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> [10¹0] Oriented Hybrid 3D ZnO Nanowalls Architecture with Enhanced Dye-Sensitized Solar Cells Performance Nanaji Islavath^{a*}
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Supporting Information

The cross-section TEM samples were prepared by first sticking two sample slides together, with nanostructure sides facing each other using glue. The sample was thinned down from 6 mm to 1 mm equally from both glass substrates without damaging the interface. The thinned sample cut and fixed in a 3-mm copper tube. The copper tube was cut to 3mm disk using an isomet cutter and thinned down to 50 µm using emery paper and diamond polishing is done to reduce the thickness to about 35-40 µm. The sample is then dimpled to the point where the dimpled region about 10-15µm thick. Later, a precision ion polishing system is used to create a small hole near the interface of nanostructure and substrate, within the dimpled region around which a very thin area (10-100 nm in thickness) which can then to viewed in the TEM and schematic of TEM sample preparation as shown in **Figure S1**.



Figure S1. Schematic diagram of the Cross-section TEM sample preparation.



Figure S2. Two probe I-V characteristics of ZnO nanostructures.



Figure S3. SEM images of ZnO nanostructure grown on FTO glass substrates with different seed layers: (a) ZnO and 1 at. % Al-ZnO, (b) 2 at. % Al-ZnO and (c) 3at. % Al-ZnO, (Scale bar 1μ m).



Figure S4. High magnification scanning and transmission electron microscopy image of ZnO nanostructure grown on the Al-ZnO and ZnO seed layer coated FTO glass substrate.



Figure S5. The SEAD pattern of FTO and Al-ZnO seed layer.



Figure S6. Cross-sectional TEM images of 1D nanowires (a) High-resolution, (b-d) SAED pattern of 1D ZnO NW/seed layer/FTO, and (e) HRTEM image of corresponding 1D ZnO NW/seed layer.



Figure S7. After dye-desorption from the electrodes (a) porphyrin (LG5), and (b) N719 dye.



Figure 8. Current–voltage characteristics of ZnO nanostructures-based N719 dye DSSCs measured under 1 sun illumination.

Table S1. Device parameters ^a and, ^b active area of the N719 dye DSSCs.

Device	Dye loading [10 ⁻⁸ mol.cm ⁻²]	V _{OC} [V]	J _{SC} [mA cm ⁻²]	FF	η[%)]
ZnO NW	1.941	0.689	4.582	0.493	1.55
3D ZnO NWL	2.681	0.700	6.250	0.514	2.24
Hybrid 3D ZnO NWL	4.729	0.717	8.741	0.519	3.25

^a All values area average of 8 cells

 $^{\rm b}$ Active area of the cell was 0.36 $\rm cm^2$

Further, reconfirming the performance of solar cells; we fabricated device using the lowerconcentration dye-solution (7.336 x 10⁻⁸ mol. cm²). This concentration was chosen from the dye-loading of 0.2 mM electrodes (Hybrid 3D ZnO NWL) for reference. **Figure S9** shows the I-V characteristics of ZnO nanostructure based Pophyrin sensitized solar cells and it have similar trends in the performance as like 0.2 mM dye-solution based solar cells. It clearly reflects the hybrid 3D ZnO nanowall architecture shown high performance as compare to the ZnO nanowire and 3D nanowall arrays. Due to the higher hybrid surface area, which holds more dye-molecules and provides the shorter path. These device parameters were listed in Table S2.



Figure 9. Current–voltage characteristics of ZnO nanostructure-based (7.336 x 10⁻⁸ mol. cm²) Pophyrin solar cells measured under 1 sun illumination.

J_{SC} [mA cm⁻²] V_{OC} [V] η[%)] Device FF 0.656 0.690 0.565 0.25 ZnO NW 0.984 0.36 3D ZnO NWL 0.653 0.572 Hybrid 3D 0.655 0.583 0.43 1.452 ZnO NWL

Table S2. Device parameters ^a and, ^b active area of the (7.336 x 10⁻⁸ mol. cm²) Pophyrin dye

DSSCs.

^a All values area average of 2 cells

 $^{\rm b}$ Active area of the cell was 0.36 $\rm cm^2$