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Supporting Information

High-Efficiency Inverted Organic Solar Cells with Polyethylene oxide-Modified Zn-doped TiO_2 as Interfacial Electron Transport Layer

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Experimental section

Synthesis of Polyethylene oxide (PEO)-modified Zn-doped TiO_2 nanocrystalline thin films: In the present study, PEO-modified Zn-doped TiO_2 nanocrystalline thin films have been prepared using sol-gel spin coating method. Titanium (IV) butoxide ($Ti(OCH_2CH_2CH_2CH_3)_4$) (0.45M) and zinc acetate dihydrate ($Zn(CH_3COO).2H_2O$) (0.01M) were dissolved in a mixture of 2-methoxyethanol ($CH_3OCH_2CH_2OH$) and acetylacetone ($CH_3COCH_2COCH_3$) (0.45M) at room temperature. The resultant solution was stirred for 1h to yield a homogeneous, clear and transparent (light yellowish color) solution using magnetic stirrer. Polyethylene oxide (PEO) (0.01 wt.%, 0.05 wt.%, 0.1 wt.% and 0.3 wt.%) was dissolved in chlorobenzene. The PEO solution was slowly added to Zn-doped TiO_2 sol and was stirred for 2h to obtain the final sol ready for deposition of thin films. The spin coating method was used to prepare thin films of PEO-modified Zn-doped TiO_2 onto ITO substrates using the prepared sol. PEO-modified Zn-doped TiO_2 thin films of thickness 30 nm was formed after post annealing at 500 °C for 1h and these films form the PEO-modified Zn-doped TiO_2 nanocrystalline thin films.

Device fabrication and characterization: Inverted organic solar cells (IOSCs) were constructed with a device structure of ITO/PEO:Zn-doped TiO_2 (ZTO)/active layer/MoO_3/Al. Patterned ITO-coated glass substrates were cleaned by a sequence of sonication in acetone, isopropyl alcohol and deionized water respectively for 15 minutes and UV-ozone cleaning for 10 minutes. A thin layer of PEO-modified ZTO (30 nm) was spin coated onto the ITO substrates and annealed at 500 ºC for 2 hours in air. The PEO-modified ZTO substrates were transferred into a glove box. The PTB7:$PC_{71}BM$ blend solution was prepared with a weight ratio of 1:1.5 in a mixed solvent of chlorobenzene/1,8-diiodooctane (97:3 vol.%). The active layer (PTB7:$PC_{71}BM$) was then spin-coated on the PEO-modified ZTO layer and the thickness was about 80 nm. After that the organic layer was slowly dried in vacuum, a layer of MoO_3 (10 nm)/Al (100 nm) as electrode was thermally evaporated on top of the

active layer through a shadow mask under a pressure of ~10^{-6} Torr. The effective area of the device was measured to be 0.0196 cm^2.

Ultraviolet photoelectron spectroscopy (UPS) measurement was performed using AXIS Ultra DLD (KRATOS Inc.) with He I (21.2 eV) as monochromatic light source. X-ray photoelectron spectroscopy (XPS, AXIS-HSi) spectra was used to identify the surface elements and their chemical state. Photoluminescence (PL) spectra of the samples were measured using a Monochromator (SP2150i) and an excitation wavelength 375 nm. Surface topography was studied using atomic force microscopy (Park systems, XE-100). The optical properties were studied using the absorbance spectra recorded using Beckman DU-70 spectrophotometer. The thickness of the films were measured using a Dektak XT surface profiler. The electrical resistivity was measured by a four-point probe method. The mobility was measured by bottom-gate top-contact thin film transistor (TFT) method with semiconductor parameter analyzer (Agilent 4155C). Current density – voltage (J-V) characteristics of the devices were recorded using a Keithley 237 source measurement unit using a 100 mW/cm^2 AM 1.5G solar simulator (Newport, 91160A). Light intensity was calibrated using a standard silicon solar cell as a reference. The incident photon to charge carrier efficiency (IPCE) spectra of the devices were recorded using a lock-in amplifier (Model 7265, Signal Recovery) and a monochromatic light from a xenon lamp through the monochromator (SpectroPro-150, Acton Research Corporation).

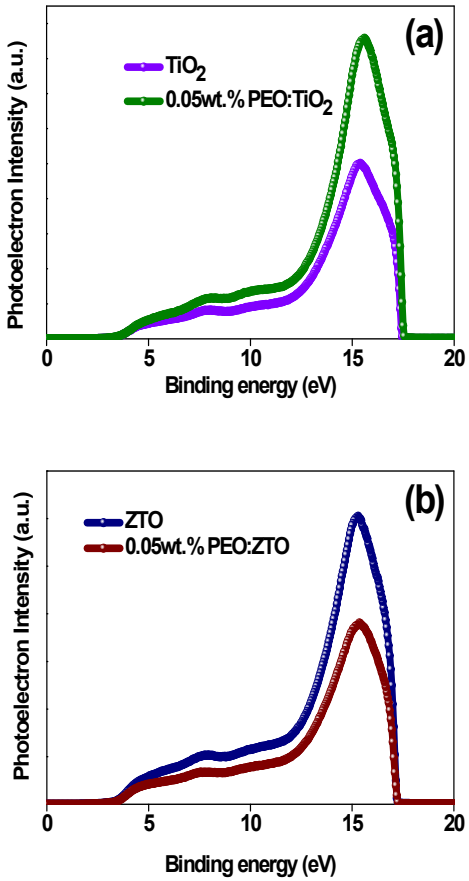

Figure S1. UPS spectra of (a) TiO_2, 0.05wt.% PEO:TiO_2 and (b) ZTO, 0.05wt.% PEO:ZTO films

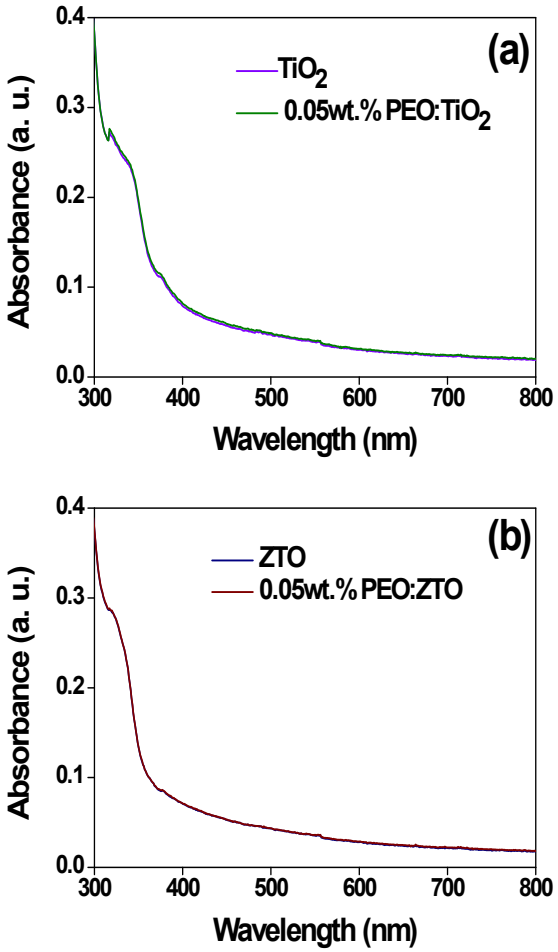

Figure S2. Absorption spectra of (a) TiO_2, 0.05wt.% PEO:TiO_2 and (b) ZTO, 0.05wt.% PEO:ZTO films

Table S1: Valance band, conduction band and band gap of TiO_2, 0.05wt.% PEO:TiO_2, ZTO and 0.05wt.% PEO:ZTO films.

ETLs	Valence band maximum (VBM) [eV]	Conduction band minimum (VBM) [eV]	Band gap (Eg) [eV]
TiO_2	-7.66	-4.46	3.20
0.05 wt.% PEO: TiO_2	-7.61	-4.41	3.20
ZTO	-7.90	-4.60	3.30
0.05 wt.% PEO: ZTO	-7.92	-4.62	3.30

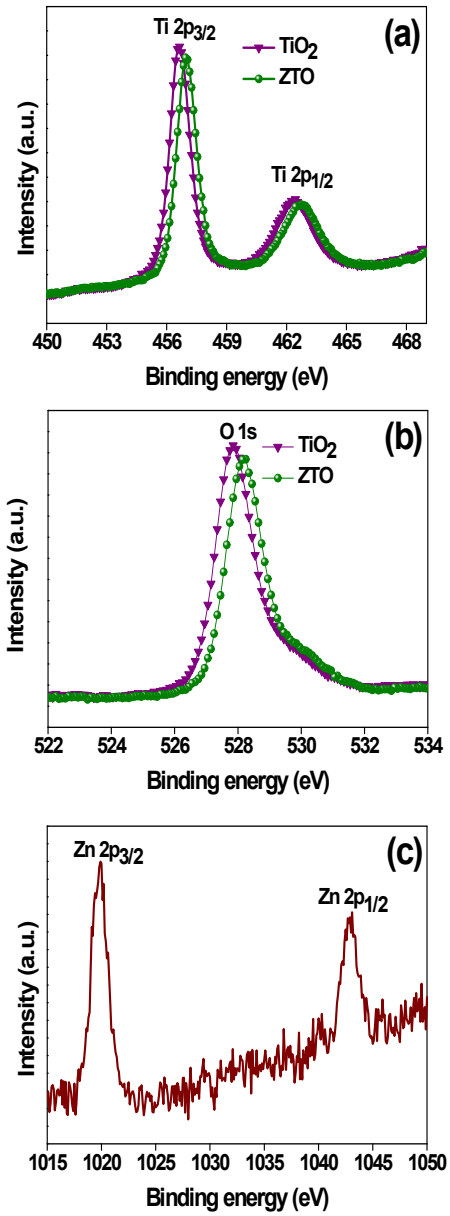

Figure S3. XPS spectra of TiO_2 and ZTO films (a) Ti2p, (b) O1s and (c) Zn2p

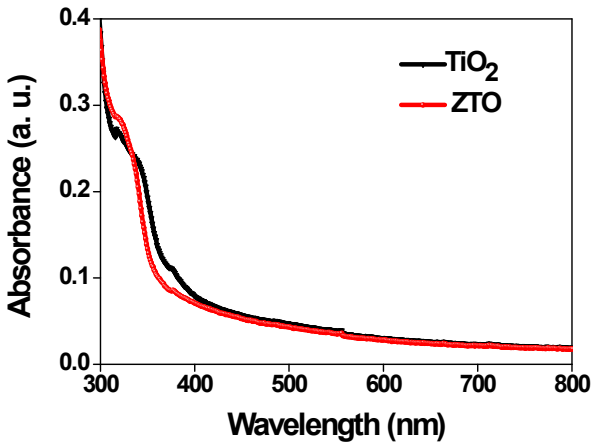

Figure S4: Absorption spectra of TiO_2 and ZTO films

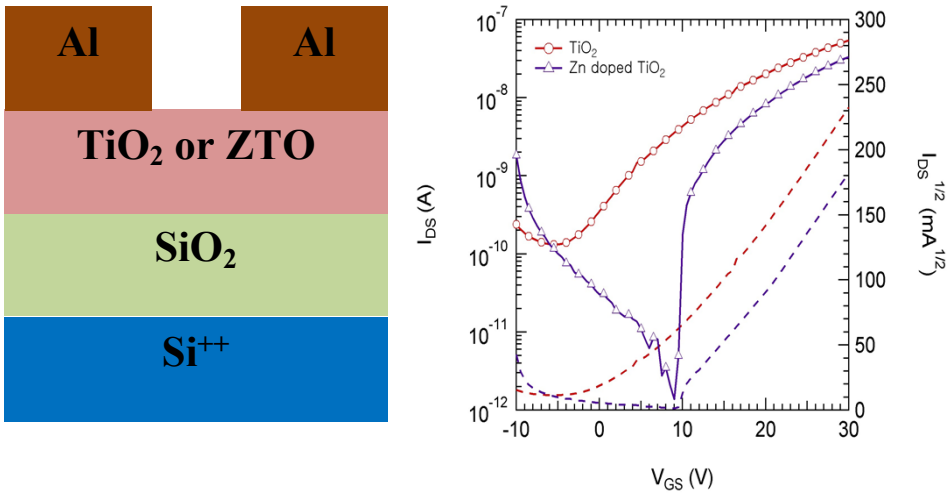

Figure S5. TFT device structure and transfer characteristics of TiO_2 and ZTO TFTs

The mobility has been measured by bottom-gate top-contact thin film transistor (TFT) method. The TFT device structure is shown in figure S5; SiO_2 was used as the gate dielectric layer, and Al was used as the source/drain electrode. Transfer characteristics of the TiO_2 and ZTO thin film transistors (TFTs) are shown in figure S5. The mobility TiO_2 and ZTO thin films are 3.15×10^{-4} $cm^2\ V^{-1}\ s^{-1}$ and $3.20 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.

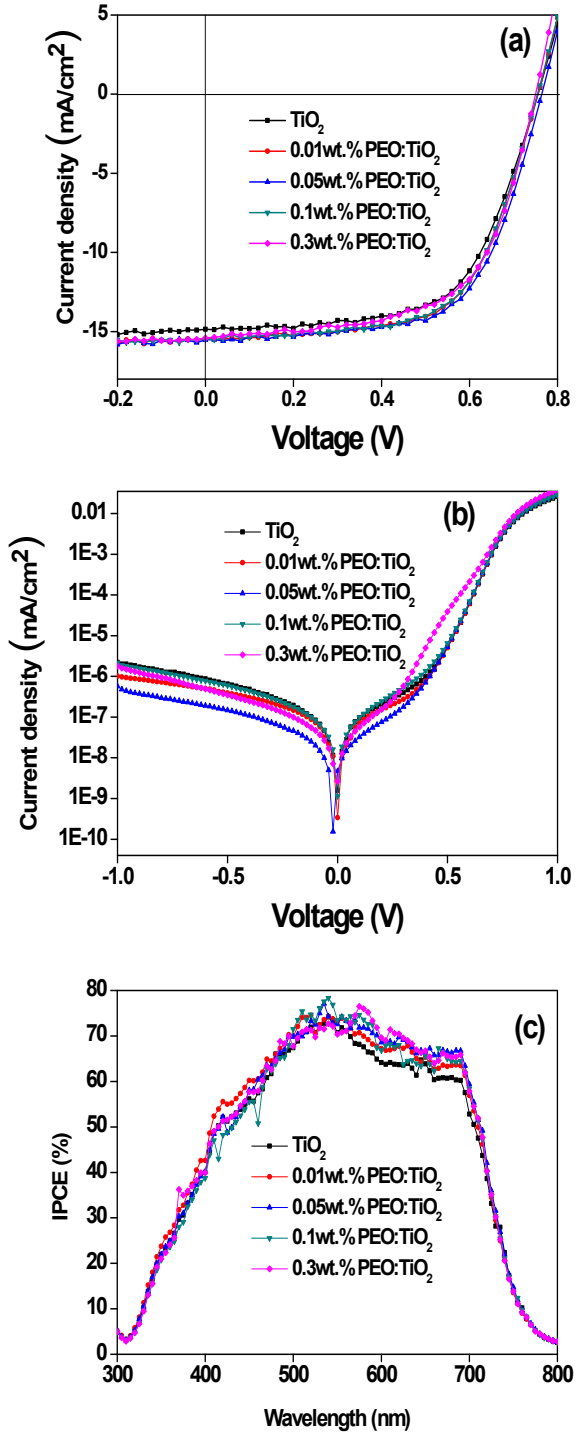

Figure S6. (a) Illuminated J-V, (b) dark J-V characteristics and (c) IPCE spectra of PTB7:$PC_{71}BM$ based IOSCs with ETLs of TiO_2 and PEO:TiO_2.

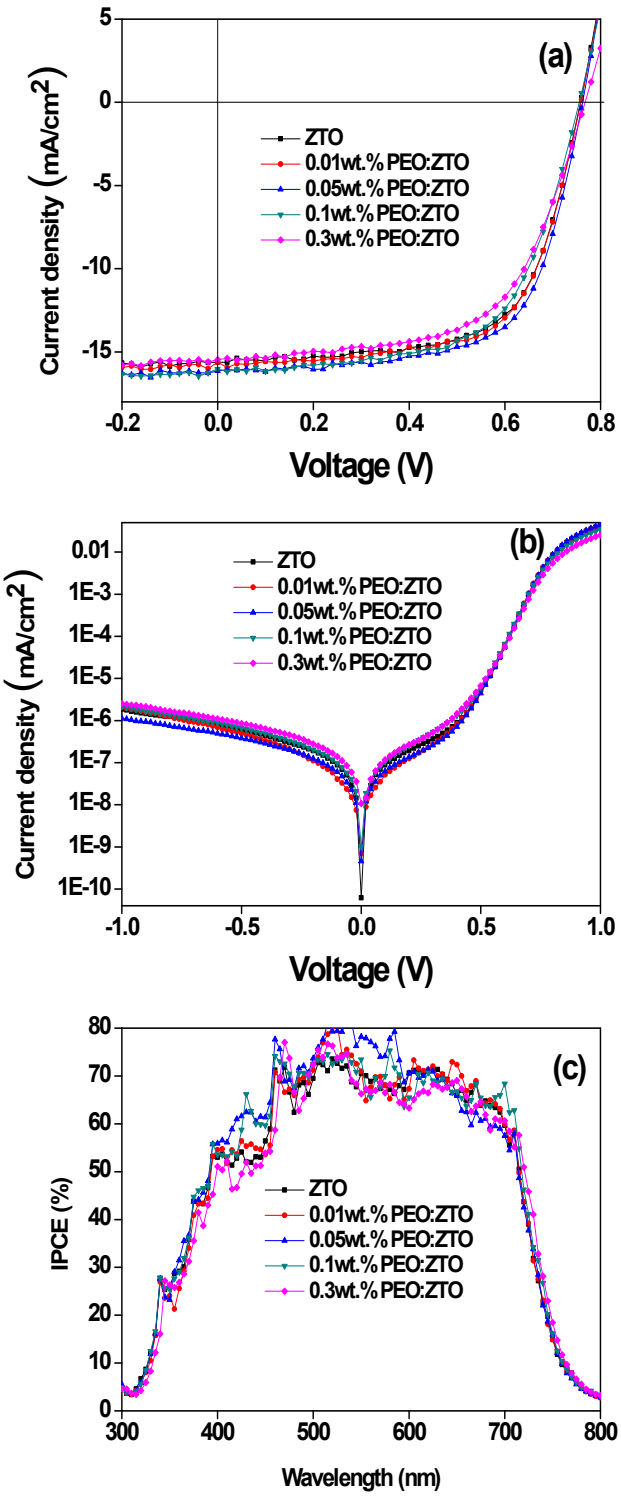

Figure S7. (a) Illuminated J-V, (b) dark J-V characteristics and (c) IPCE spectra of PTB7:$PC_{71}BM$ based IOSCs with ETLs of ZTO and PEO:ZTO.

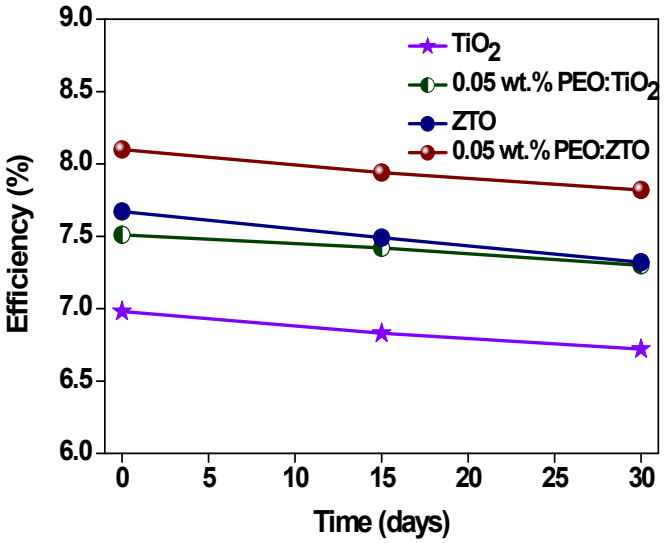

Figure S8. The stability of the PTB7:$PC_{71}BM$ based inverted device fabricated using TiO_2, 0.05 wt.% PEO:TiO_2, ZTO and 0.05 wt.% PEO:ZTO as an electron transport layer

The use of metal oxides on both sides of the PTB7:$PC_{71}BM$ layer prevents the diffusion of moisture into the active layer. The stability of the inverted PTB7:$PC_{71}BM$ solar cells (with MoO_3 as the hole transport layer and TiO_2, 0.05 wt.% PEO:TiO_2, ZTO or 0.05 wt.% PEO:ZTO as the electron transport layer) is shown in Figure S8. The solar cells were exposed continuously to air at room temperature (without any encapsulation barrier). We observed that TiO_2, 0.05 wt.% PEO:TiO_2 based devices almost retains its original efficiency even after 30 days under ambient conditions with reduction of power conversion efficiency (PCE) from 6.98 to 6.72 % and 7.51 to 7.30 %, while for the device fabricated using ZTO and 0.05 wt.% PEO:ZTO ETL the PCE decreased 7.67 to 7.32 % and 8.10 to 7.82 % under the same conditions. This clealy shows that TiO_2, PEO:TiO_2, ZTO and PEO:ZTO based devices exhibit good stability.

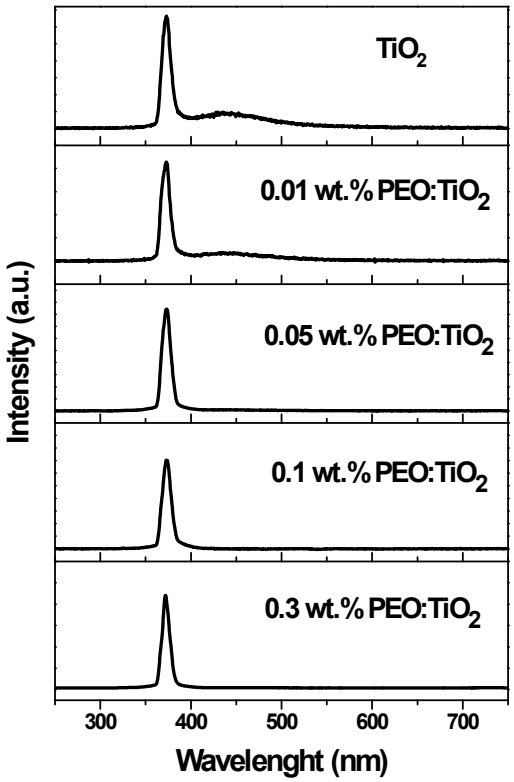

Figure S9: PL spectra of TiO_2 and PEO:TiO_2 films

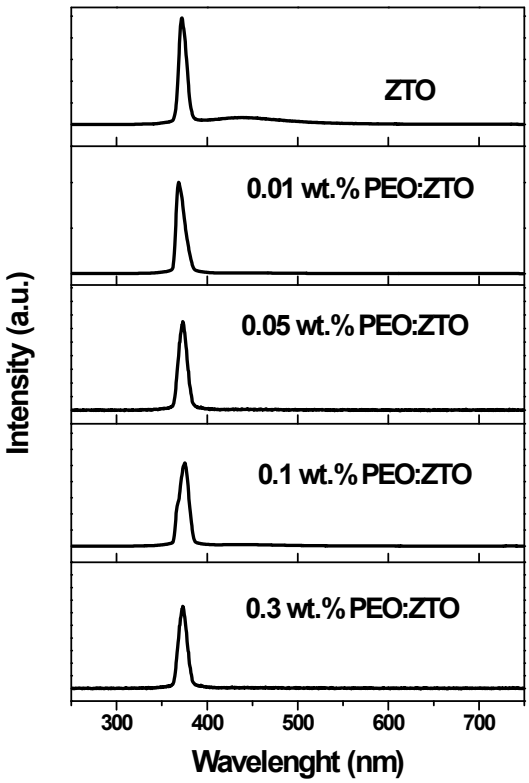

Figure S10: PL spectra of ZTO and PEO:ZTO films

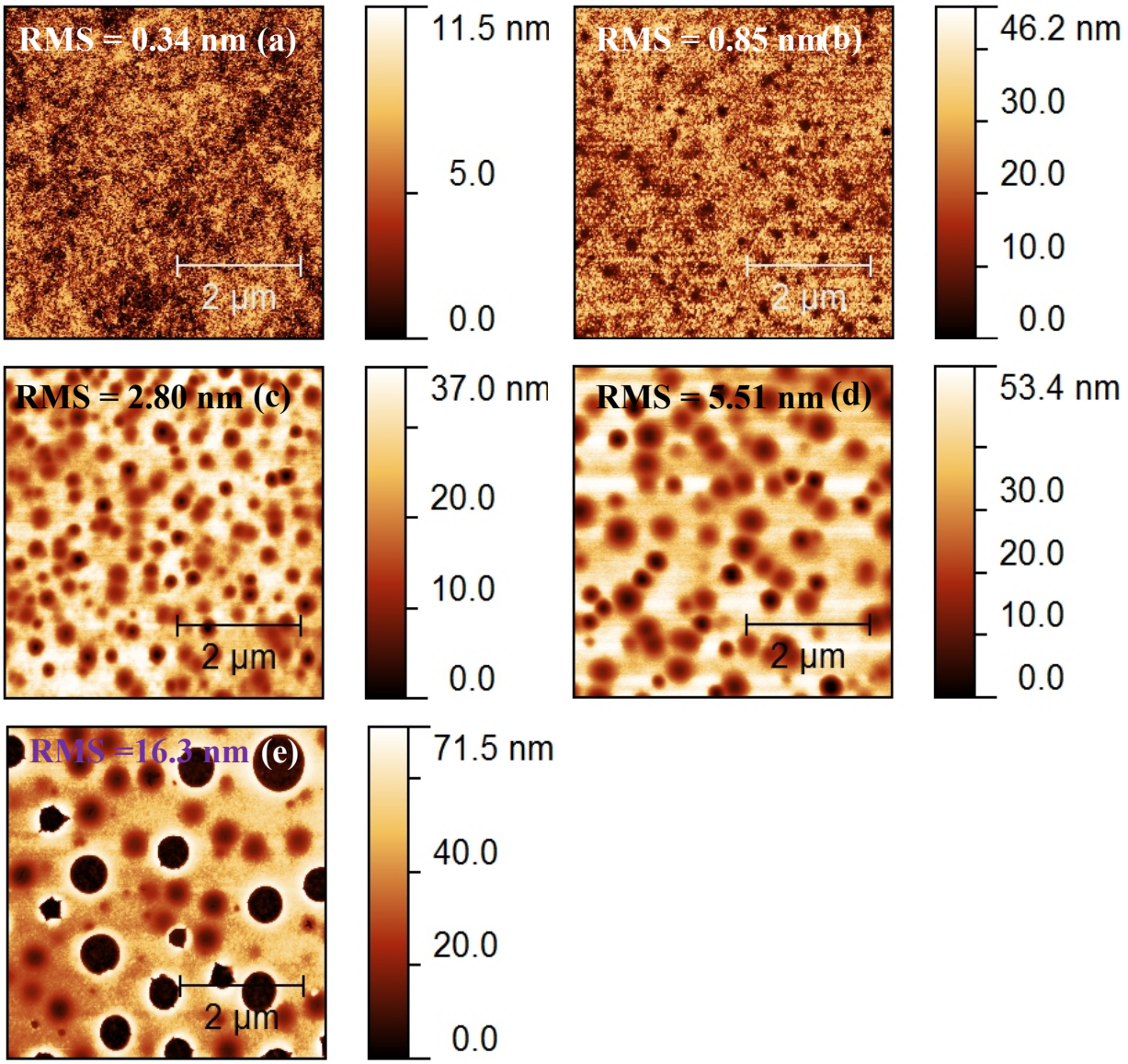

Figure S11: AFM images of (a) TiO_2 and PEO:TiO_2 films (b) 0.01 wt.% PEO, (c) 0.05 wt.% PEO, (d) 0.1 wt.% PEO, (e) 0.3 wt.% PEO

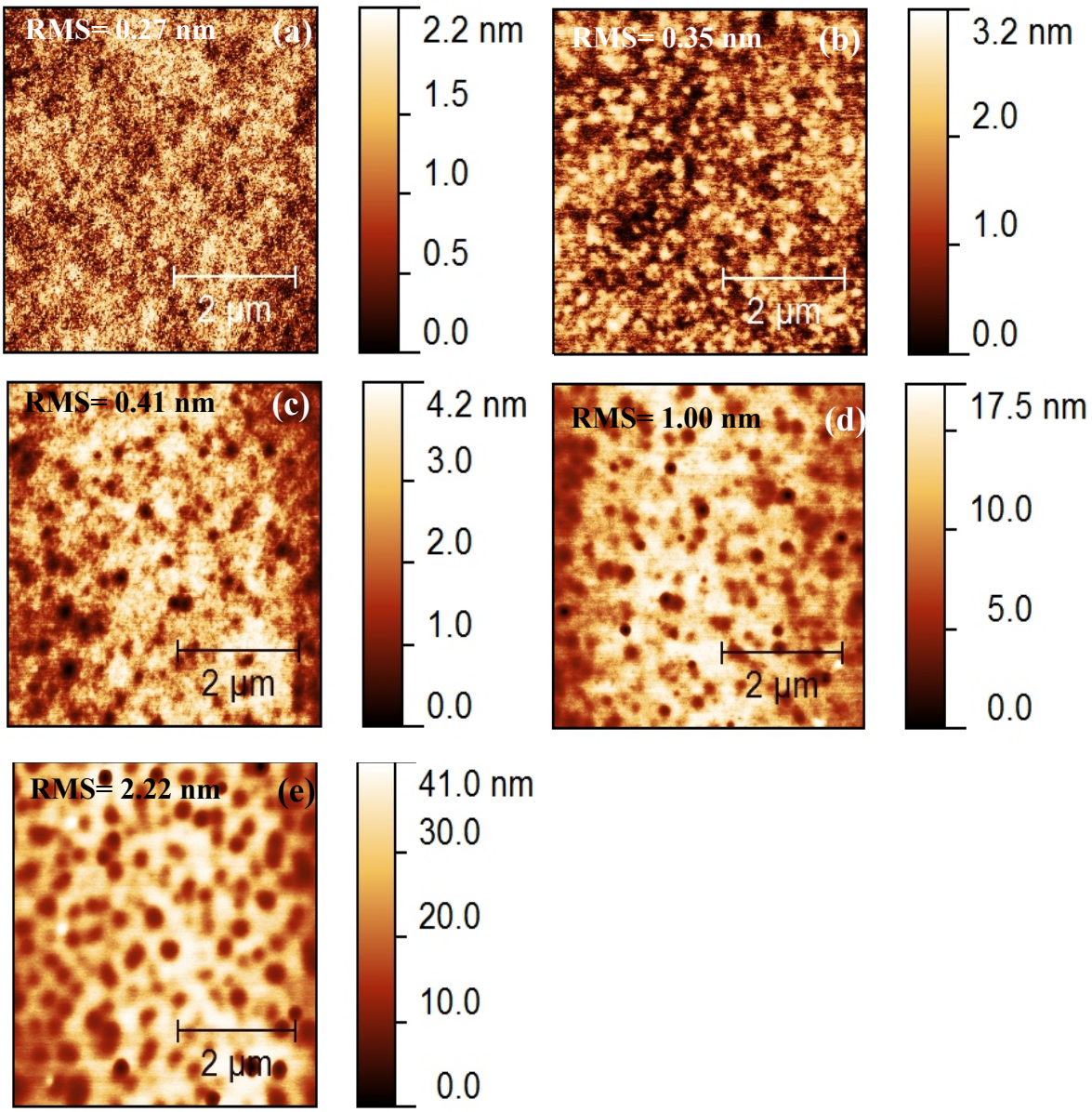

Figure S12: AFM images of (a) ZTO and PEO:ZTO films (b) 0.01 wt.% PEO, (c) 0.05 wt.% PEO, (d) 0.1 wt.% PEO, (e) 0.3 wt.% PEO