

**Electronic Supplementary Information
(ESI)**

**Room-Temperature Chemical Integration of ZnO Nanoarchitectures
on Plastic Substrates for Flexible Dye-Sensitized Solar Cells**

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Experimental Details

A butanolic solution of ZnO NPs was prepared for the spin coating of seed layers on ITO/PET substrates. A 60 ml of methanolic solution of 0.2 M KOH was added dropwise into a 125 ml of methanolic solution of 0.013 M zinc acetate at 60°C and the solution was kept stirring for 2 h at 60°C. After aging for another 2 h, the as-prepared colloidal solution was then centrifuged at a rate of 3000 rpm for 5 min. The precipitated ZnO NPs were redispersed in 30 ml of butanol by sonication. ZnO NW arrays were grown on the seeded ITO/PET substrates by CBD in a 0.02M aqueous solution of zinc acetate and hexamethylenetetramine at 95°C. To form the NC array, the ZnO NW array/ITO/PET substrate was immersed in a vigorously stirred aqueous solution of 0.062 M zinc acetate and 0.479 M NaOH at RT for 3 min. The top ZnO particle film was prepared by the drop casting of an ethanolic solution of ZnO particle on the top of NC array. The ZnO particles were hydrothermally synthesized using an aqueous solution of 0.125 M zinc acetate and 0.83 M NaOH at 180°C for 10 h. The product was centrifuged and dried at 80°C for 12 h followed by redispersed in ethanol. Finally, another RTCBD was carried out by immersing the ZnO nanoarchitecture into the stirred aqueous solution of 0.062 M zinc acetate and 0.5 M NaOH at RT for 4 min. The morphologies of the ZnO nanostructures were examined using scanning electron microscopy (SEM, JEOL JSM-7000F and ZEISS AURIGA-39-50). Structural characterizations of the ZnO nanostructures were performed using TEM (JOEL 2100F and FEI E.O Tecnai F20 G2 MAT S-TWIN). Optical properties of the ZnO nanostructures were measured using a UV-Vis-IR spectrophotometer (JASCO V-670).

Dye adsorption was carried out by immersing the anode in a 0.5 mM acetonitrile/t-butanol (1:1) solution of D149 at RT for 40 min. The sensitized electrode and platinized ITO/PET counter electrode were sandwiched together with

25- μm -thick hot-melt spacers (SX 1170-25, Solaronix SA). Liquid electrolyte solutions composed of 0.5 M tetrapropylammonium iodide (TPAI) and 50 mM I_2 in a 1:4 volume ratio of ethylene carbonate and acetonitrile was employed for the D149-sensitized DSSCs. The cells are full sealed by cyanoacrylate glue. A mask on the PET substrate side was used to create an exposed area of 0.16 cm^2 for all cells. Photographs of the flexible ZnO NC-TP anode and the corresponding DSSCs on ITO/PET substrates are shown in Fig. S3. Photovoltaic properties of the DSSCs were measured under AM 1.5 simulated sunlight at 100 mWcm^{-2} (300 W, Model 91160A, Oriel).

IPCE spectra were measured using 500 W xenon light source (Oriel) and a monochromator (Oriel Cornerstone) equipped with Si (Model 71640, Oriel) detector. Intensity modulated photocurrent spectroscopy (IMPS) measurements were conducted under a modulated green LED light (530 nm) driven by a source supply (Zahner, PP210) and a potentiostat (Zaher, IM6ex) with a frequency response analyzer. The experimental procedure and the method for extraction of electron transit times of the DSSCs from the IMPS responses have been described in detail elsewhere.¹

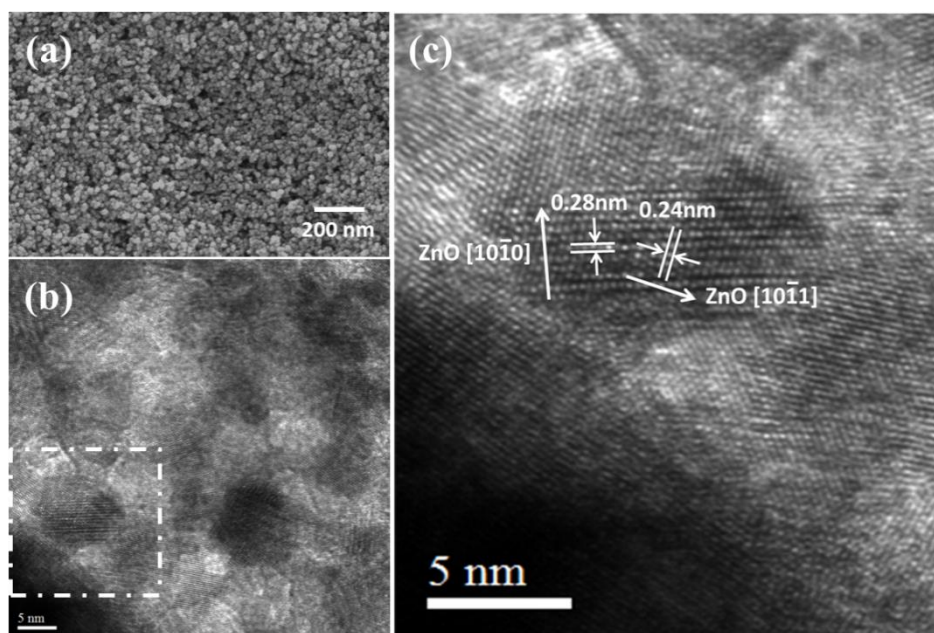


Fig. S1 (a) SEM and (b) TEM images of ZnO NP seed layer. (c) HRTEM image of the ZnO NPs denoted in (b).

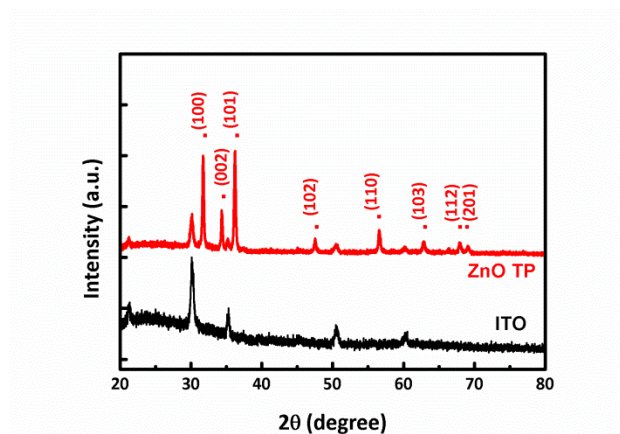


Fig. S2 XRD patterns of ZnO TP film on ITO substrate and ITO substrate.

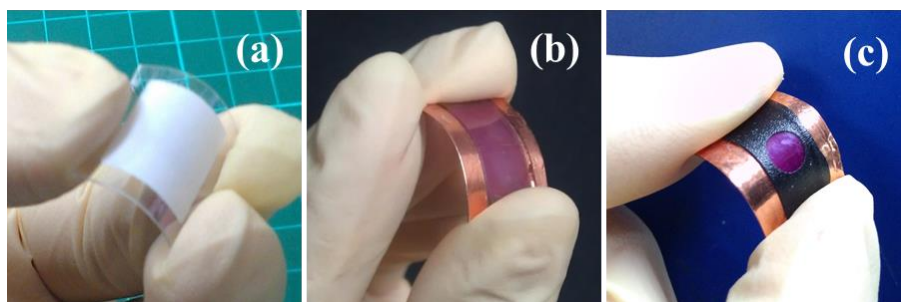


Fig. S3 Photographs of (a) flexible ZnO NC-TP anode, (b) the corresponding DSSC, and (c) flexible ZnO NC-TP DSSC with mask for photovoltaic measurements.

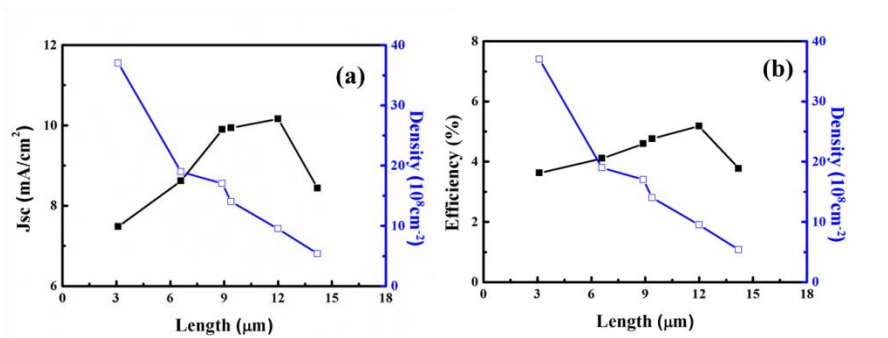


Fig. S4 Influences of array length on density of primary NW array as well as J_{sc} and efficiency of the ZnO NC DSSCs fabricated on ITO/glass substrates.

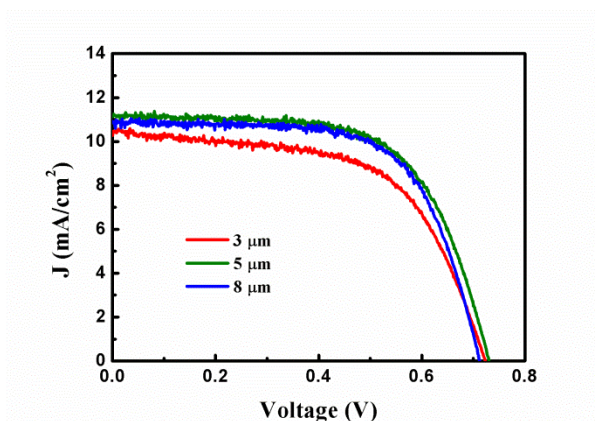


Fig. S5 J-V curves of flexible D149-sensitized ZnO NC-TP DSSCs fabricated using 10- μm -thick ZnO NC arrays and ZnO TP films with various thicknesses.

Table S1 Photovoltaic properties of flexible D149-sensitized ZnO NC-TP DSSCs

Thickness of ZnO TP film in Flexible ZnO NC-TP DSSC	Voc (V)	Jsc (mA/cm ²)	F.F.	η (%)
3 μm	0.72	10.28	0.61	4.51
5 μm	0.73	11.19	0.64	5.24
8 μm	0.71	10.89	0.66	5.11

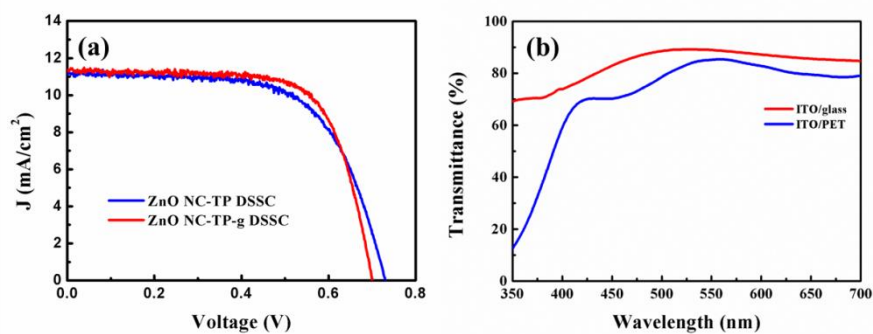


Fig. S6 (a) J-V curves of flexible D149-sensitized ZnO NC-TP and ZnO NC-TP-g DSSCs. The ZnO NC-TP-g DSSC exhibits an efficiency of 5.64 % with a J_{sc} of 11.34 mA cm^{-2} , a V_{oc} of 0.70V, and an FF of 0.71. (b) Transmittance spectra of ITO/PET and ITO/glass substrates. The sheet resistances of ITO/PET and ITO/glass substrates are 15 and 10 ohm/sq , respectively.

Bending Test

It is well known that the leakage of electrolyte due to the poor adhesion of sealing material with plastic substrate surface is one of the major issues for the poor stability of the flexible DSSC fabricated using plastic substrates.² We found that the liquid electrolyte leaks from the ZnO NC-TP DSSC during bending even though the cell is sealed by glue. The performance of the cell is therefore degraded during bending test, which is mainly due to the electrolyte deficiency. An expedient method for examining the flexible nature of the ZnO TP-NC photoanode is to conduct the bending test on an unsealed liquid-electrolyte ZnO NC-TP DSSC cell. While the liquid electrolyte leaks from the unsealed cell during bending, it is refillable into the flattened cell after bending.

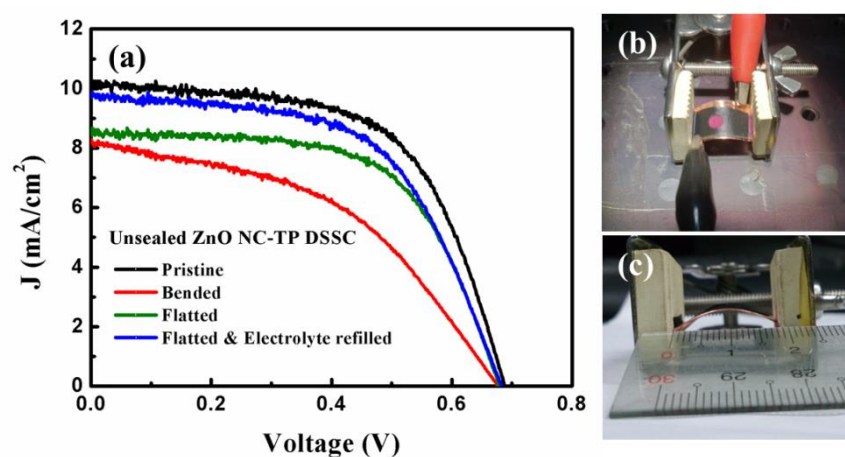


Fig. S7(a) Bending test results of unsealed liquid-electrolyte ZnO NC-TP DSSC cell. (b) Top-view and (c) cross-sectional photographs of bended cell with a bending radius of 12.5 mm.

Fig. S7(a) and Table S2 show the bending test results of the unsealed liquid-electrolyte ZnO NC-TP DSSC cell. The pristine unsealed cell possesses an efficiency of 4.25%, which is lower than that of ZnO NC-TP DSSC shown in Fig. 3(a) due to the evaporation of the electrolyte in the unsealed cell. The performance of unsealed ZnO NC-TP DSSC is then monitored with a bending radius of 12.5 mm as shown in Fig. S7(b) and (c). An efficiency of 2.43% is measured in the bended ZnO NC-TP DSSC in which the leakage of electrolyte is significant occurring. Both J_{sc} and FF of the cell in the bending condition are decreased compared to those of pristine cell as shown in Fig. S7(a) and Table S2. When the unsealed cell is flatted, an

efficiency of 3.59% is attained. The degradation of the efficiency after bending is mainly attributed to the decrease of the J_{sc} . After refilling the electrolyte into the cell, the efficiency of the unsealed ZnO NC-TP DSSC is recovered by 90% compared to the first measurement for the pristine cell. As shown in Fig. S7(a) and Table S2, the J_{sc} and FF are respectively recovered by 96% and 93%. The electrolyte is not possible refilled completely in the unsealed cell, which may mainly lead to the decrease of FF and therefore the degradation of the efficiency of the unsealed ZnO NC-TP DSSC. Nevertheless, the bending test results of the unsealed ZnO NC-TP DSSC demonstrate the good bending stability of the ZnO TP-NC photoanode.

Table S2 Bending test results of unsealed liquid-electrolyte ZnO NC-TP DSSC cell.

Monitor Condition	Voc (V)	Jsc (mA/cm ²)	F.F.	η (%)
Pristine	0.69	10.18	0.61	4.25
Bended	0.68	8.01	0.45	2.43
Flatten	0.68	8.49	0.62	3.59
Flatten & Electrolyte refilled	0.68	9.74	0.58	3.85

References:

1. D.-K. Wong, C.-H. Ku, Y.-R. Chen, G.-R. Chen and J.-J. Wu, *ChemPhysChem*, 2009, **10**, 2698-2702.
2. H. C. Weerasinghe, F. Huang and Y.-B. Cheng, *Nano Energy*, 2013, **2**, 174-189.