

Chemical Design of Efficient Photoelectrodes by Nucleation and Growth of Carbon Dots in Mesoporous Ordered Titania Films

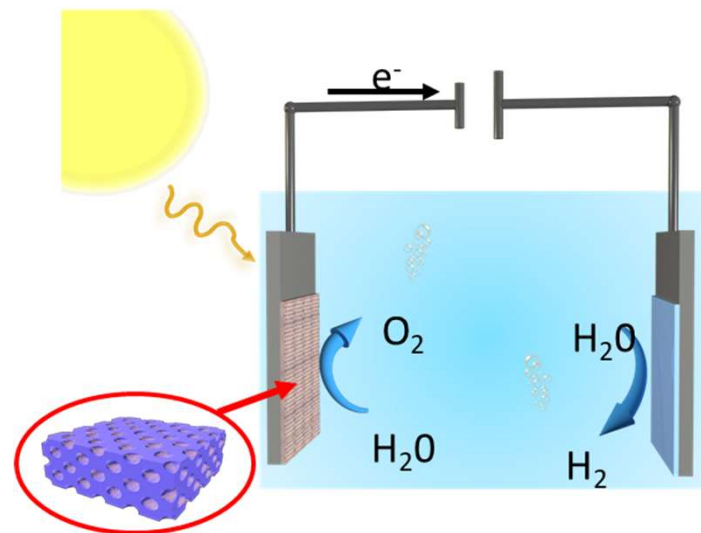
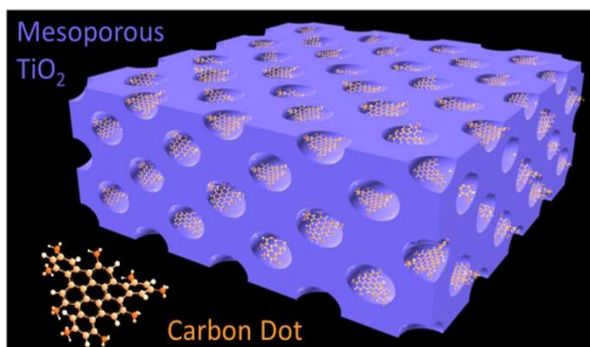
Luca Malfatti,¹ F. Herrera,² V. Sireus,¹ P. Rasso,¹ L. Stagi,¹ M. Reale,³ A. Sciortino,³ F. Messina,³ G. J. J. Soler-Illia,² L. Stagi,¹ P. Innocenzi¹

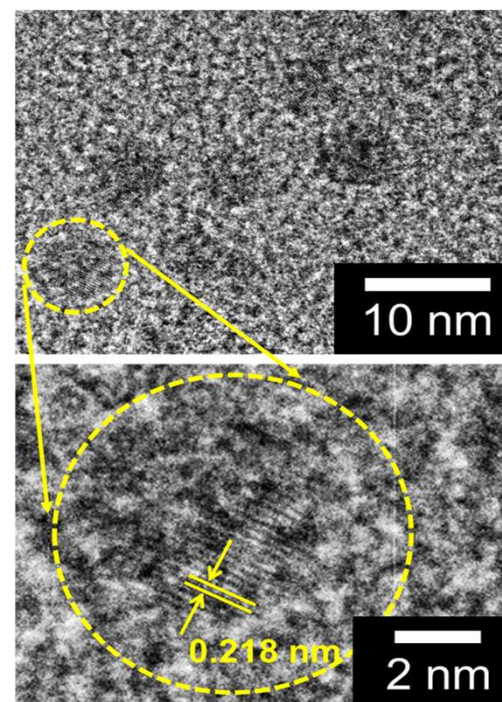
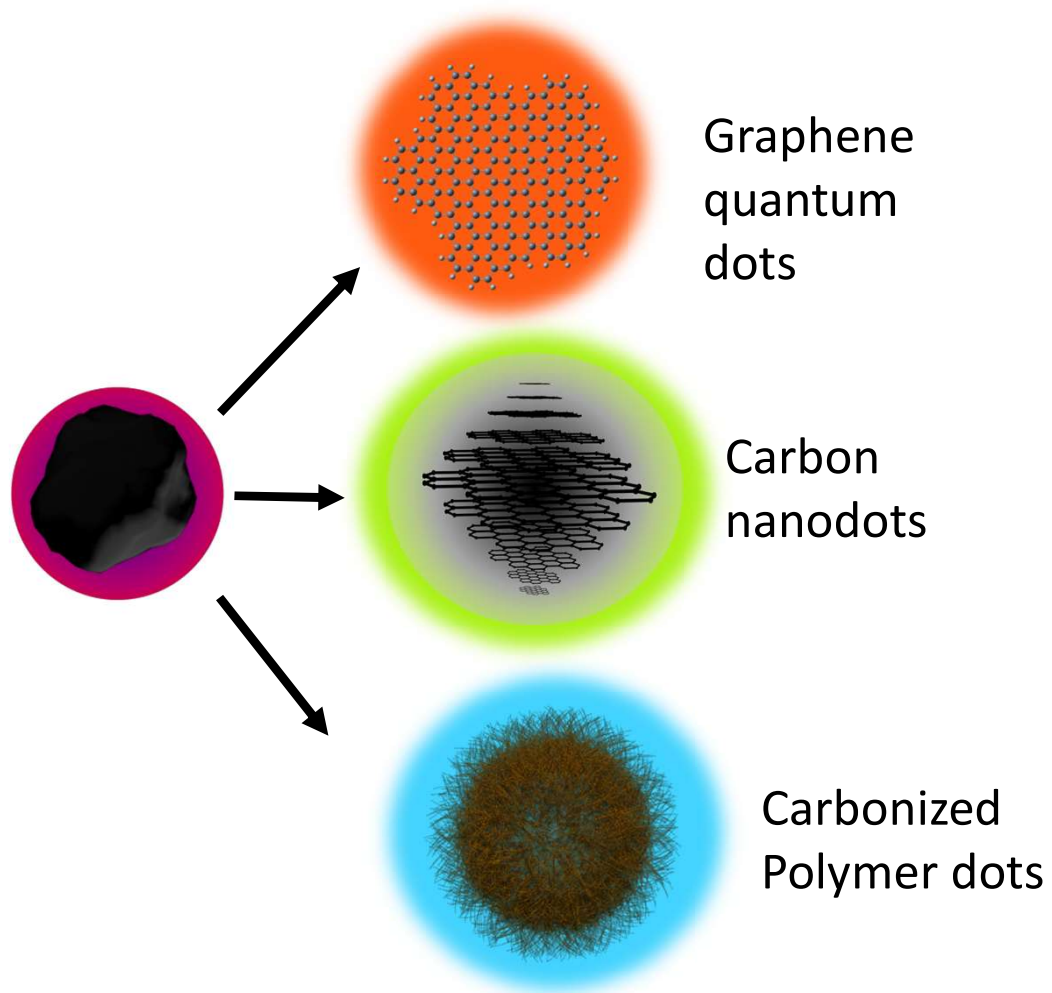
¹*LMNT-Department of Biomedical Sciences, University of Sassari, Italy*

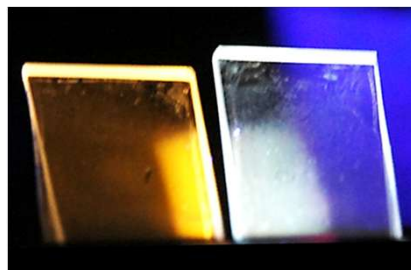
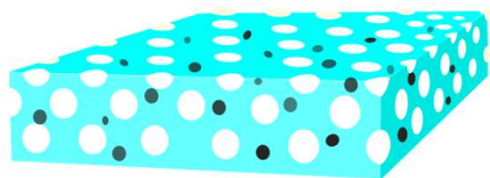
²*Instituto de nanosistemas, Universidad Nacional de San Martín, Argentina*

³*Department of Physics and Chemistry, University of Palermo, Italy*

Email: luca.malfatti@uniss.it

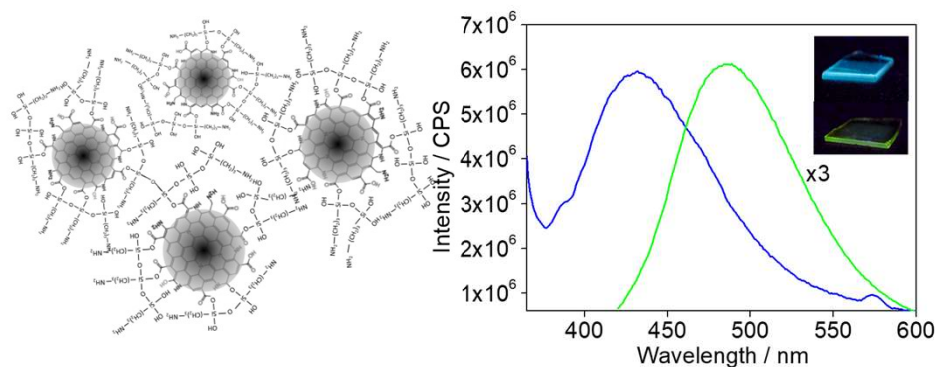






Post-impregnated C-dots onto macroporous film

K. Suzuki, *et al*, *RSC Adv.*, 6, (2016) 55393

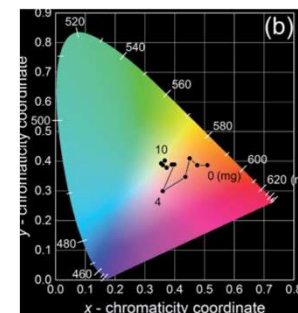
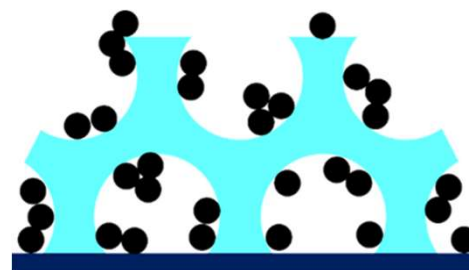


Design of C-dots with customized photo-physical properties

K. Suzuki, *et al*, *Sci. Rep.*, 7, (2017) 5469.

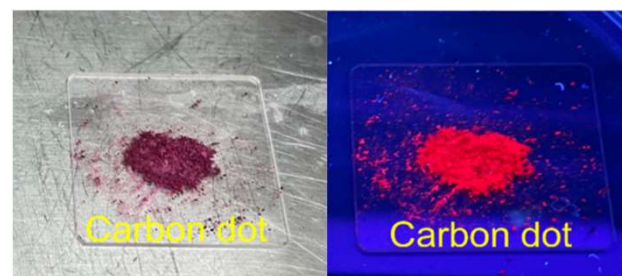
One-pot synthesis of mesoporous nanocomposite film

Suzuki, *et al*, *J. Phys. Chem. C*, 119, (2015) 2837.



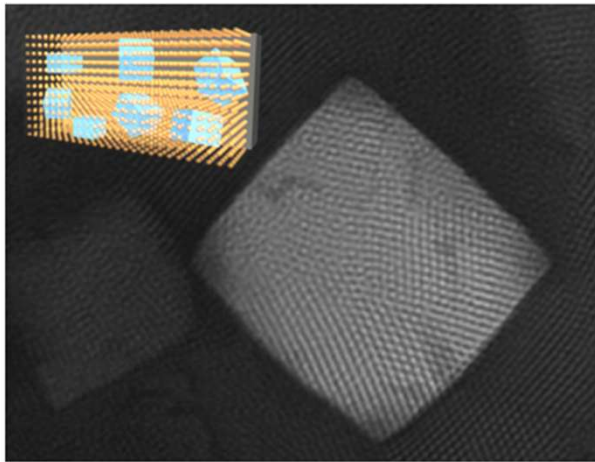
Design of C-dots surface for incorporation in sol-gel films

S. Mura, *et al*, *Sci. Rep.*, 10, (2020) 4770

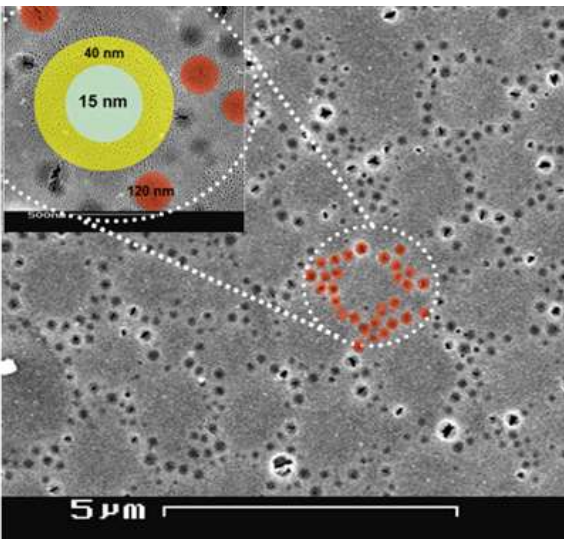


M. Meloni *et al*, *Nanomaterials* 12 (2022) 2351.

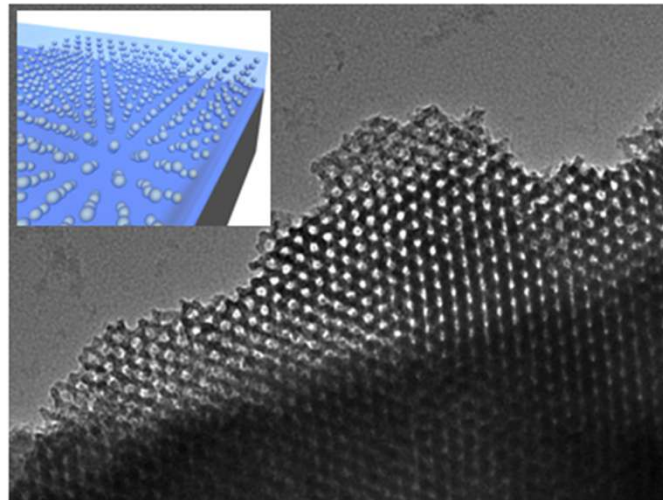
Sol-gel based self-assembled porous films



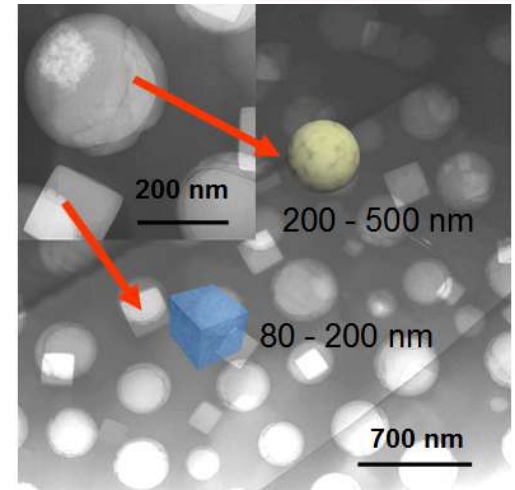
Malfatti et al, *Chem. Mater.*, **2009**, *21*, 4846



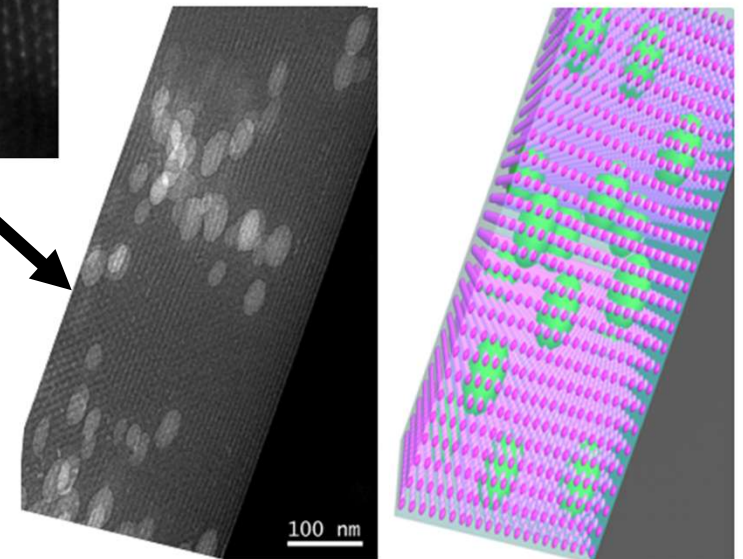
Malfatti et al, *Chem. Mater.*, **2009**, *21*, 2763



Innocenzi, Malfatti *Chem. Soc. Rev.*, 2013, **42**, 4198-4216



Innocenzi et al, *N. J. Chem.*, **2011**, *35*, 1624



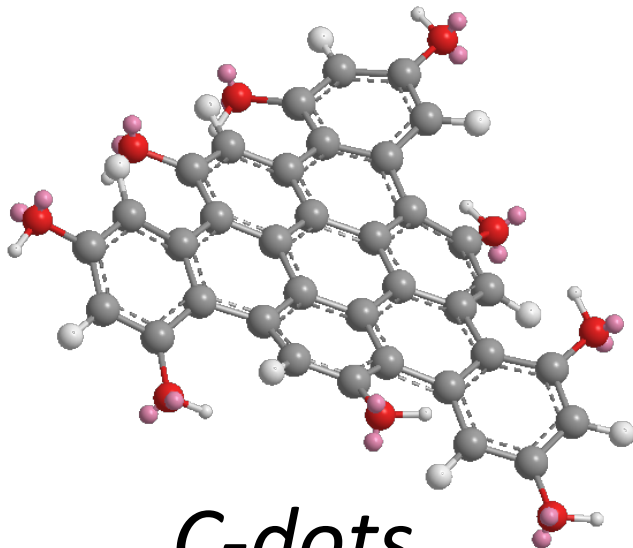
Falcaro et al, *Chem. Mater.*, **2009**, *21*, 2055



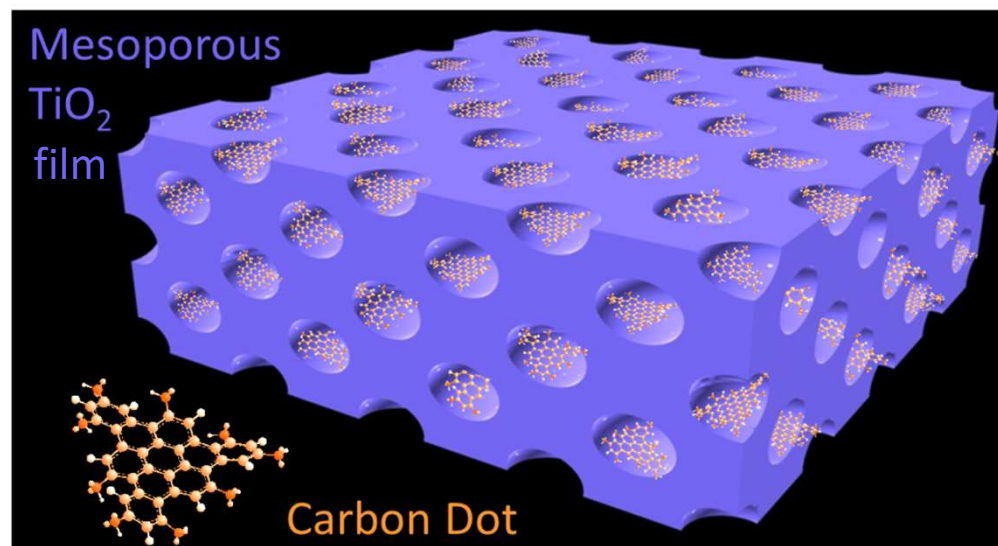
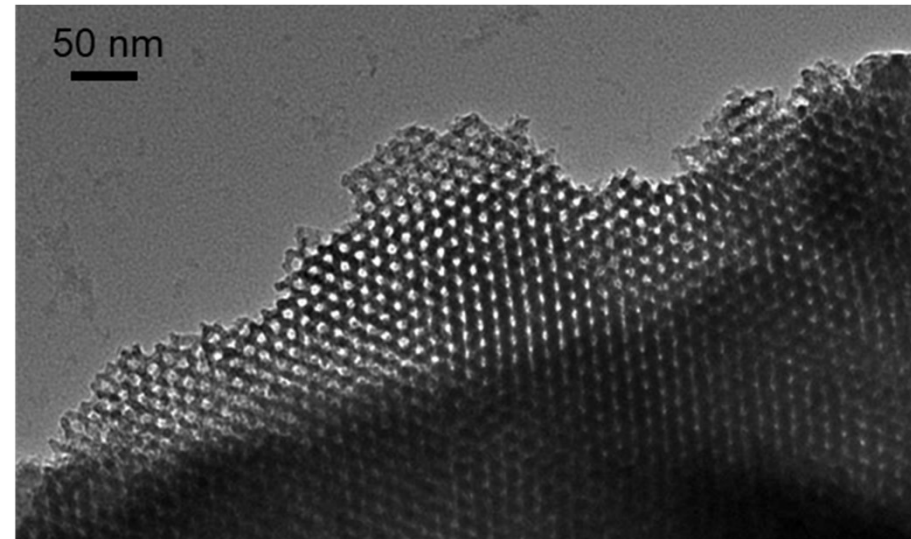
Heterogenous nucleation of C-dots in mesoporous films



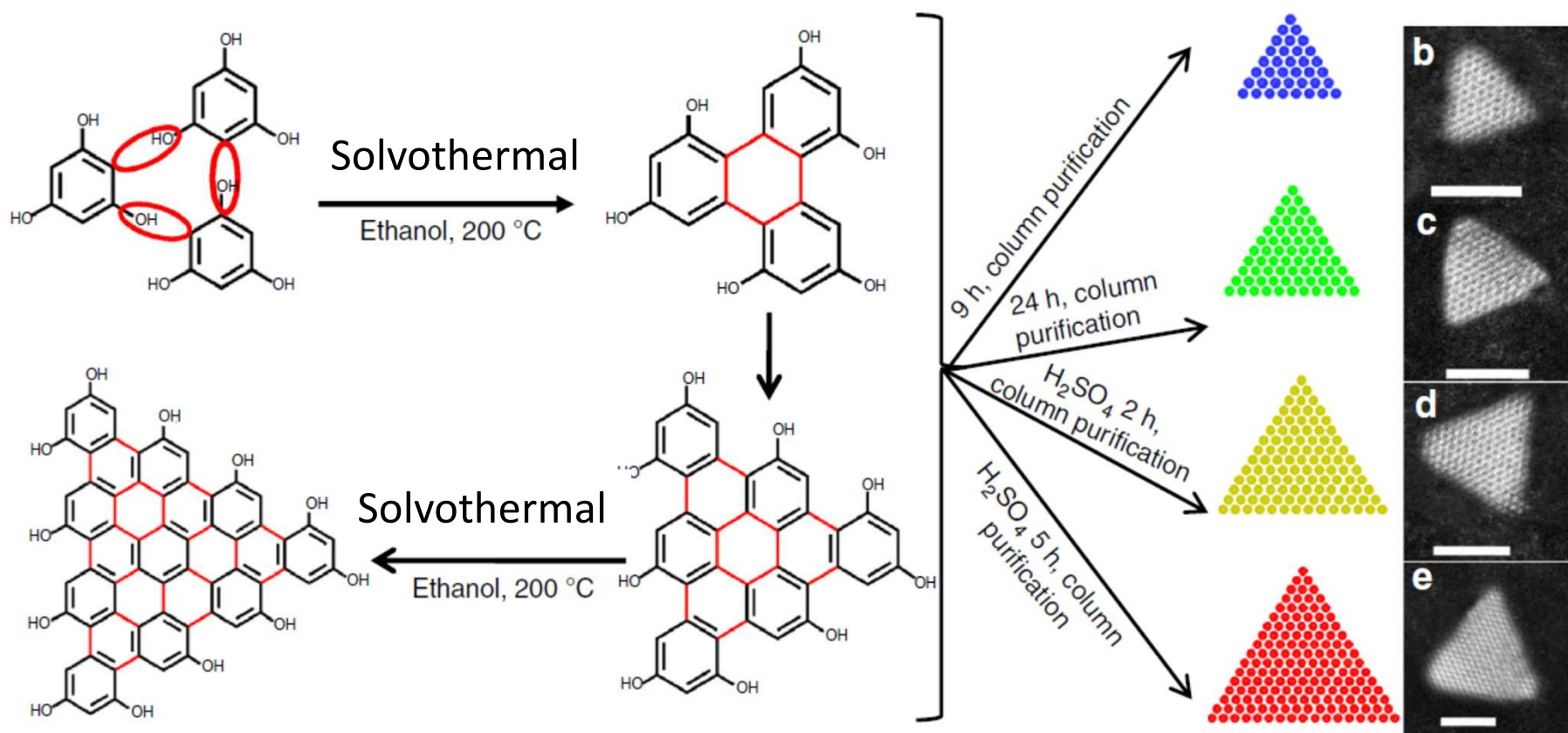
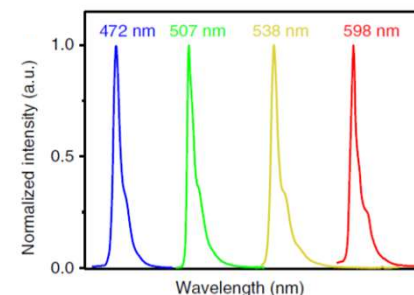
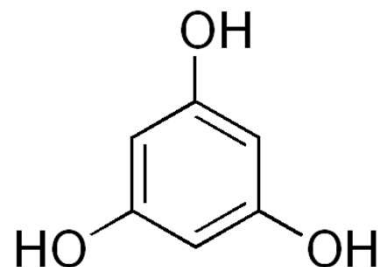
Mesoporous film



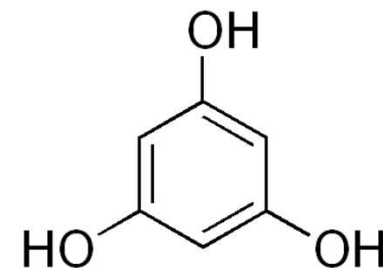
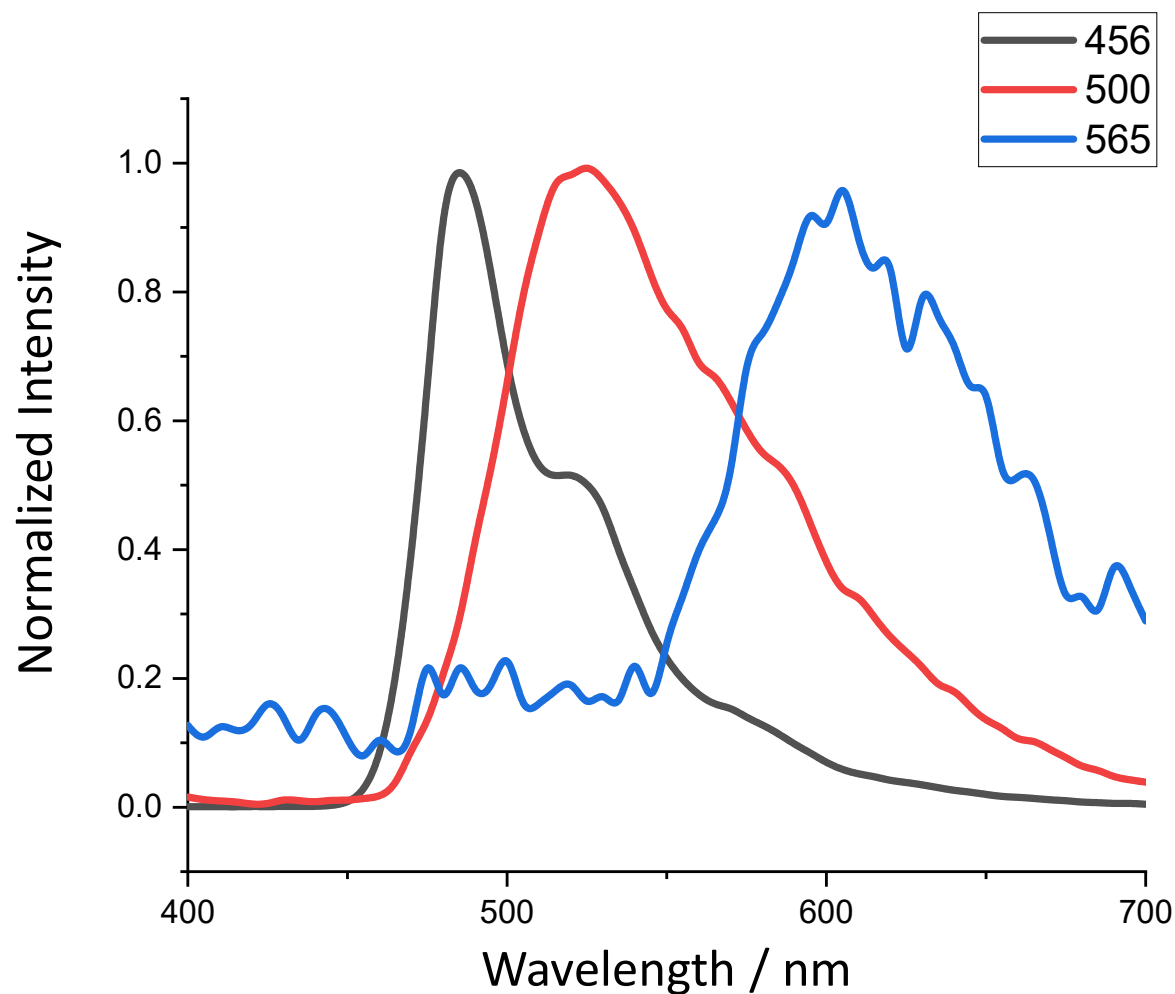
C-dots



1,3,5-Trihydroxybenzene Phloroglucinol



F. Yuan et al Nature Communications 2018, 9, 2249

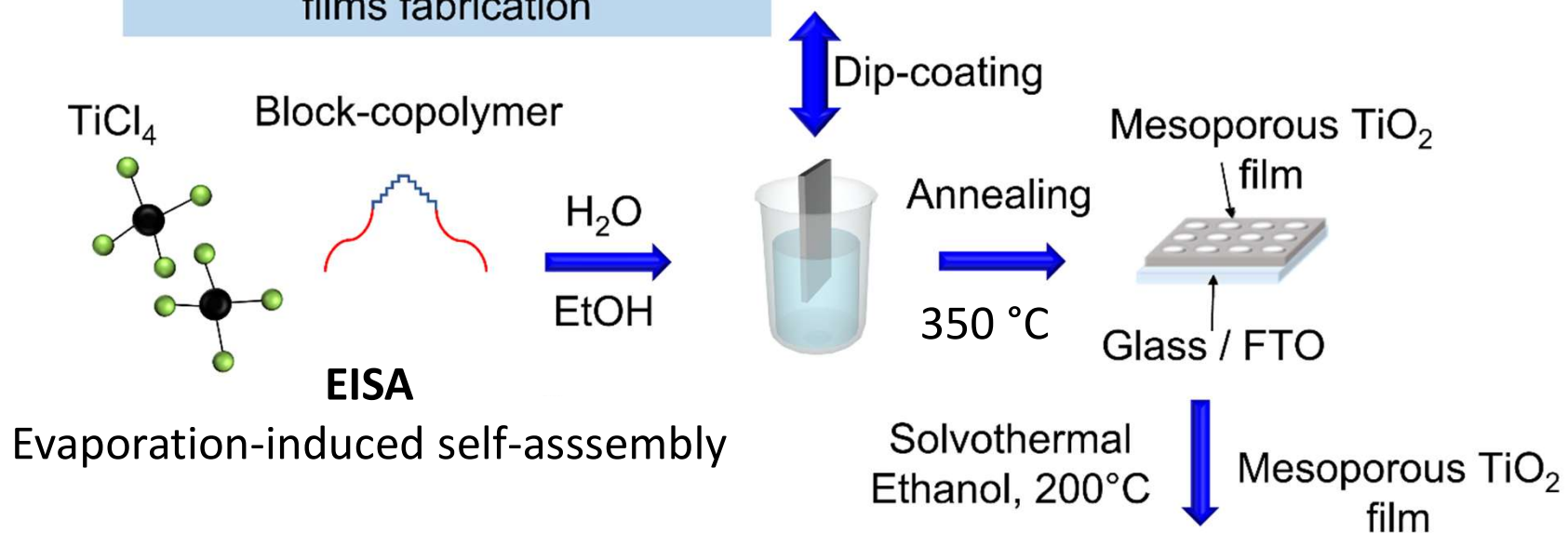


500 mg in 50 mL EtOH
3 h 200 °C

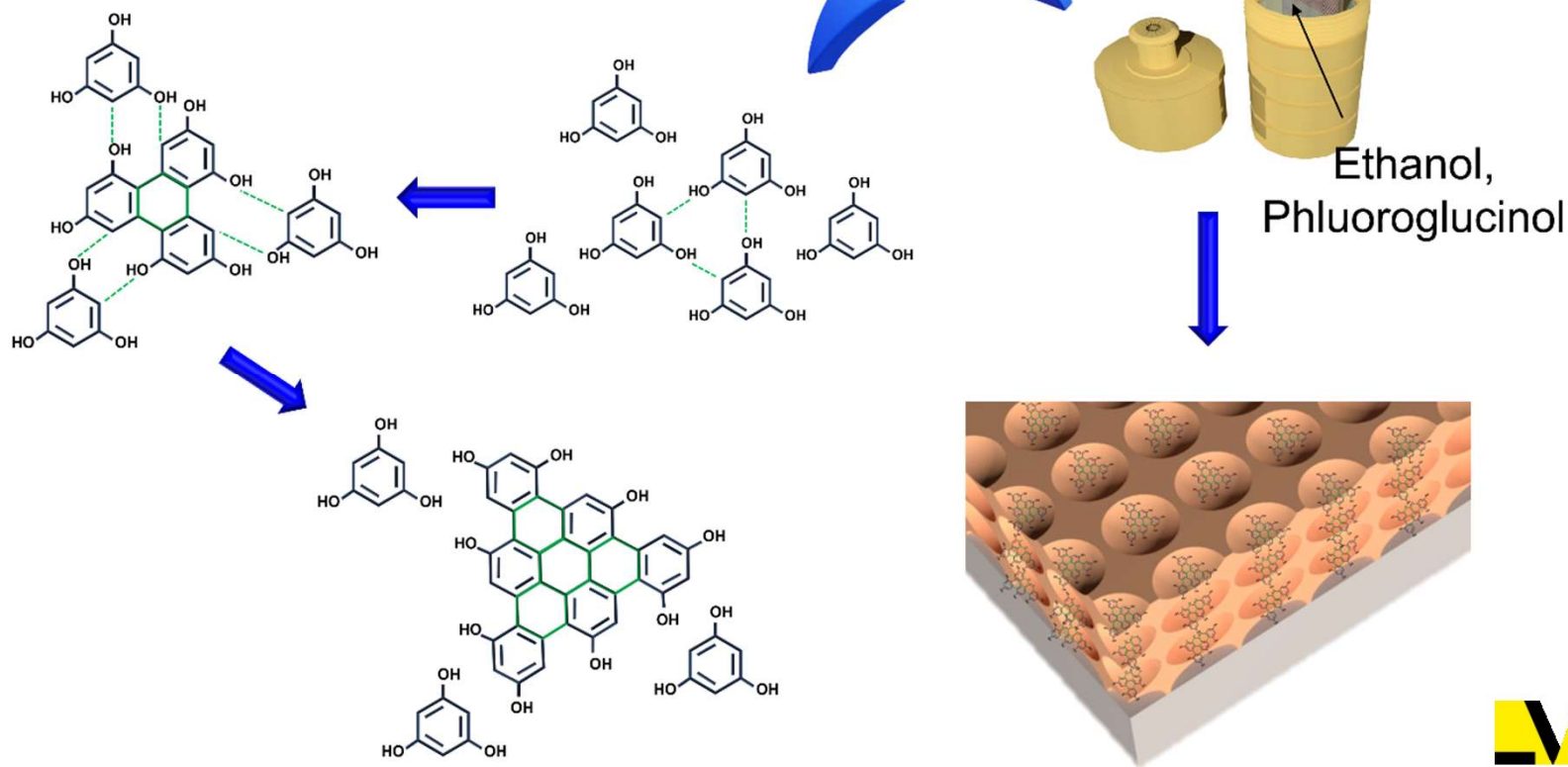
QY = 51%



Stage 1: Mesoporous TiO₂ thin films fabrication

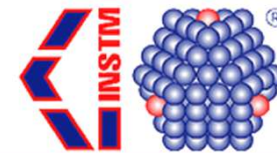


Stage 2: *In situ* solvothermal synthesis





Solvothermal synthesis

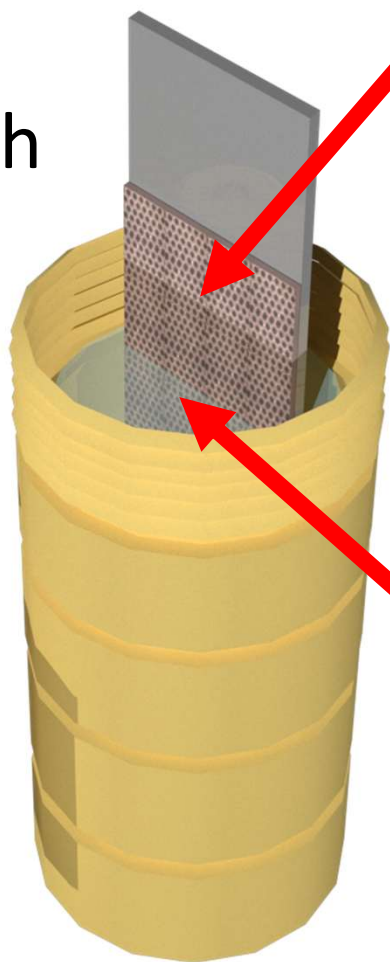


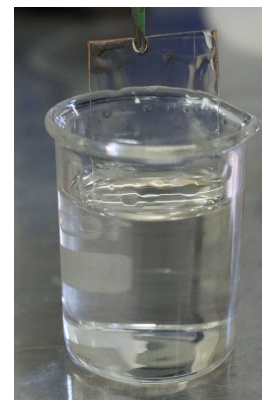
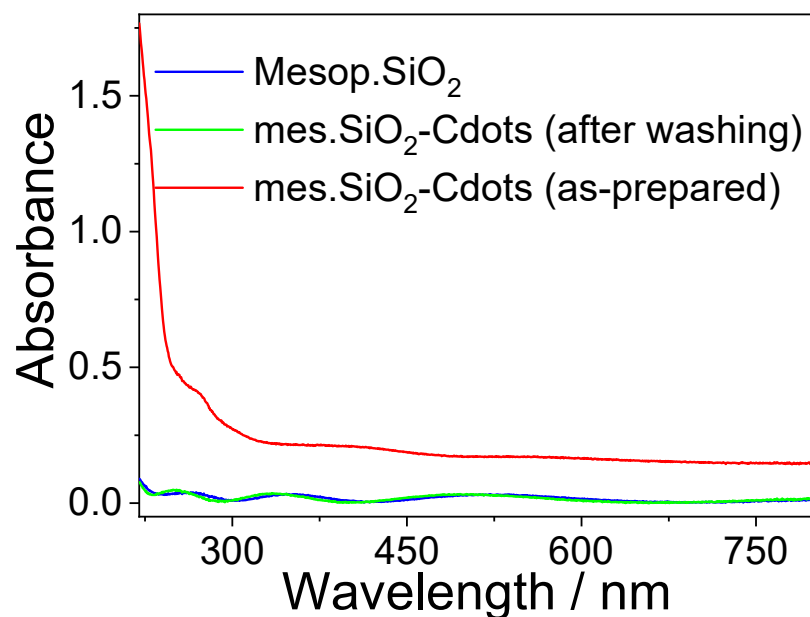
*Mesoporous TiO_2 film
and
Mesoporous SiO_2 film*

200° for 3h

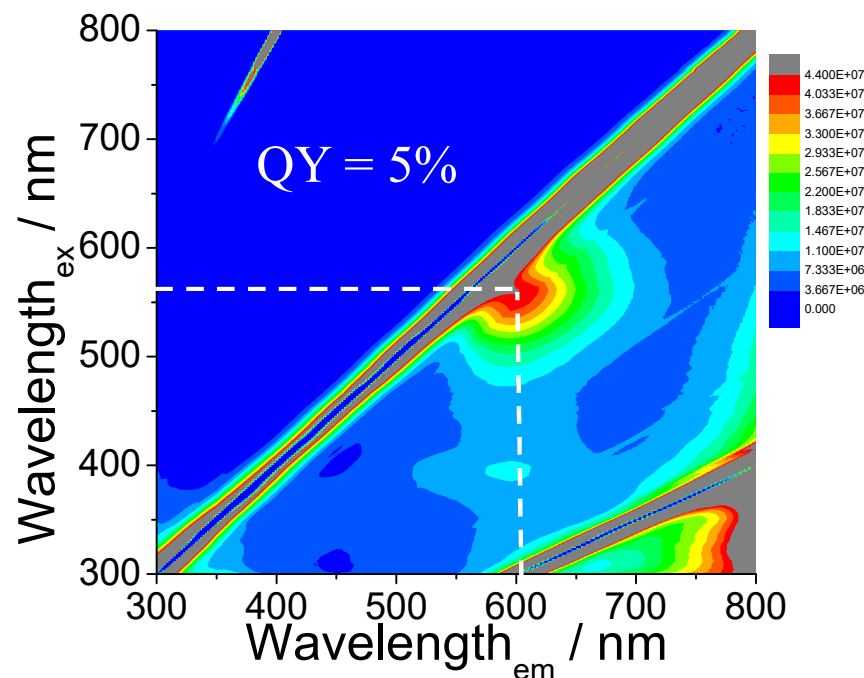
*Si, fused-silica and ITO substrates
F127-templated
Thickness ≈ 160 nm
Treated at 350°C for 3h*

*Ethanol,
Phloroglucinol*





The SiO_2 films are inhomogeneous and fluorescent (unwashed)!

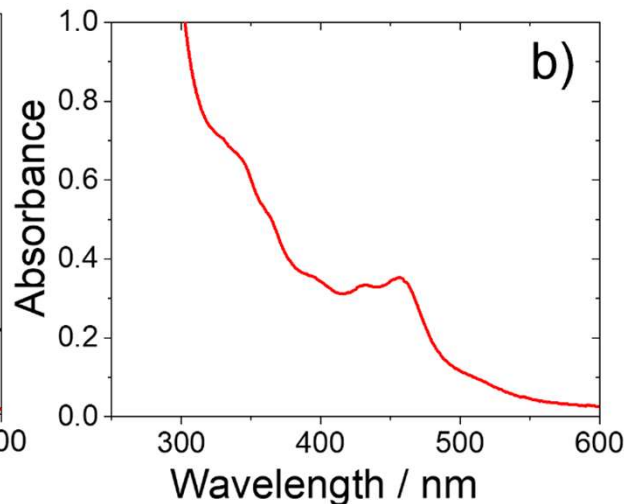
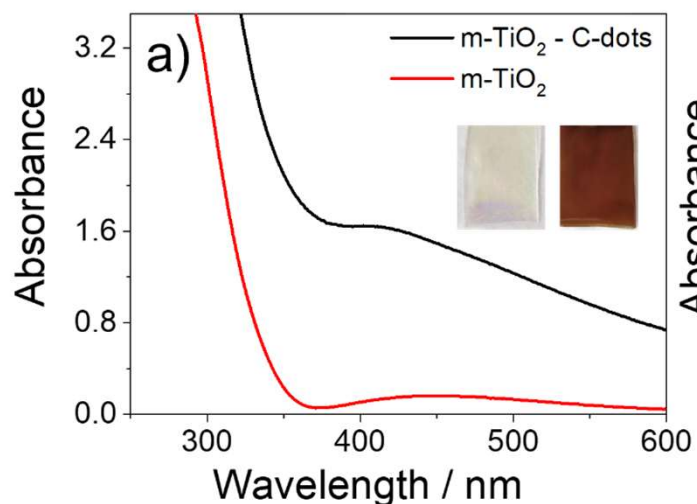
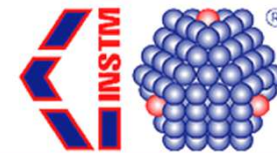


Exc 560 nm
Em 600 nm

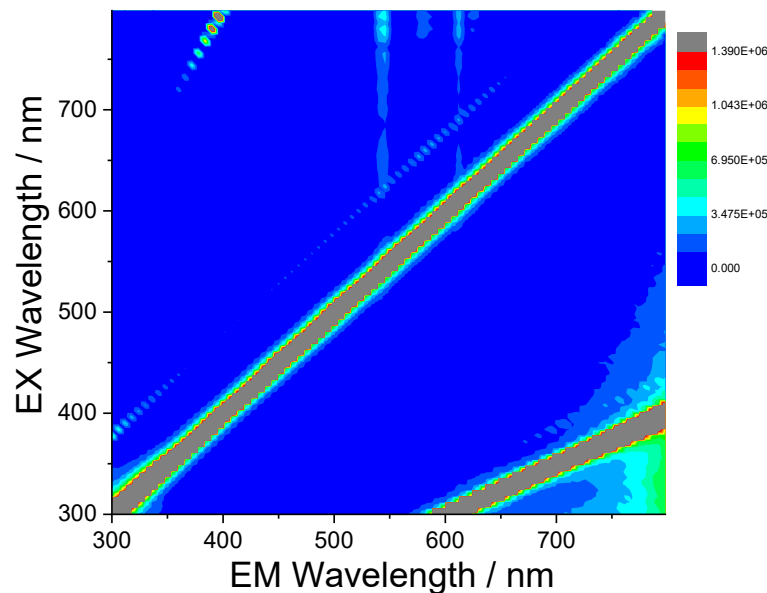


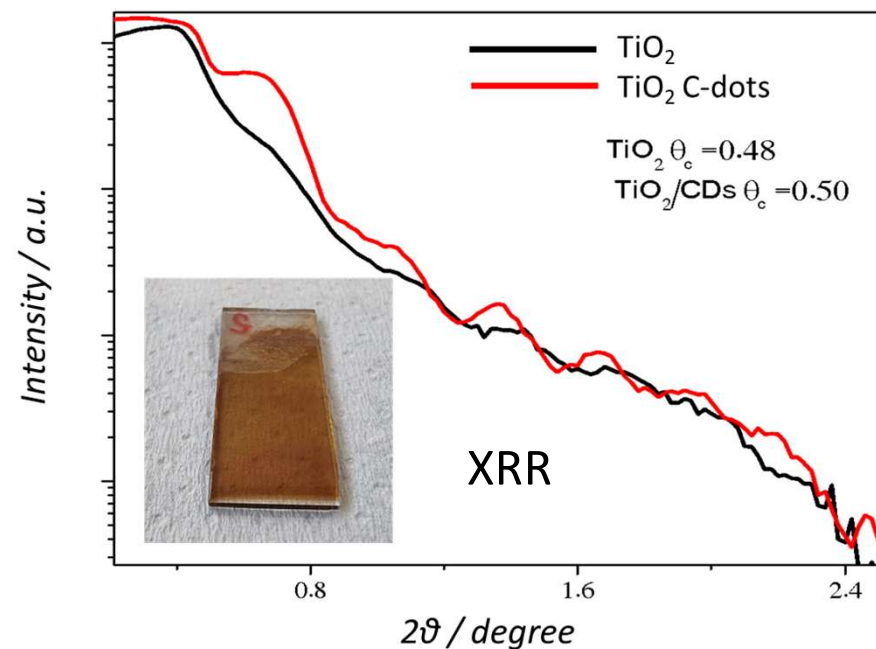
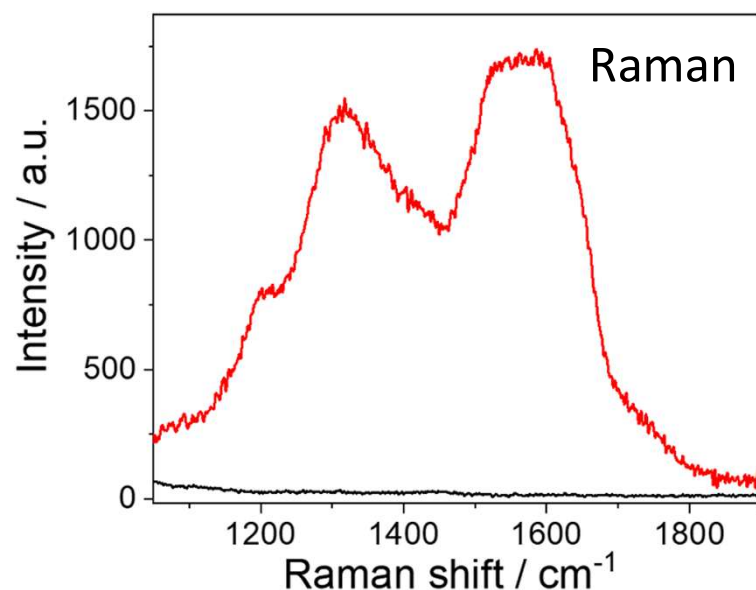


UV-Vis of the TiO_2 nanocomposite



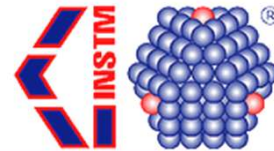
The TiO_2 nanocomposite films are homogenous, but the fluorescence is completely quenched



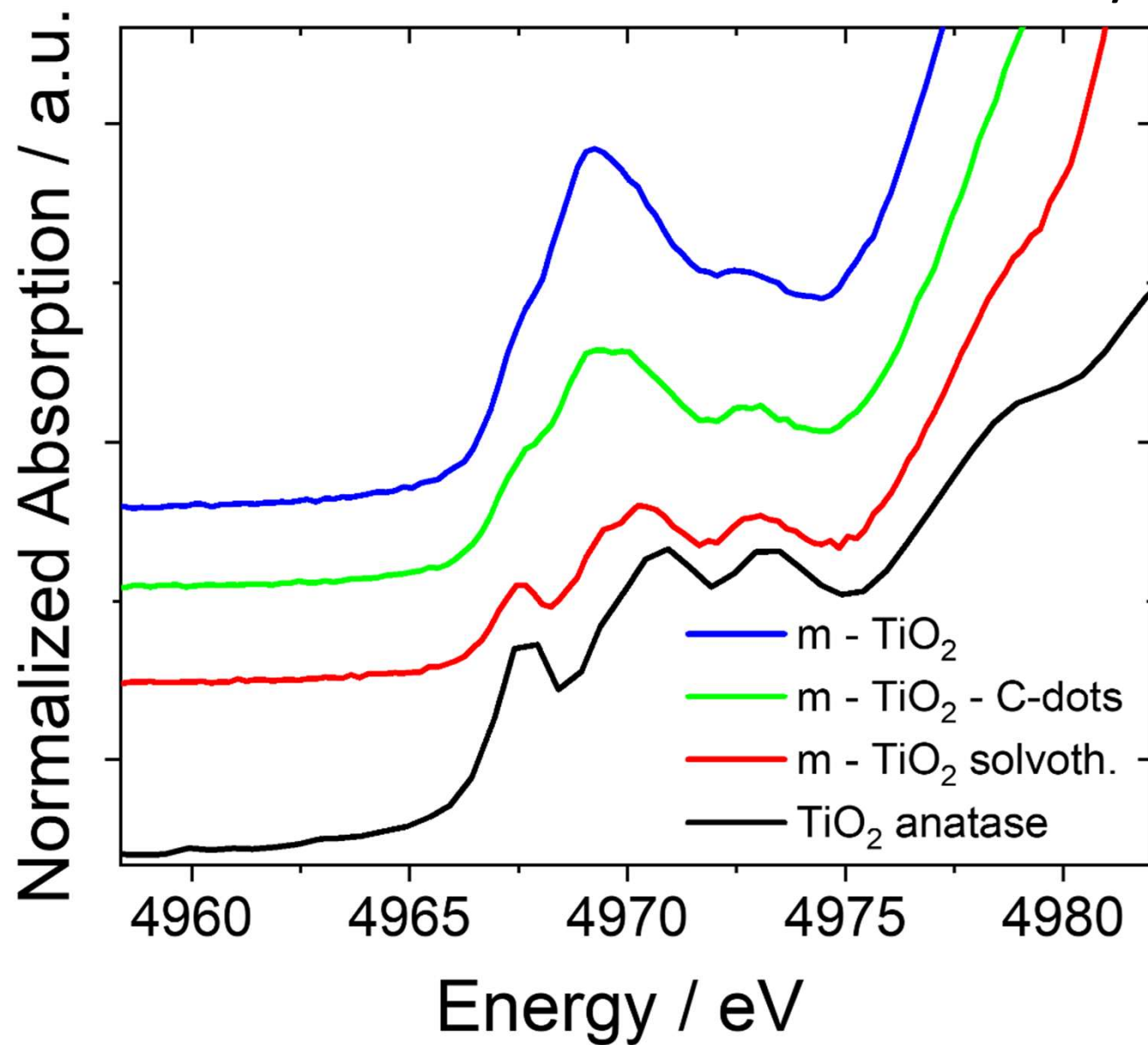


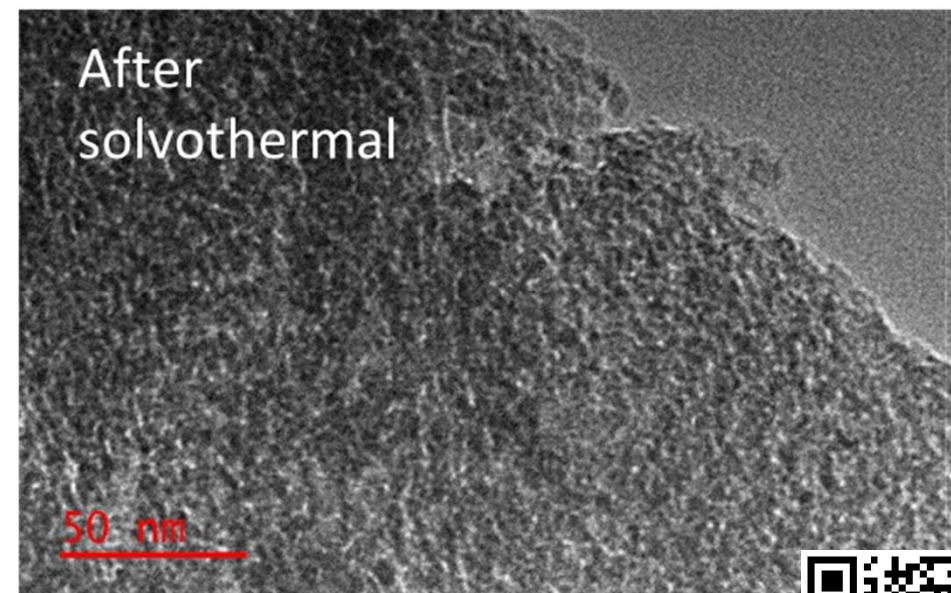
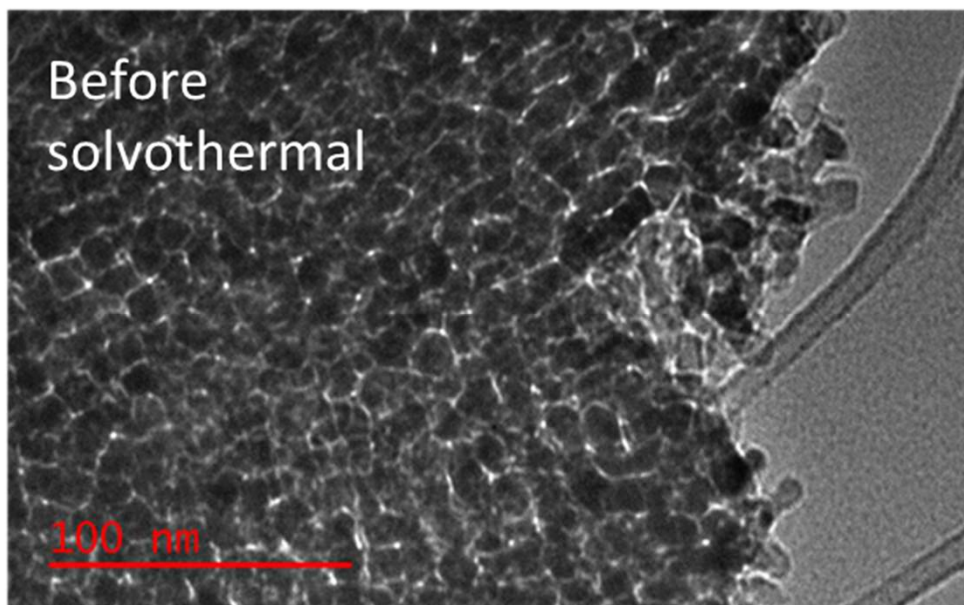
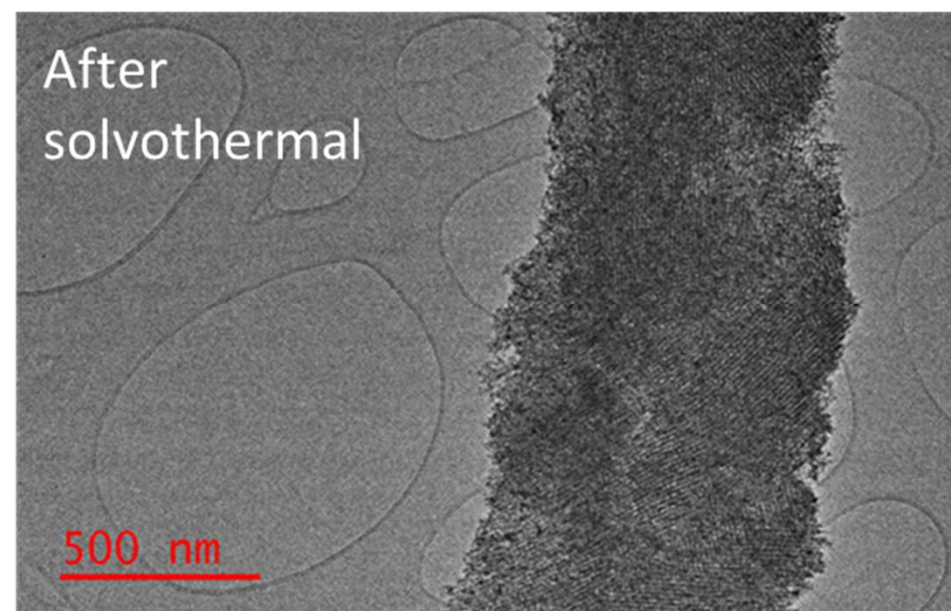
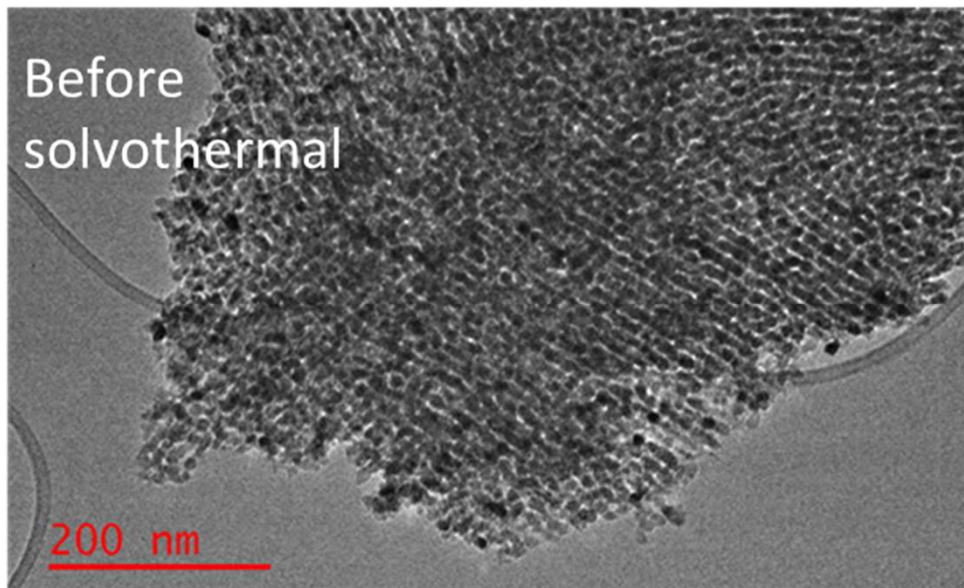
Ellipsometry	Before solvothermal	After solvothermal
Thickness / nm	161.4 ± 1.7	162.3 ± 2.0
Pore Volume / %	26 ± 2	12.0 ± 5





XAFS Beamline – Elettra synchrotron Facility



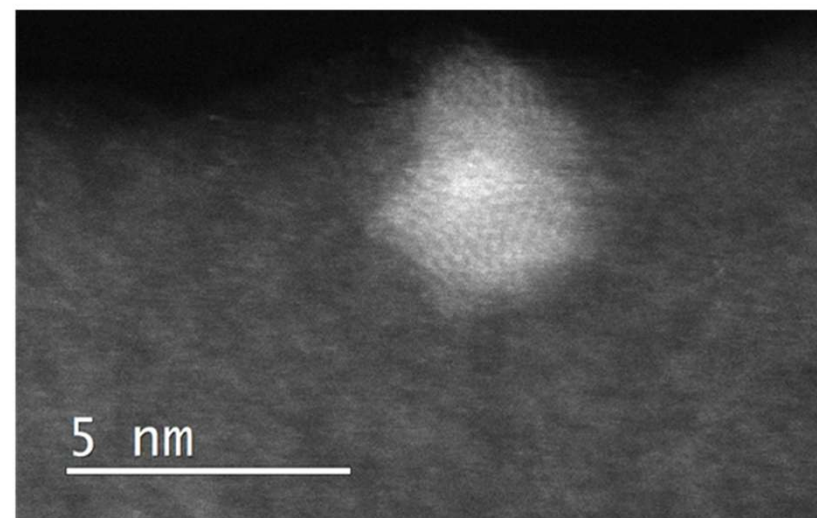
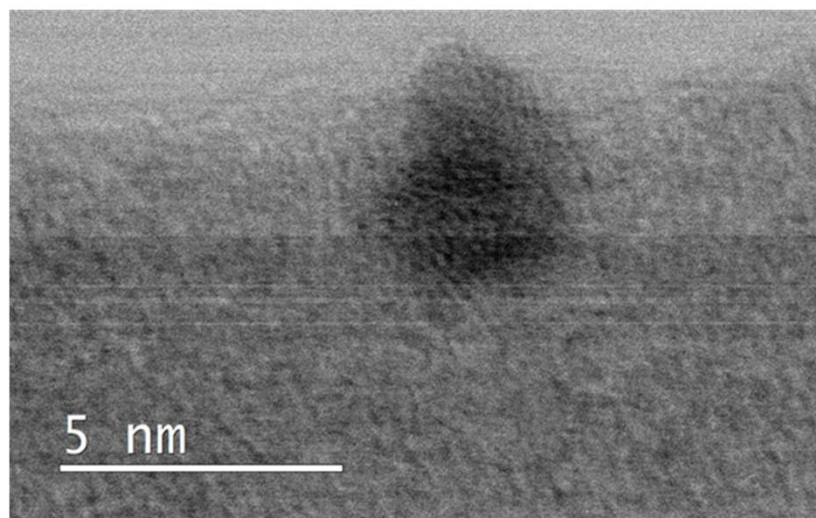
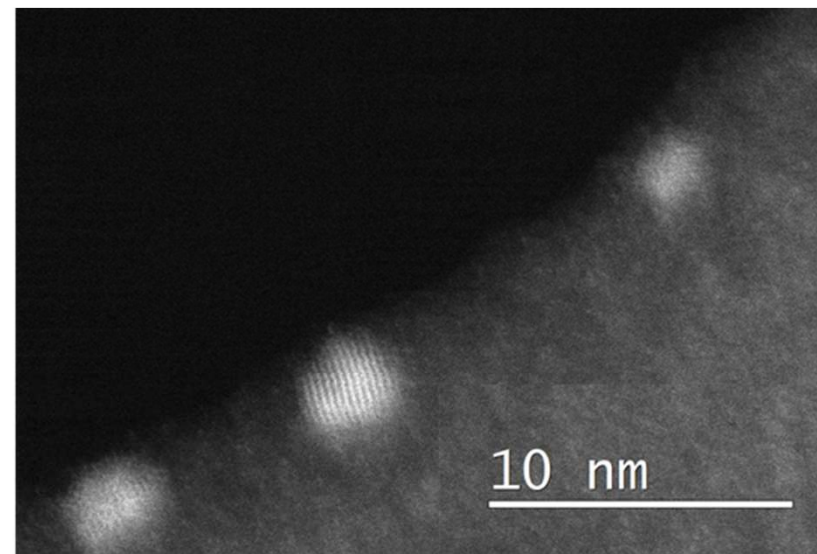
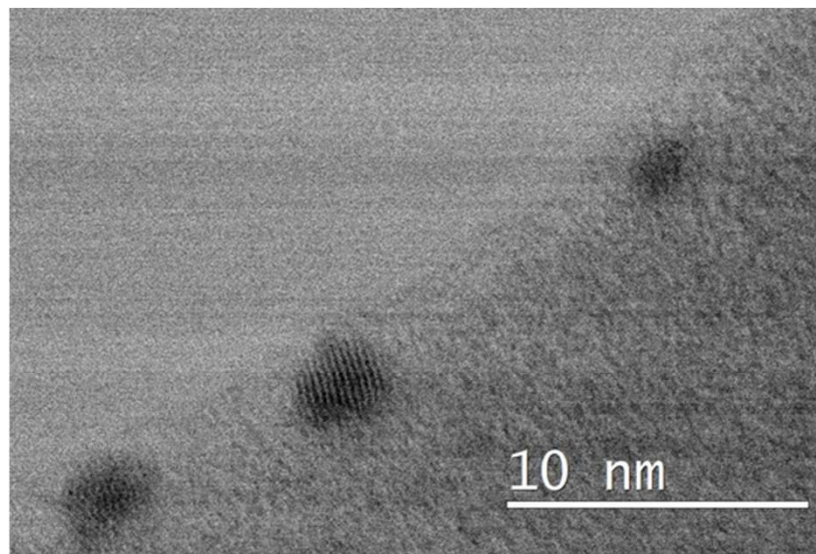
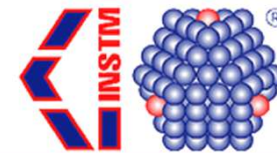


wall-to-wall distance $\sim 10.75 \pm 0.7$ nm

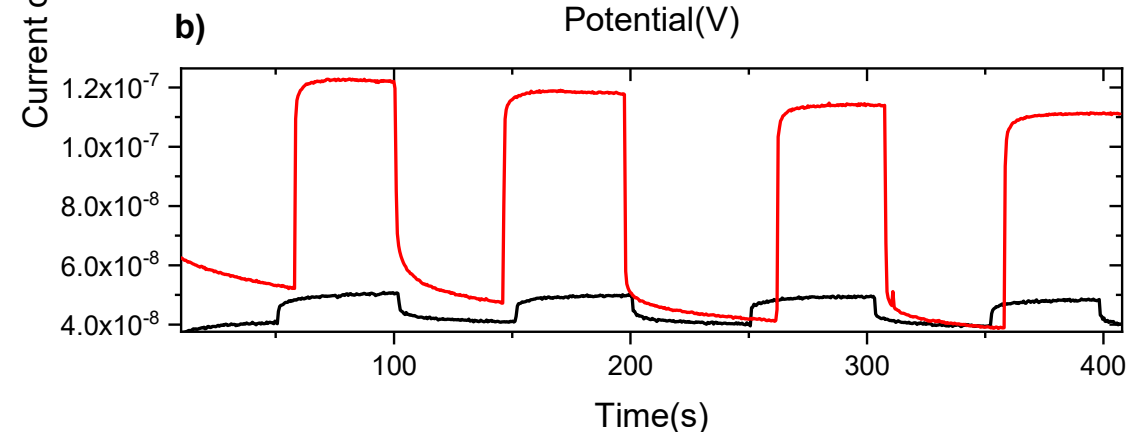
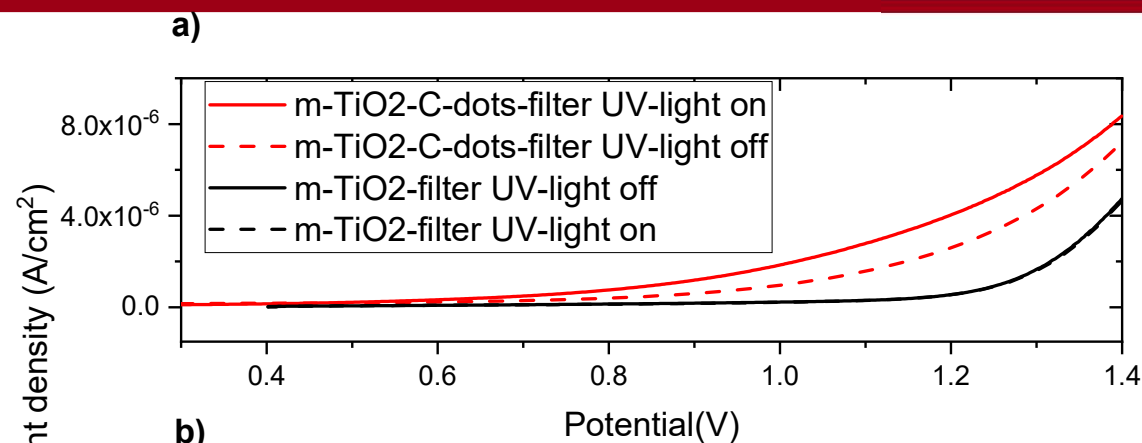
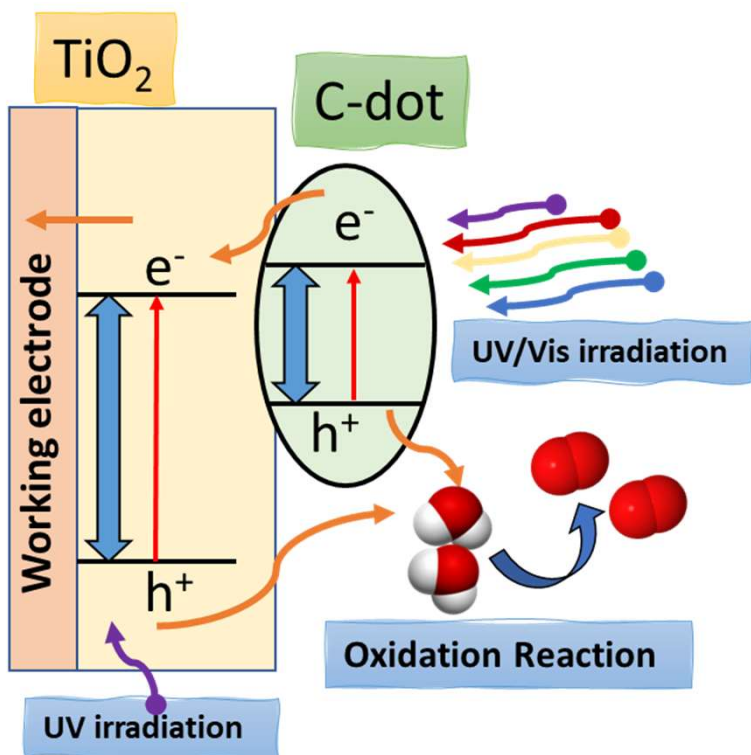
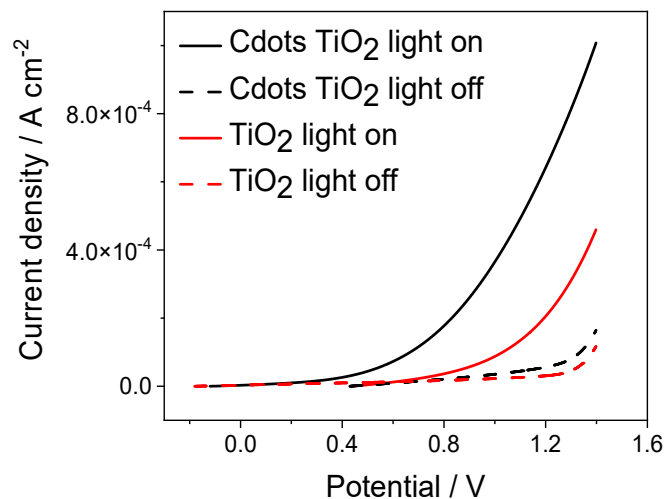




TEM - Phloroglucinol C-dots

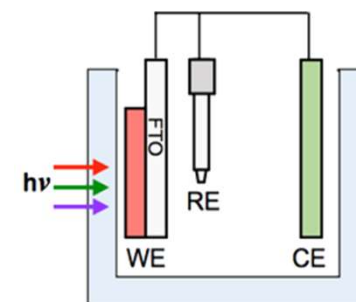


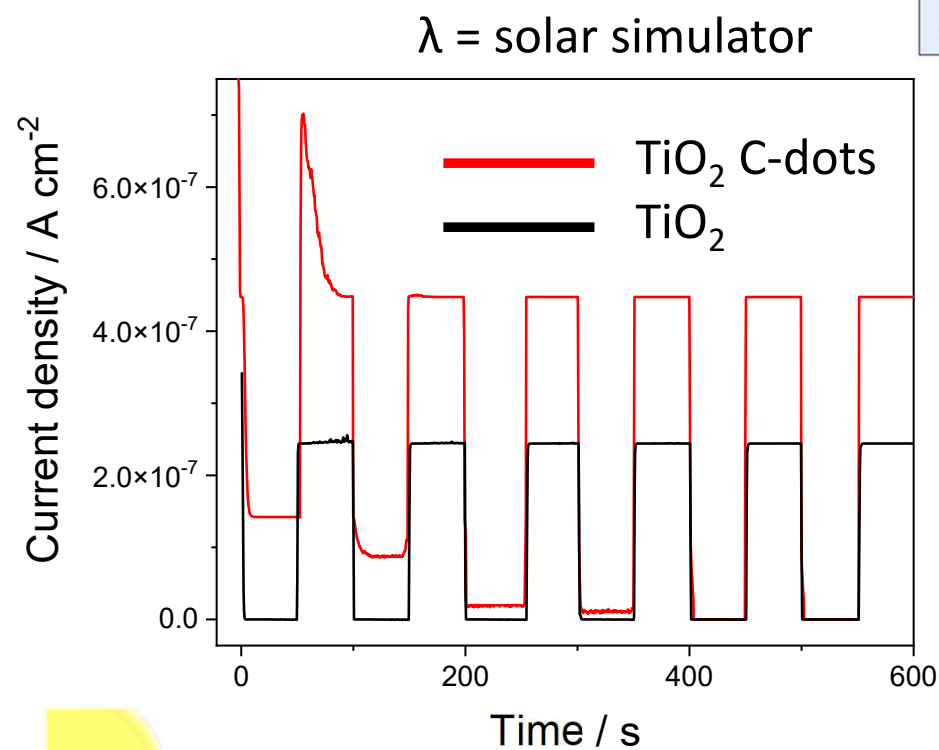
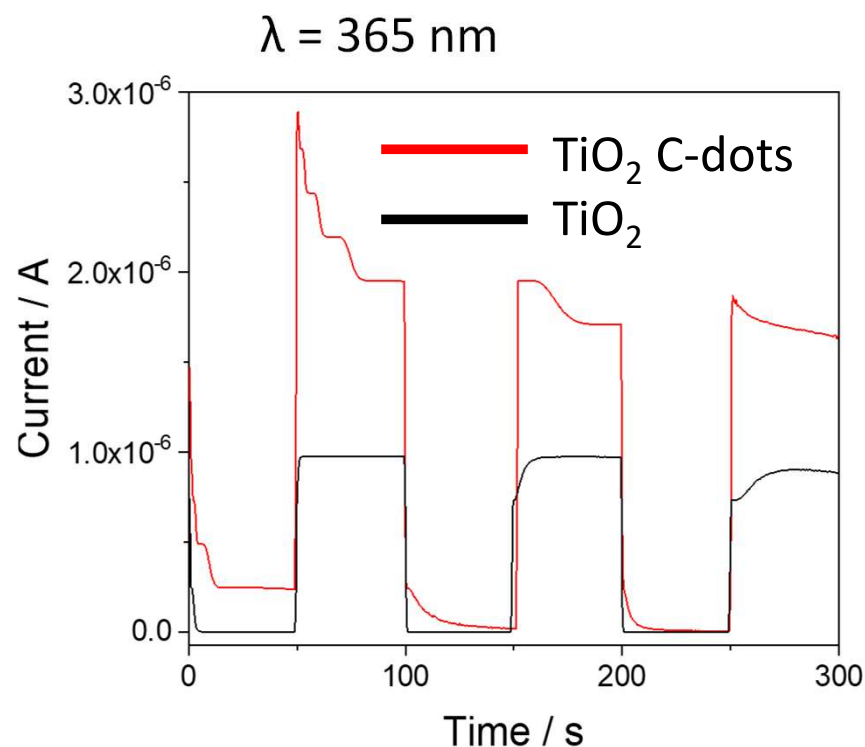
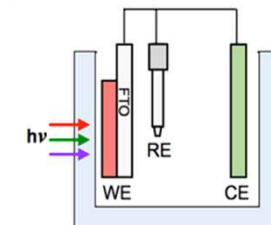
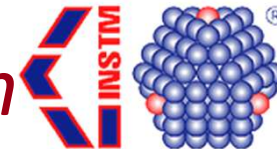
Cdots size 3 – 5 nm



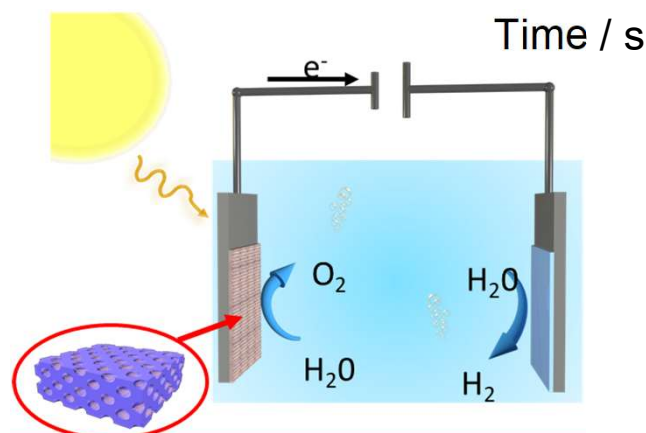
xenon lamp with UV filter

TiO₂ C-dots
Lower overpotential for OER
Higher current density



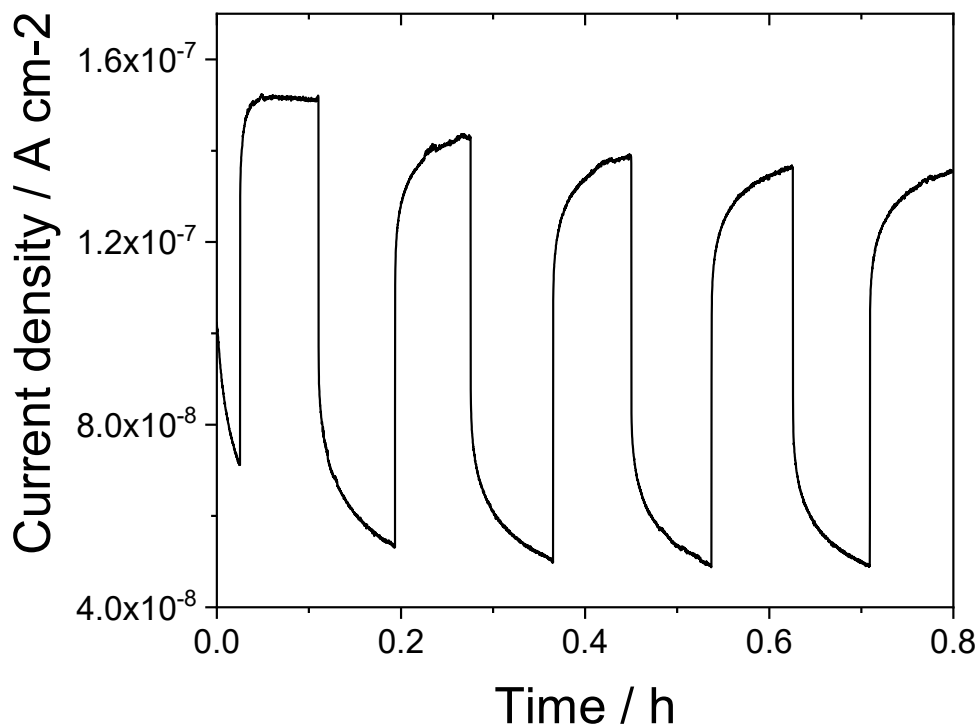


TiO_2 C-dots
Lower overpotential for OER
Higher current density





Carbon dots/mesoporous
titania thin film

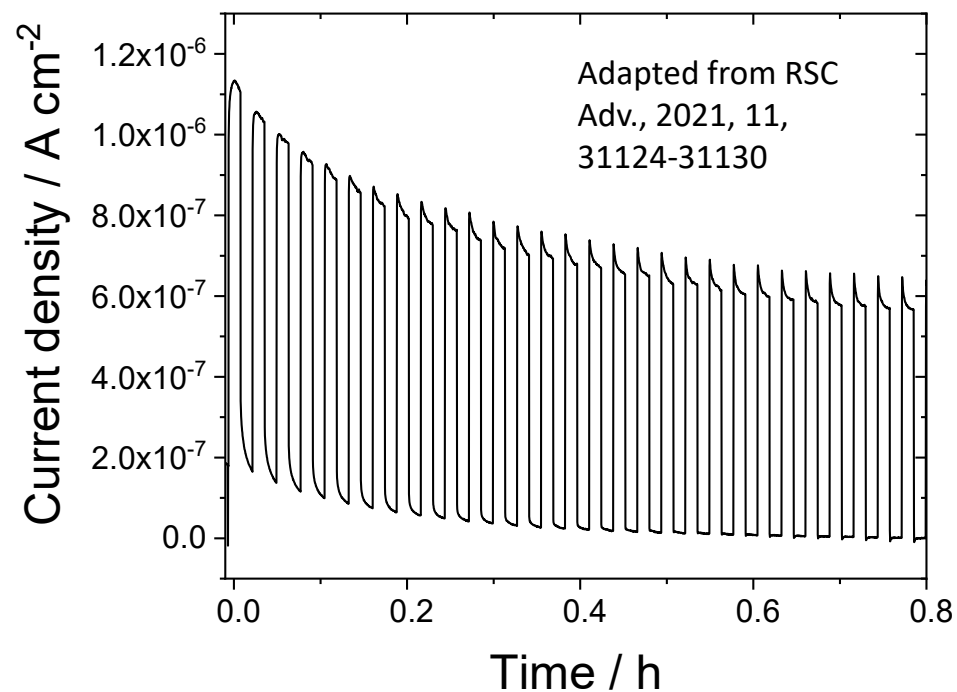


Stability for 50 min
Loss of current density < 10%

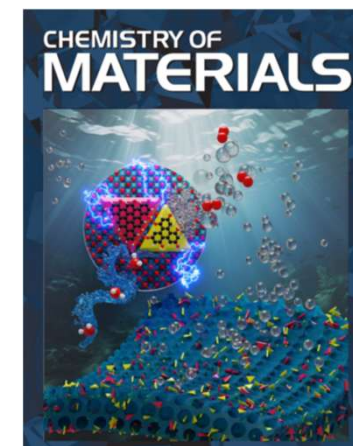
No C-dots leakage

Vs.

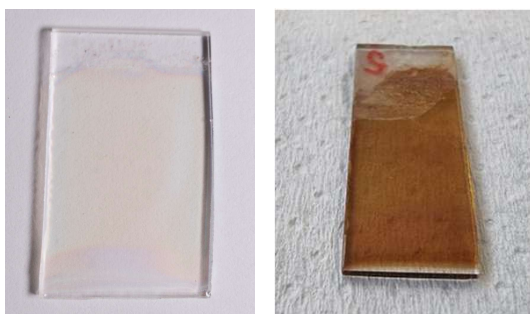
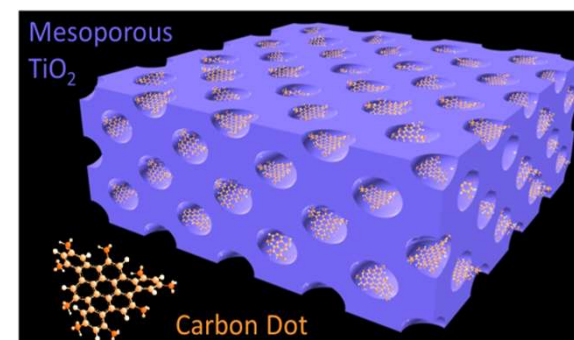
Zinc porphyrin/mesoporous
titania thin film



Stability for 50 min
Loss of current density > 40%

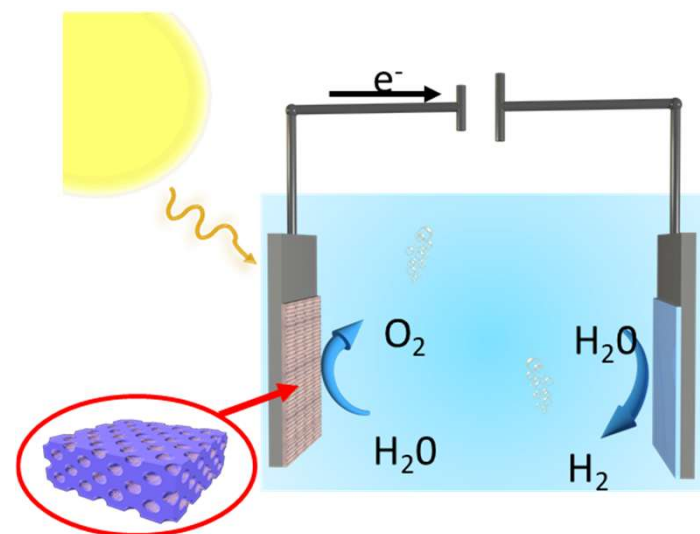


Mesoporous films embedding C-dots have been obtained by in situ growth of the nanoparticles during solvothermal synthesis



The interaction between Ti and C-dots allows preparing optical-quality nanocomposites which are not fluorescent

Photochemical characterization reveals a remarkable stability of the nanocomposites when used as electrode for OER

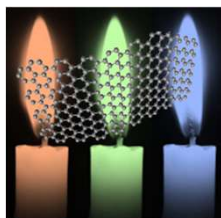




Thank you for your attention!



Fundings



Regione Autonoma
della Sardegna



Fondazione
di Sardegna

Acknowledgements

Luca Olivi (XAS beamline, Elettra)

Sebastiano Garroni (University of Sassari)

Miran Ceh (Jozef Stefan Institute)