Supporting Information:

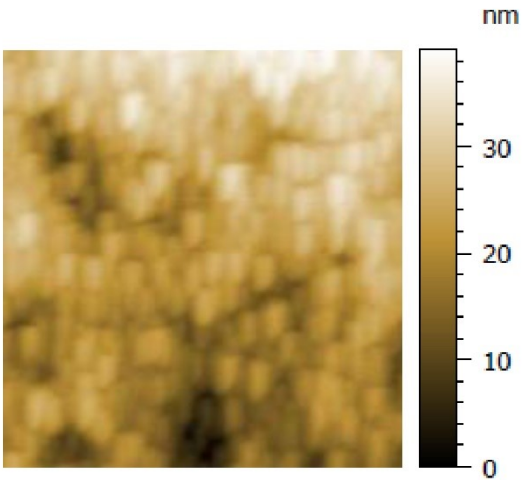

FIGURE S1. AFM images of thermally decomposed WO_3 film, the area shown is 1.5x1.5 µm array.

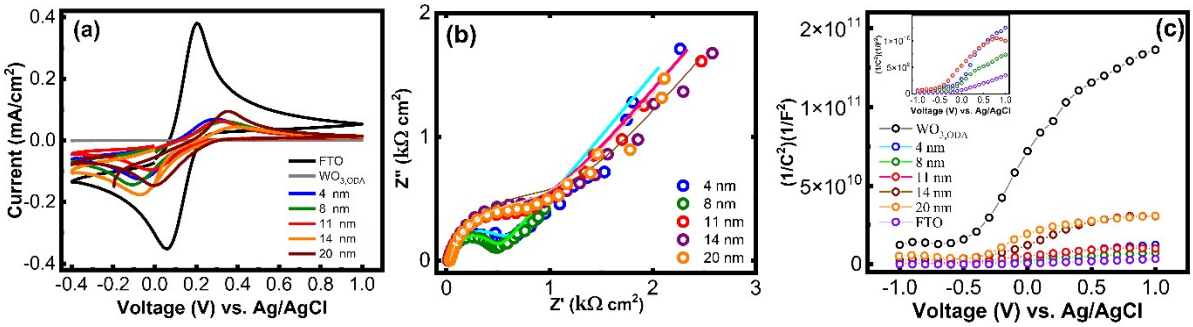

FIGURE S2. (a) cyclic voltammogram, (b) EIS spectra and (c) Mott-Schottky plots of the WO_3 blocking layer as a function of thickness

The cyclic voltammograms of WO_3 coated FTO reveals decrease in the anodic current, which is accompanied by simultaneous increase in the peak-to-peak separation, ΔE. No significant increase in the ΔE value with increase in the BL thickness rules out electron tunneling (Figure S2a). Further, appearance of two-slopes in Mott–Schottky plots are characteristics of FTO covered with compact film of WO_3 (Figure S2c). The larger slope can be attributed to FTO while smaller slope to the WO_3 film. A significant change in the slope corresponding to WO_3 film curve occurs when thickness of the film increases beyond 11 nm.

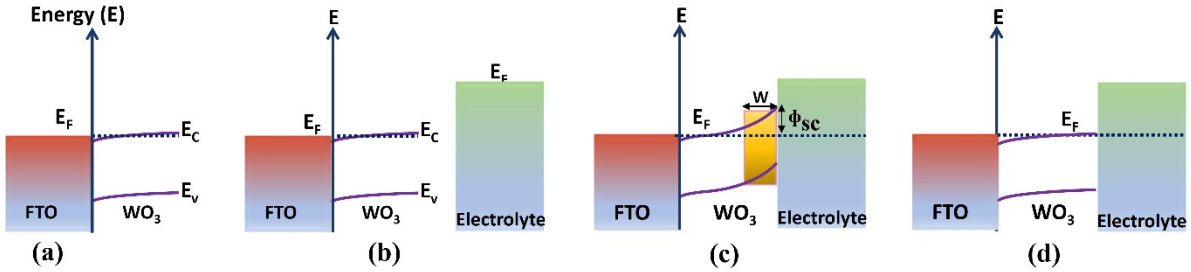

FIGURE S3. Energy level diagram of (a) FTO/WO_3 ohmic contact, (b) FTO/WO_3 -electrolyte, before contact and FTO/WO_3 -electrolyte interface, after contact for WO_3 thickness (c) $\geq L_D$ and, (d) $< L_D$, respectively.

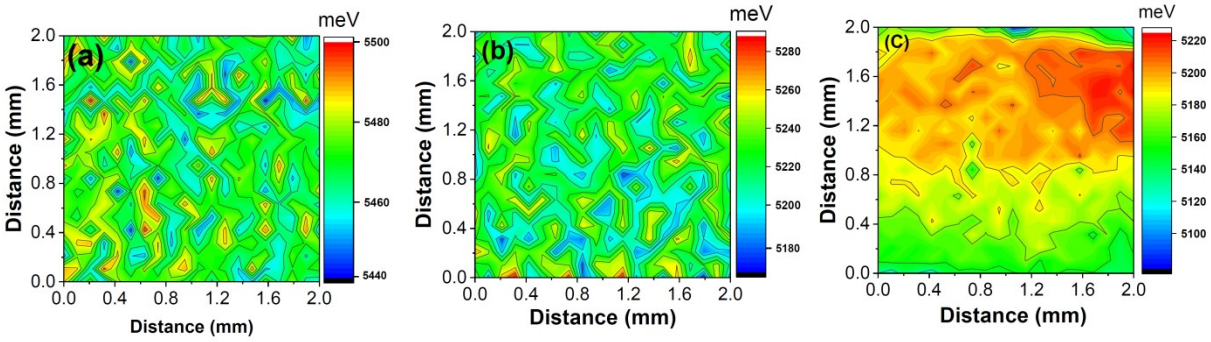

FIGURE S4. Contour Kelvin probe work function plots of (a) FTO, (b) spin cast WO_3 and LB WO_3.

The estimated average work function (Φ) value of LB WO_3 was 5.195 eV, which is close to that of FTO (5.1 eV), suggesting Fermi level alignment of BL with FTO substrate. Owing to the small difference Φ_{WO3}–Φ_{FTO}, the formation of ohmic-like contact (Figure S1a) is favoured between FTO and WO_3 BL. In the absence of built-in potential at FTO/BL interface, band bending is negligible and therefore, tunneling will not have significant contribution to charge carrier transport. This is also corroborated by the fact that short circuit current (J_{SC}) does not increase upon reducing the thickness of the WO_3 layer to 4nm, thereby ruling out the contribution of the tunnelling event to the J_{SC}. The contour plots for WO_3 LB film in scanning area of 2 mm x2 mm exhibit < 0.05% variation in the work function from the average value, suggesting excellent homogeneity. The homogeneity in LB WO_3 is much better than that of the spin cast film, which shows >1.5% variation in the work function from the average value (5.2 eV). Further, the Φ of the both WO_3 LB and spin cast films are similar to that of TiO_2 (5.2 eV), which suggests that WO_3 films are suitable for replacing TiO_2 in DSCs.

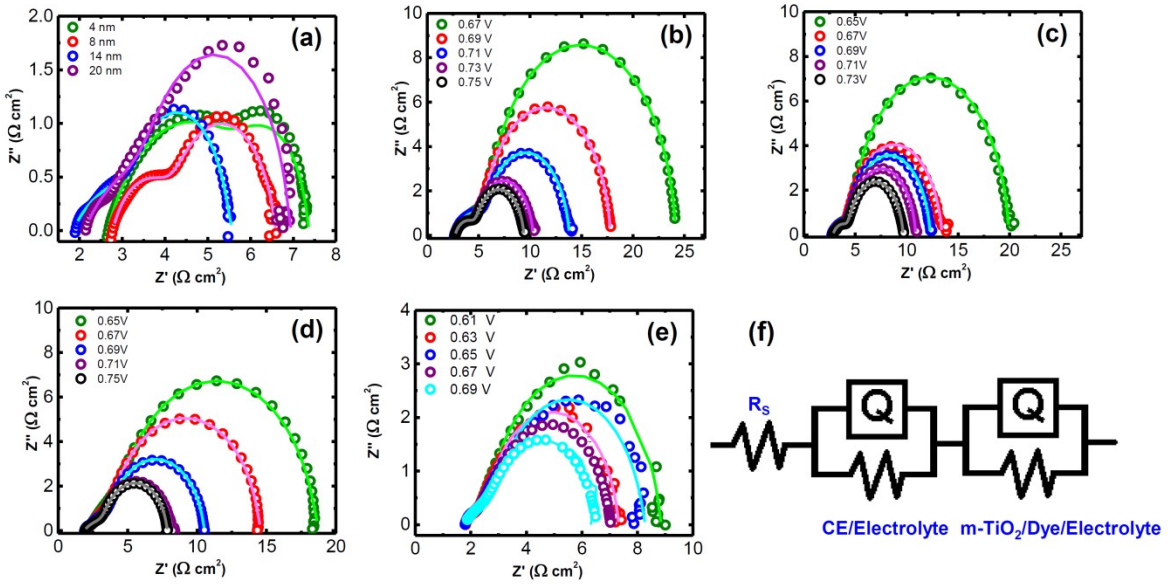

FIGURE S5. EIS spectra of DSCs under (a) AM 1.5 sun illumination as a function of number of layers and (b-e) dark at V_{OC}, V_{OC}±0.02V and V_{OC}±0.04V. The solid lines in figure represent fitted data using a model shown in (f), two randle circuits represent charge transfer behavior at the CE/electrolyte interface and m-TiO_2/dye/electrolyte interface and series resistance (Rs) includes BL, FTO and contact resistance.

The EIS in presented in Fig. S5, were measured at V_{OC}, $V_{OC} \pm 0.02$V and $V_{OC} \pm 0.04$V in dark. At these potentials the photoanode is sufficiently conductive and therefore, $C_{m\text{-}TiO2} >> C_{TCO}$, where $C_{m\text{-}TiO2}$ and C_{TCO} are the capacitances of m-TiO_2 and exposed FTO substrate respectively. The estimated chemical capacitance in dark, which is the sum of $C_{m\text{-}TiO2}$ and $C_{TCO,}$ therefore reduces to $C_{m\text{-}TiO2}$ only.

References:

S1: R. van de Krol1, A. Goossens1 and J. Schoonman1 Mott-Schottky Analysis of Nanometer-Scale Thin-Film Anatase TiO_2, Journal of The Electrochemical Society, 144 (5), 1723, 1997.