Supporting Information for

Surface Passivation Effect by Fluorine Plasma Treatment on ZnO for Efficiency and Lifetime Improvement of Inverted Polymer Solar Cells

Ermioni Polydorou,[1,2] Angelos Zeniou,[1] Dimitris Tsikritzis,[3] Anastasia Soultati,[1,4] Ilias Sakellis,[1,5] Spyros Gardelis,[5] Theodoros A. Papadopoulos,[6] Joe Briscoe,[7] Leonidas C. Palilis,[2] Stella Kennou,[3] Evangelos Gogolides,[1] Panagiotis Argitis,[1] Dimitris Davazoglou,[1] Maria Vasilopoulou[1,*]

[1]*Institute of Nanoscience and Nanotechnology, National Center for Scientific Research Demokritos, 15310, Aghia Paraskevi, Attiki, Greece*

[2]*Department of Physics, University of Patras, 26504 Patras, Greece*

[3]*Department of Chemical Engineering, University of Patras, 26500 Patras, Greece*

[4]*Department of Chemical Engineering, National Technical University of Athens, 15780, Athens, Greece*

[5]*Physics Department, Solid State Physics Section, University of Athens Panepistimiopolis, GR, 15784 Athens, Greece*

[6]*Department of Natural Sciences, University of Chester, Thornton Science Park, CH2 4NU, Chester, U. K.*

[7]*Materials Research Institute, School of Engineering and Materials, Queen Mary University of London, U. K.*

**email: m.vasilopoulou@inn.demokritos.gr*

Table of Contents

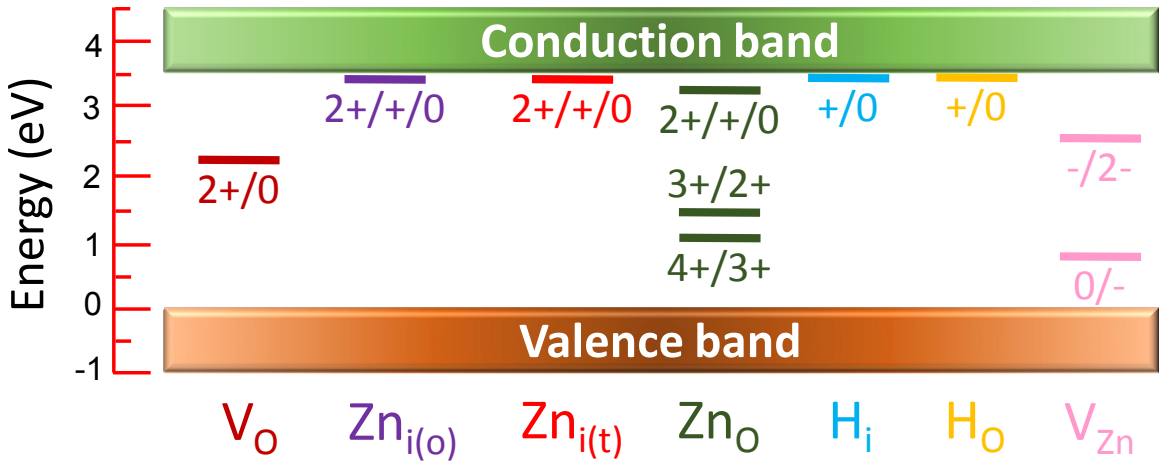
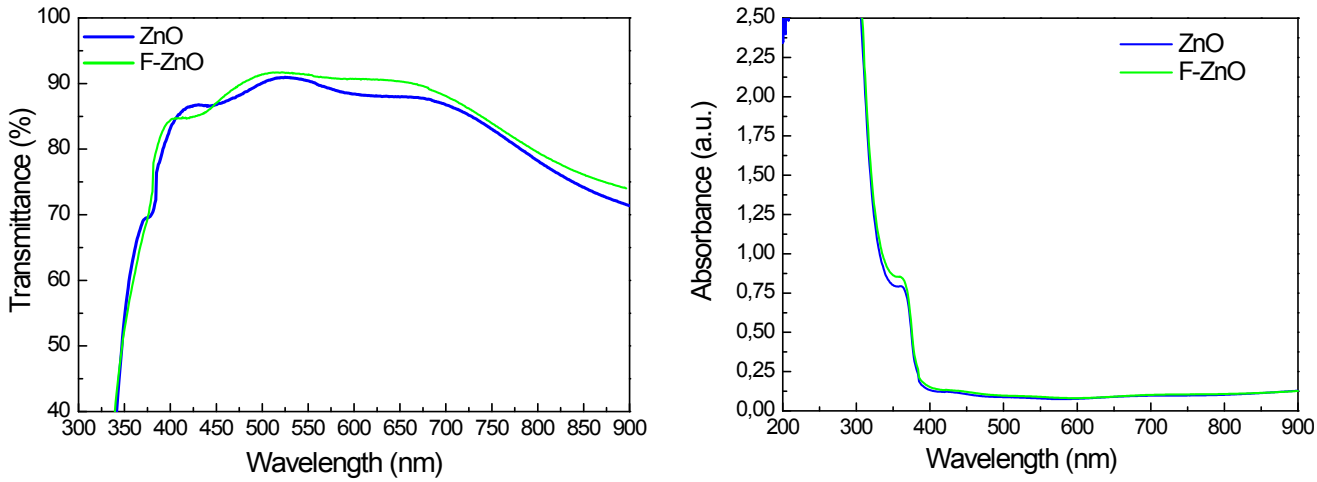
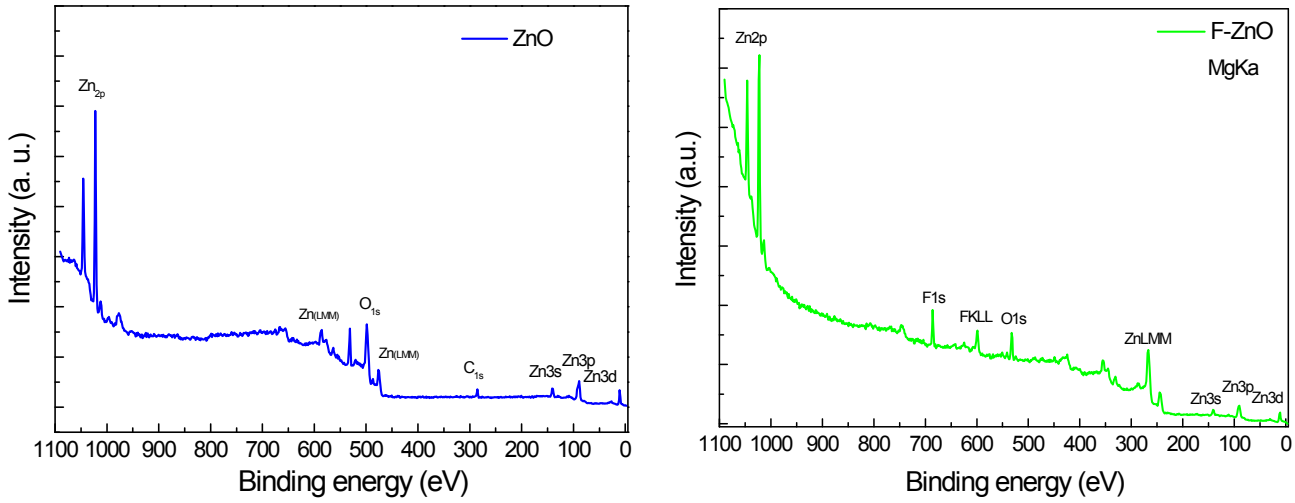


Figure S1 Schematic diagram depicting the various defect states in ZnO. Zinc interstitials (Z_{ni}) are 0.22 eV below the CB while oxygen vacancies (V_O) are 0.8-1.0 eV below the CB and zinc vacancies (V_{Zn}) are 1.0 eV below the CB and above the VB, for a typical band gap of 3.3 eV. [1-6]



(a) **(b)**

Figure S2 (a) Transmission spectra and (b) UV-vis absorption measurements of solution-processed ZnO and SF_6 plasma treated (F-ZnO) ~40 nm thick films.



(a) **(b)**

Figure S3 Wide scan XPS spectra of ZnO films (a) before and (b) after SF_6 plasma surface treatment.

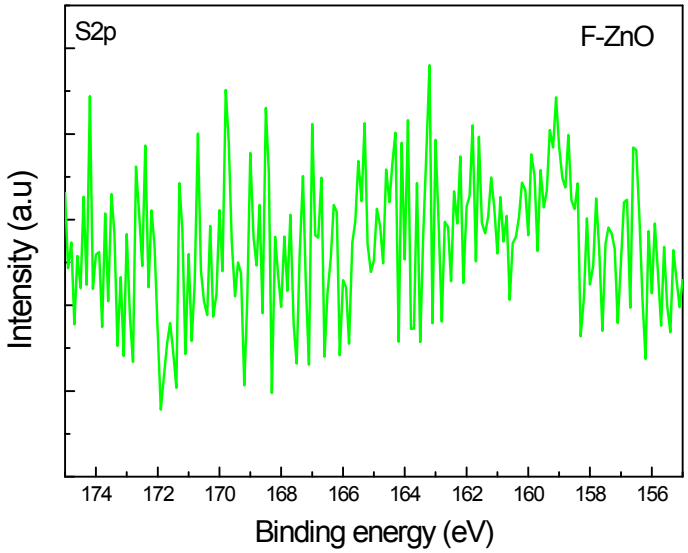
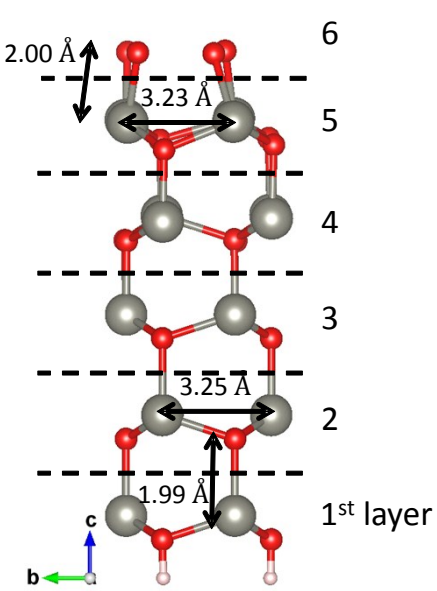
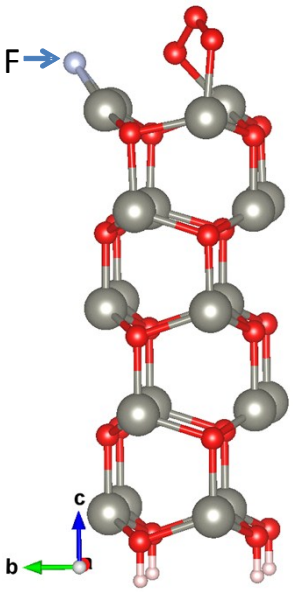


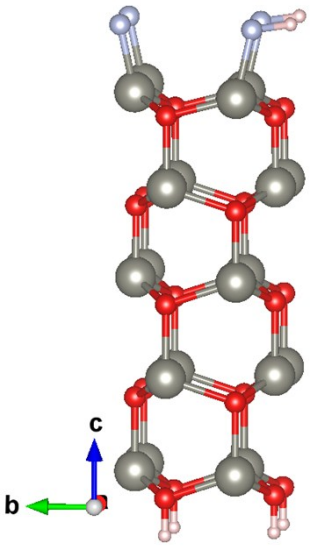
Figure S4 XPS S2p core level peaks of the SF_6 treated ZnO film.

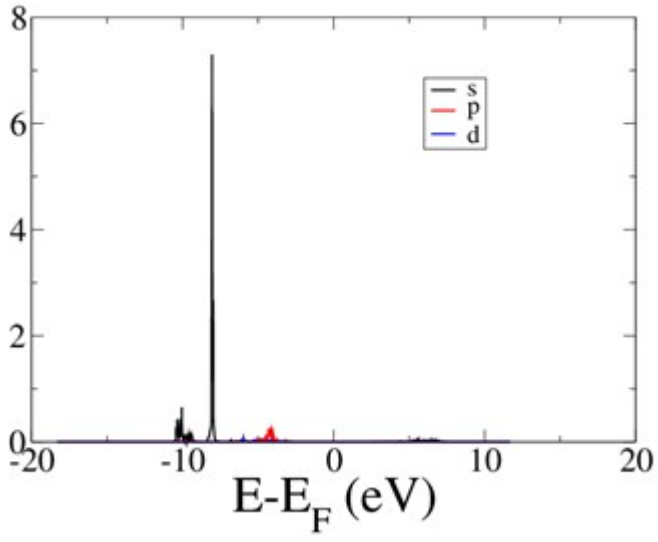




(a) **(b)**

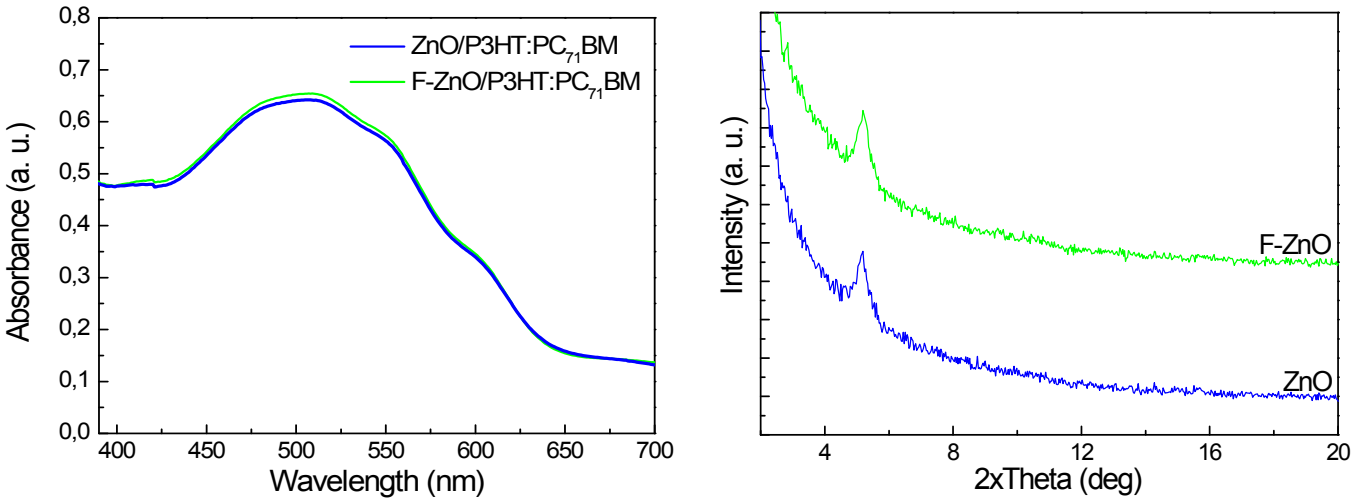
Figure S5 (a) The crystal structure of the O-terminated ZnO (0002) surface. Grey spheres represent zinc (Zn) atoms and red spheres represent oxygen (O) atoms. (b) The same crystal structure with a fluorine (F) atom substituting an O atom.





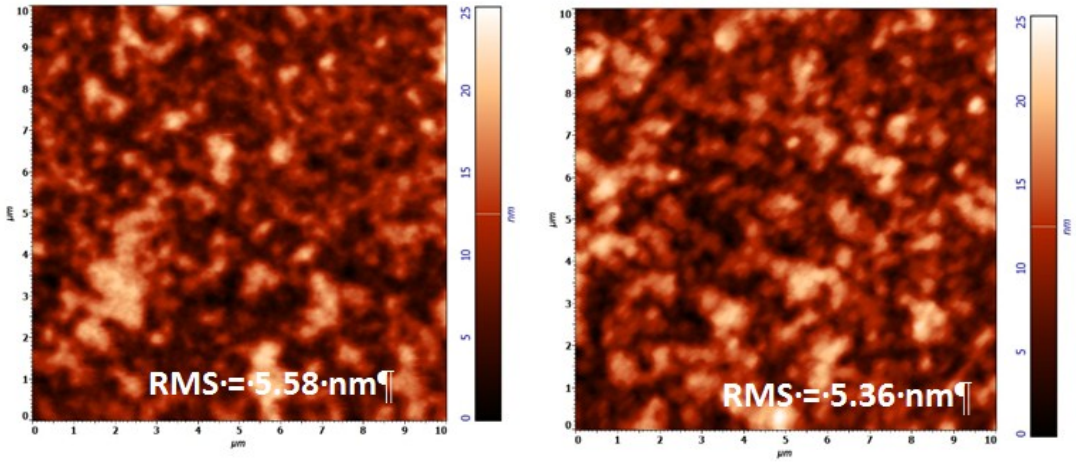
(a) **(b)**

Figure S6 (a) The crystal structure of the fully fluorinated ZnO surface with two H atoms bonded to nearest F atom., and (b) Partial density of states corresponding to the hydrogen atoms adsorbed on the surface. The x-axis is shifted with reference to the Fermi level, $E_F = 0$ eV (right panel).



(a) **(b)**

Figure S7 (a) UV-vis absorption spectra and (b) XRD patterns of 150 nm thick P3HT:$PC_{71}BM$ films deposited on ZnO films without and with SF_6 plasma surface treatment.



(a) **(b)**

Figure S8 2D AFM surface topographies (10x10 μm) of P3HT:$PC_{71}BM$ films with a thickness of 150 nm (similar to that used in the devices) deposited on ZnO films (a) without and (b) with SF_6 plasma surface treatment.

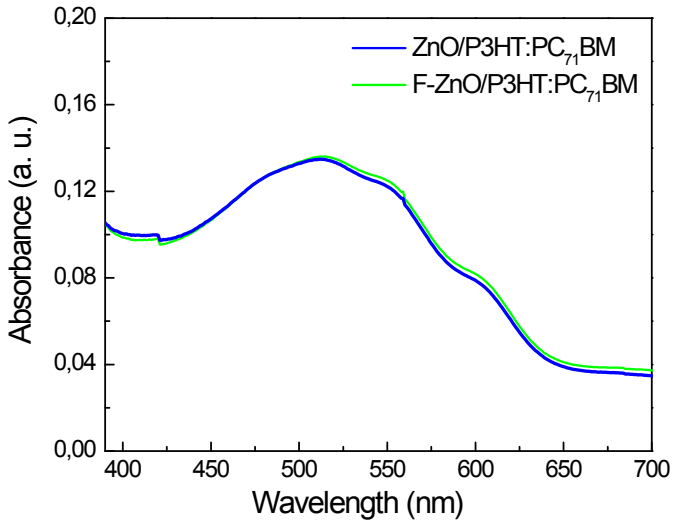
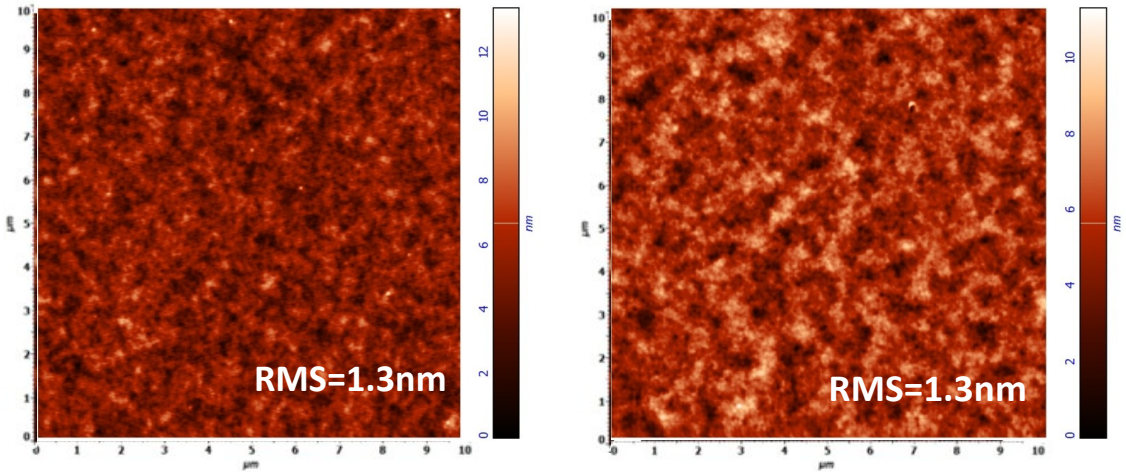


Figure S9 UV-vis absorption spectra of ~30 nm P3HT:$PC_{71}BM$ films deposited on ZnO films without and with SF_6 plasma surface treatment.



(a) **(b)**

Figure S10 2D AFM surface topographies (10x10 μm) of thin P3HT:$PC_{71}BM$ films with a thickness of ~30 nm deposited on ZnO films (a) without and (b) with SF_6 plasma surface treatment.

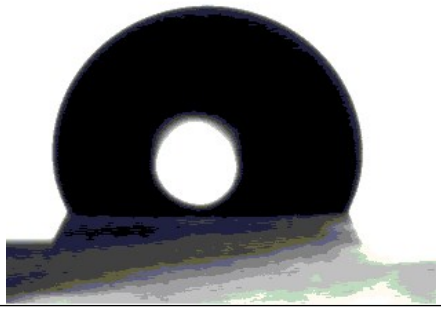
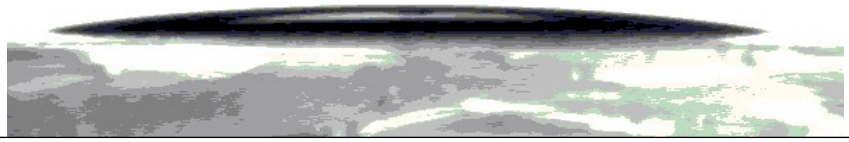
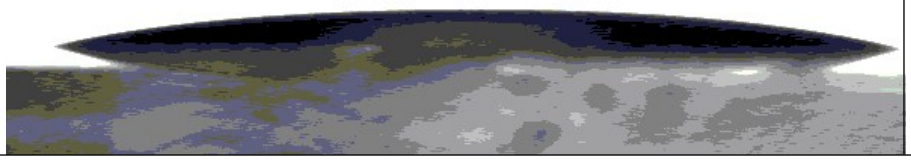
Sample		Contact Angle	
	(a)	Water	P3HT:$PC_{71}BM$
ZnO		111.2°	
			5.7°
	(b)		
F-ZnO		68.8°	
			11.6°

Figure S11 Contact angle measurements of a drop of deionized water and of a P3HT:$PC_{71}BM$ blend taken on (a) untreated ZnO and (b) SF_6 surface treated ZnO films.

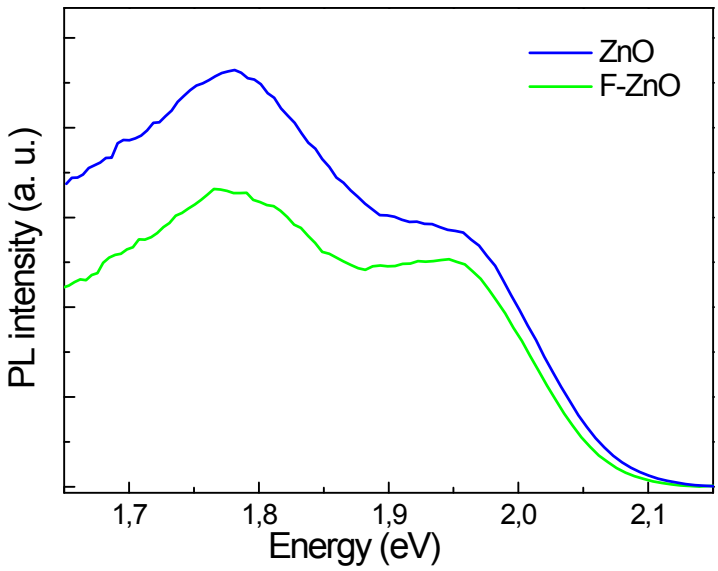


Figure S12 Steady-state PL spectra of P3HT:$PC_{71}BM$ blend (150 nm) on different ZnO layers.

References

1. J. D. Ye, S. L. Gu, F. Qin, S. M. Zhu, S. M. Liu, X. Zhou, W. Liu, L. Q. Hu, R. Zhang, Y. Shi and Y. D. Zheng, *Appl. Phys. A: Mater. Sci. Process.,* 2005, **81**, 759.
2. S. Vempati, J. Mitra, P. Dawson, *Nanoscale Res. Lett*., 2012, **7**, 470.
3. L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, D. A. Shirley, *Phys. Rev. B: Solid State*, 1974, **9**, 600.
4. F. Kayaci, S. Vempati, I. Donmez, N. Biyikliab, T. Uyar, *Nanoscale*, 2014, **6**, 10224.
5. M. K. Nowotny, L. R. Sheppard, T. Bak, J. Nowotny, *J. Phys. Chem. C*, 2008, **112**, 5275.
6. J. Wang, P. Liu, X. Fu, Z. Li, W. Han, X. Wang, *Langmuir*, 2009, **25**, 1218.