Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Control of morphology and defect density in ZnO for improved dye sensitized solar cells

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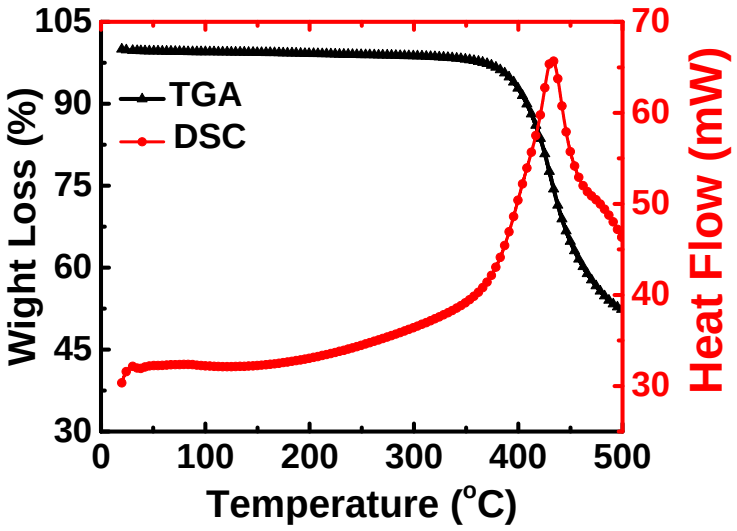

Fig. S1 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of Zn-complex.

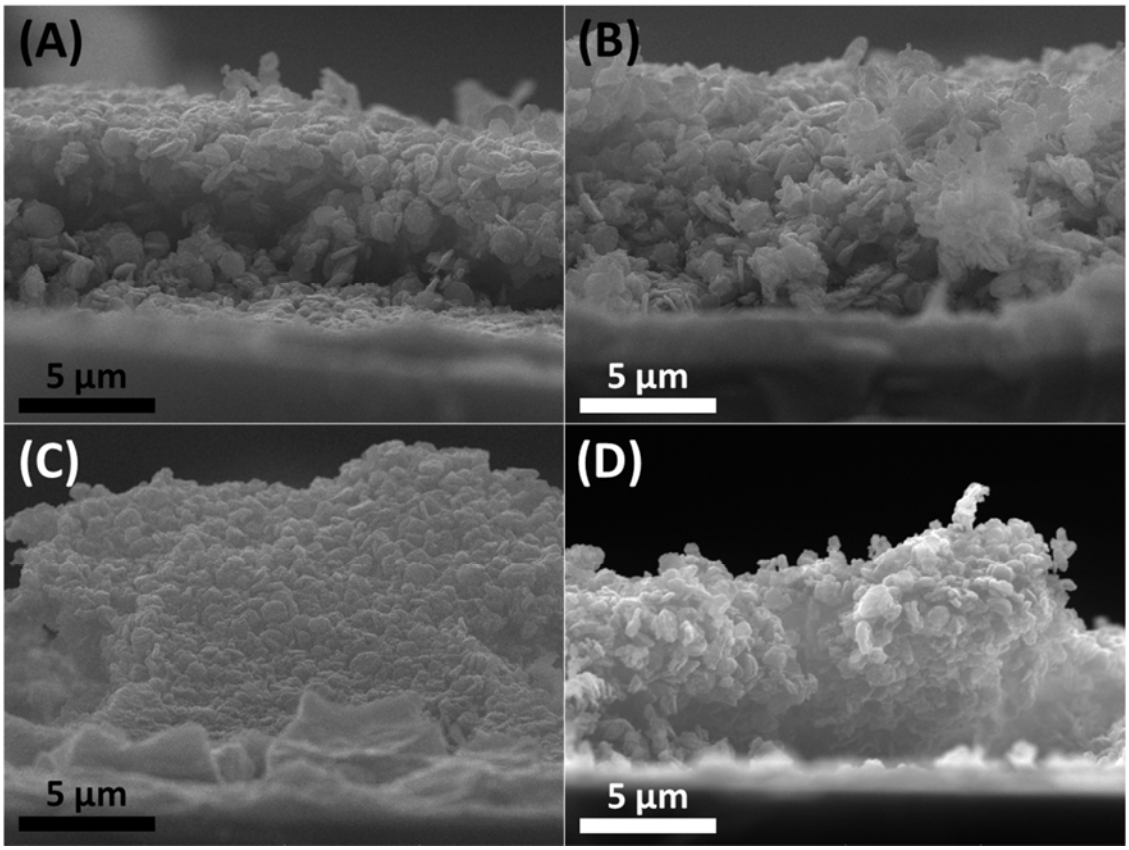

Fig. S2 Cross-sectional images of nanodisk-ZnO and nanodisk-ZnO-$TiCl_4$ films, which clearly shows improved connection between ZnO particles after $TiCl_4$ treatment. (A-B) nanodisk-ZnO and (C-D) nanodisk-ZnO-$TiCl_4$.

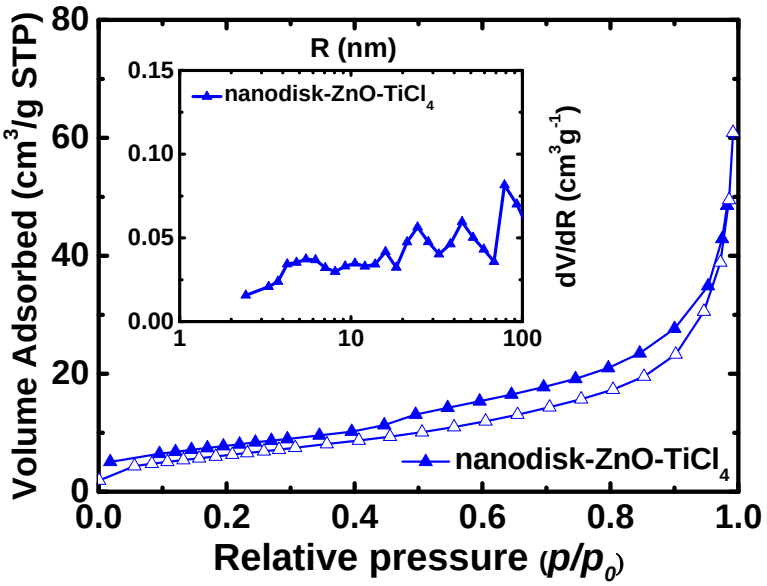

Fig. S3 N_2 adsorption/desorption isotherms of the $TiCl_4$-treated nanodisk-ZnO. The open symbols in the isotherms represent the adsorption curves, and the solid symbols represent the desorption curves. The inset of (B) provides the pore size distribution of nanodisk-ZnO-$TiCl_4$.

Table S1. Summary of BET surface area of various zinc oxides used in current work. It also shows the gain in the electrode surface area as a result of $TiCl_4$ treatment.[a]

Parameter	*Comm-ZnO*	*nanodisk-ZnO*	*nanodisk-ZnO-TiCl4*
BET area (m^2/g)	34.39	24.75	23.81
Avg. Pore diameter (nm)	34.48	15.11	15.03
TiO_2 mass gain (wt %)	---	---	60
Gain in Electrode Area (%)	---	---	54

[a]After the $TiCl_4$ treatment, even though gravimetric surface area was decreased; however, additional TiO_2 was deposited on the nanodisk-ZnO surface. This increased the packing density of the electrode film and led to the overall increase in electrode area.

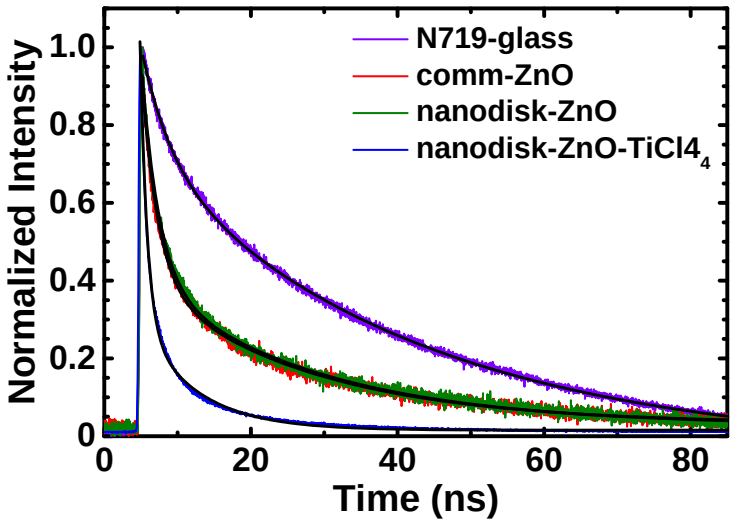

Fig. S4 Photoluminescence decay of N719 dye adsorbed onto three different mesoporous films. Solid black lines in each curve shows fitted lines. Faster decay on nanodisk-ZnO-$TiCl_4$ indicates faster electron transfer to $TiCl_4$-treated nanodisk-ZnO as compared to other two ZnO films.

Table S2. Photoluminescence lifetime parameters of N719 dye used in current work on glass slide and adsorbed onto various mesoporous films.[a]

Sample	τ_1 *(%)*	τ_2 *(%)*	$\tau_{avg.}$ *(ns)*	k_c [b]
N719 on Glass	4.04 (26)	37.68 (74)	28.78	---
comm-ZnO	2.19 (58)	22.40 (42)	10.59	5.97×10^7
nanodisk-ZnO	2.36 (58)	23.45 (42)	11.17	5.48×10^7
nanodisk-ZnO-$TiCl_4$	0.96 (72)	7.63 (28)	2.83	3.19×10^8

[a]The PL decay curves were fitted with the following equation: $f(t) = A_1 e^{-k\tau_1} + A_2 e^{-k\tau_2}$. [b]Calculated using the following equation: $k_c = 1/\tau_{ZnO} - 1/\tau_{Glass}$.

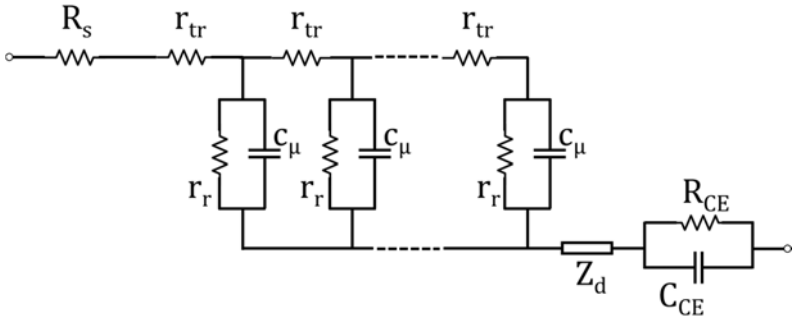

Fig. S5 Equivalent circuit used for fitting the EIS data. R_S is the series resistance, R_{CE} and C_{CE} are the charge transfer resistance and the chemical capacitance at the counter electrode/electrolyte interface, R_{tr} ($=r_{tr}.L$) is the transport resistance through mesoporous TiO_2 network, R_r ($=r_r.L$) and C_μ ($=c_\mu.L$) are the recombination resistance and the chemical capacitance at the TiO_2/dye/electrolyte interface.[1,2]

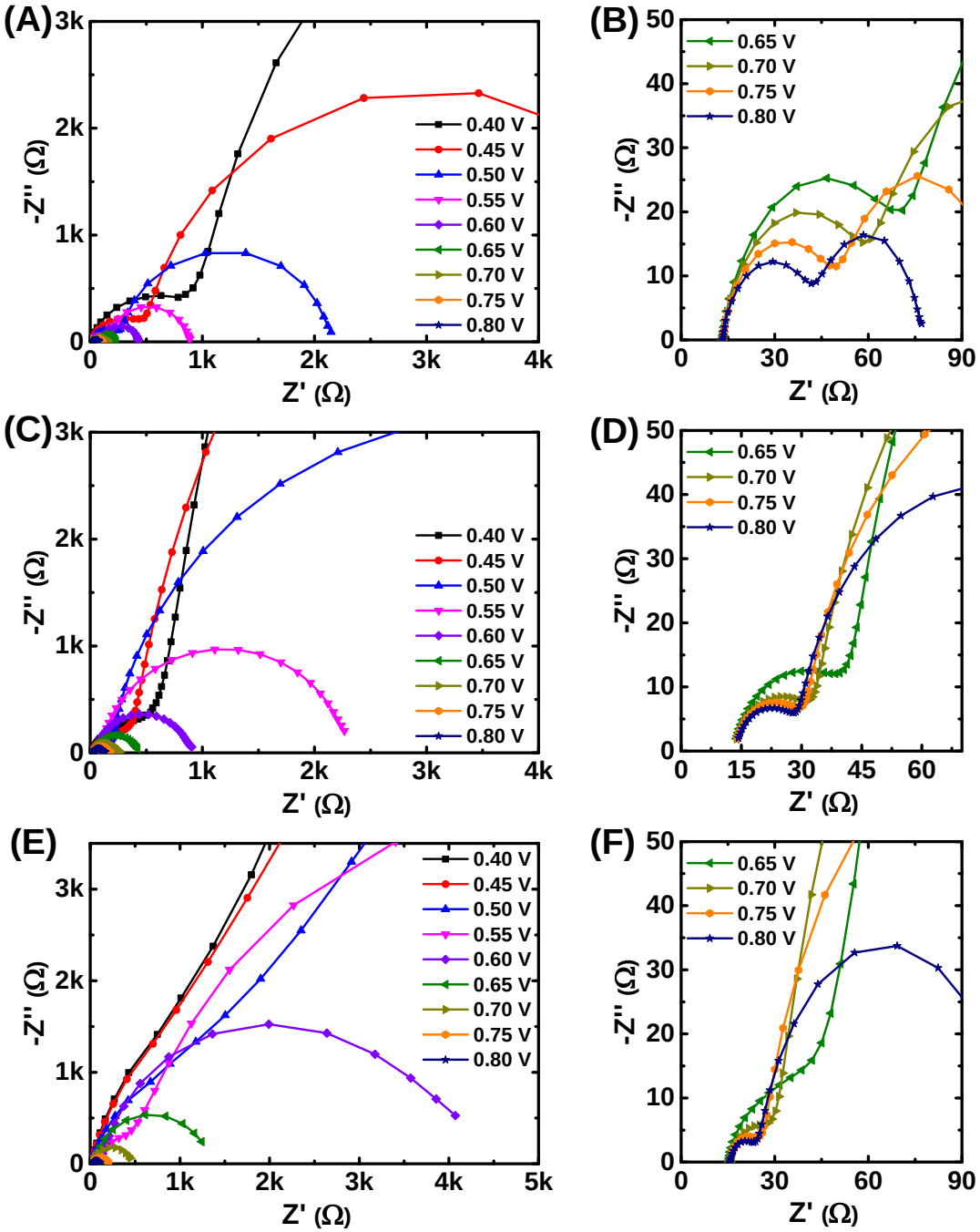

Fig. S6 Nyquist plots of three different solar cells studied in current work. (A-B) comm-ZnO, (C-D) nanodisk-ZnO, and (E-F) nanodisk-ZnO-$TiCl_4$. Figures (B), (D), and (F) are zoom in of the Nyquist plots on left side of the respective figures to show the linear region used to estimate the transport resistance.

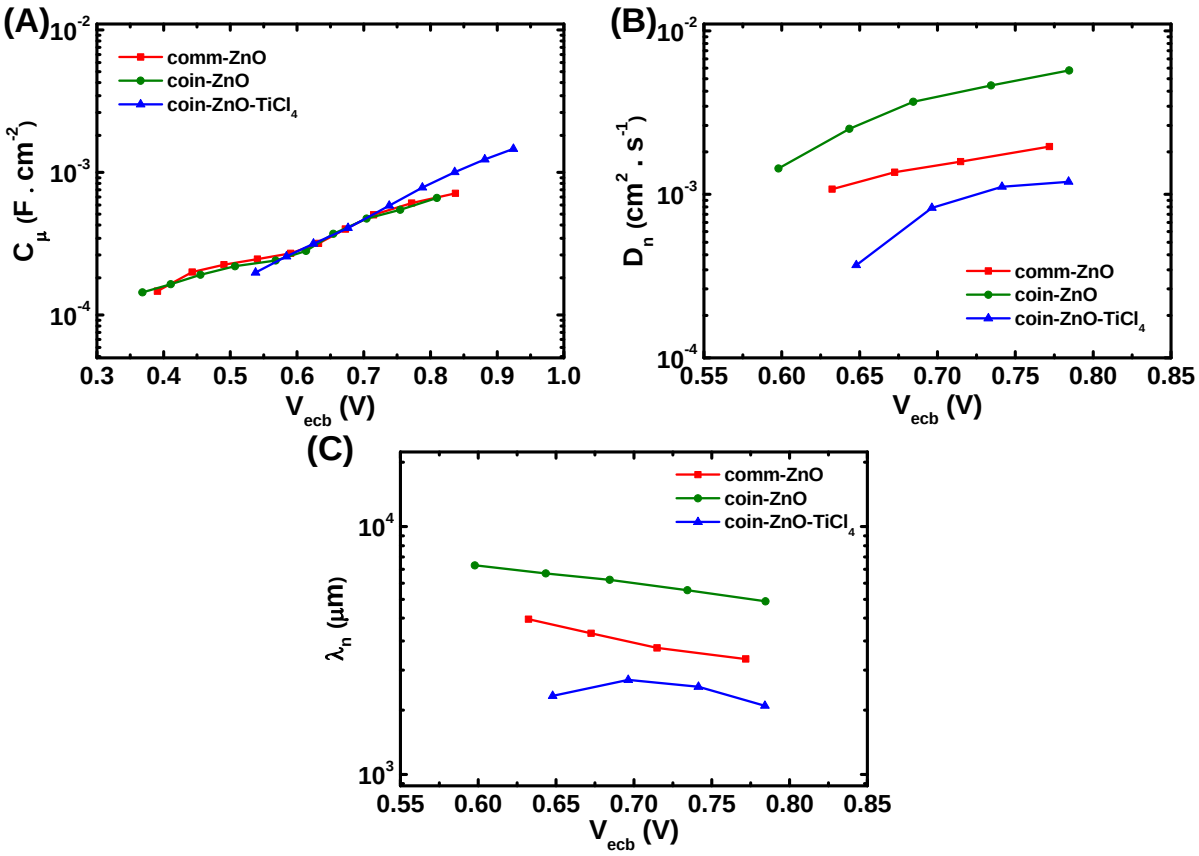

Fig. S7 (A) Chemical capacitance in equivalent conduction band position to calculate the shift in the V_F for comparison of various parameters extracted from EIS. (B) Electron diffusion coefficient and (C) small perturbation diffusion length as calculated from EIS.

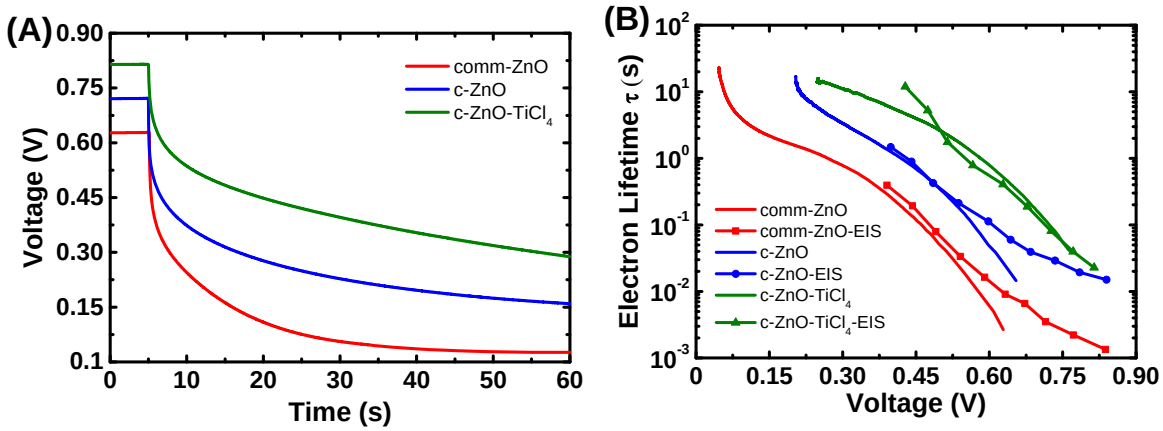

Fig. S8 (A) Open circuit voltage decay (OCVD) data of various ZnO-based DSSC studied in the current work. (B) Comparison of electron lifetimes measured by OCVD and EIS measurements.

References

1. F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo and A. Hagfeldt, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 117-131.
2. V. González-Pedro, X. Xu, I. Mora-Seró and J. Bisquert, *ACS Nano*, 2010, **4**, 5783-5790.