

ELECTRONIC SUPPORTING INFORMATION

Soft plasma processing of organic nanowires: a new route for the fabrication of 1D organic heterostructures and the template synthesis of inorganic 1D nanostructures.

Maria Alcaire,^a Juan R. Sanchez-Valencia,^{a,b} Francisco J. Aparicio,^a Zineb Saghi,^c Juan C. Gonzalez-Gonzalez,^a Angel Barranco,^a Youssef Oulad,^a Agustin R. Gonzalez-Elipe,^a Paul Midgley,^c Juan P. Espinos,^a Pierangelo Groening^b and Ana Borrás^{a*}

^a *Nanotechnology on Surfaces Lab. Materials Science Institute of Seville (CSIC-University of Seville). C/ Americo Vespucio 49, 41092 Seville, Spain*

E-mail: anaisabel.borras@icmse.csic.es

^b *Nanotech@surfaces Lab., EMPA, Swiss Federal Laboratories for Materials Science and Research Überlandstrasse 129, 8600 Dübendorf, Switzerland*

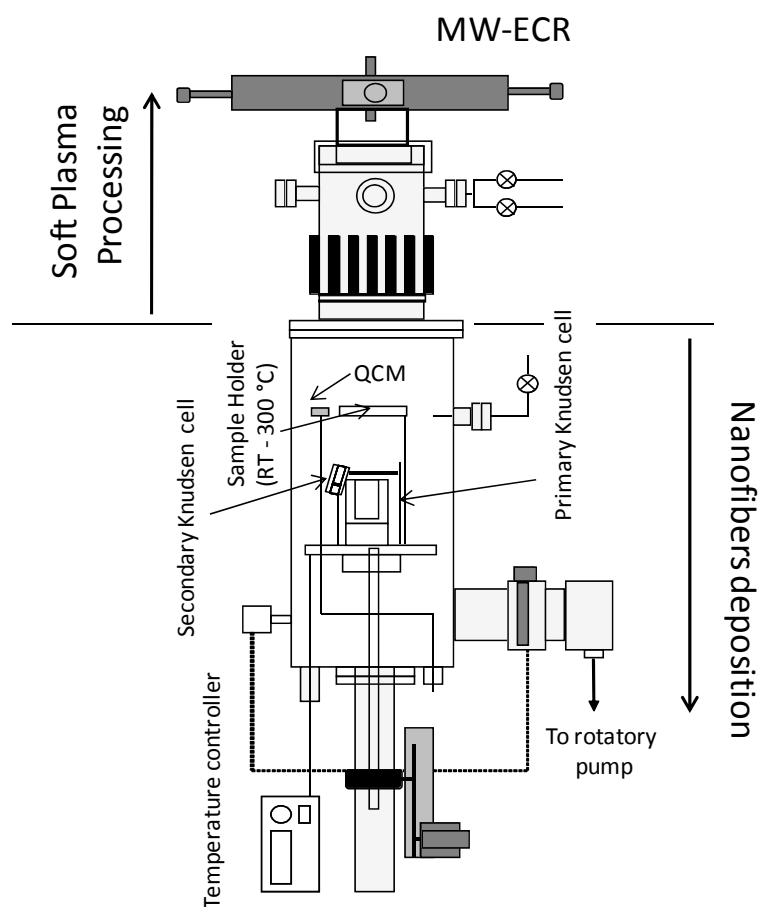
^c *Department of Materials Science and Metallurgy University of Cambridge, Pembroke Street CB2 3QZ Cambridge, United Kingdom*

Experimental Section

ONWs by PVD: The procedure development has been fully described in previous references.³ Perylene diimide (2,9-dimethyl-anthra[2,1-def:6,5,10-d'ef']diisoquinoline-1,3,8,10-tetrone (Me-PTCDI) from Sensient Imaging Technologies.), Pd Octaethyl porphyrin (Frontier Sci.), and Co phthalocyanine (Aldrich) were used as purchased (See Figure 1 for their molecular structures). ONWs were grown simultaneously on different substrates ITO, TiO₂ thin films prepared by CVD and GLAD and Si(100), fused silica and Au TEM grids previously coated with silver nanoparticles by dc-sputtering. Substrates temperature (T_s) for the ONWs formation depended on the organic molecule: a) for the Me-PTCDI T_s ~ 175 ± 5°C; b) for the PdOEP T_s ~ 150 ± 5°C and c) for the CoPc T_s ~ 260 ± 5°C.

Plasma treatments: Our experimental set up (see refs. 3 and 7) allows in situ MW (2.45 GHz) plasma treatments at controlled power. All the experiments gathered at this work were carried out at 150 W, plasma gas composition 80% Oxygen – 20% Argon, total pressure at the chamber 0.020 mbar and downstream configuration, i.e. substrates emplaced out the plasma discharge, concretely at 5 cm.

Characterization: SEM characterization was carried in Hitachi S-4800; TEM and HAADF-STEM electron tomography was performed on a FEI Tecnai F20 field-emission gun transmission electron microscope operated at 200 kV. Data collection was carried out by tilting the specimen about a single axis from -64° to +62° with a 2° increment, using a Fischione ultrahigh-tilt tomography holder, and acquiring the images with the FEI software package Xplore3D. The tilt series was then exported to the FEI software Inspect3D for the cross-correlation alignment and the tomographic reconstruction using the iterative routine SIRT. Slice viewing after a global thresholding was undertaken using Amira software. ONWs were analyzed by TEM and STEM directly grown on TEM grids or after removed from the substrates by scratching and dispersion in ethanol and then “fished” in a holey carbon grid. Fluorescence microscopy images were obtained with an Olympus BX51 fluorescence microscope. Fluorescence spectra were recorded in a Jobin Yvon Fluorolog3 spectrofluorometer using the front face configuration and grids of 4 and 2 nm for the excitation and emission mono-chromators respectively.



Scheme S1. Experimental system schematic. The system was pumped up to $5 \cdot 10^{-6}$ mbar base pressure before the deposition. The distance between the substrate and the sublimation source was 8 cm. During the experiments Argon was dosed using a calibrated mass flow controller. The pressure in the system during deposition was fixed at 0.020 mbar by a VAT controller. The growth rate was controlled by a quartz crystal microbalance located in parallel to the substrates. The growth of the hierarchical nanowires was carried out combining two different Knudsen cells. The soft plasma processing was carried out in situ.

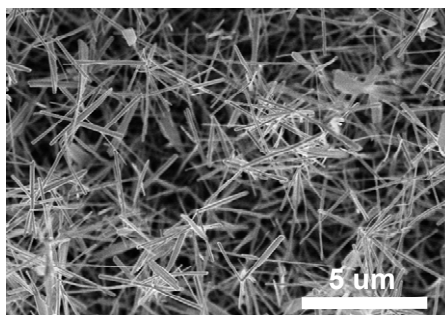


Figure S1. Low magnification SEM micrograph demonstrating a high density of hierarchical perylene/PdOEP-NWs.

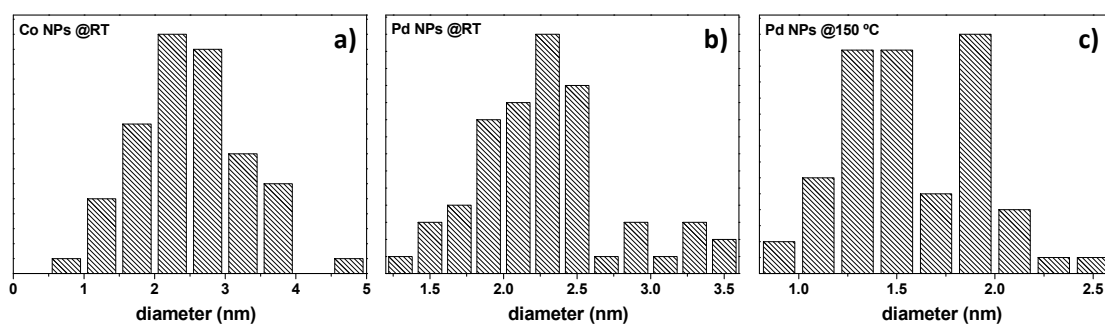


Figure S2. Size histograms for Co (a) and Pd (b-c) nanoparticles formed at: a) room temperature after 1 minutes; b) room temperature after 5 minutes and c) 130 °C after 5 minutes. The mean diameter for the Co NPs in a) is ~2.5 nm; for the Pd NPs in b) ~2.3 nm and c) 1.6 nm. Statistics were carried out by direct measurement of the diameters in ~100 nanoparticles in micrographs acquired by STEM at high magnification.

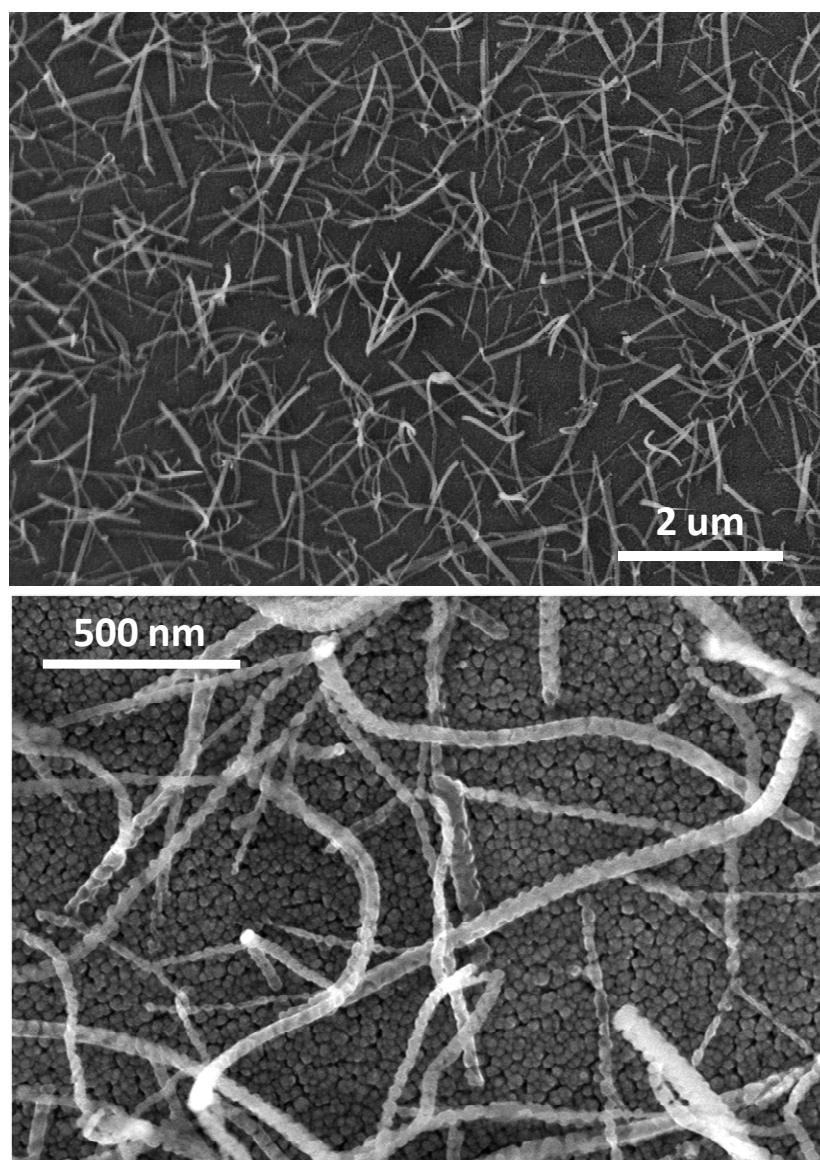


Figure S3. SEM micrographs at different magnifications showing PdOEP nanowires grown on the surface of TiO_2 thin films after plasma treatment at 130 °C during 8 minutes.