

SUPPORTING INFORMATION

Filling Nanoporous Polymer Thin Films: An Easy Route Toward the Full Control of the 3D Nanostructure

Giovanni Li-Destri^{a}, Andrea Tummino^{ab}, Antonio A. Malfatti Gasperini^{ac}, Laura Parellada^a,
Grazia M.L. Messina^b, Valentina Spampinato^d, Giacomo Ceccone^d, Oleg Kononov^{a*}*

a ESRF-The European Synchrotron 71, Avenue des Martyrs Grenoble, France

b Laboratory for Molecular Surfaces and Nanotechnology (LAMSUN), Department of Chemistry, University of Catania and CSGI, V.le A Doria 6, 95125 Catania, Italy

c Brazilian Synchrotron Light Laboratory, CNPEM, Caixa Postal 6192, CEP 13.083-970, Campinas, São Paulo, Brazil

d European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Via E. Fermi 2749, 21027, Ispra (VA), Italy

MATERIALS AND METHODS

Materials Regioregular poly(3-hexylthiophene) (P3HT), average Mn 54000-75000, electronic grade and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), purity >99.5%, were purchased by Sigma Aldrich and used as received. P3HT was dissolved in chloroform, purity >99.9% from Sigma-Aldrich, at a concentration of 6mg/mL and then gently heated at 40°C until the solution became clear. PCBM was dissolved in dichloromethane, purity

>99.9% from Sigma-Aldrich, at concentrations ranging between 1.5 and 4.5 mg/mL. A 5% w/v aqueous suspension of silica nanoparticles, nominal diameter 140 nm, was purchased by Microparticles GmbH, Berlin (Germany), and used as received. Hydrofluoric acid, 48% wt in water, purity $\geq 99.99\%$, was purchased from Sigma-Aldrich and used as received.

Methods The substrates were prepared by treating a <100> silicon wafer (from Wacker Siltronic, Burghausen, Germany) with a basic ‘‘piranha’’ mixture (3mL NH_4OH , 3mL H_2O_2 , and 15mL H_2O at 60°C for 10 min). The nanoparticle monolayer was prepared by spin coating the as received dispersion onto the substrate according to the following recipe: 1 s at 400 rpm, 10 s at 800 rpm and 30 s at 2200 rpm. The monolayer was then baked at 90°C for 1 hour to completely remove the residual water.

P3HT solution was spin coated onto the nanoparticle monolayer at 1500 rpm, partially embedding the close packed nanoparticles film, whilst the silica particles were etched by hydrofluoric aqueous solution for 6 minutes followed by a thorough rinsing with ultrapure MilliQ water. Finally, PCBM solutions were spin coated onto the nanoporous film at 1500 or 1000 rpm.

XPS measurements were performed by means of an Axis Ultra spectrometer (Kratos, Manchester, UK), using the K_α Al monochromatic source ($h\nu=1486.6$ eV) operating at 150 W and X-ray spot size of $400 \times 700 \mu\text{m}^2$ in hybrid mode. The residual pressure of the analysis chamber during the analysis was less than 8×10^{-9} Torr. For each sample, both survey spectra (0–1150 eV, pass energy 160 eV) and high-resolution spectra (pass energy at 20 eV) were recorded. Surface charge was compensated by a magnetic charge compensation system and the energy scale was calibrated by setting the C 1s hydrocarbon peak to 285 eV. The take-off angle for the acquisitions was 90° with respect to the sample surface.

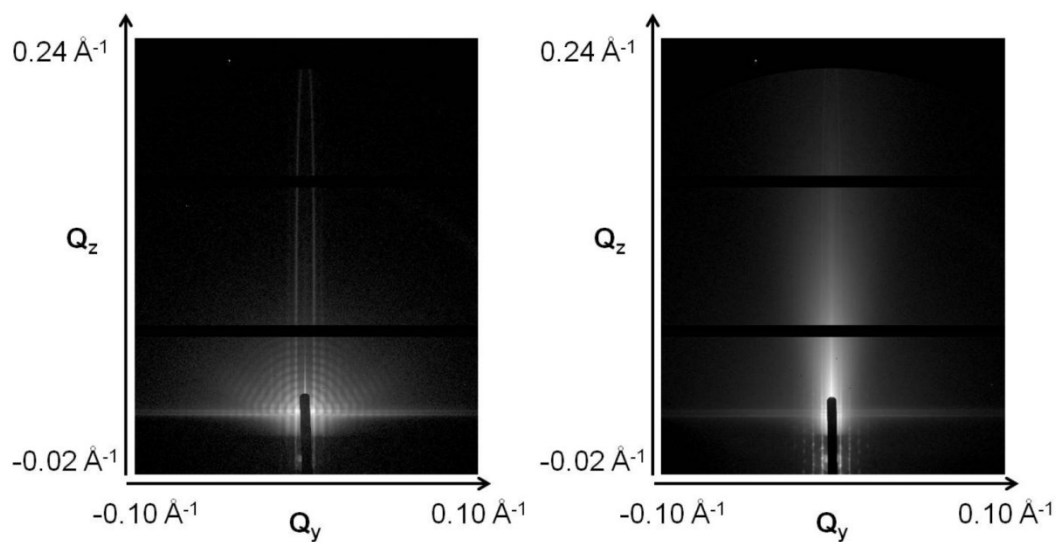
The data were processed using Vision2 software (Kratos Analytical, UK) and the analysis of the XPS peaks was carried out using a commercial software package (Casa XPS v2.3.16PR1,

Casa Software Ltd., UK). Peak fitting was performed with no preliminary smoothing. Symmetric Gaussian–Lorentzian (70% Gaussian and 30% Lorentzian) product functions were used to approximate the line shapes of the fitting components after a Shirley-type background subtraction.

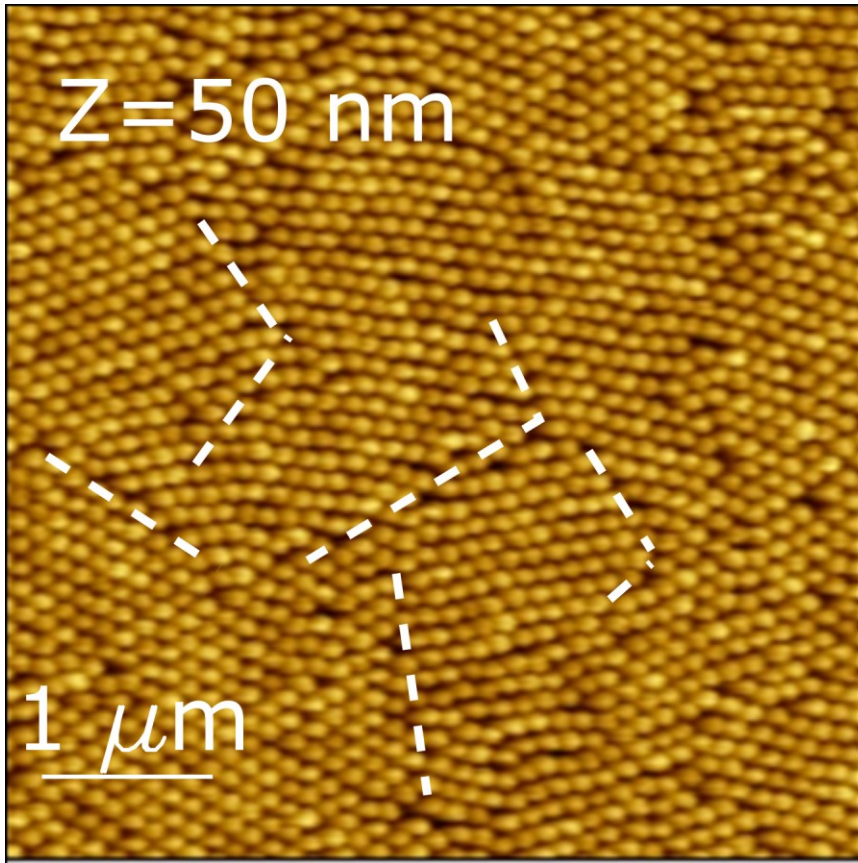
AFM images were obtained with an MFP-3D microscope from Asylum Research (Santa Barbara, USA) used in tapping mode in air. NSC15 silicon cantilevers from Mikromash (Sofia, Bulgaria) with a nominal resonance frequency of 325 kHz were employed. All the images were obtained using oscillation amplitude of 100 nm at a set point of 36 nm.

GISAXS data were recorded at ID 10 beamline of the European Synchrotron (ESRF), the energy of the incoming beam was 10 keV. The 2D GISAXS patterns were recorded with a Pilatus 300k detector from Dectris (Baden, Switzerland) at a distance of 2160 mm from the sample. The incident beam was 0.16° , 90% of the silicon oxide critical angle (0.18°), to minimize the substrate contribution. GISAXS simulations were performed with BornAgain software package¹.

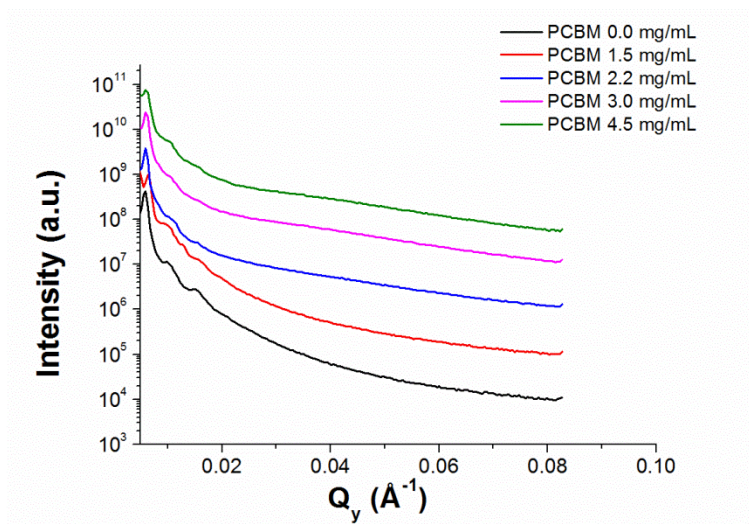
[1] C. Durniak, M. Ganeva, G. Pospelov, W. Van Herck and J. Wuttke, BornAgain – Software for simulating and fitting X-ray and neutron small-angle scattering at grazing incidence, version 1.3 2015, <http://www.bornagainproject.org>.



S1. GISAXS patterns of the silica nanoparticles monolayer (left) and of the P3HT nanoporous film (right). After the removal of the nanoparticles the intense spherical form factor disappears but the series of the long structure factor rods are kept, confirming the preservation of the 2D lattice order.



S2. AFM height image on a $25 \mu\text{m}^2$ area. Some of the boundaries between the different crystalline domains are highlighted with dashed lines.



S3. GISAXS cuts at $Q_z 0.028 \text{\AA}^{-1}$. By increasing the PCBM concentration the three peaks at $Q_y 0.0055 \text{\AA}^{-1}$, 0.01\AA^{-1} and 0.015\AA^{-1} are progressively weaker because of the reduced electron density contrast.