



Visible light active FeO_x-TiO₂ photonic crystal photocatalysts

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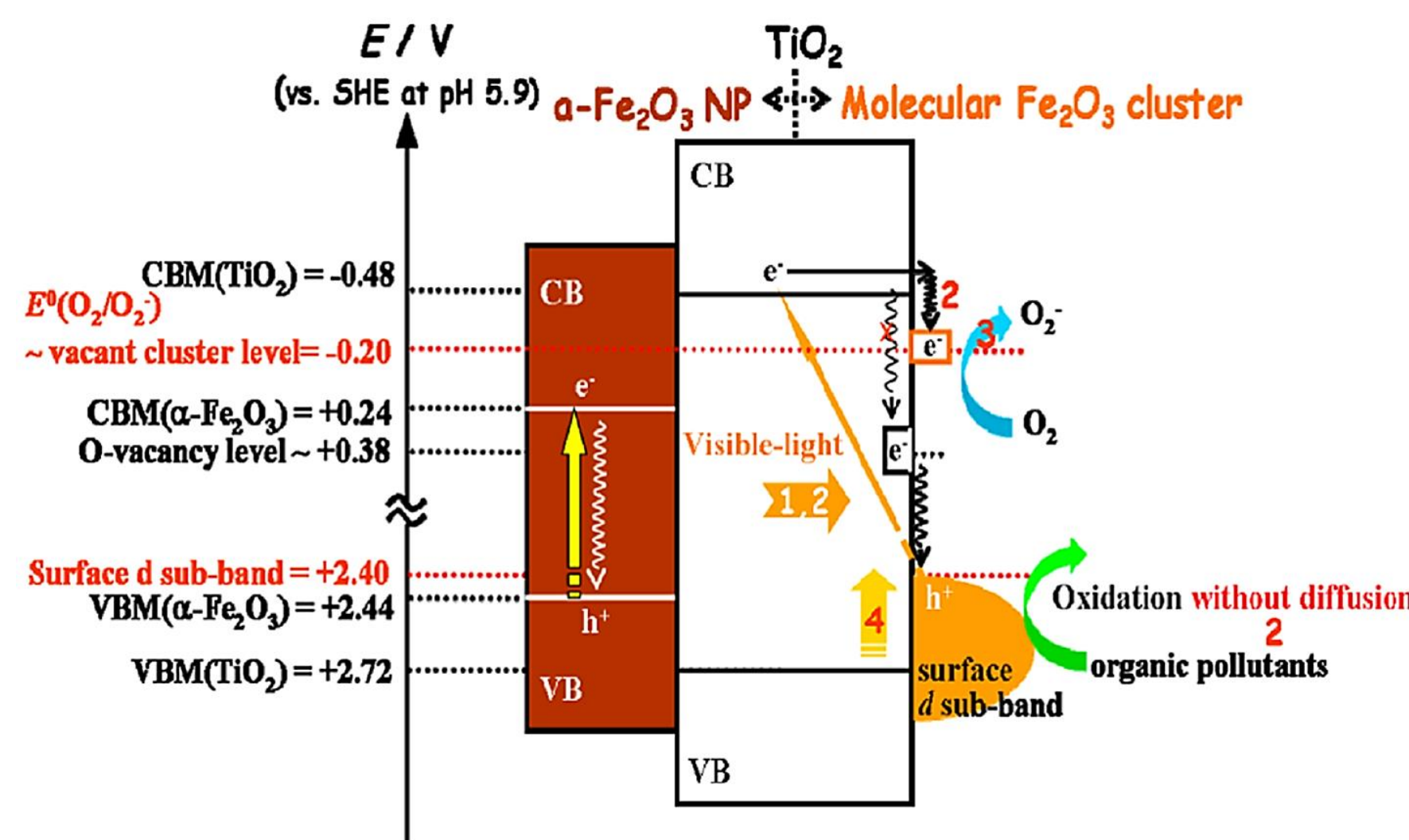
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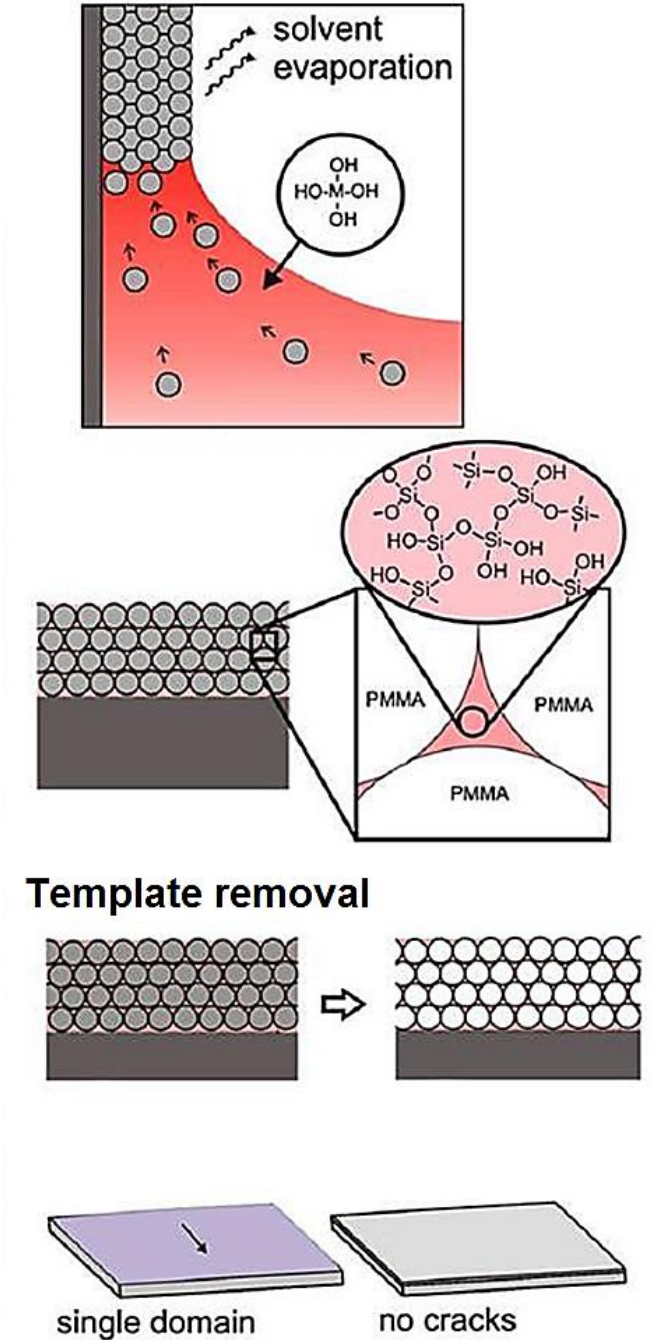
Photonic crystal-assisted semiconductor photocatalysis has emerged as an advanced structural modification for the development of high performance UV and recently visible light active (VLA) photonic catalysts exploiting slow photons i.e. light propagation at reduced group velocity near the edges of the photonic band gap [1]. These materials combine the slow photon-assisted light harvesting, mass transport and high adsorption capacity of macro-mesoporous structures with compositional tuning of the catalysts for enhanced charge separation and visible light activation. In this work, controlled surface modification of TiO₂ photonic crystals by "molecular" scale FeO_x nanoclusters was implemented using the chemisorption-calcination-cycle (CCC) method [2] in order to develop efficient VLA FeO_x-TiO₂ photocatalysts. In the molecular scale FeO_x cluster-TiO₂ coupling system titania's surface modification by extremely small Fe₂O₃ clusters raises the VB maximum leaving the CB minimum unchanged, due to the effective electronic coupling through the surface Fe-O-Ti interfacial bonds formed by the strong nanocluster - TiO₂ interaction. The resulting decrease in the band gap shifts the light absorption to the visible region while leaving intact the O₂ reduction potential [2].



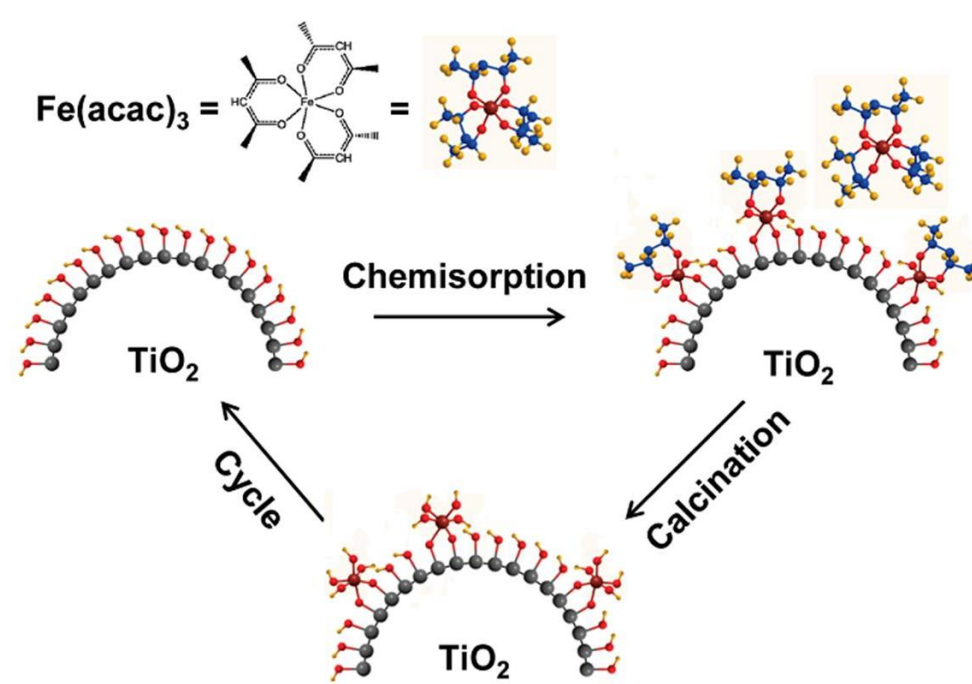
TiO₂ inverse opal fabrication and FeO_x surface modification

TiO₂ inverse opals of variable photonic gap were fabricated using the evaporation-induced co-assembly of polymer colloidal spheres of three different diameters (220, 260 and 330 nm) with a hydrolyzed Ti alkoxide (TiBALDH) [4]. According to this method, cleaned glass substrates are placed nearly vertically in vials containing 8 ml of 0.125w/v % dilute PMMA and PS aqueous sphere suspension and 0.07 ml of the titania precursor (0.5 ml HCL, 1 ml EtOH and 0.25 ml TiBALDH). The vials were kept at 55 °C until the solvent fully evaporated over 3 days resulting in the self assembly of close packed PMMA/PS opal structures.

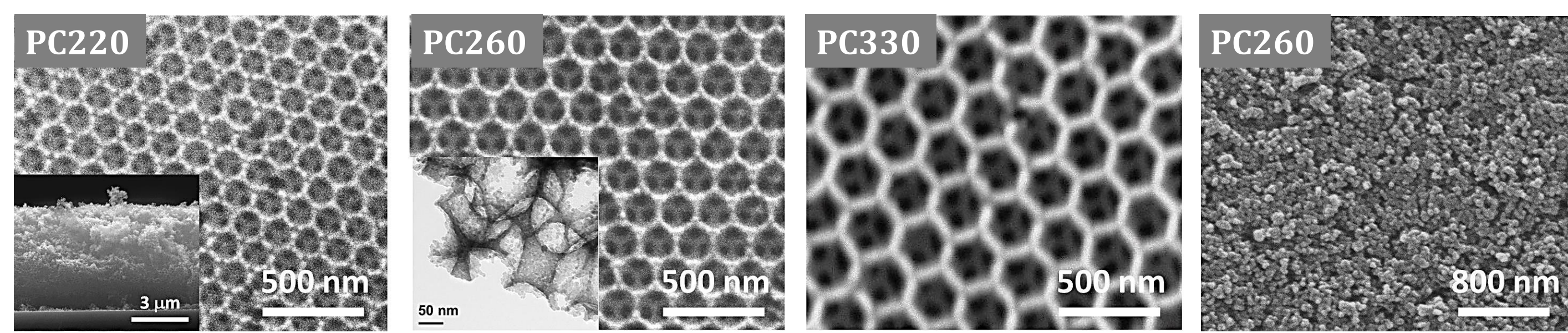
Template/matrix co-assembly [4]



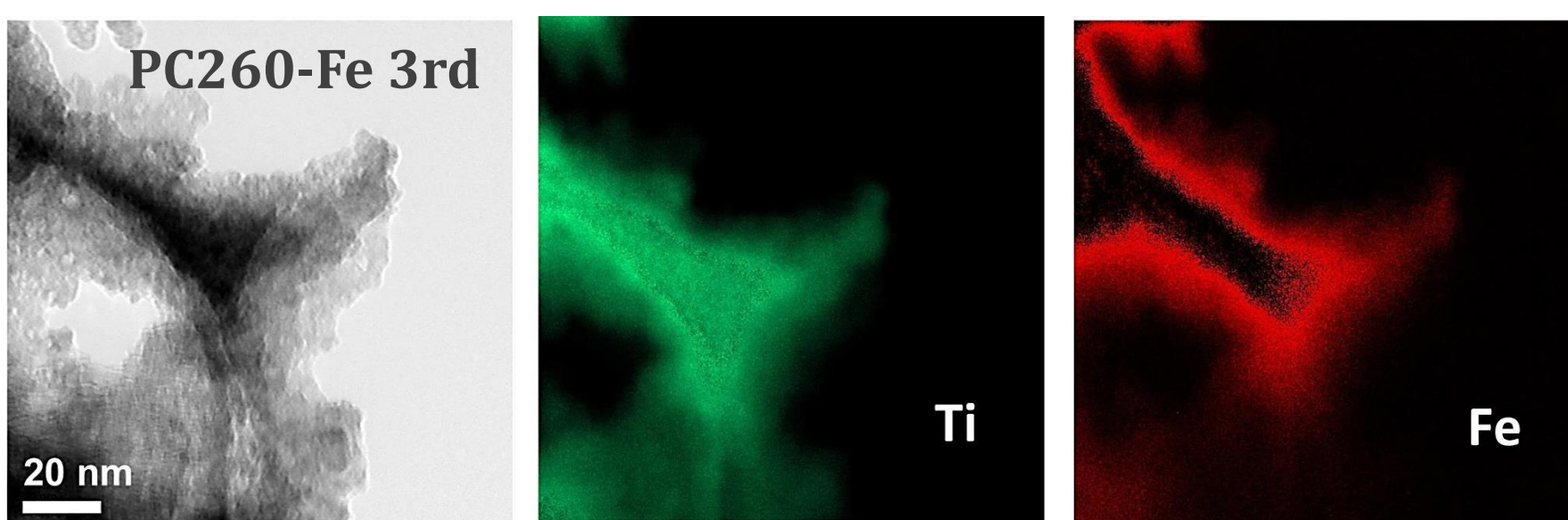
These films are calcinated at 500°C for 2 h in air at a heating rate of 1 °C/min, in order to remove the polymer matrix and crystallize titania in the inverse opal structure. To evaluate the performance of inverse opals, P25 mesoporous films were prepared as reference samples, by the spin-coating method using Aeroxide®P25 (Evonik) nanocrystalline titanium reference paste on the substrate. For surface modification, the TiO₂ films were immersed for 24 h at room temperature in 100 ml of a volatile solution of 6x10⁻⁴ M Fe(acac)₃ prepared from 23 mg of Fe(acac)₃ in a solvent consisting of 15 ml EtOH and 85 ml normal hexane (ethanol:n-hexane=3:17v/v). Copious rinsing of the films with the same solvent is followed to remove the naturally adsorbed molecules to surface of TiO (without chemical bond) and heat to 500°C for 1 h at a rate of 1 °C/min.



Morphology and structure



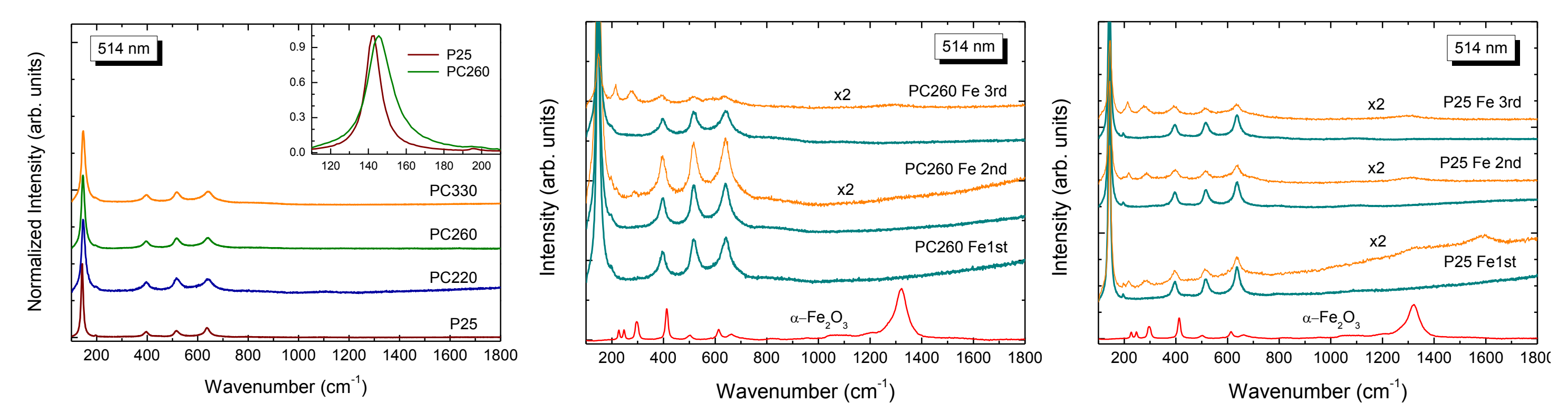
SEM images verify the formation of highly ordered 3D periodic structures corresponding to the (111) planes of an *fcc* lattice consisting of void spheres within the titania framework. The macropores were well interconnected through smaller pores 40-90 nm (dark circular areas), while the surface of the mesoporous P25 films is highly rough due to the formation of extensive aggregates. TEM reveals that the inverse opal skeleton consists of ~10 nm nanoparticles.



EDX	Ti (at %)	Fe (at %)	Fe /Ti
PC220-Fe 1 st	94.55	5.45	0.058
PC330-Fe 1 st	94.98	5.02	0.053
PC260-Fe 1 st	94.91	5.09	0.054
PC260-Fe 2 nd	92.7	7.3	0.079
PC260-Fe 3 rd	86.7	13.3	0.153
P25-Fe 1 st	97.26	2.74	0.028
P25-Fe 2 nd	94.15	5.85	0.062
P25-Fe 3 rd	90.26	9.74	0.108

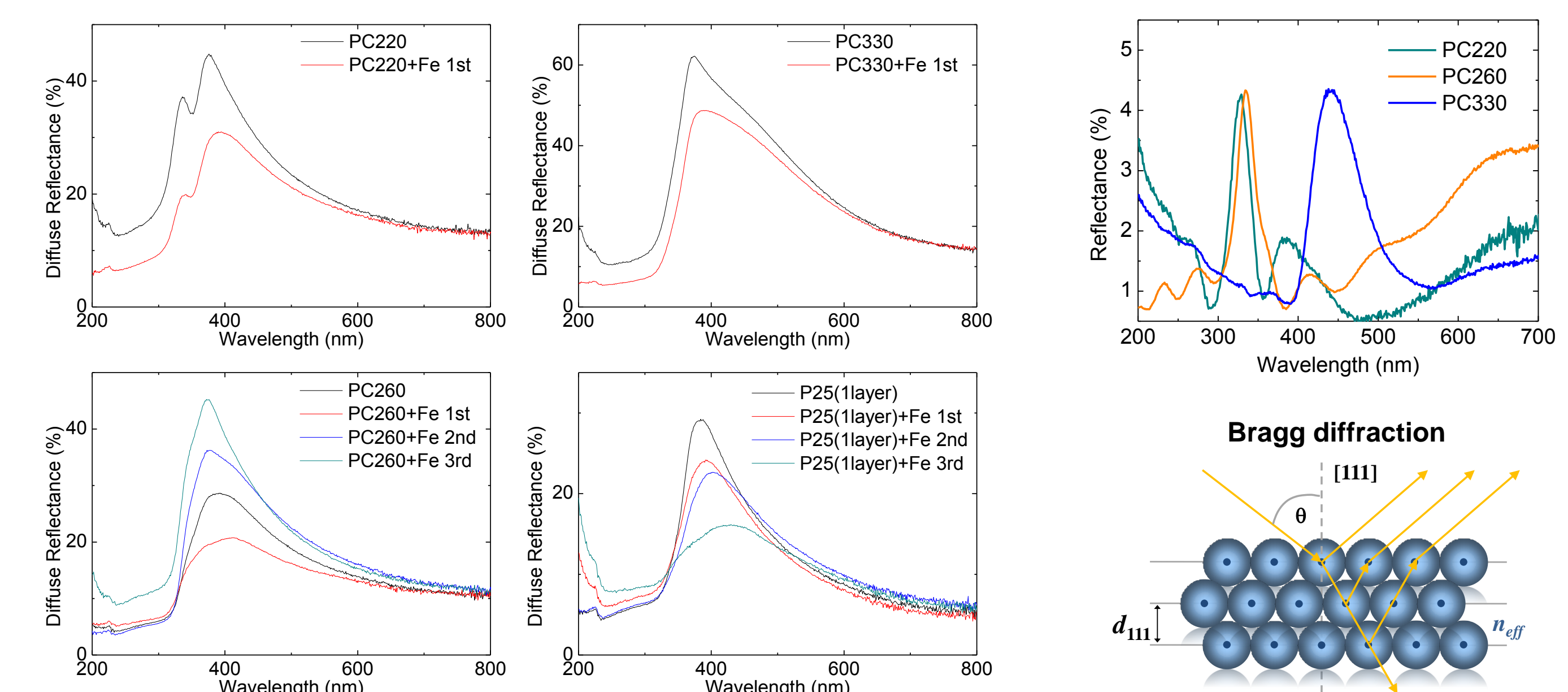
The deposition and spatial distribution of Fe species on the nanocrystalline titania walls was investigated by Energy-filtered EF-TEM, as shown by the Ti and Fe elemental maps of the area corresponding to the bright field TEM image of PC260 after 3 modification cycles. Furthermore, EDX analysis confirmed the controlled loading of Fe surface species on the TiO₂ photonic films with the number of successive CC cycles.

Micro-Raman spectroscopy - identification of FeO_x



The characteristic Raman modes corresponding to the crystalline anatase TiO₂ phase were observed, while the iron oxide Raman peaks were absent in all modified photonic films, indicating the formation of FeO_x nanoscale complexes of low crystallinity. To further study the formation of Fe oxides in the modified films, local heating experiments were performed focusing the laser beam at full power to achieve strong local heating. The appearance of new peaks was observed, in the case of the P25 films at 214, 283 and 1310 cm⁻¹ from the first modification cycle, which are close to the characteristic Raman modes of hematite *α*-Fe₂O₃.

Optical properties - PBG engineering vs Visible light activation



Sample	D (nm)	$\lambda_{\text{exp}}(15^\circ)$ (nm)	n_{eff} (air)	1-f	$\lambda(0^\circ)$ (air)	n_{eff} (H ₂ O)	$\lambda(0^\circ)$ (H ₂ O)
PC220	135	325	1.50	0.23	330	1.68	371
PC260	150	334	1.39	0.17	340	1.60	392
PC330	200	440	1.37	0.16	448	1.59	519

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

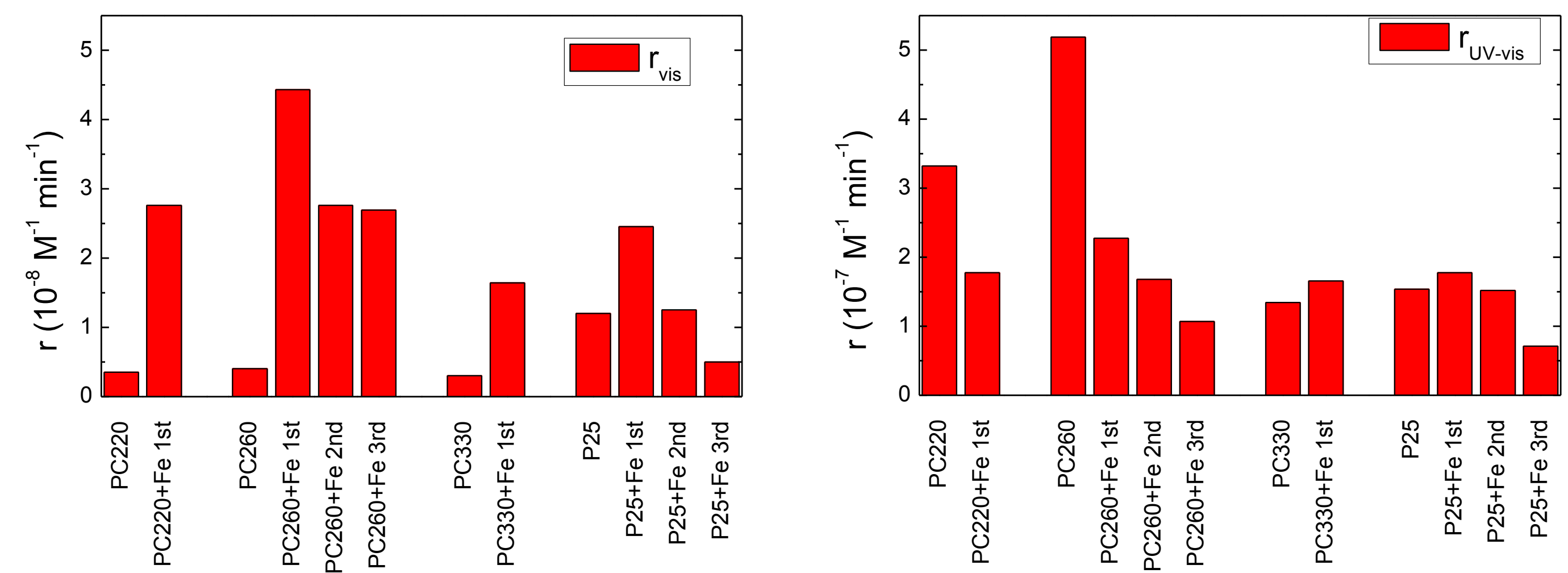
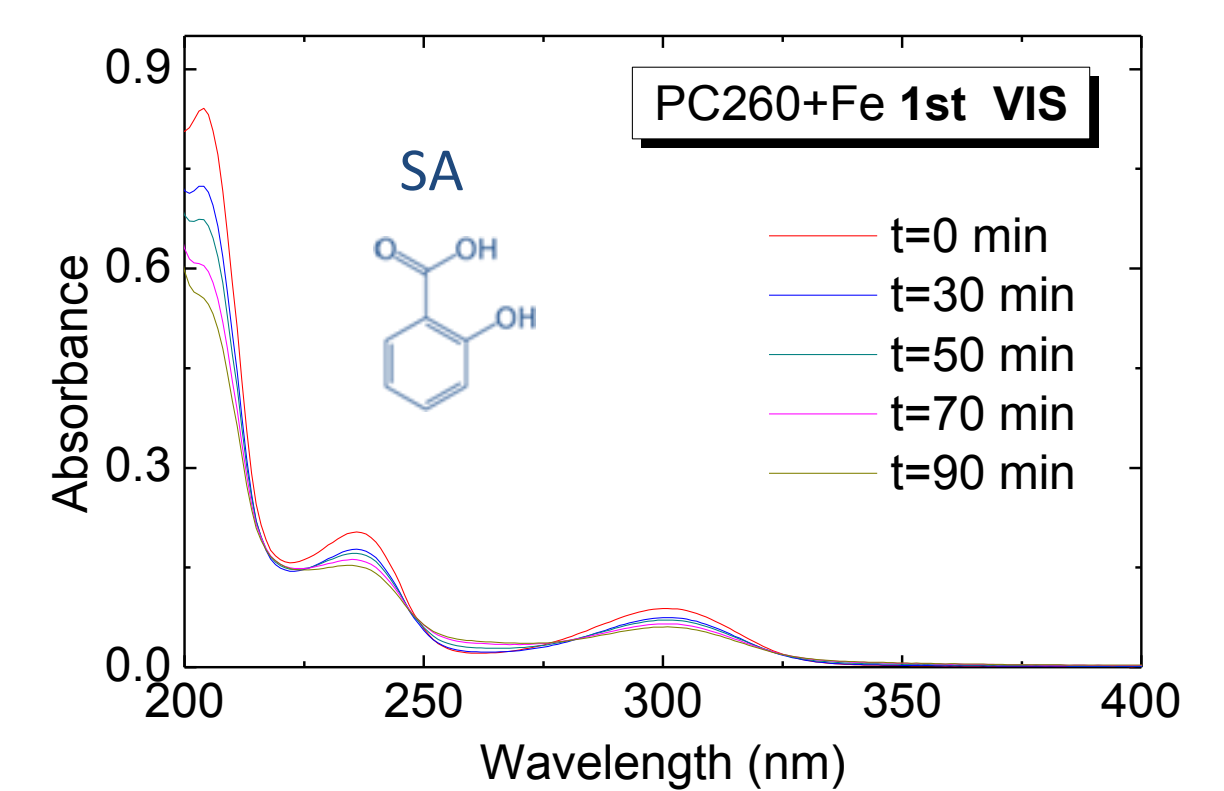
λ_{exp} = stop band wavelength determined from the 15° incidence specular spectra.

$\lambda(0^\circ)$ = stop band wavelength predicted from modified Bragg law $\lambda = 2d_{111}\sqrt{n_{\text{eff}}^2 - \sin^2\theta}$,

$n_{\text{eff}}^2 = n_{\text{sphere}}^2 f + n_{\text{solid}}^2 (1 - f)$ for $\theta=0^\circ$ incidence angle and $d_{111} = \sqrt{2/3}D$ the spacing of (111) planes.

Photocatalytic activity

The photocatalytic activity of the photonic films was evaluated on the aqueous phase degradation of salicylic acid (SA), a colorless water pollutant rarely investigated by photonic crystal photocatalysts, under UV-Vis and visible light. The photonic films (~1.5 cm²) were placed at the bottom of beakers containing SA (3 ml, 25 μM) aqueous solutions, where they were left for 30 min under dark conditions to reach adsorption-desorption equilibrium. The solution pH was stabilized at 3 to enhance SA adsorption on the TiO₂ surface and direct oxidation by holes. The power density of the incident beam from a Xe lamp and suitable filters was nearly 1 sun (96 mW/cm²).



The deposition of low amounts of nanoscale FeO_x clusters on the TiO₂ inverse opals leads to high visible light photocatalytic activity, exceeding mesoporous P25 films and evading the loss of holes oxidizing ability, frequently identified in VLA doped TiO₂ photocatalysts due to localized states. The VLA enhancement is related to the synergy of slow photons and surface states induced by the strong FeO_x-TiO₂ interfacial coupling. However, rising the visible light electronic absorption by increasing the FeO_x loading competes with the photonic enhancement, especially under UV-Vis light that is crucial for colorless pollutant photodegradation.

Acknowledgments

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[1] V. Likodimos, Photonic crystal-assisted visible light activated TiO₂ photocatalysis, *Appl. Catal. B* 230, 269–303 (2018).

[2] H. Tada and Q. Jin, "First-Transition Metal oxocomplex-surface-modified titanium(iv) oxide for solar environmental purification," in *Advanced Catalytic Materials - Photocatalysis and Other Current Trends, IntechOpen*, (2016).

[3] 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, 12077–12086 (2014).

[4] B. Hatton, L. Mishchenko, S. Davis, K.H. Sandhage, J. Aizenberg, Assembly of large-area, highly ordered, crack-free inverse opal films, *PNAS* 107, 10354–10359 (2010).