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Metal-organic frameworks derived hierarchical ZnO parallelepipeds as efficient scattering layer in dye-sensitized solar cells

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Experimental

Photoanode preparation. All reagents were of analytical grade and were used without further purification. MOF-5 nanoparticles were fabricated according to the procedures reported in the literatures.[1] The procedure used to prepare the paste is as follows: ZnO nanoparticles (20 nm, Wako) or MOF-5 (as-prepared), ethyl cellulose (10 wt%) and α-terpineol (5 wt%) were added into the ethanol solvent successively. A homogeneous paste was obtained by dispersing the mixture of these components sufficiently with a homogenizer (Ultra-turrax T18 basic, IKA). The paste was concentrated by a rotary evaporator (EYELA N-1100S, Tokyo rikakikai) to a final concentration of 20 wt%. The paste was printed on FTO glass (8–10 Ω/□, Nippon sheet glass) using a screen printer (Mitani Electronics) and then sintered at 525 ^{o}C for 2 h.

For the preparation of ZnO scattering layer, MOF-5 paste was screen printing on the ZnO film formed on the first step, and then calcined at 525 ^{o}C for another 2 h.

For the coating of ZIF-8, the photoanode with a structure of FTO/ZnO/ZnO scatter layer was immersed in a fresh methanol solution containing 1 mM $Zn(NO_3)_2$ and 2 mM 2-methyl imidazole for a given time. It was found that about 15 min growth time was best for the improvement of cell performance.

Cell Assembly. The ZnO electrode was immersed in the 0.3 mM ethanolic solution containing the dye N719 (Solaronix) and D131 (Mitsubishi Paper) for 2 h to ensure a saturated adsorption. The sensitized ZnO photoanode was incorporated into a thin-layer, sandwiched solar cell with an active area of 0.25 cm^2. The Pt sputtered on FTO glass was used as a counter electrode. A 38 μm thick polyethylene spacer was placed between the working electrode and the counter electrode to prevent the cell from short-circuiting. The electrolyte consisted of 0.6 M 1,2-dimethyl-3-n-

propylimidazolium iodide, 0.1 M LiI, and 0.05 M I_2 in acetonitrile with 0.5 M 4-tertbutylpyridine.

Cell Characterization. The photovoltaic performance of the solar cells was measured with a source meter (Keithley 2400). A PEC-L11 AM1.5 solar simulator (Peccell, with a 1000 W Xe lamp and an AM 1.5 filter) was used as the light source (100 mW cm^{-2}). UV-vis spectra were investigated with Lambda-950 (Perkin-Elmer). To compare the loading amount of dyes, the sensitized photoanode was immersed in the 0.1 M NaOH solution with water and ethanol (v/v = 1/1) as solvents. The dyes could be desorbed from the ZnO photoanode completely after immersion for about 1 h. X-ray diffraction patterns were recorded on a PANalytical X'Pert spectrometer. Scanning electron microscopy images were taken from S4800 (Hitachi) with an accelerated voltage of 10 kV. Electrochemical impedance spectroscopy was taken on an IM6 (Zahner). The incident photon-to-electron conversion efficiency (IPCE) spectra were collected by PEC-S20 (Peccell).

1 T. Tachikawa, J. R. Choi, M. Fujitsuka and T. Majima, *J. Phys. Chem. C*, 2008, **112**, 14090.

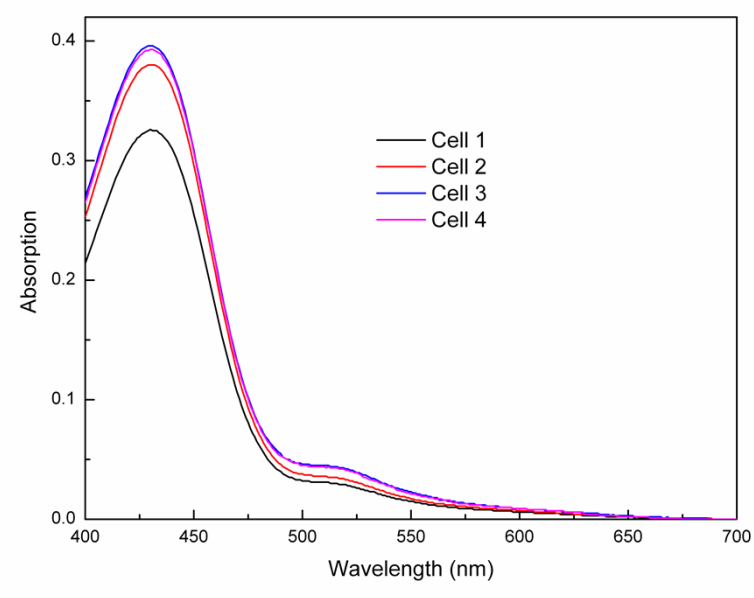

Fig. S1. Absorption spectra of the desorbed dyes of cells. The cell 4 consisted of ZnO nanoparticles and its film thickness (16.0 μm) is almost the same with that of cell 2.

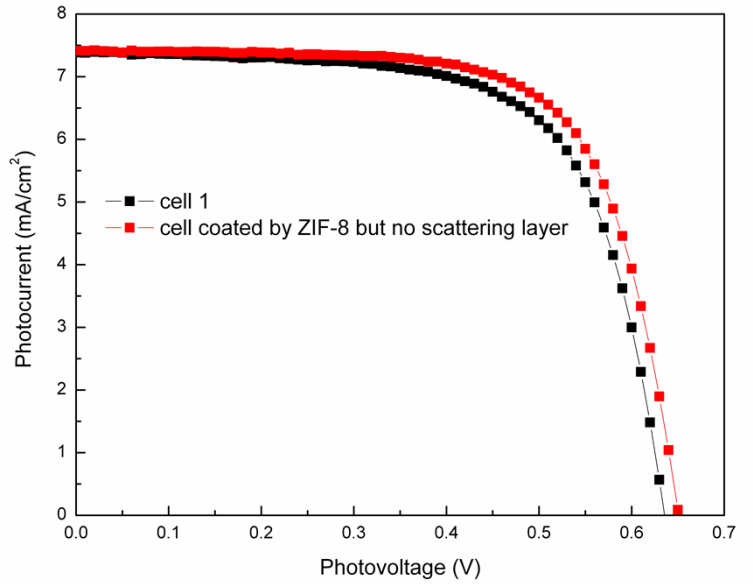

Fig. S2. *I-V* curves of cells with and without the coating of ZIF-8.

Table S1. Photovoltaic performance of ZnO films with different thicknesses.

Thickness (μm)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	Fill Factor	Efficiency (%)
7.3±0.2	5.72±0.08	642±4	0.68±0.00	2.50±0.02
9.1±0.3	6.43±0.11	638±6	0.66±0.01	2.71±0.04
10.6±0.4	6.94±0.13	640±5	0.68±0.01	3.02±0.04
12.0±0.2	7.39±0.09	636±6	0.67±0.00	3.15±0.02
13.2±0.2	7.21±0.08	632±7	0.65±0.00	2.96±0.03
14.0±0.3	7.12±0.12	630±6	0.65±0.01	2.92±0.04
16.0±0.2	6.89±0.10	628±7	0.65±0.01	2.81±0.04

Table S2. The relationship between the thicknesses of scattering layer and photovoltaic properties of cells.

Thickness (μm)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	Fill Factor	Efficiency (%)
0	7.39±0.09	636±6	0.67±0.00	3.15±0.02
2.2±0.2	7.57±0.21	637±7	0.67±0.01	3.23±0.05
3.1±0.4	7.78±0.15	646±5	0.66±0.00	3.32±0.03
3.8±0.3	7.95±0.17	646±6	0.68±0.01	3.49±0.04
4.4±0.2	7.81±0.18	644±6	0.68±0.01	3.42±0.05

Table S3. The calculated dye loading amounts from Fig. S1.

Device	Dye loading amounts (10^{-7} mol/cm^2)	
	N719	D131
Cell 1	0.90	0.32
Cell 2	1.05	0.37
Cell 3	1.09	0.46
Cell 4	1.08	0.45