Textured ZnO films from evaporation-triggered aggregation of nanocrystal dispersions and their use in solar cells

Junfeng Yan[a], Qing Lian[a], Muhamad Z. Mokhtar[a], Amir H. Milani[a], Eric Whittaker[b], Bruce Hamilton[b], Paul O'Brien[a,c], Nam T. Nguyen[a] and Brian R. Saunders[a,]*

[a] *School of Materials, MSS Tower, The University of Manchester, Manchester, M13 9PL, U.K.*

[b] *Photon Science Institute, University of Manchester, Alan Turing Building, Oxford Road, Manchester, M13 9PL, U.K.*

[c] *School of Chemistry, The University of Manchester, Manchester, M13 9PL, U.K.*

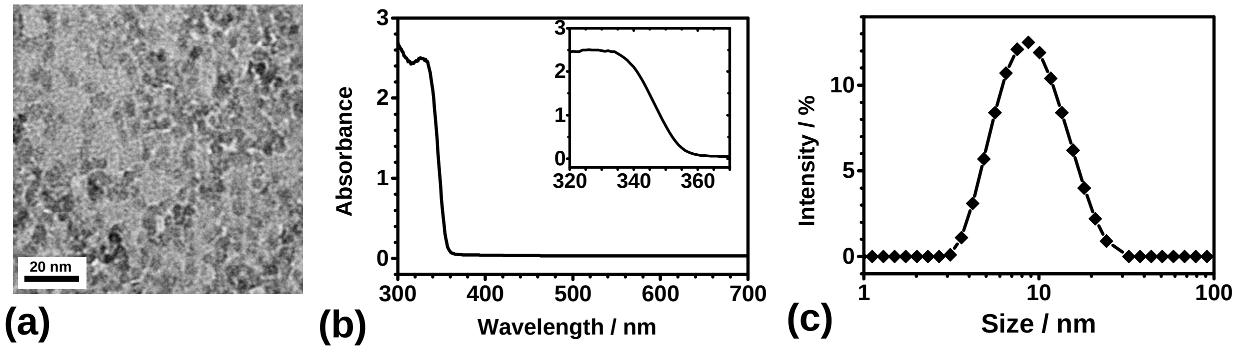


Figure S1. (a) Representative TEM image of ZnO nanocrystals (NCs) deposited from methanol. (b) UV-visible spectrum for ZnO dispersed in $CHCl_3$/PA. (Note that PA is 1-propylamine). (c) Size distribution measured for the dispersion from (b) using dynamic light scattering.

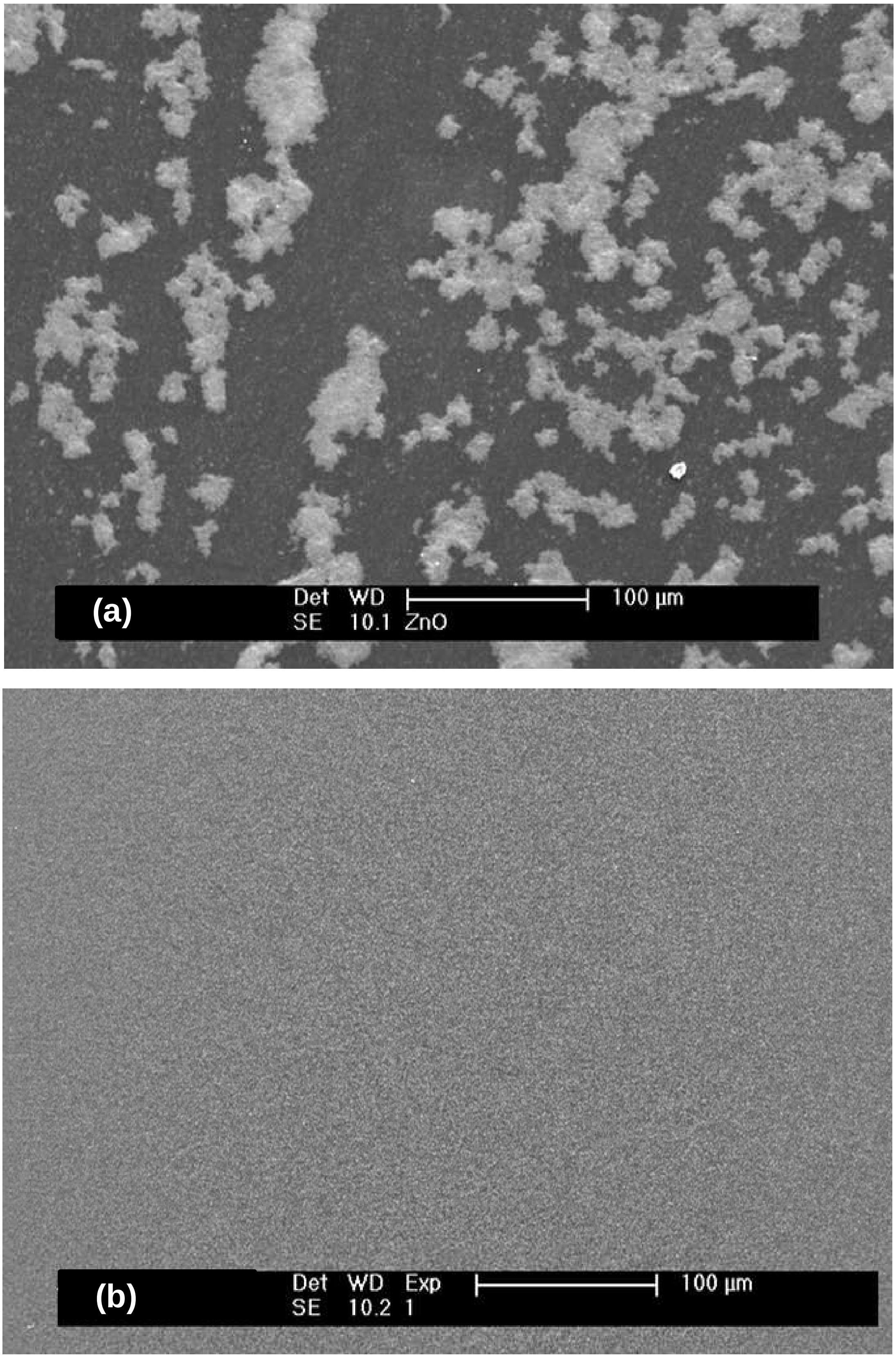


Figure S2 Low magnification SEM images for ZnO films deposited from (a) $CHCl_3$ and (b) $CHCl_3$/PA.

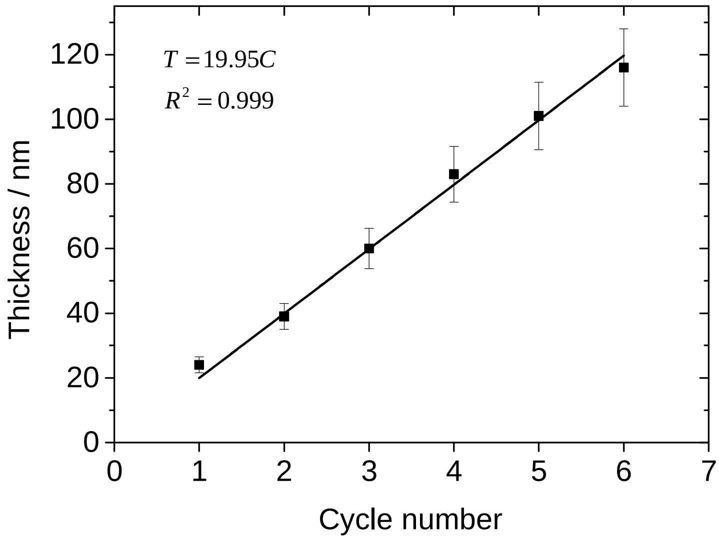


Figure S3. Thickness of textured porous ZnO (tp-ZnO) films as a function of deposition cycle number.

Derivation of equation for estimating the volume ratio of ligand to nanocrystal

The volume fraction occupied by the ligand in a deposited film of ligand-stabilised nanocrystals (NCs) can be estimated from the fraction of volume occupied by a collapsed ligand shell surrounding a NC (ϕ_L) assuming a spherical core-shell model. The latter can be estimated using the geometry shown in Fig. S4. This simplified treatment assumes the NCs are spherical and that all surfaces are equivalent and have a similar tendency for binding ligands and ignores specific interactions of different crystal facets for ligands. The steps required for the derivation are to first determine the volume of the NC (V_{NC}) in terms of d_{NC}. Then, an expression is required for the volume of the ligand (V_L) surrounding the NC. The ratio of the two expressions (V_L/V_{NC}) can then be used to determine ϕ_L. These steps are outlined in the following.

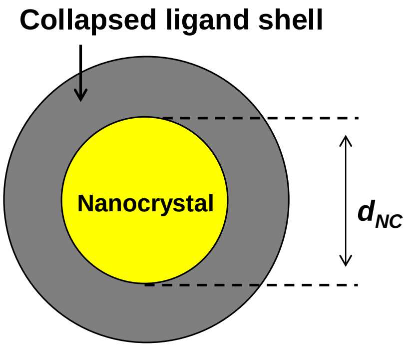


Figure S4. Depiction of a NC with a collapsed ligand shell.

The expression for V_{NC} is:

$$V_{NC} = \frac{\pi d_{NC}^3}{6} \qquad \text{(S1)}$$

An expression for V_L requires the number of ligands bound per NC particle ($n_{L,P}$) as well as the volume of a ligand molecule in the collapsed state (v_L), i.e., $V_L = n_{L,P}\, v_L$ An expression for v_L follows from the ligand molecular weight (M_L) and density (ρ_L).

$$v_L = \frac{M_L}{\rho_L N_A} \qquad \text{(S2)}$$

For the above equation, N_A is Avogadro's number. A value for $n_{L,P}$ can be estimated using the ligand surface concentration in the dispersed state (Γ_L) using $n_{L,P} = \pi\, d_{NC}^2 \Gamma_L$. It follows from the above that:

$$\frac{V_L}{V_{NC}} = \frac{6\Gamma_L M_L}{d_{NC} N_A \rho_L} \qquad \text{(S3)}$$

Use of $\phi_L = (V_L/(V_L + V_{NC}))$ gives the following equation:

$$\phi_L = \frac{1}{1+\frac{1}{\left(V_L/V_{NC}\right)}} \qquad \text{(S4)}$$

Equations S3 and S4 were used to calculate the values for V_L/V_{NC} and ϕ_L shown in Table S1. The value used for Γ_L was 22 Å^2, which is a value obtained for a monovalent ligand on NCs with a similar diameter to those studied here[1].

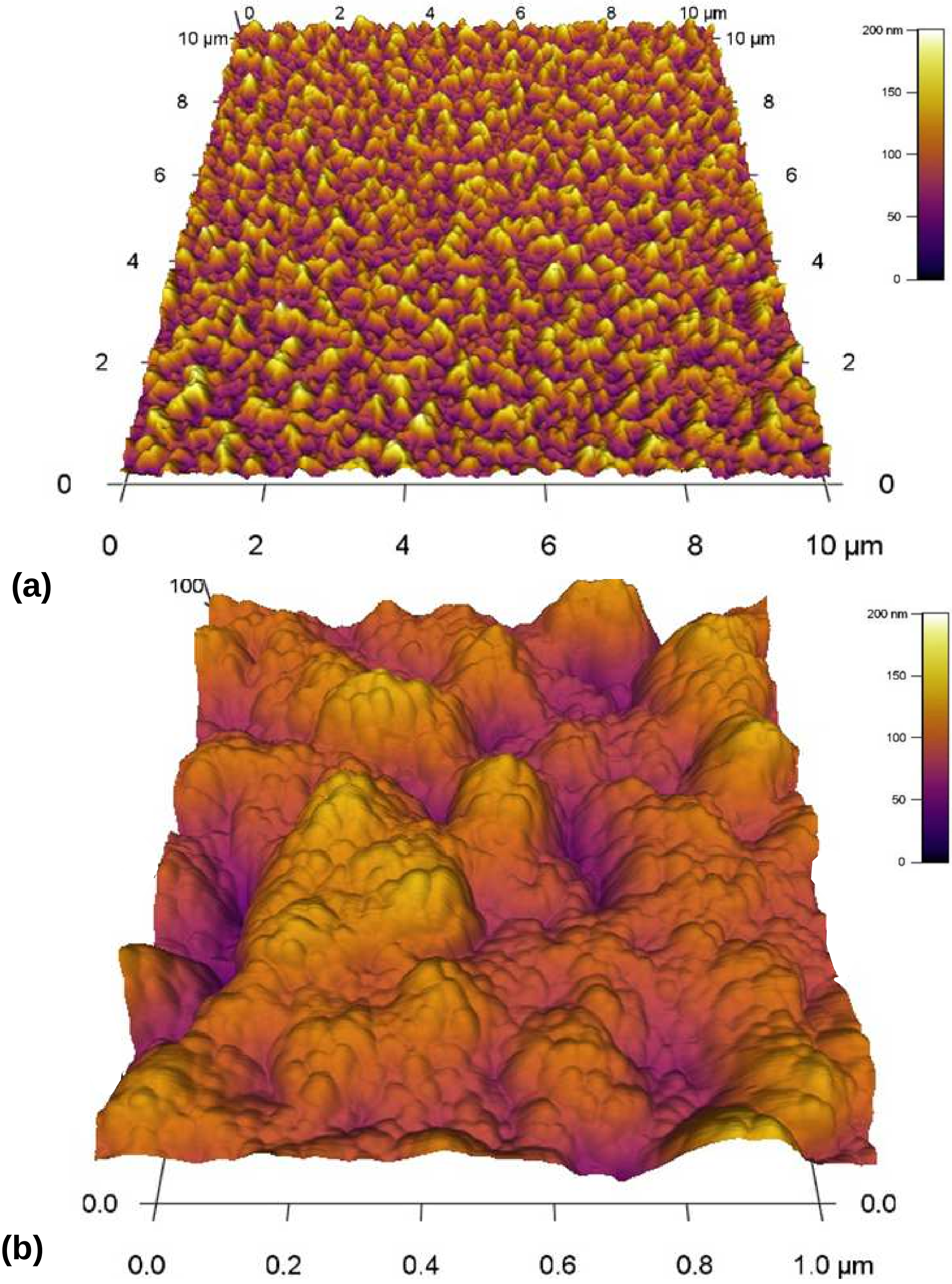


Figure S5. (a) and (b) show 3D AFM images for the tp-ZnO films from Fig. 1d and f, respectively.

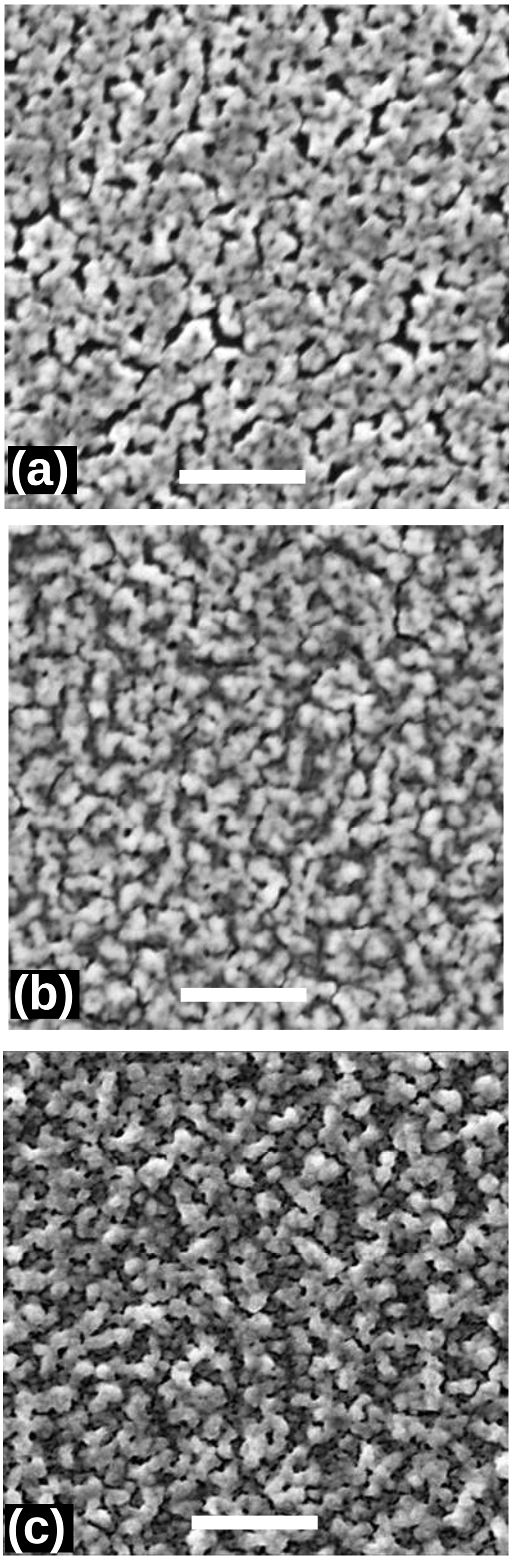


Figure S6. SEM images for as-prepared (a) 1 layer, (b) 3 layer and (c) 6 layer tp-ZnO films. The scale bar is 2 μm.

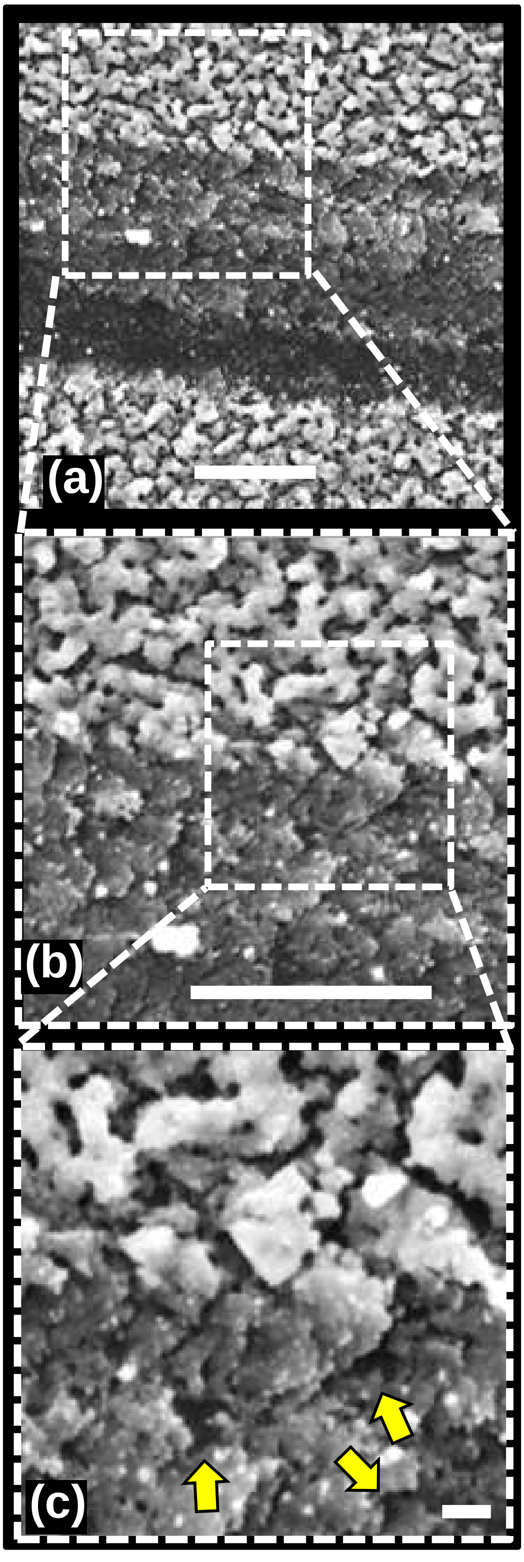


Figure S7. SEM images of a tp-ZnO film after it had been scratched. Shear removed the upper layers of the film and smaller pores are evident in the lower layers of the film (arrows). Scale bars: (a) and (b): 2 μm; (c) 200 nm.

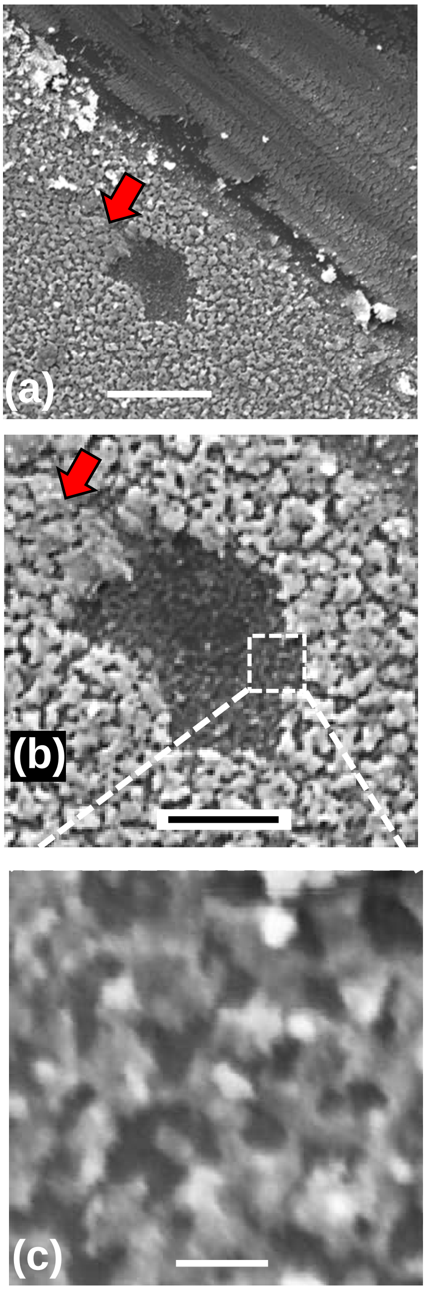


Figure S8. SEM images showing a region near a scratch. The red arrows in (a) and (b) show that the nearby region had been sheared which deformed the surface aggregates. This resulted in the fortuitous removal of a surface layer which revealed the sub-surface layer, which was porous Scale bars: (a) 5 µm; (b) 2 µm; (c) 200 nm.

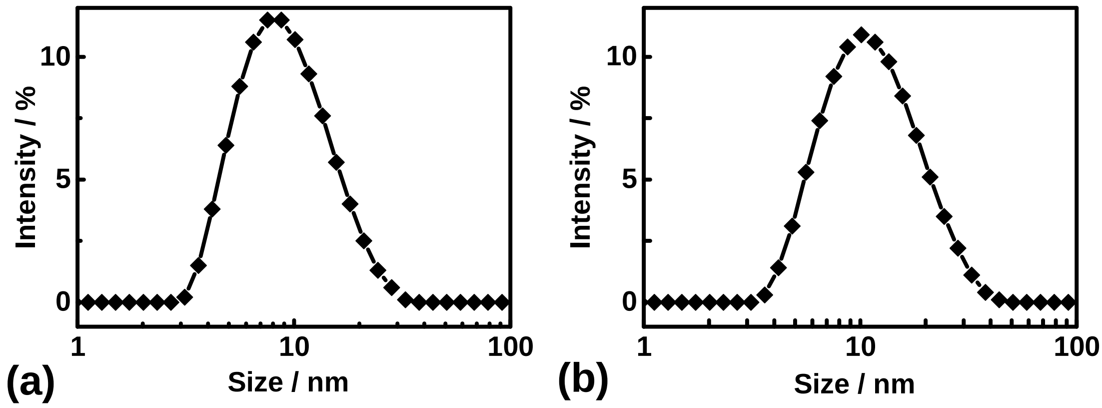
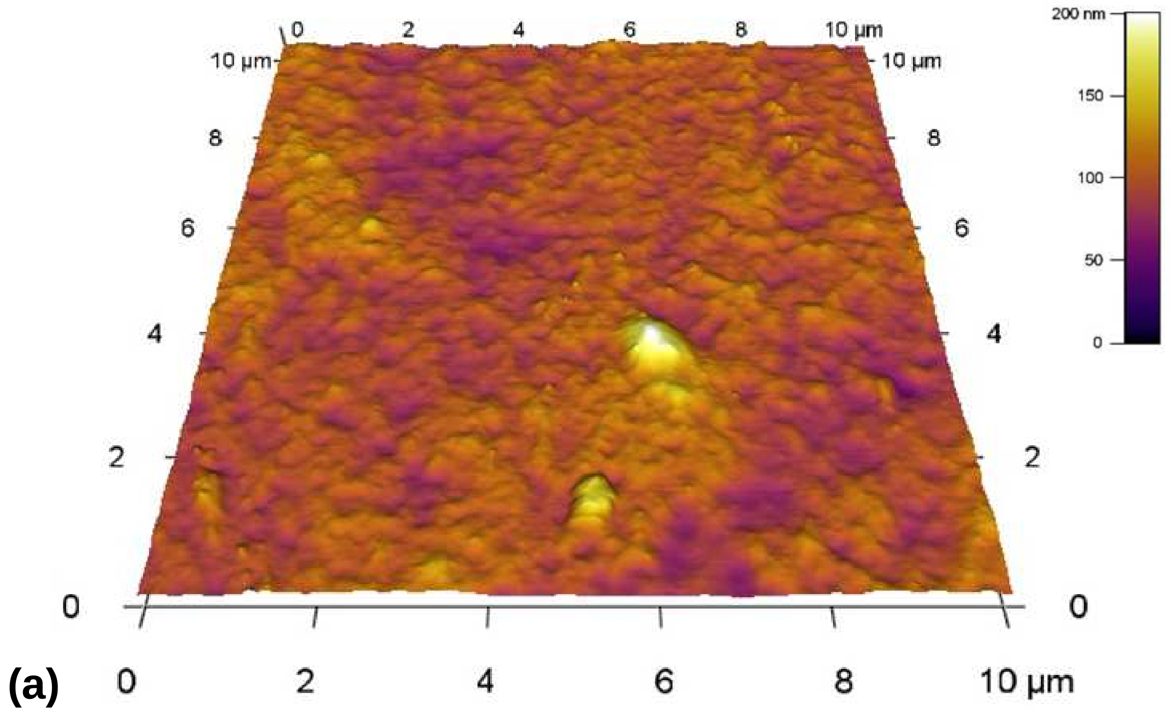


Figure S9 DLS data for ZnO NCs dispersed in (a) $CHCl_3$/BA or (b) $CHCl_3$/DA solutions. BA and DA are *n*-butylamine and *n*-dodecylamine, respectively.



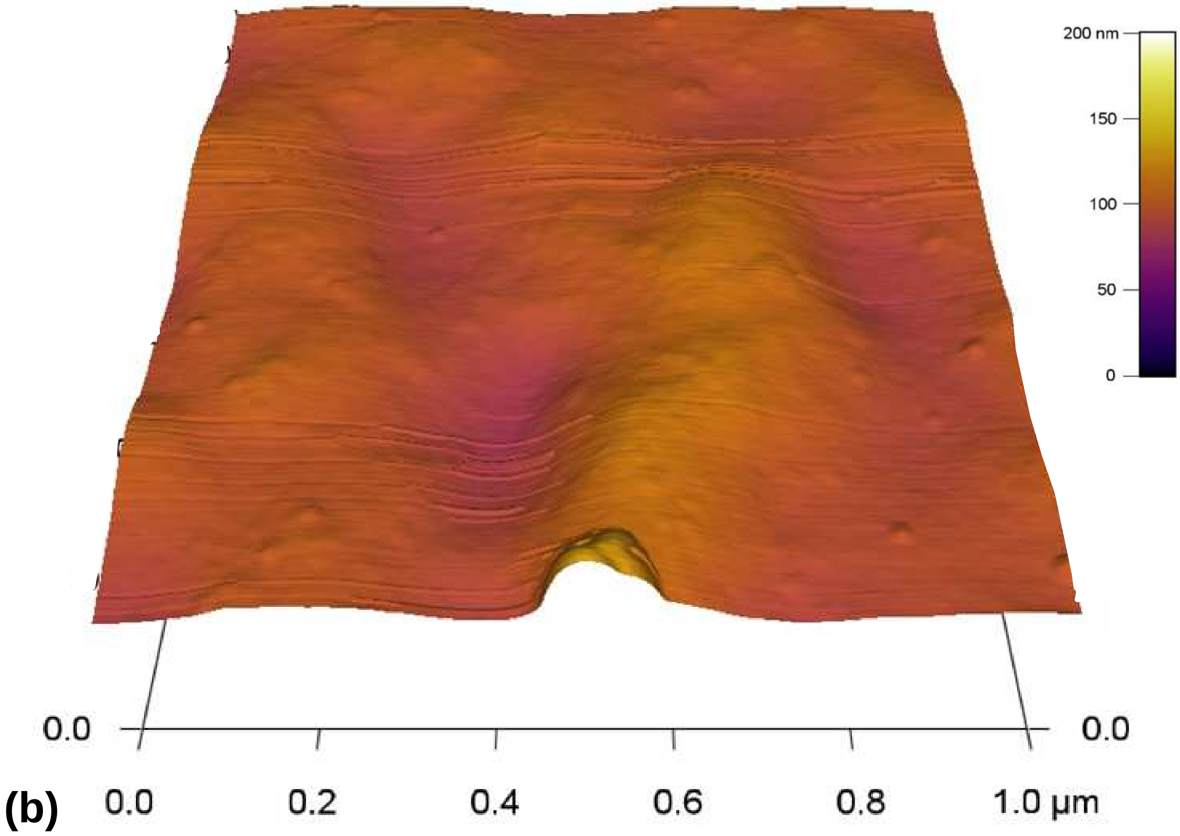


Figure S10 (a) 3D AFM image for the ZnO/P3HT film prepared using 15 mg/mL P3HT. (b) shows a higher magnification image of the film (1.0 x 1.0 μm^2).

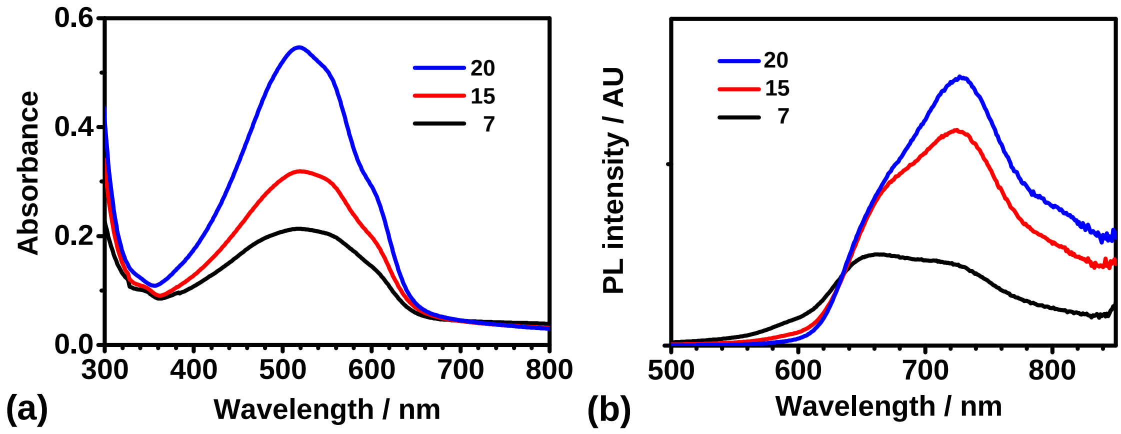


Figure S11. (a) UV-visible spectra (b) photoluminescence (PL) spectra for tp-ZnO/P3HT films prepared using P3HT concentrations of 7, 15 and 20 mg/mL (legends). The excitation wavelength used for (b) was 430 nm.

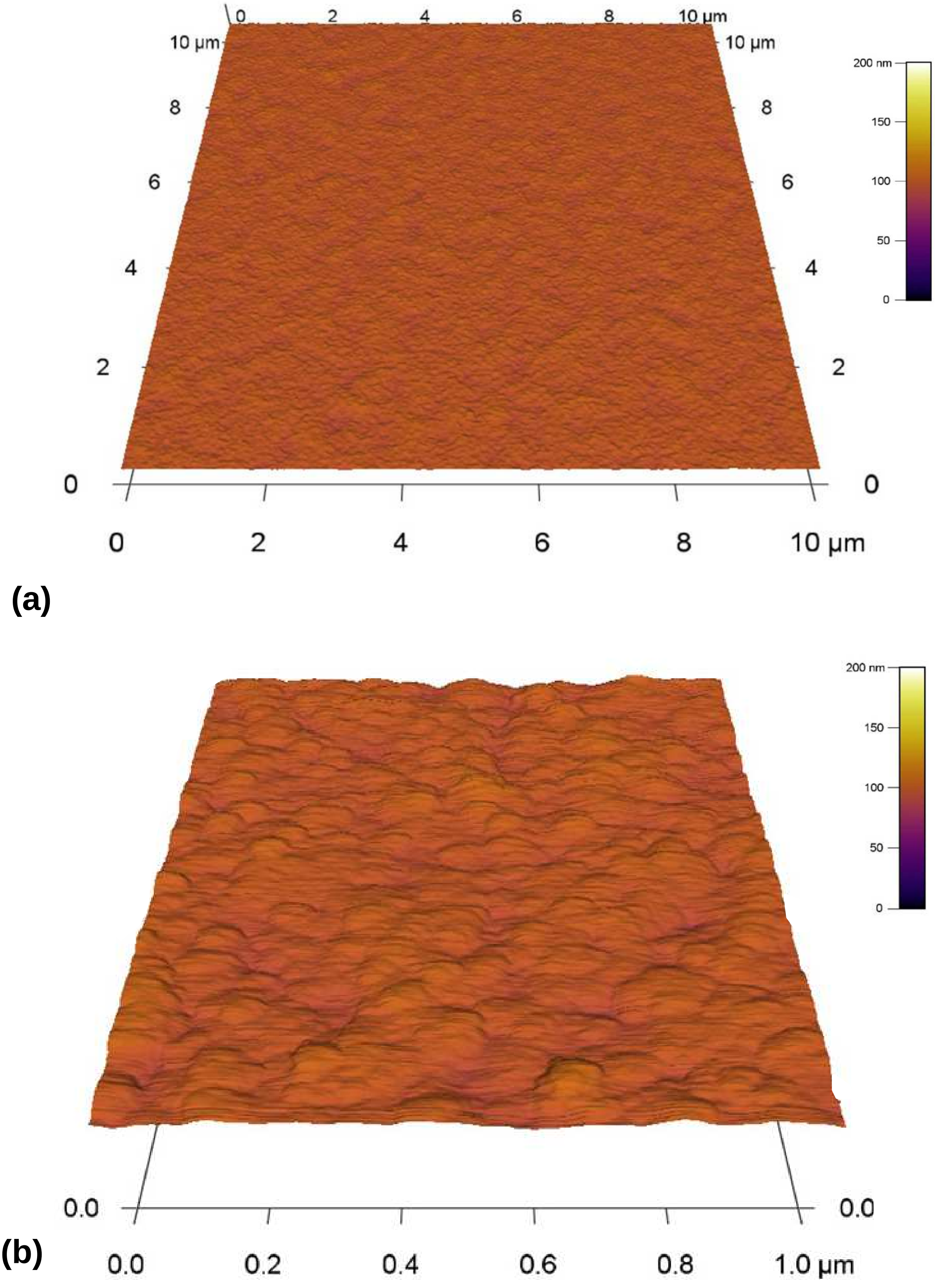


Figure S12. (a) 3D AFM image for the ZnO sol-gel film used to construct control devices (Fig. 6). (b) shows a higher magnification image of the film (1.0 x 1.0 μm^2).

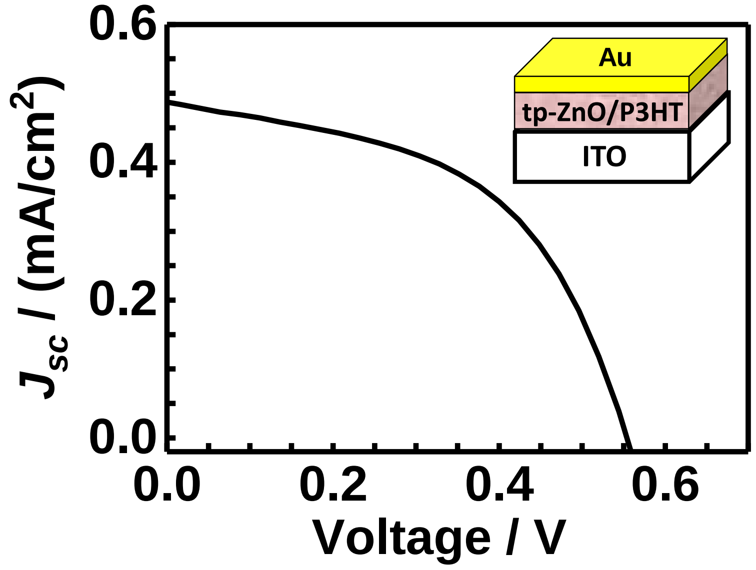


Figure S13. Representative *J*-*V* data for an ITO/tp-ZnO/P3HT/Au device. The device geometry is shown.

TABLES

Table S1. Ligand and ligand-stabilised ZnO nanocrystal properties

Ligand	$M_L{}^a$ / g/mol	$\rho_L{}^b$/ g/ml	V_L / $V_{NC}{}^c$	$\phi_L{}^d$/ vol.%
PA	59	0.72	0.92	48
BA	73	0.74	1.11	53
DA	185	0.81	2.57	72

[a] Molecular weight of ligand. [b] Density from provided by supplier. [c] Ratio of volume of ligand to nanocrystal. [d] Calculated volume fraction of ligand within the ZnO NCs containing adsorbed ligand.

Table S2. Performance data for the tp-ZnO/P3HT solar cells.

C_{P3HT} / (mg/mL)	J_{sc} / (mA/cm^2)	V_{oc} / V	FF	PCE / %
7[a]	0.33 ± 0.09	0.34 ± 0.06	0.37 ± 0.01	0.044 ± 0.009
15[a]	0.46 ± 0.07	0.41 ± 0.03	0.39 ±0.01	0.078 ± 0.010
20[a]	0.34 ± 0.02	0.59 ± 0.02	0.51 ±0.05	0.107 ± 0.012
20[b]	0.52 ± 0.02	0.55 ± 0.03	0.51 ± 0.03	0.146 ± 0.017
20[c]	0.24 ± 0.03	0.29 ± 0.03	0.47 ± 0.05	0.033 ± 0.007

[a] ITO/bl-ZnO/tp-ZnO/P3HT/Ag, [b] ITO/tp-ZnO/P3HT/Au and [c] ITO/bl-ZnO/P3HT/Ag.

Reference

1. U. K. Gautam, M. Rajamathi, F. Meldrum, P. Morgan, and R. Seshadri. *Chem. Commun.* 2001, 629-630.