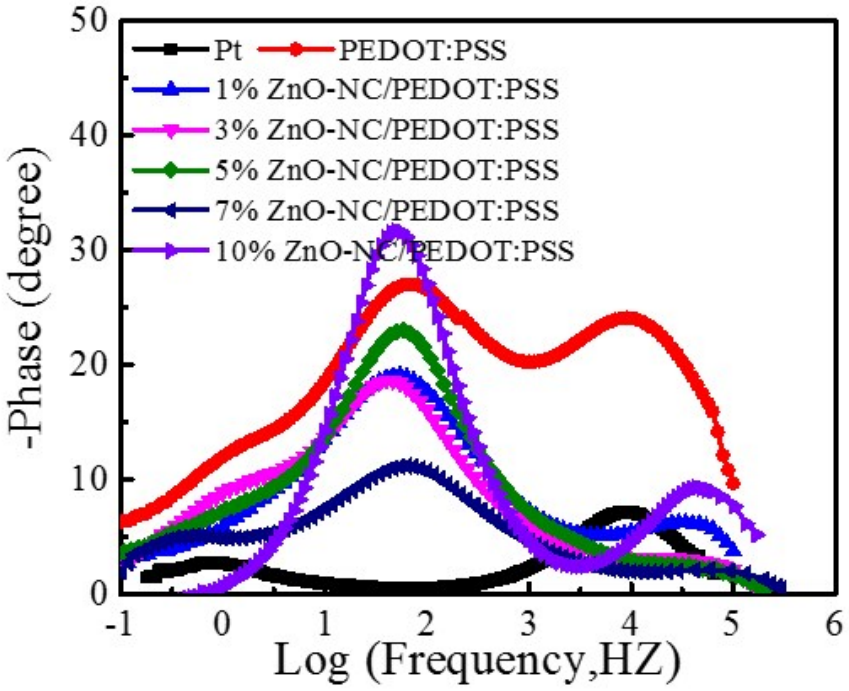


Fig. S5 Bode plot of Pt, PEDOT: PSS and ZnO-NC/PEDOT: PSS based symmetric cells.

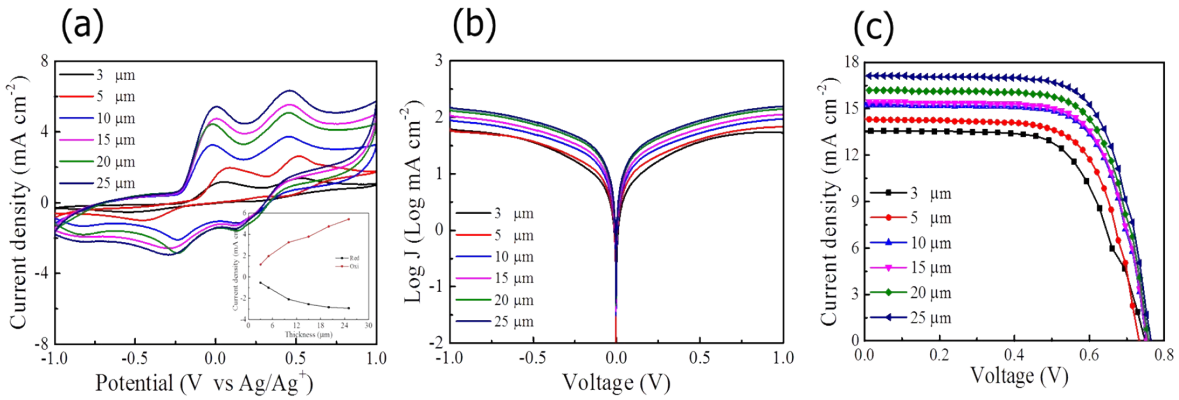


Fig. S6 (a) CV curves, (b)Tafel polarization curves and (c) J-V curves of the DSSCs with 7% ZnO-NC/PEDOT: PSS CEs with different thickness.

Table S1 CV, Tafel and Photovoltaic parameters of DSSCs with 7% ZnO-NC/PEDOT: PSS CEs different thickness. [a*]

a* the photovoltaic parameters are averages of three cells assembled in the same batch

CEs thickness(µm)	J_{PC} (mA cm^{-2})	Log J_O ($mAcm^{-2}$)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
3 µm	-0.53	1.13	0.74±0.00	13.55±0.02	64.65±0.14	6.53±0.01
5 µm	-1.00	1.18	0.72±0.01	14.28±0.02	69.04±0.14	7.16±0.06
10 µm	-2.09	1.31	0.74±0.01	15.20±0.03	70.88±0.26	8.05±0.10
15 µm	-2.56	1.41	0.75±0.06	15.43±0.21	70.97±0.09	8.18±0.09
20 µm	-2.85	1.54	0.74±0.02	16.17±0.14	71.28±0.07	8.62±0.09
25 µm	-2.94	1.58	0.74±0.06	17.11±0.22	71.64±0.13	9.16±0.11

Cobalt based electrolyte

- **Synthesis of $[Co(bpy)_3]$ $(TFSI)_2$ complex**

This complex was synthesized based on the approach used in previously.[1] By dissolve both of CoCl2.6H2O and 2,20-bipyridine in ration 1:1 in a minimum amount of methanol, reflux for 1 h with constant stirring. An excess amount of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt was added to the above solution to precipitate the cobalt complex. The obtained solid precipitate was filtered, washed with water and diethyl ether, then subjected to vacuum drying for 24 h. Slightly more than one molar equivalent of $NOBF_4$ was added to an acetonitrile solution of the complex to oxidize the Co (II) complex before rotary evaporation of the solvent. The resulted complex was re-dissolved in acetonitrile and a 10-fold excess of LiTFSI was added to precipitate the product. The product was filtered, washed with diethyl ether and water, and then dried under vacuum for 24 h. These two compounds were used without further purification.

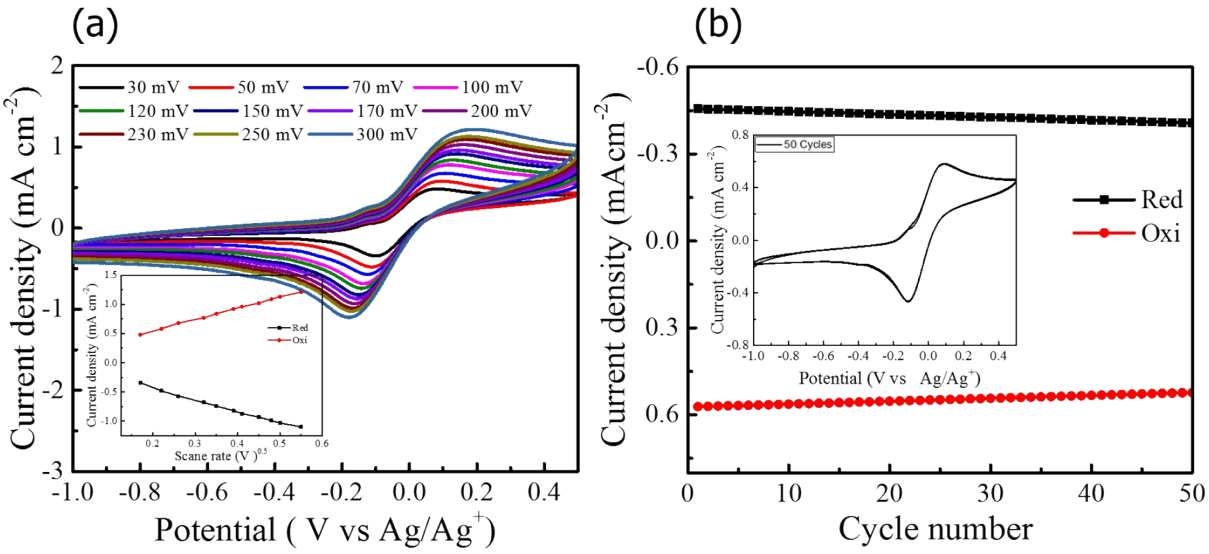


Fig. S7 (a) CV curves at different scan rates; inside the relationship between peak current density and the square root of scan rates, and (b) 50 times continuous cycle scans CVs of the 7% ZnO-NC/PEDOT: PSS CE with the scan rate of 50 mV s^{-1}.

Table S2. Photovoltaic performances of DSSCs $[Co(bpy)_3]^{2+/3+}$ electrolyte with different CEs under AM1.5G illumination.

CEs	DSSCs	Voc mV	Jsc (mA/cm^2)	FF (%)	Eff (%)
Pt	Cell (1)	824	12.78	72.30	7.61
	Cell (2)	823	12.49	72.40	7.44
	Cell (3)	823	12.66	71.29	7.43
	Average	**823**	**12.64**	**72.00**	**7.49**
	SD (±)	0.58	0.15	0.61	0.10
PEDOT: PSS	Cell (1)	828	10.12	70.27	5.89
	Cell (2)	828	10.13	70.26	5.89
	Cell (3)	828	10.26	69.81	5.91
	Average	828	10.17	70.11	5.90
	SD (±)	0	0.08	0.26	0.01
1% ZnO-NC/PEDOT: PSS	Cell (1)	834	10.74	70.11	6.28
	Cell (2)	834	10.75	70.14	6.29
	Cell (3)	834	10.85	70.00	6.33
	Average	834	10.78	70.08	6.3
	SD (±)	0	0.06	0.074	0.03
3% ZnO-NC/PEDOT: PSS	Cell (1)	845	12.32	70.00	7.28
	Cell (2)	846	12.41	69.98	7.35
	Cell (3)	853	12.54	68.31	7.31
	Average	848	12.42	69.43	7.31
	SD (±)	4.36	0.11	0.97	0.04
5% ZnO-NC/PEDOT: PSS	Cell (1)	832	13.09	71.73	7.81
	Cell (2)	831	12.80	70.56	7.51
	Cell (3)	834	12.98	71.35	7.72
	Average	832.33	12.96	71.21	7.68
	SD (±)	1.53	0.15	0.60	0.15
7% ZnO-NC/PEDOT: PSS	Cell (1)	835	13.72	71.70	8.21
	Cell (2)	836	13.43	70.64	7.93
	Cell (3)	837	13.59	72.14	8.22
	Average	**836**	**13.58**	**71.49**	**8.12**
	SD (±)	1	0.16	0.77	0.16
10% ZnO-NC/PEDOT: PSS	Cell (1)	831	13.41	71.93	8.02
	Cell (2)	832	13.11	70.69	7.71
	Cell (3)	833	13.28	71.55	7.92
	Average	832	13.27	71.39	7.88
	SD (±)	1	0.15	0.64	0.16

References

1. X. L. Zhang, W. Huang, A. Gu, W. Xiang, F. Huang, Z. X. Guo, Y.-B. Cheng and L. Spiccia, *Journal of Materials Chemistry C*, 2017, 5, 4875-4883.