ORDERED ORGANIC-INORGANIC SOLAR CELLS

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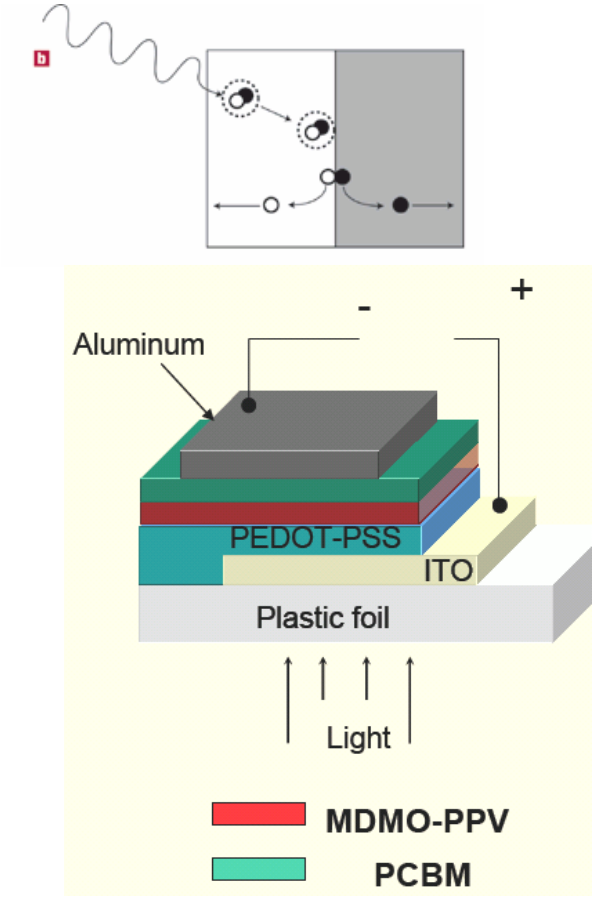
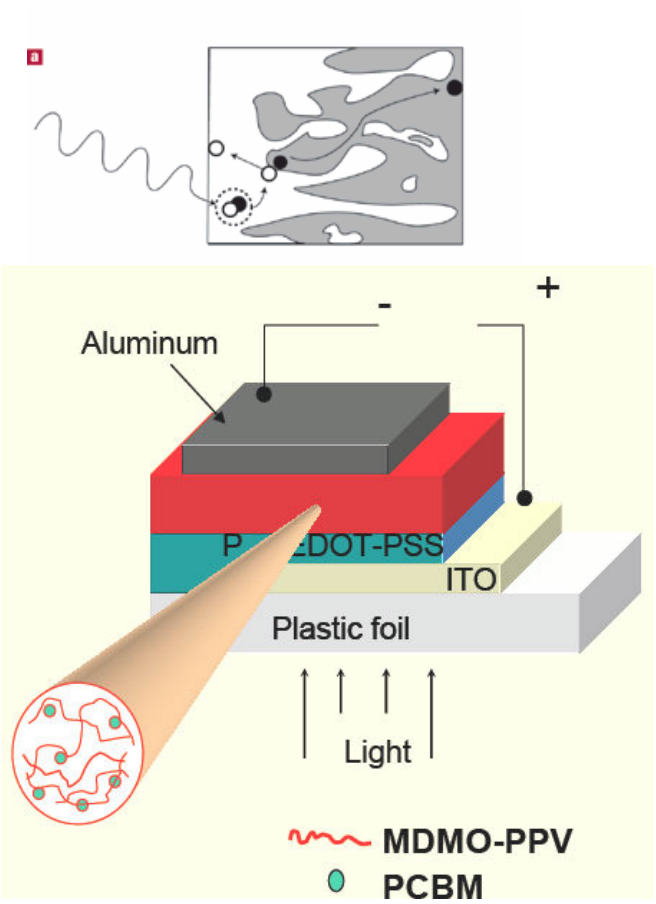
OPV: device geometries

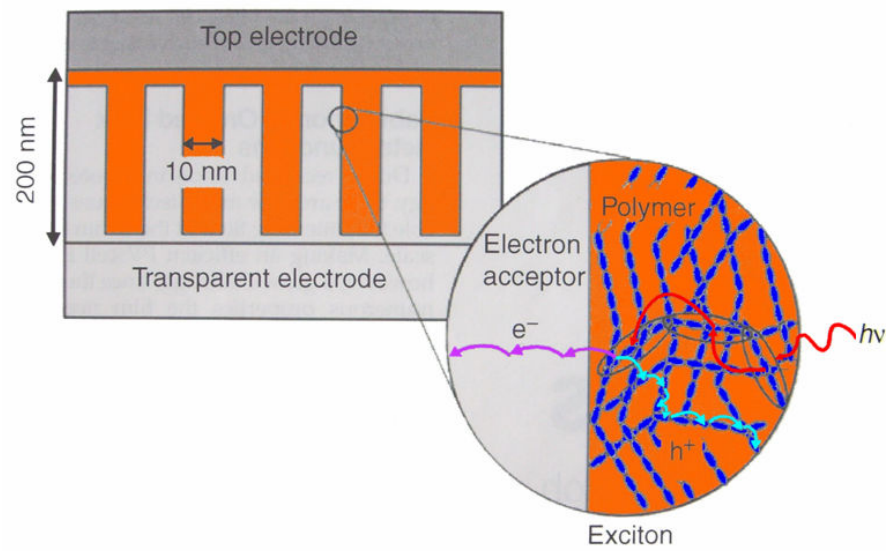
PLANAR HETEROJUNCTION



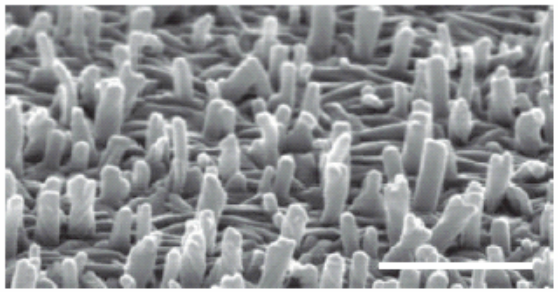
BULK HETEROJUNCTION



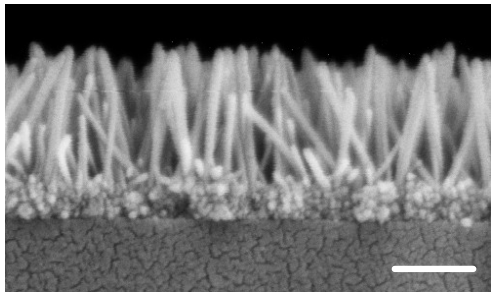
Ordered Bulk Heterojunction PV



Schematic illustration of an ideal ordered bulk heterojunction photovoltaic cell.The enlarged circle represents an exciton [KM Coakley, Y Liu, C Goh, MD McGehee, MRS Bulletin, 30 (2005) 37]

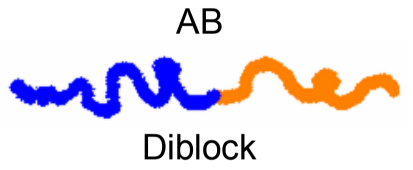


Short needle-like crystals of CuPc grown on a silicon wafer surface by organic vapour phase deposition (OVPD). Scale bar: 500 nm. [F. Yang, M. Shtein, S.R. Forrest, Nature Materials, 2005, 4, 37].

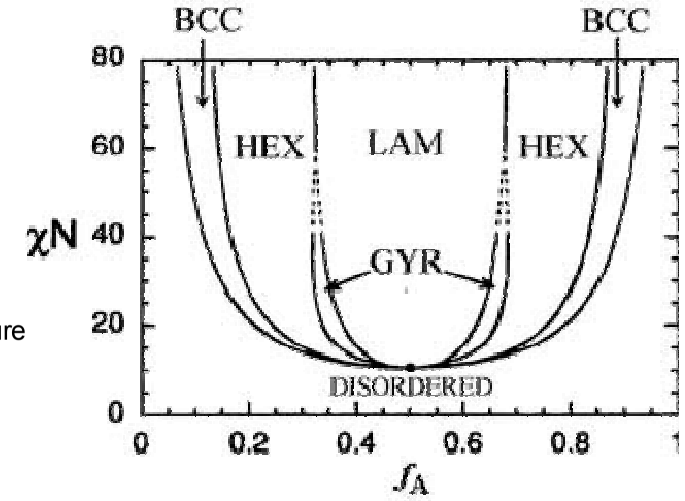


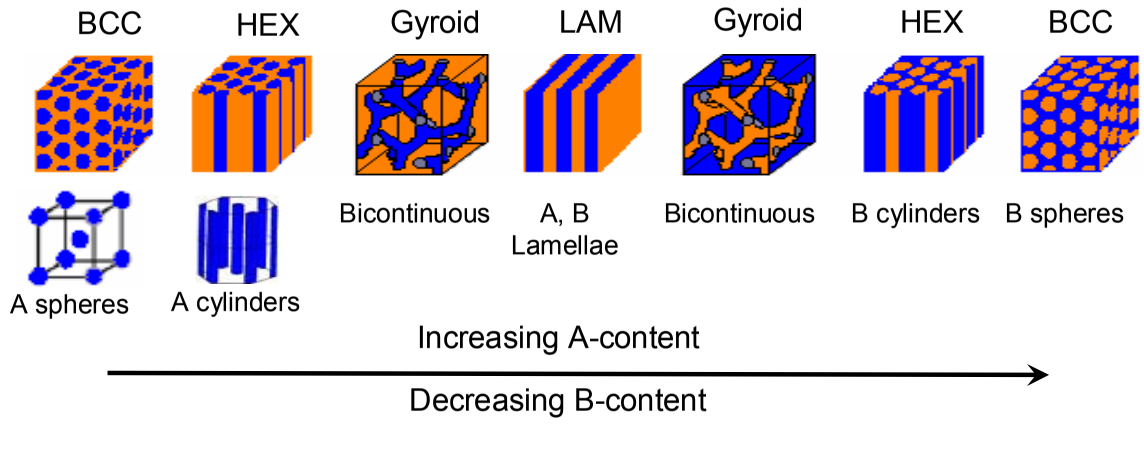
ZnO nanowires grown on a transparent conducting oxide using a chemical solution growth technique. Scale bar: 200 nm. [S. Shaheen et al., Conference Paper NREL/CP-520-37042, January 2005].

Self-assembling block-copolymers

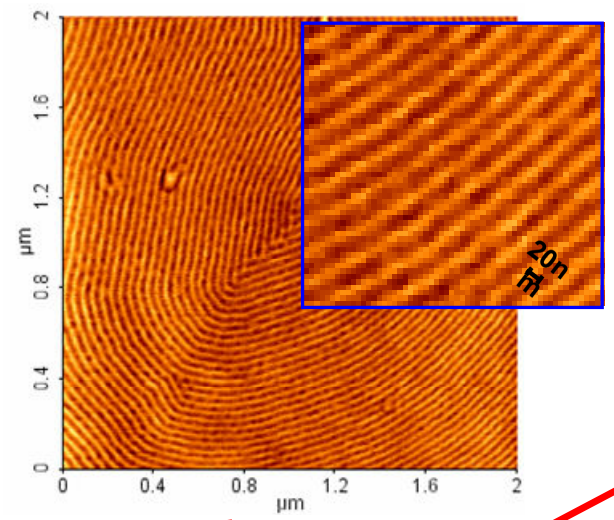


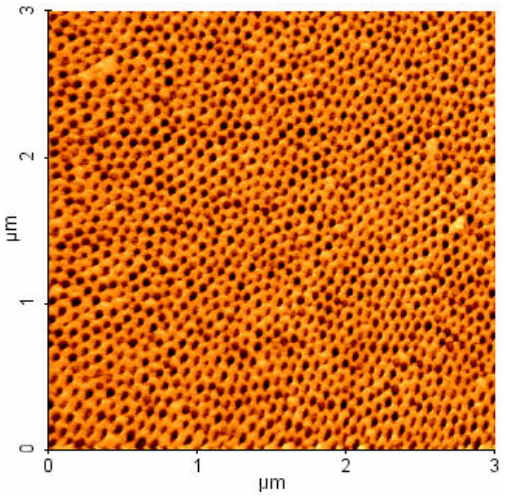
LAM: Lamellar
HEX: Hexagonal-packed cylinder
BCC: Body-centred cubic spherical structure
GYR: Gyroid

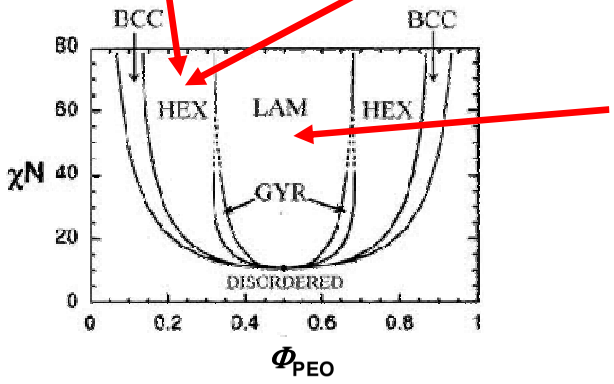


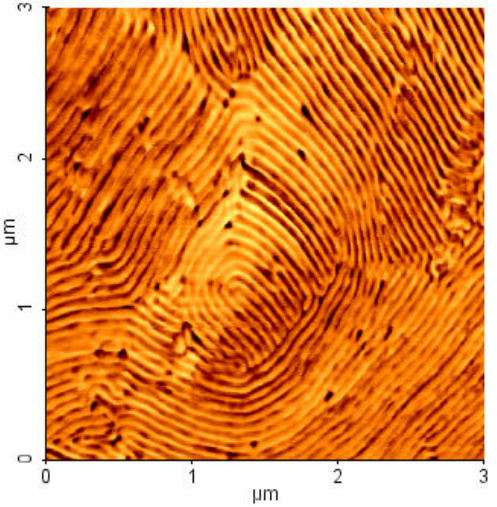


PS-*b*-PEO nanostructured films









Alignment and large-scale ordering of BCs

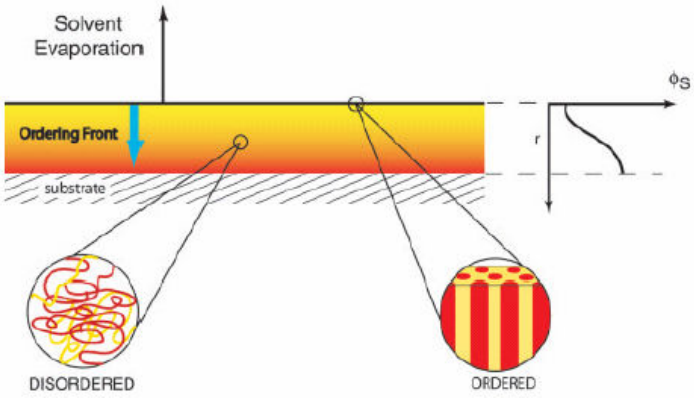
To fully realize the potential of block copolymers in nanotechnology **morphology**, **orientation** and **lateral ordering** of the nanoscopic domains must be controlled.

In general, structural order over large extension can be obtained by exploiting molecular interactions including:

- ❖ hydrophilic and hydrophobic effects
- ❖ **hydrogen bonding**
- ❖ columbic interactions
- ❖ van der Waals forces.

The level of ordering can be increased by directional external fields:

- ➢electric and magnetic fields
- ➢flow fields
- ➢thermal treatments
- ➢directional crystallization
- ➢epitaxy
- ➢chemically patterned substrates
- ➢**solvent evaporation and annealing**

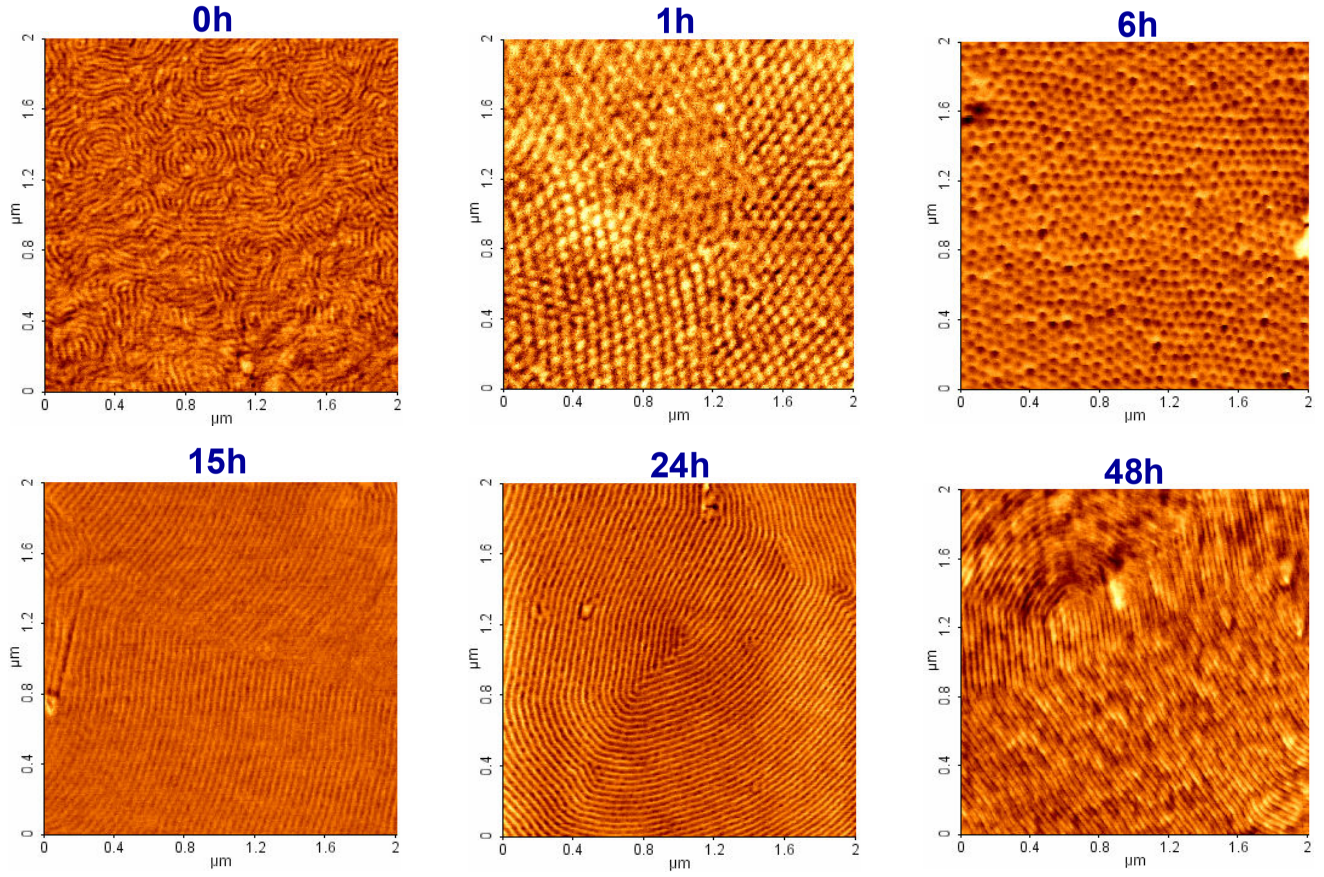


Kim S.H.; Misner M.J.; Xu T.; Kimura M.; Russell T.P., *Advanced Materials* **2004**, 3, 226.

Xuan Y.; Peng J.; Cui L.; Wang H.; Li B.; Han Y., *Macromolecules* **2004**, 37, 7301.

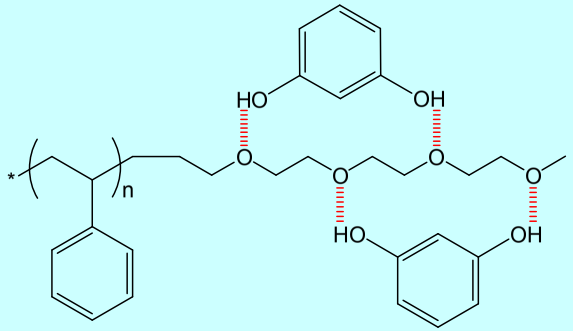
Orientation vs solvent annealing time

PS-*b*-PEO (32000-*b*-11000 g/mol)
annealing under benzene atmosphere at 60°C for 1h, 6h, 15h, 24h and 48h



Scalarone D. et al., *Study of the morphology and cristallinity development in thin films of PS-b-PEO copolymers and PS-b-PEO/resorcinol molecular complexes*, in preparation, 2008

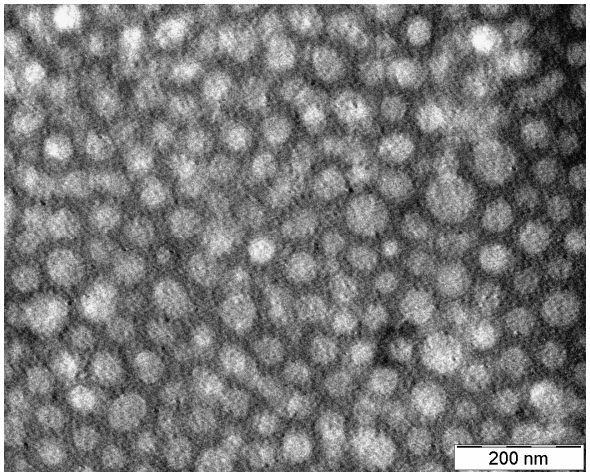
Supramolecular Assembly of PS-*b*-PEO and Resorcinol

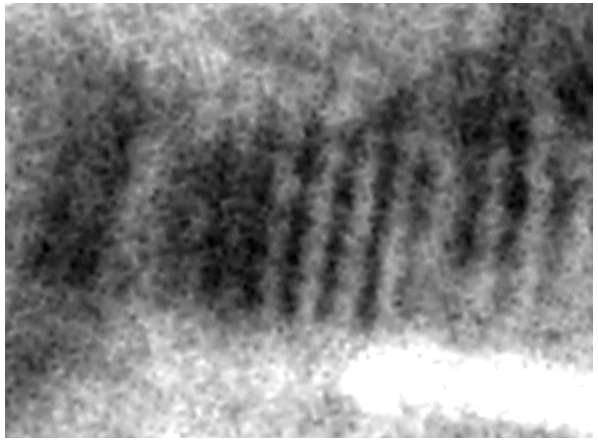


5 wt% benzene solutions of PS-*b*-PEO & Resorcinol with Res/EO molar ratio 1:2.

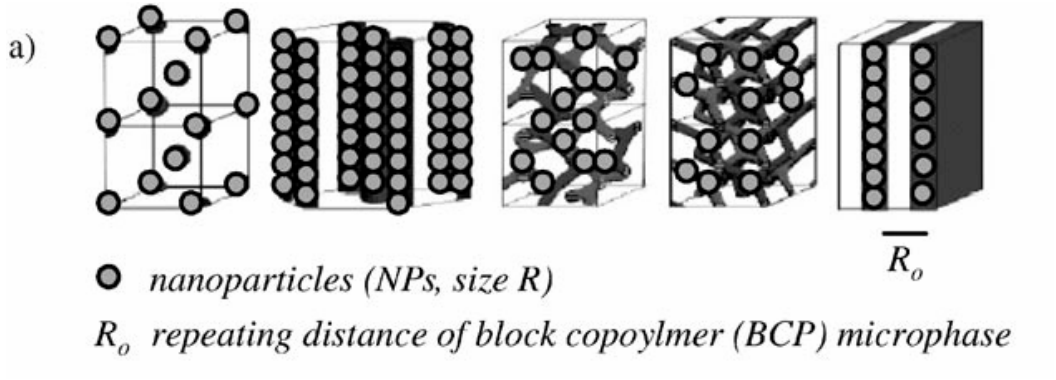
A. Sidorenko et al., J. Am.Chem Soc., 125 (2003) 12211

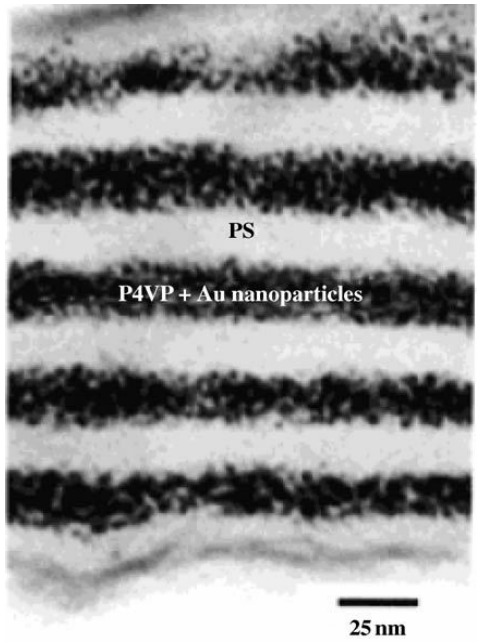
C. Liang et al.., *Angew. Chem. 116* (2004) 5909





…from self-assembling BCs to hybrid nanostructured materials

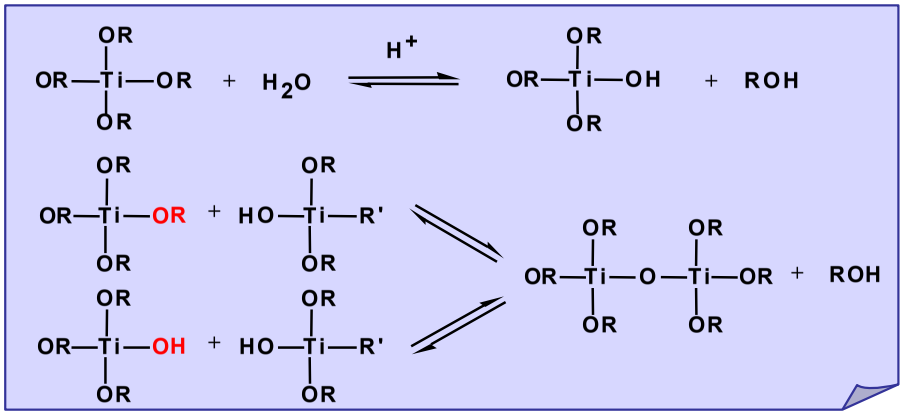




Cross-sectional TEM images of thin PS-b-P4VP films containing Au NPs (R3 nm). The Au NPs are enriched in the P4VP microphase after direct formation within the matrix via reduction from a HAuCl4/NaBH4 solution.
[H. Shen, L. Zhang, A. Eisenberg, J. Am. Chem. Soc. 1999, 121, 2728]

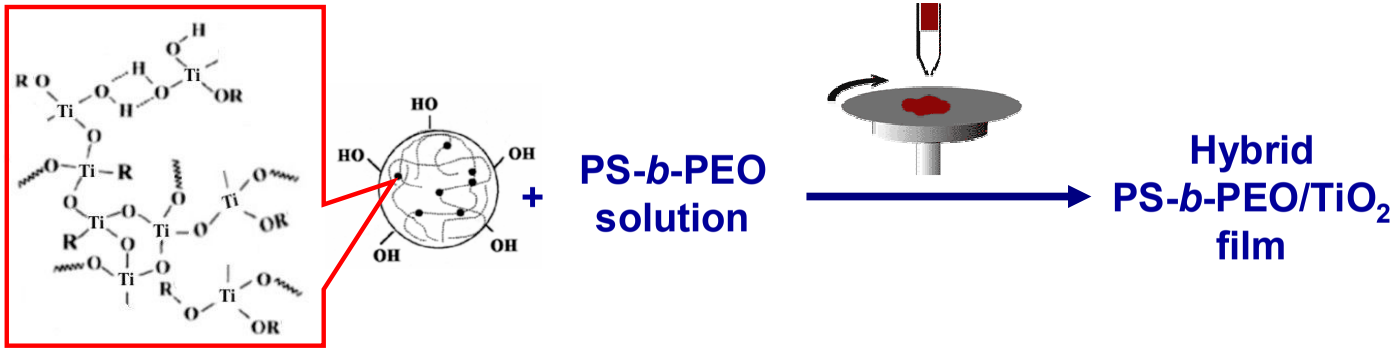
Hybrid PS-*b*-PEO/TiO_2 nanostructured films: nanoparticle synthesis and film preparation

NANOPARTICLE SOL-GEL SYNTHESIS

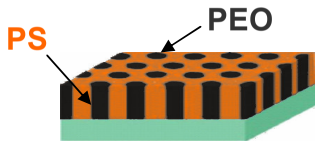


$TTIP/HCl_{aq(37\%)}$ = 0.8;0.5;0.2

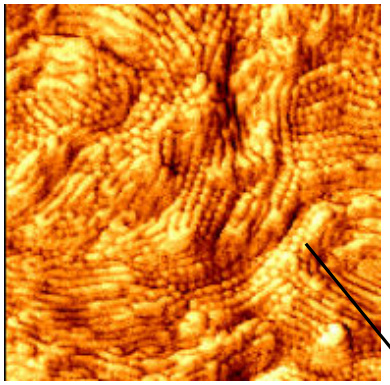
NANOSTRUCTURED HYBRID FILM PREPARATION



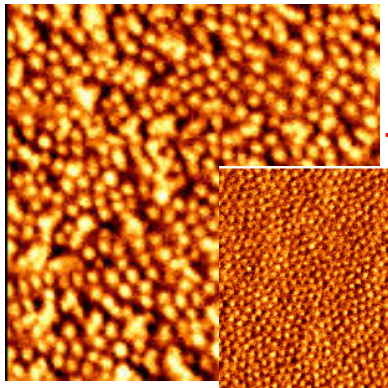
Hybrid PS-*b*-PEO/TiO_2 nanostructured films: morphology

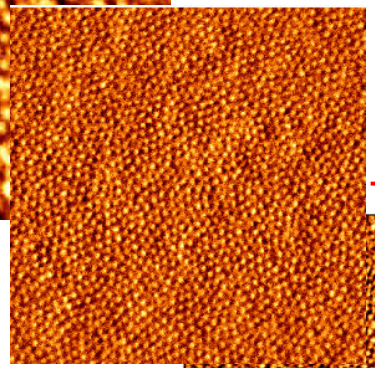


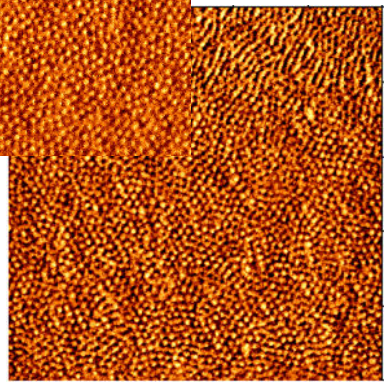
PS-*b*-PEO
(58600-b-31000 g/mol)

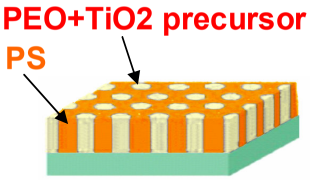


+ sol-gel solution

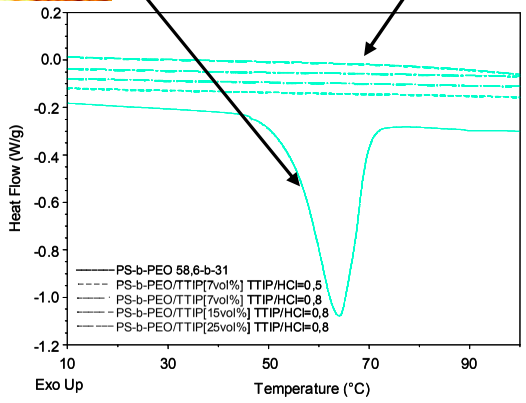






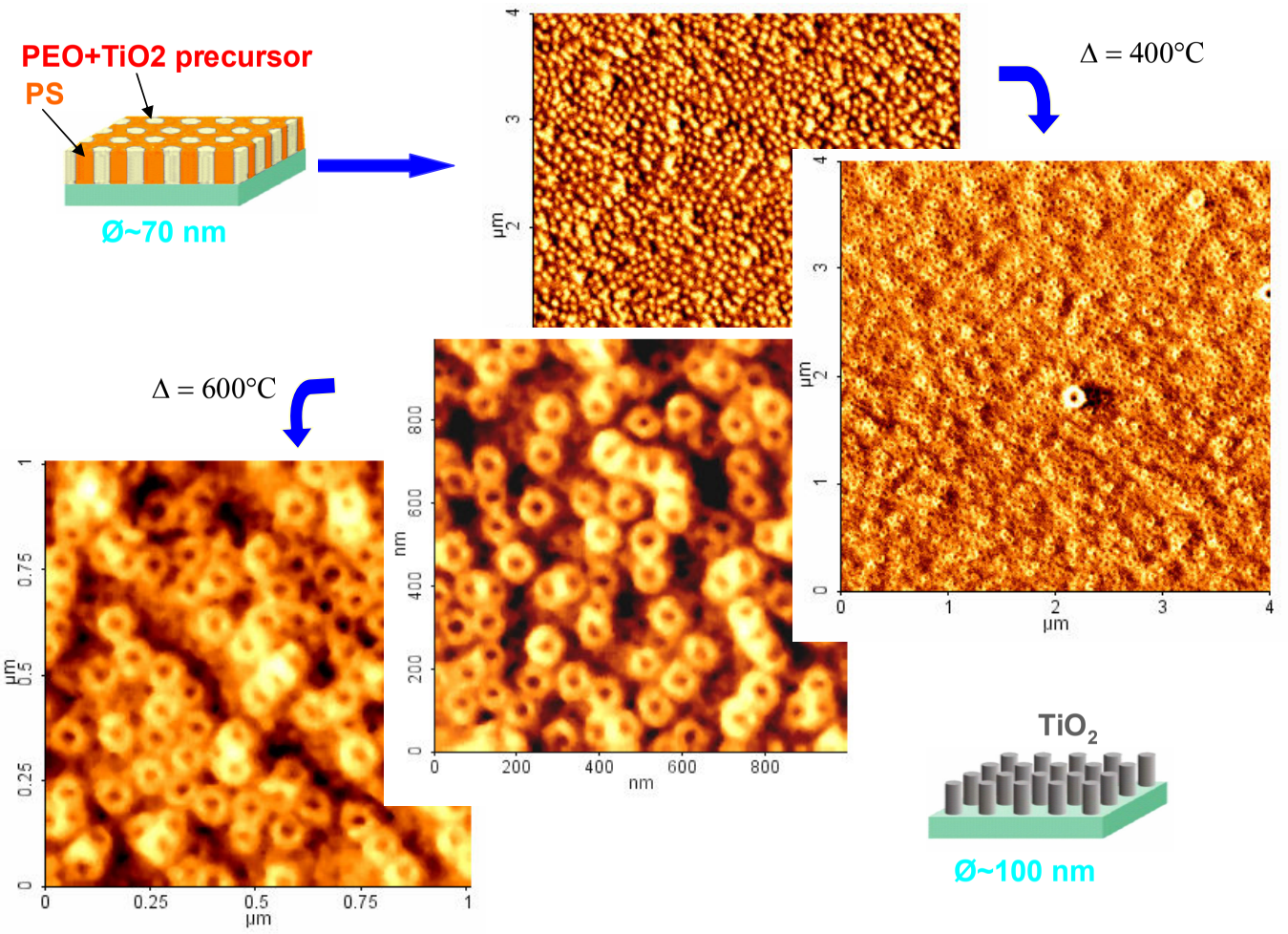


TTIP content



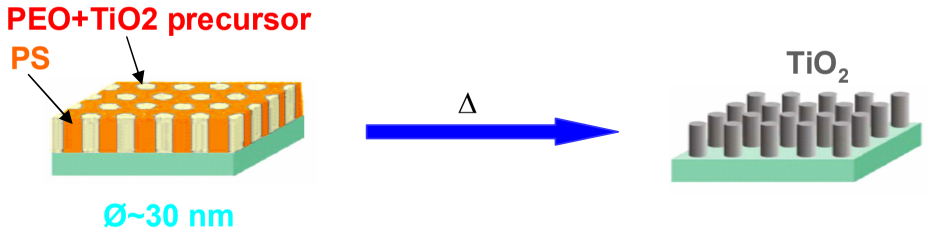
From hybrid PS-*b*-PEO/TiO_2 nanostructured films to titania nanoparticle arrays

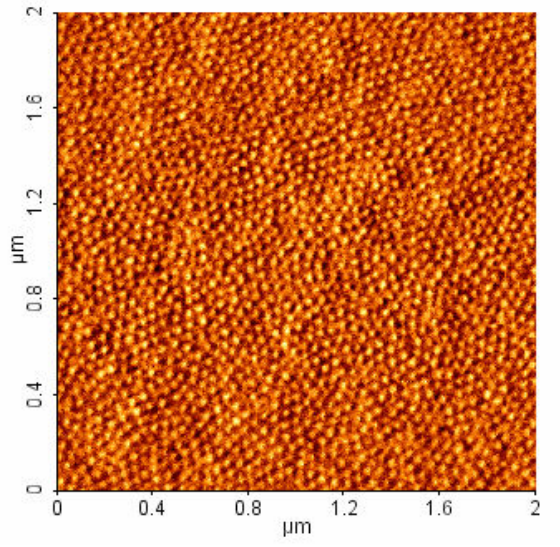
PS-*b*-PEO (Mn=58600-*b*-31000 g/mol) + TTIP (25%vol) [TTIP/HCl=0,8]

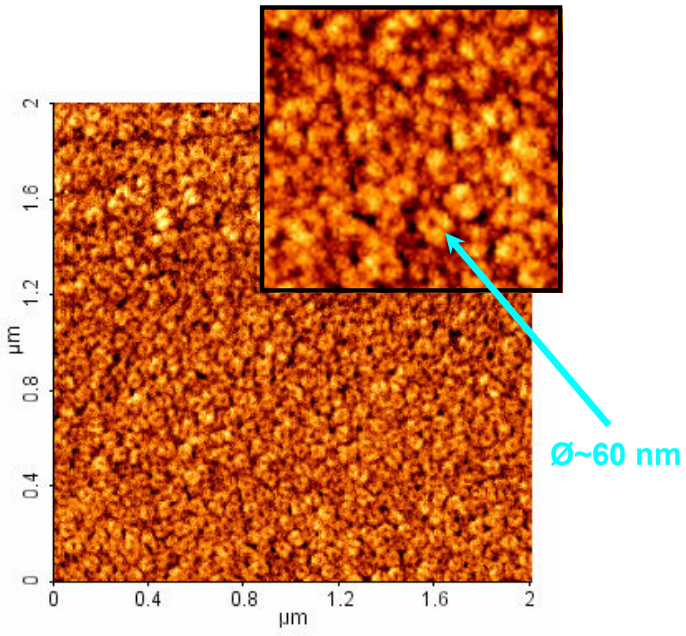


From hybrid PS-*b*-PEO/TiO_2 nanostructured films to titania nanoparticle arrays

PS-*b*-PEO (Mn=58600-*b*-31000 g/mol) + TTIP (15%vol) [TTIP/HCl=0,8]

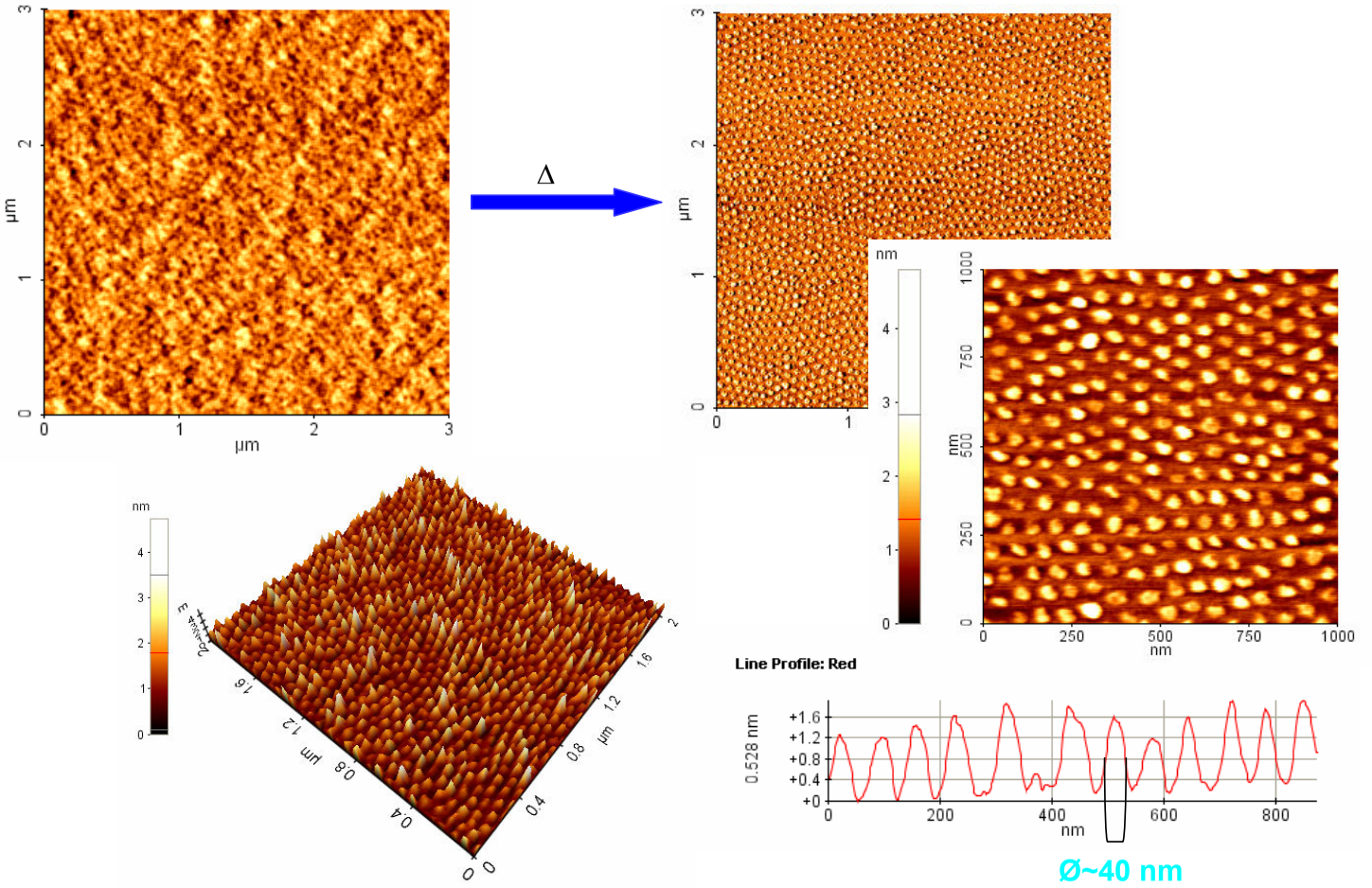






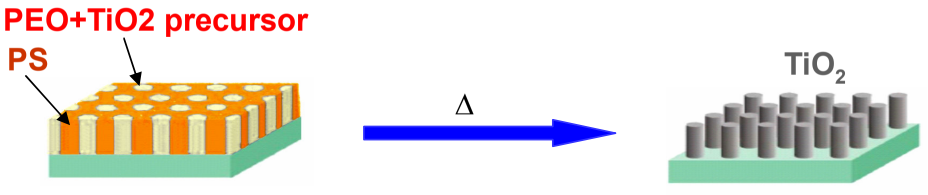
From hybrid PS-*b*-PEO/TiO_2 nanostructured films to titania nanoparticle arrays

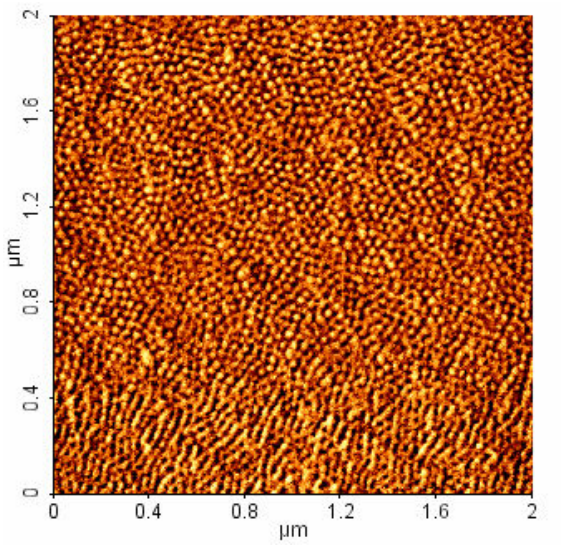
PS-*b*-PEO (Mn=58600-*b*-31000 g/mol) + TTIP (7%vol) [TTIP/HCl=0,8]



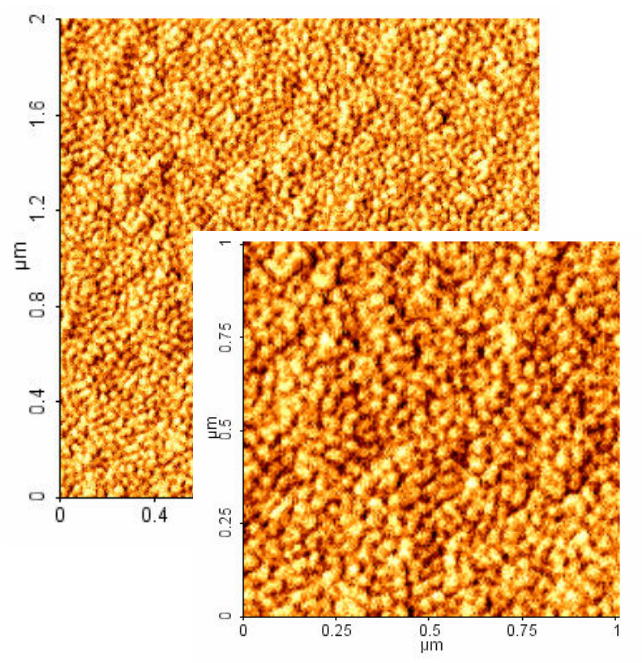
From hybrid PS-*b*-PEO/TiO_2 nanostructured films to titania nanoparticle arrays

PS-*b*-PEO (Mn=58600-*b*-31000 g/mol) + TTIP (7%vol) [TTIP/HCl=0,5]





Ø~30 nm



Ø~30 nm

Conclusions and perspectives

❑ The self-assembling capability of PS-*b*-PEO BCs has been used to drive the arrangement of TiO_2 nanoparticles in a polymer matrix.

❑ Hybrid nanostructured films with the Ti rich phase confined in perpendicular cylindrical domains have been prepared.

❑ Elimination of the polymer template by calcination has produced ordered arrays of TiO_2 nano-rings or nano-dots with diameters ranging from 30 to 100 nm.

❑ After the BC template removal, a new hybrid film can be obtained by incorporation of a polymer filling the space between the conducting domains. Diffusion and spin casting of semiconductive polymer solutions have been proposed as simple methods for the preparation of photoactive polymer films.

❑ Ordered organic-inorganic BHJ photovoltaic films should allow a better electronic interfacial transfer, optimized dissociation of charge carriers, optimized charge paths from the interfaces to the contacts and minor probability of electron-hole recombination.