



Surface modified TiO₂ photonic crystal photocatalysts by cobalt oxide nanoclusters

A. Toumazatou¹, E. Sakellis², N. Boukos², P. Falaras², V. Likodimos^{1*}

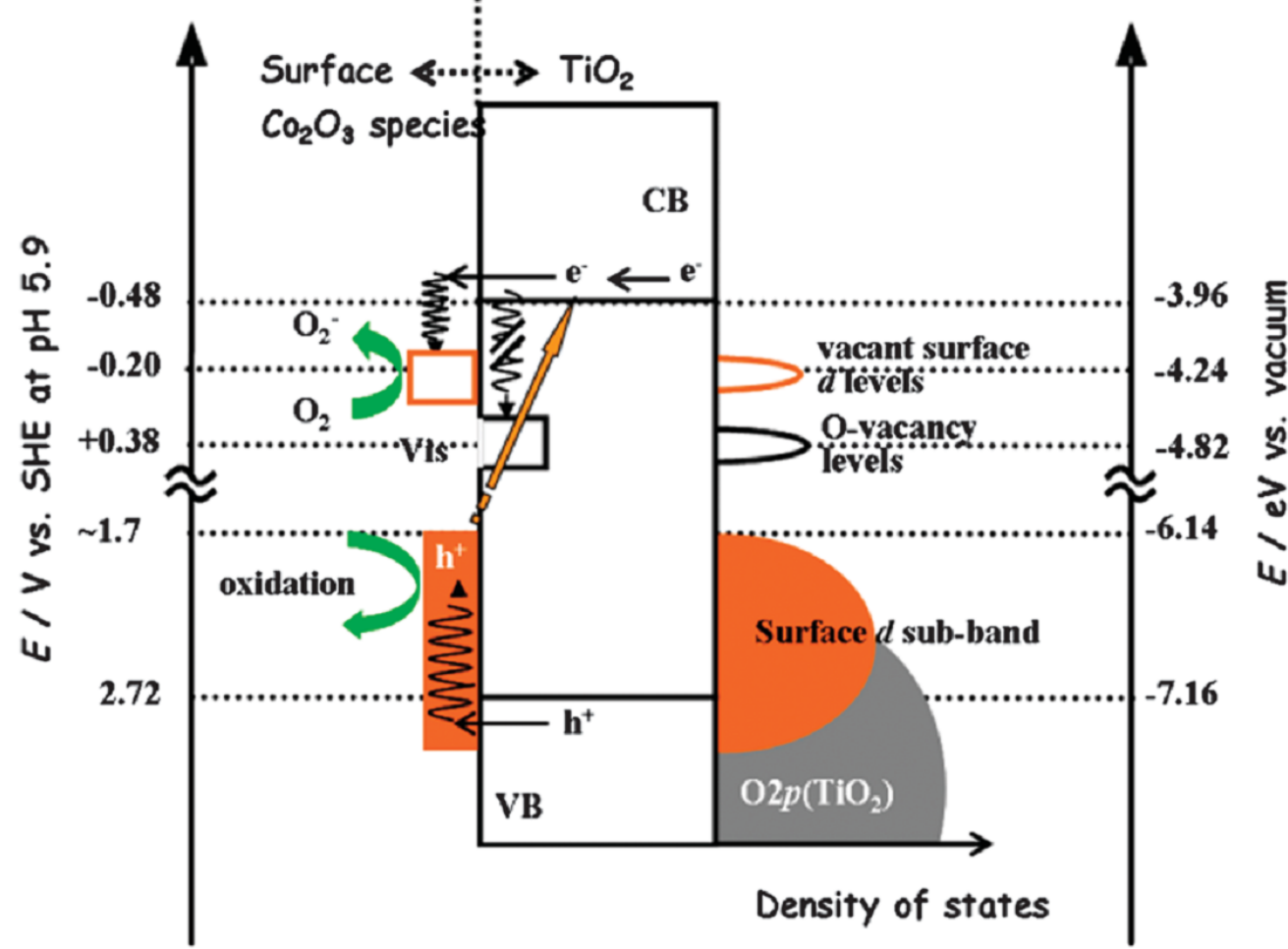
¹ Section of Solid State Physics, Department of Physics, National and Kapodistrian University of Athens, Panepistimiopolis, 15 784, Greece

² Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Patriarchou Grigoriou & Neapoleos 27 Str., 15310, Athens, Greece

* Corresponding author: vlkodimos@phys.uoa.gr

Photonic crystal assisted - visible light activated TiO₂ photocatalysis

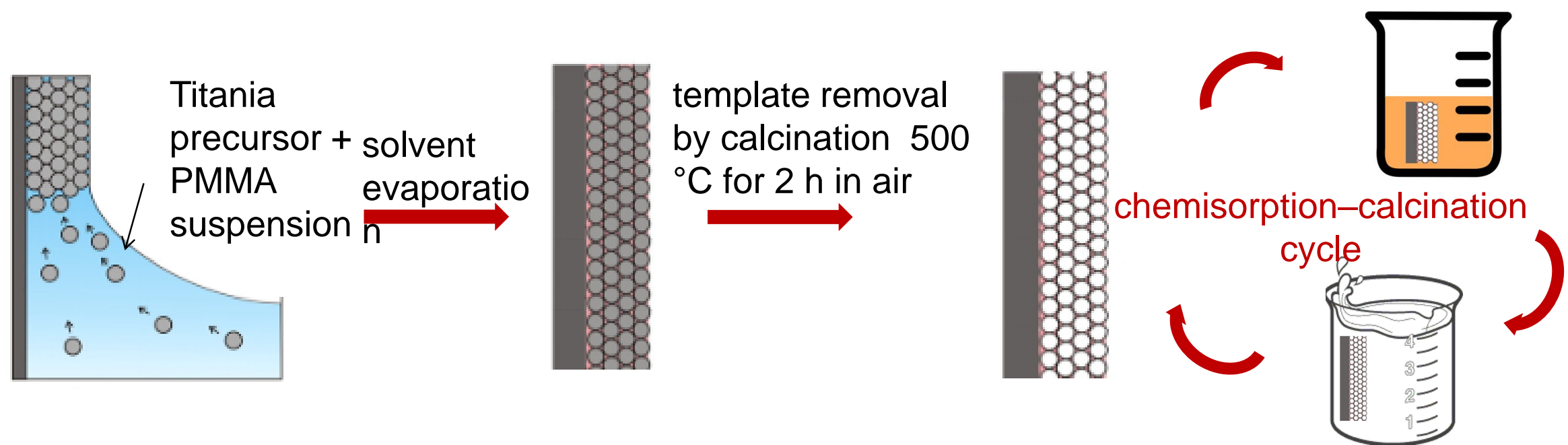
Photonic crystals have recently immersed as a distinct class of nanostructured materials of topical interest in the field of semiconductor photocatalysis [1]. In this work, surface modification of photonic band gap (PBG) engineered TiO₂ inverse opal films was performed by cobalt oxides. Molecular scale Co-oxide clusters were deposited on anatase TiO₂ photonic crystals by the chemisorption–calcination cycle (CCC) method, where visible light activation (VLA) can be achieved by raising titania's valence band without introducing impurity/vacancy states of low oxidation potential, while leaving intact the conduction band and O₂ reduction potential [2].



Jin et al. Phys. Chem. Chem. Phys. 15 (2013) 20313

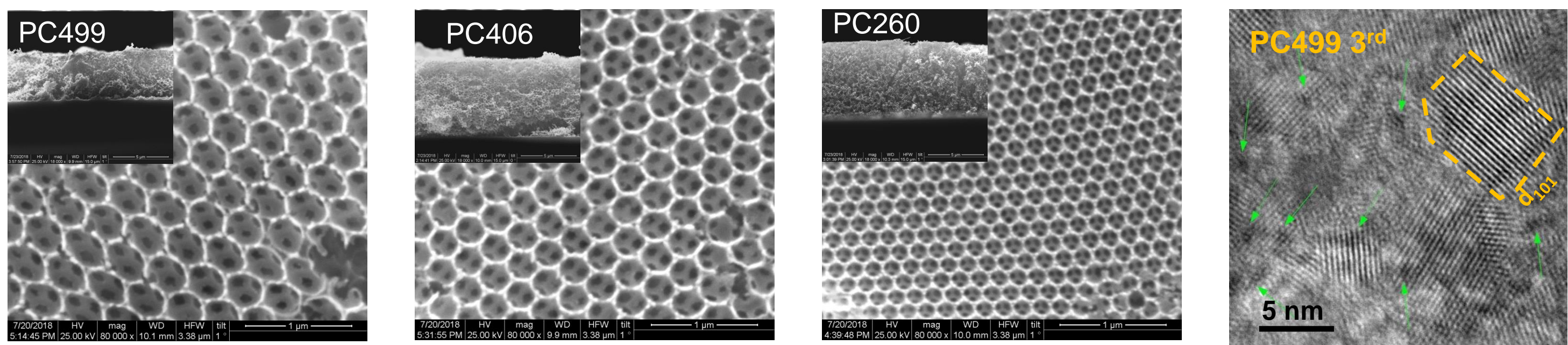
Inverse opal fabrication and CoO_x surface modification

Titania inverse opal films were fabricated by the convective evaporation-induced co-assembly of PMMA colloidal spheres with a hydrolyzed titania (TIBALDH) sol-gel precursor. Cleaned glass slides were vertically suspended in vials containing the colloidal suspension and the titania precursor and were kept at 55 °C until the solvent fully evaporated over 3 days. The composite films comprising the titania gel within the interstices of the close packed opal were then calcined at 500 °C, to remove the polymer matrix and crystallize TiO₂ in the inverse opal structure.



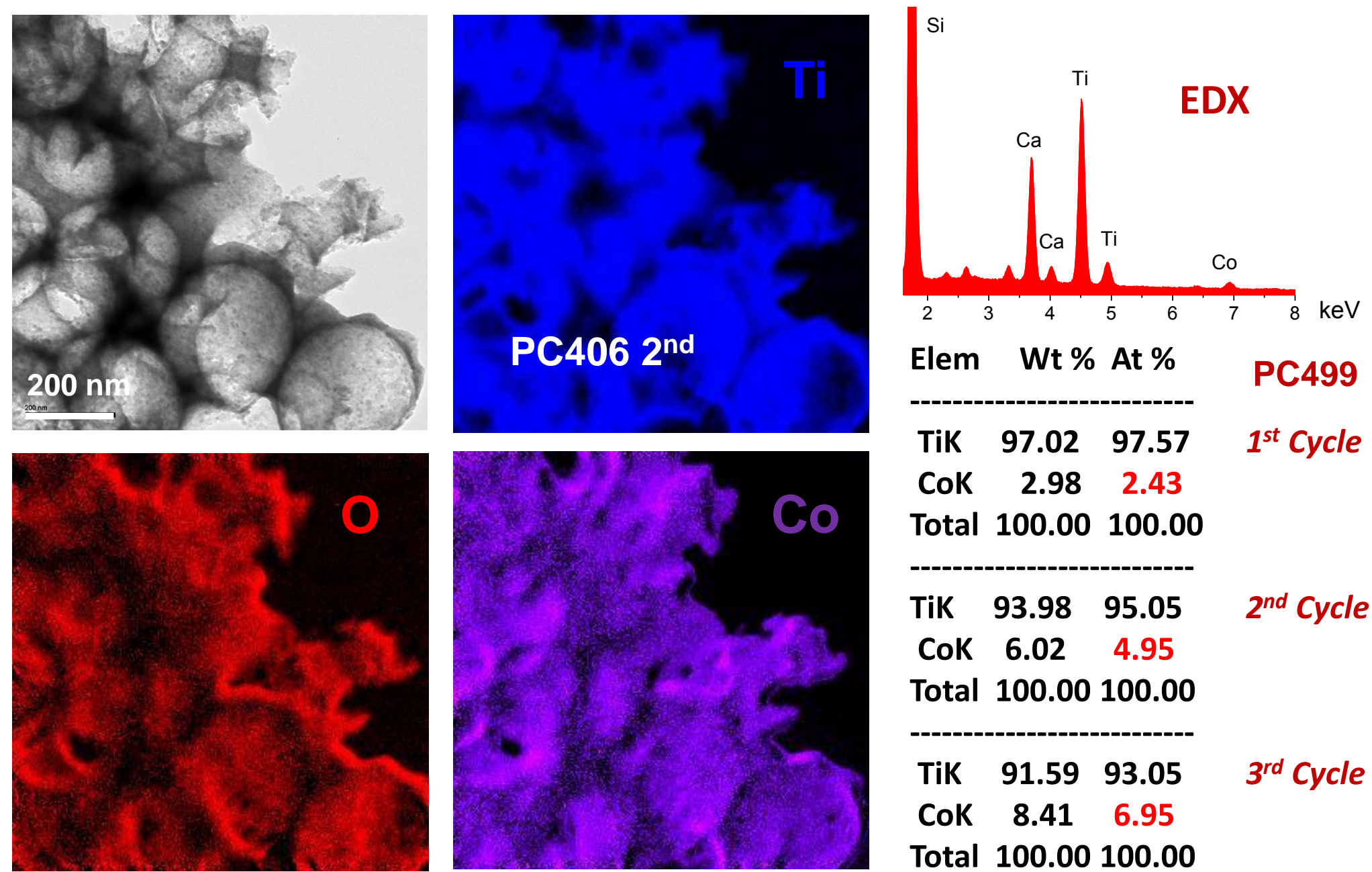
Co oxide modification was performed by immersing the TiO₂ inverse opals to 100 ml of 10⁻³ M Co(acac)₃(H₂O)₂ solution for 24 h. The films were repeatedly washed with the solvent for the physisorbed complexes to be removed and dried, followed by heating in air at 500 °C for 1 h.

Morphology and surface characteristics



SEM images disclose highly ordered 3D periodic structures corresponding to the (111) planes of an *fcc* lattice consisting of void spheres within the titania skeleton. The hexagonally arranged macropores were well interconnected through smaller pores 40-90 nm (dark circular areas). HR-TEM reveals that the skeleton consistw of ~10 nm nanoparticles with distinct *d*-spacings, the most common being 0.35 nm due to the (101) planes of the anatase TiO₂ phase, while even smaller dark inclusions of ~1 nm (arrows) indicate the formation of "molecular" nanoscale CoO_x.

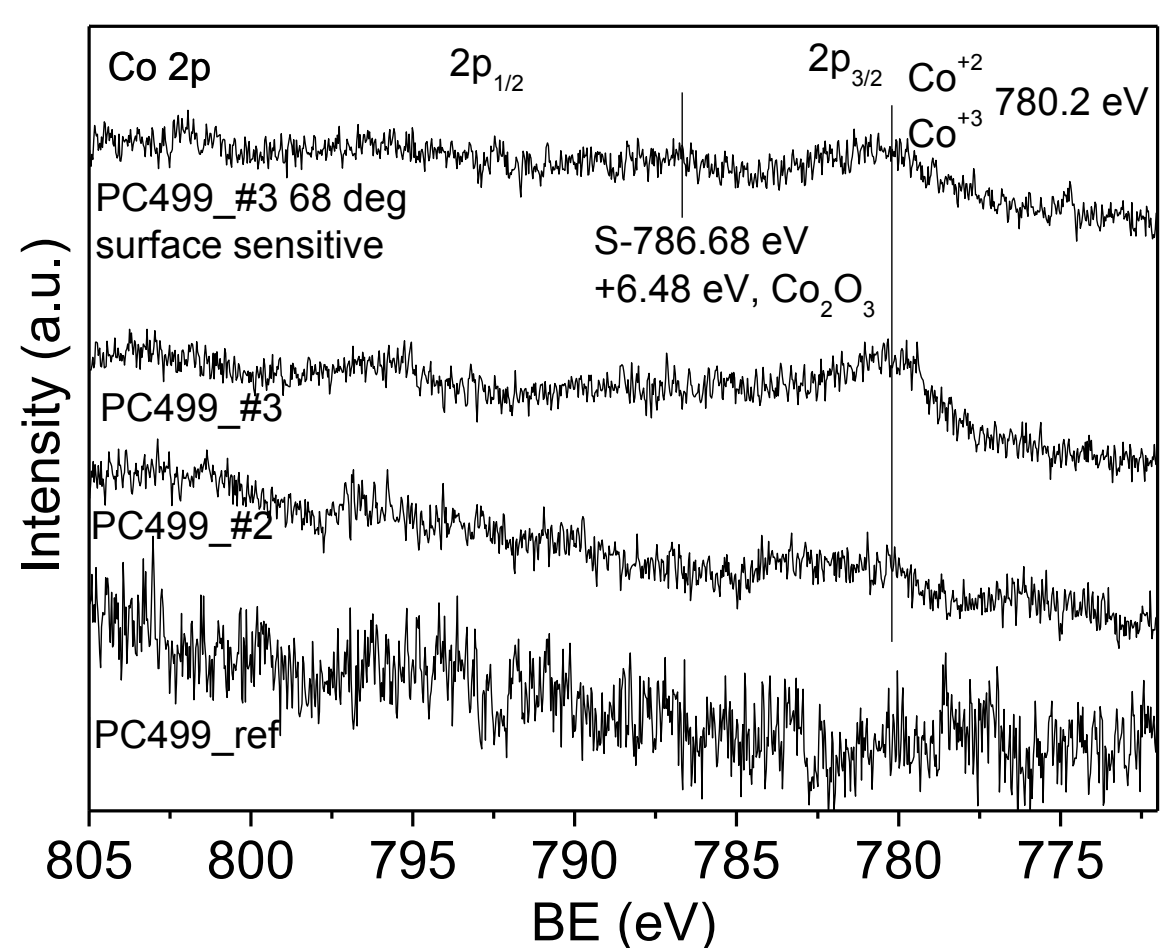
CoO_x surface modification EF-TEM, EDX



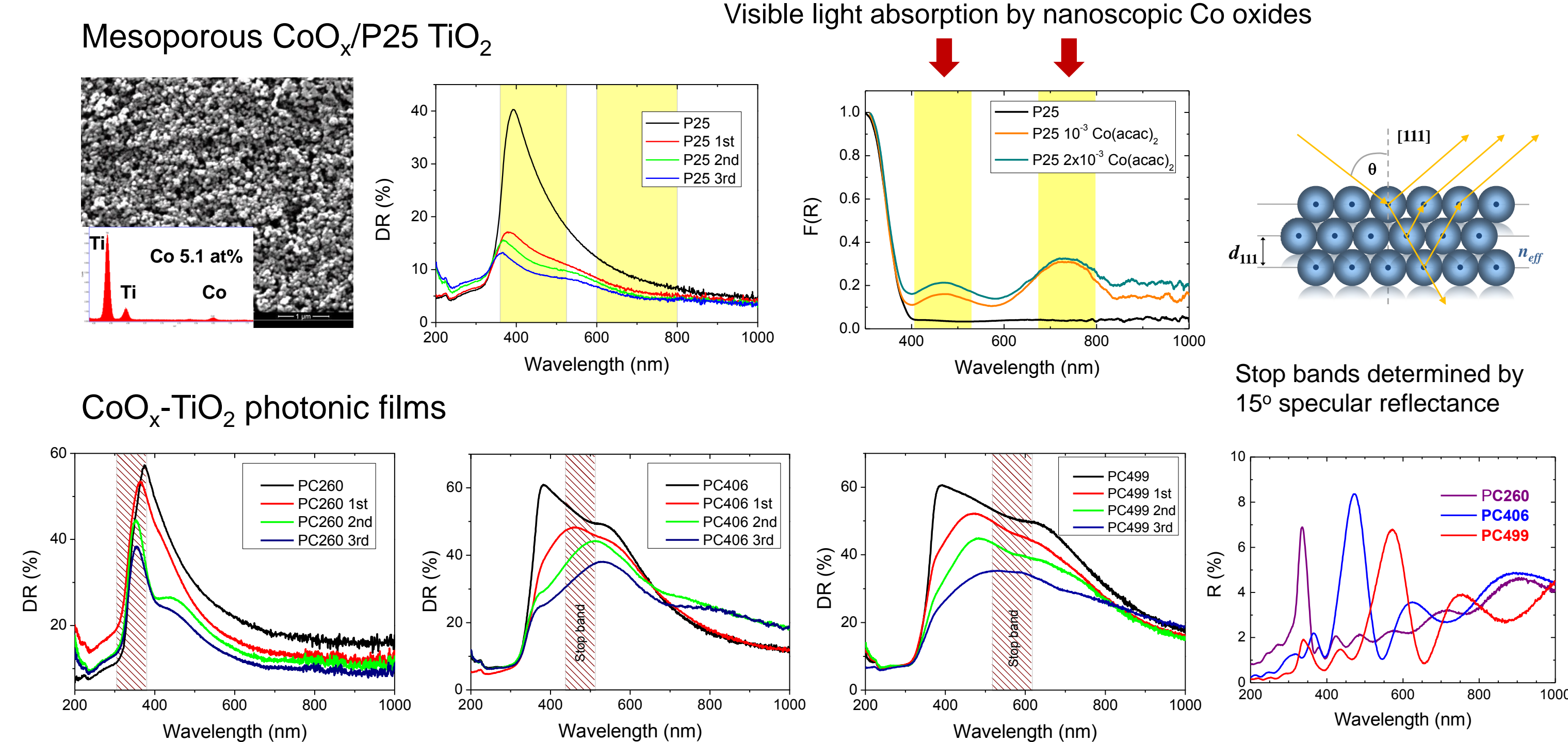
Energy-filtered EF-TEM mapping verified the uniform deposition of Co species on the modified photonic films, as shown by the Ti, O and Co elemental maps of the area corresponding to the bright field TEM image of PC406 after 2 cycles. EDX analysis shows the controlled loading of Co-oxides that increases with the number of CC cycles.

XPS spectroscopy

The Co ions oxidation state was investigated by XPS measurements even at 68° incidence. The main Co2p_{3/2} peak is located at 780.2 eV, which is indicative of both Co⁺² and Co⁺³ ions (CoO, Co₂O₃, Co₃O₄). Nevertheless, a satellite S peak seems to be present at +6.48 eV from the main Co 2p_{3/2} peak, indicating the formation of Co₂O₃ species (6.3 eV), rather than CoO species where the S peak should have come at +7.9 eV.



Optical properties - PBG engineering vs Visible light activation



Sample	D _{PMMA} ^a (nm)	D ^b (nm)	λ _{exp} (15°) ^c (air)	n _{eff} (air)	1-f	n _{eff} (H ₂ O)	λ _{th} (0°) ^d (air)	λ _{th} (0°) ^d (H ₂ O)
PC260	260	150	335	1,39	0,170	1,60	341	393
PC406	406	250	472	1,18	0,073	1,45	484	594
PC499	499	310	572	1,16	0,062	1,44	587	727

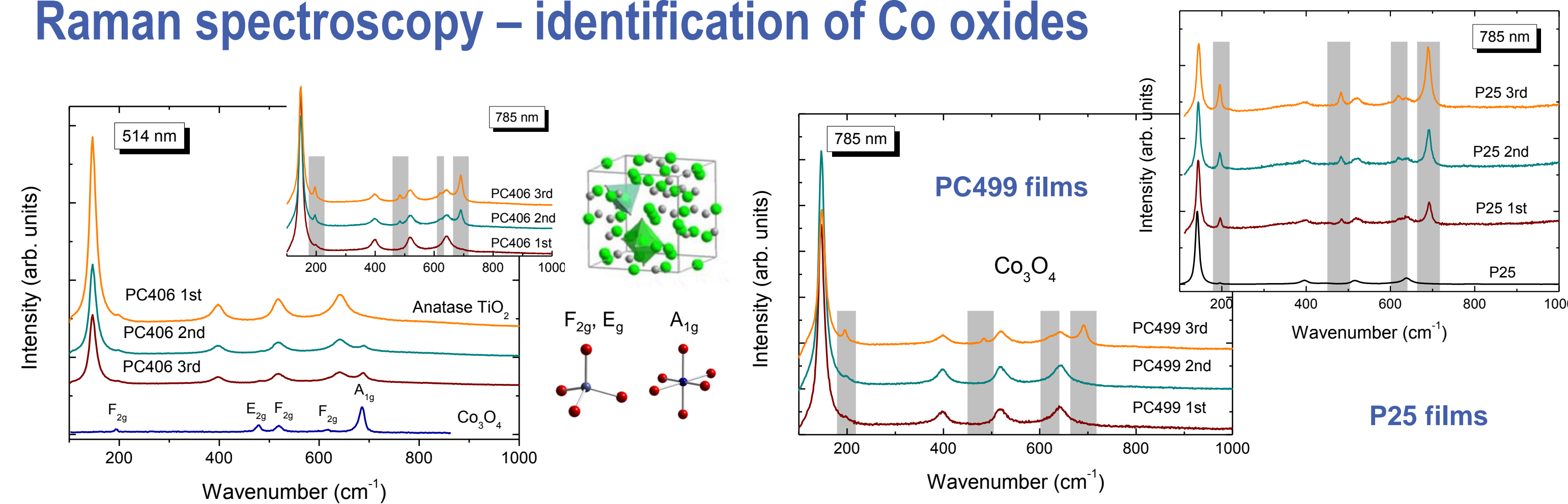
^a D_{PMMA} = diameter of colloidal PMMA spheres.

^b D = macropore diameter of the TiO₂ inverse opal films determined by SEM.

^c λ_{exp} = stop band wavelength determined from the 15° incidence specular spectra.

^d λ_{th} = stop band wavelength predicted from modified Bragg law $\lambda = 2d_{111}\sqrt{n_{eff}^2 \sin^2 \theta}$, where $n_{eff}^2 = n_{sphere}^2 f + n_{solid}^2 (1-f)$ for $\theta=0^\circ$ incidence angle and $d_{111} = \sqrt{2/3}D$ the spacing of the (111) crystal planes.

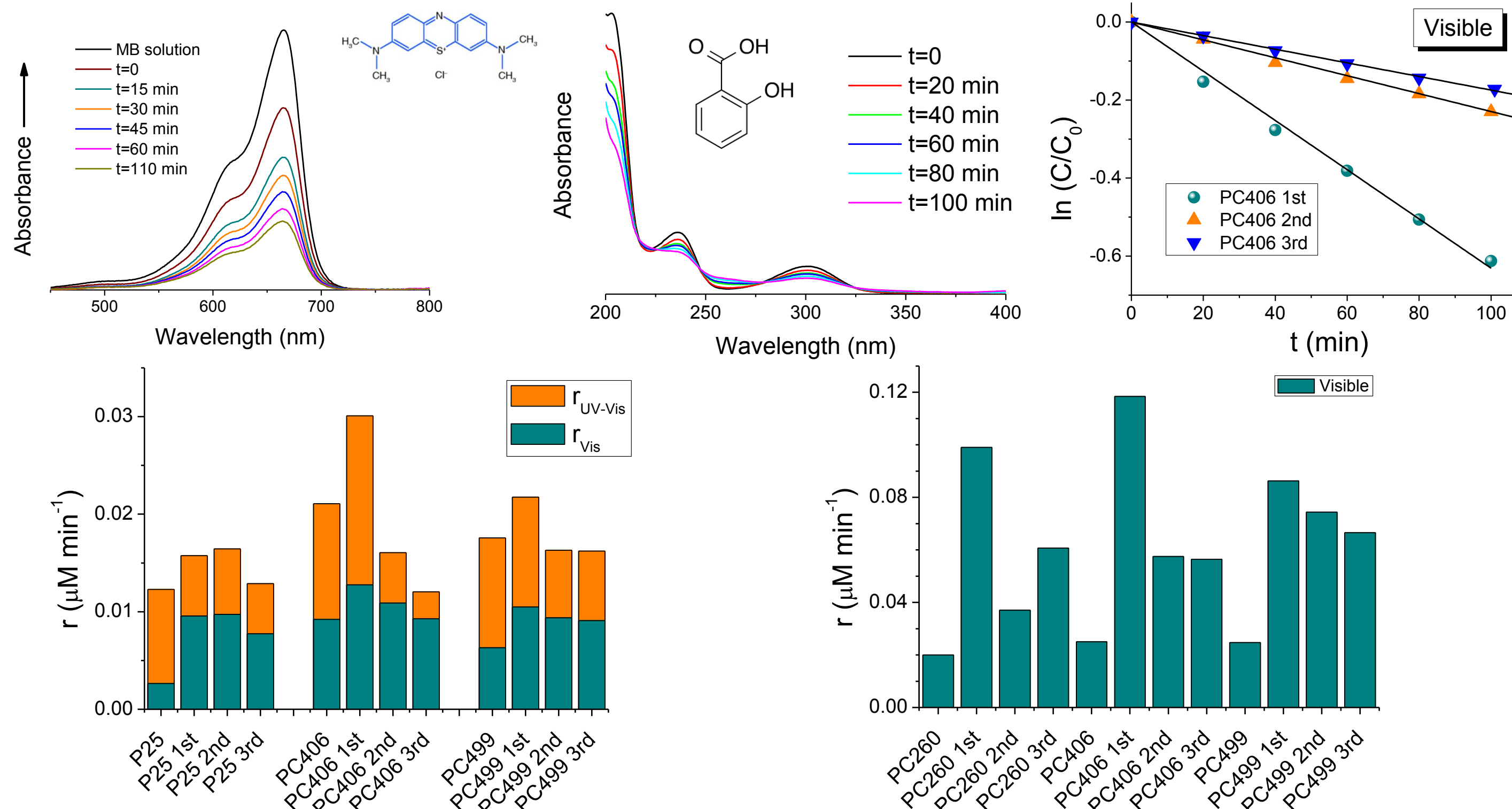
Raman spectroscopy – identification of Co oxides



Vibrations at 194, 482 and 691 cm⁻¹ arise from the F_{2g}, E_g and A_{1g} modes of the tetrahedral (CoO₄) and octahedral (CoO₆) units in the Co₃O₄ = [Co²⁺][Co³⁺]₂[O₂]₄ spinel. In defect-free CoO, first-order Raman scattering is forbidden due to its centrosymmetric cubic NaCl-type structure. The higher intensity of Co₃O₄ Raman bands at 785 nm is due to the optical absorption and the resonant enhancement of Raman scattering by the surface Co-oxides.

Photocatalytic activity

The photocatalytic activity of the photonic films was evaluated on the aqueous phase degradation of methylene blue (MB) and salicylic acid. The photonic films (~1.5 cm²) were placed horizontally at the bottom of beakers containing MB (4 ml, 3 μM) or SA (3 ml, 25 μM) aqueous solutions, where they were left for 60 min under dark conditions to reach adsorption-desorption equilibrium. The power density of the incident beam from a Xe lamp on the film surface was 2.8 mW/cm² in the case of MB degradation and nearly 1 sun (96 mW/cm²) for SA in the visible spectral range, respectively.



Fine tuning of the films' photonic-electronic properties by varying the inverse opal diameter and the number of CC cycles resulted in a marked improvement in the photocatalytic activity. This effect was related to the synergy of slow photon-assisted light harvesting and mass transport of the macroporous inverse opals in combination with the enhanced charge separation and visible light absorption due to the Co oxide nanoclusters. However, enhancement of the visible light electronic absorption by increasing the surface oxide loading competes with the photonic enhancement.

Acknowledgments

Alexia Toumazatou is deeply indebted to the National and Kapodistrian University of Athens for their financial support to participate to the 6th Nano Today Conference and to the Onassis Foundation scholarship for doctoral studies. D. Tsoutsou and A Dimoulas are gratefully acknowledged for availing XPS experiments.



[1] V. Likodimos, Photonic crystal-assisted visible light activated TiO₂ photocatalysis, Appl. Catal. B: Environ. 230 (2018) 269.

[2] H. Tada, Q. Jin, A. Iwaszuk, M. Nolan, Molecular-scale transition metal oxide nanocluster surface-modified titanium dioxide as solar-activated environmental catalysts, J. Phys. Chem. C 118 (2014) 12077.