



Metal (Mo, Ca)-doped BiVO₄ photonic crystal photocatalysts

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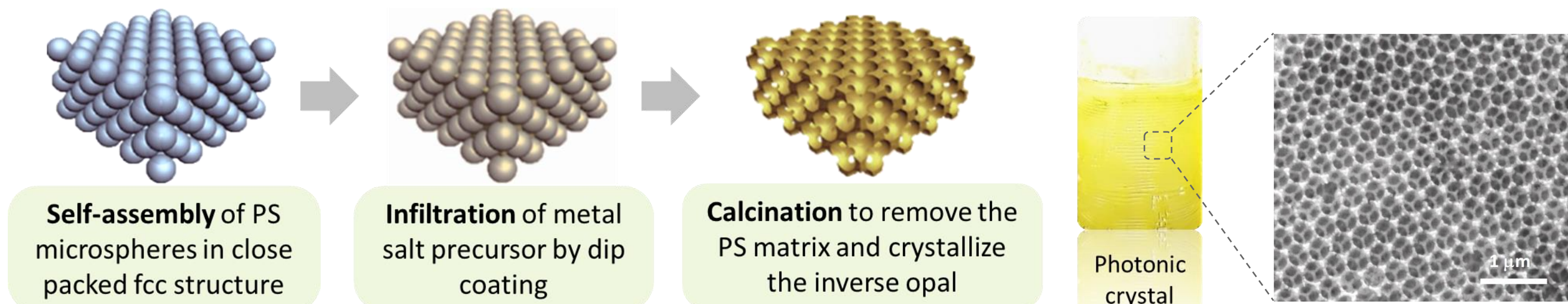


Metal doped BiVO₄ photonic crystal catalysts

Photonic crystal (PC) catalysts have been attracting significant attention as they can combine slow photon-assisted light harvesting, mass transport and the high adsorption capacity of macroporous periodic structures such as inverse opals with compositional tuning of the catalysts' electronic properties for enhanced charge separation [1]. Bismuth vanadate (BiVO₄) has emerged as a promising, environmentally benign visible-light photocatalyst that has been widely investigated for water oxidation and organics degradation [2]. Nevertheless, its photocatalytic performance is significantly impaired by the extremely low carrier mobility that leads to electron-hole recombination losses.

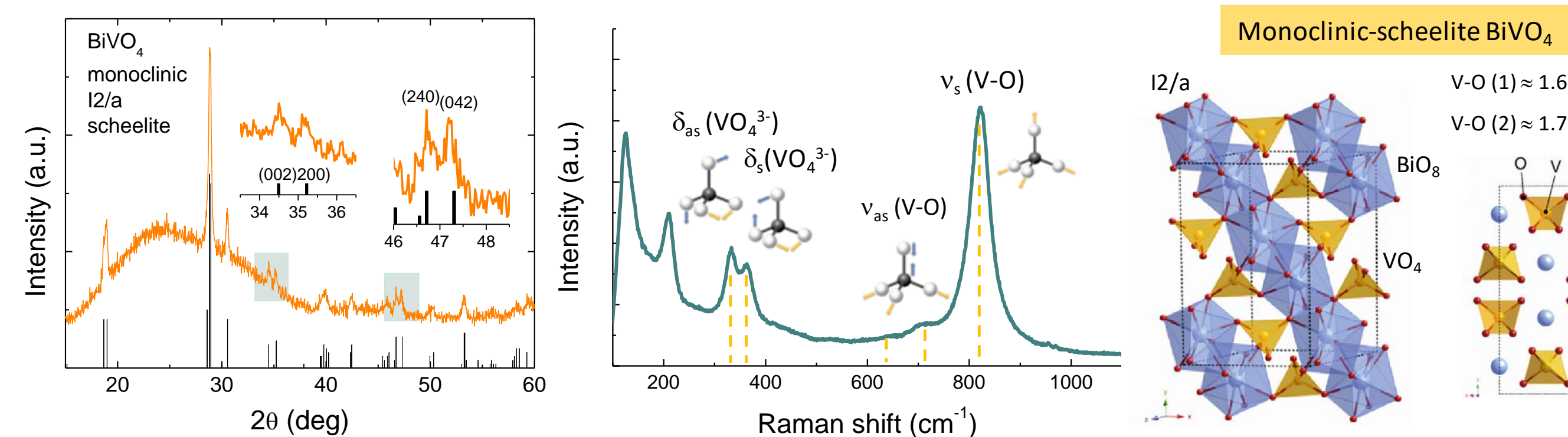
In this work, homojunction formation on the nanocrystalline walls of photonic band gap (PBG) engineered metal (Mo/Ca) doped BiVO₄ inverse opals is demonstrated as a promising means to synergistically combine light trapping with the improved charge separation of optimally doped BiVO₄ for enhanced photocatalytic performance on water pollutant degradation and water splitting applications.

Photonic crystal film fabrication

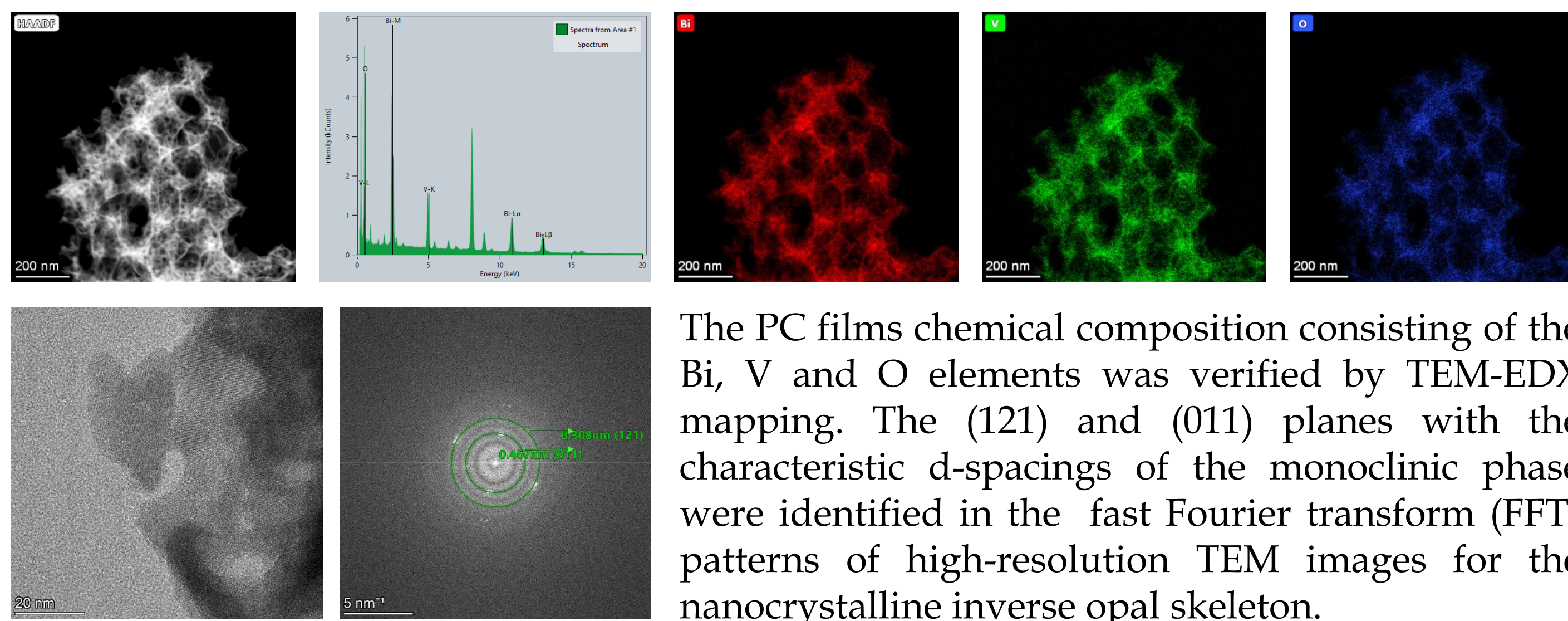


Controlled fabrication of BiVO₄ photonic films was performed by the convective evaporation-induced self-assembly on polystyrene (PS) colloidal templates [3]. Liquid phase infiltration of a metal salt precursor based on Bi(NO₃)₃·5H₂O and NH₄VO₃ was carried out by dip coating on self-assembled PS opal templates on glass or FTO substrates. Calcination was performed at 375 °C to remove the PS matrix and crystallize the amorphous precursor in the monoclinic scheelite BiVO₄ phase. PBG engineering was realized using monodisperse PS microspheres of different diameters (300-500 nm) in order to tune the photonic stop band across the BiVO₄ electronic absorption edge and thus allow exploitation of slow photon effects.

Phase composition

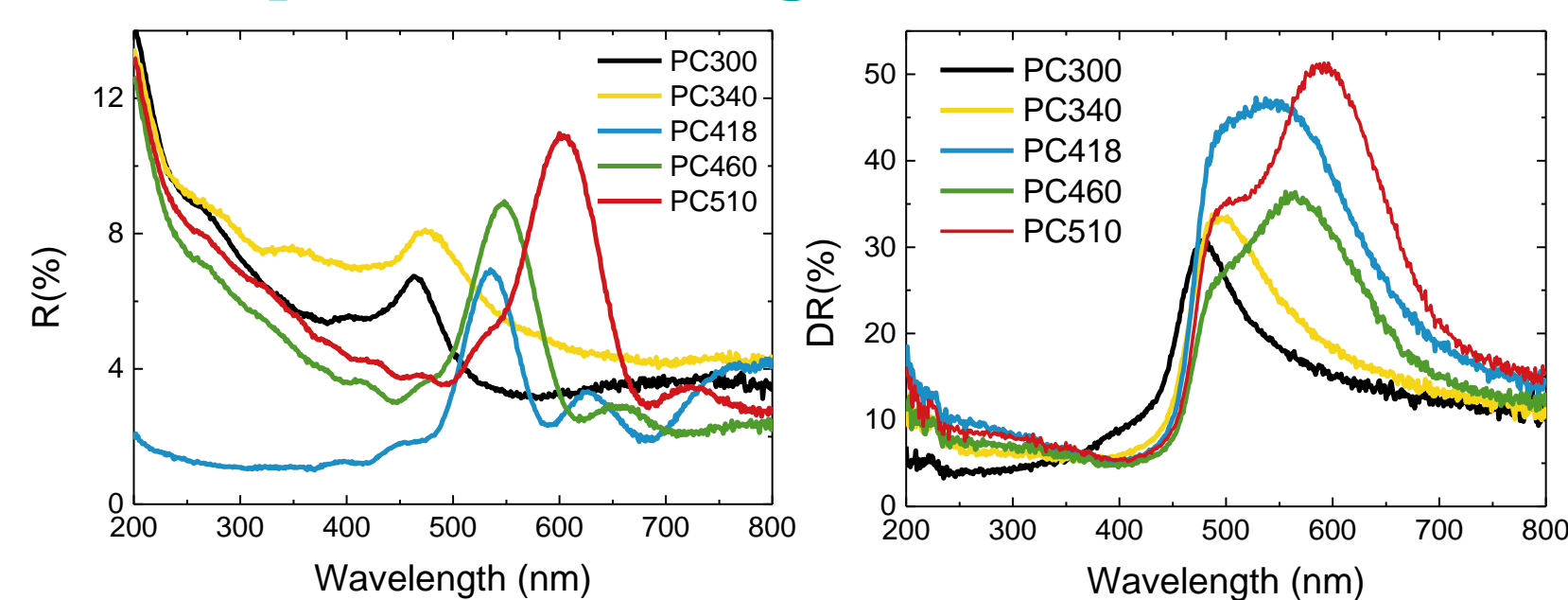


X-ray powder diffraction showed that the films crystallized in the single monoclinic scheelite phase (I2/a) [4] with clearly observed splitting of characteristic diffraction peaks. This was firmly corroborated by Raman spectroscopy, where all the characteristic Raman-active modes of the monoclinic scheelite BiVO₄ were identified with the clear splitting of the VO₄ tetrahedra bending modes and no traces of polymeric species or other polymorphic phases.

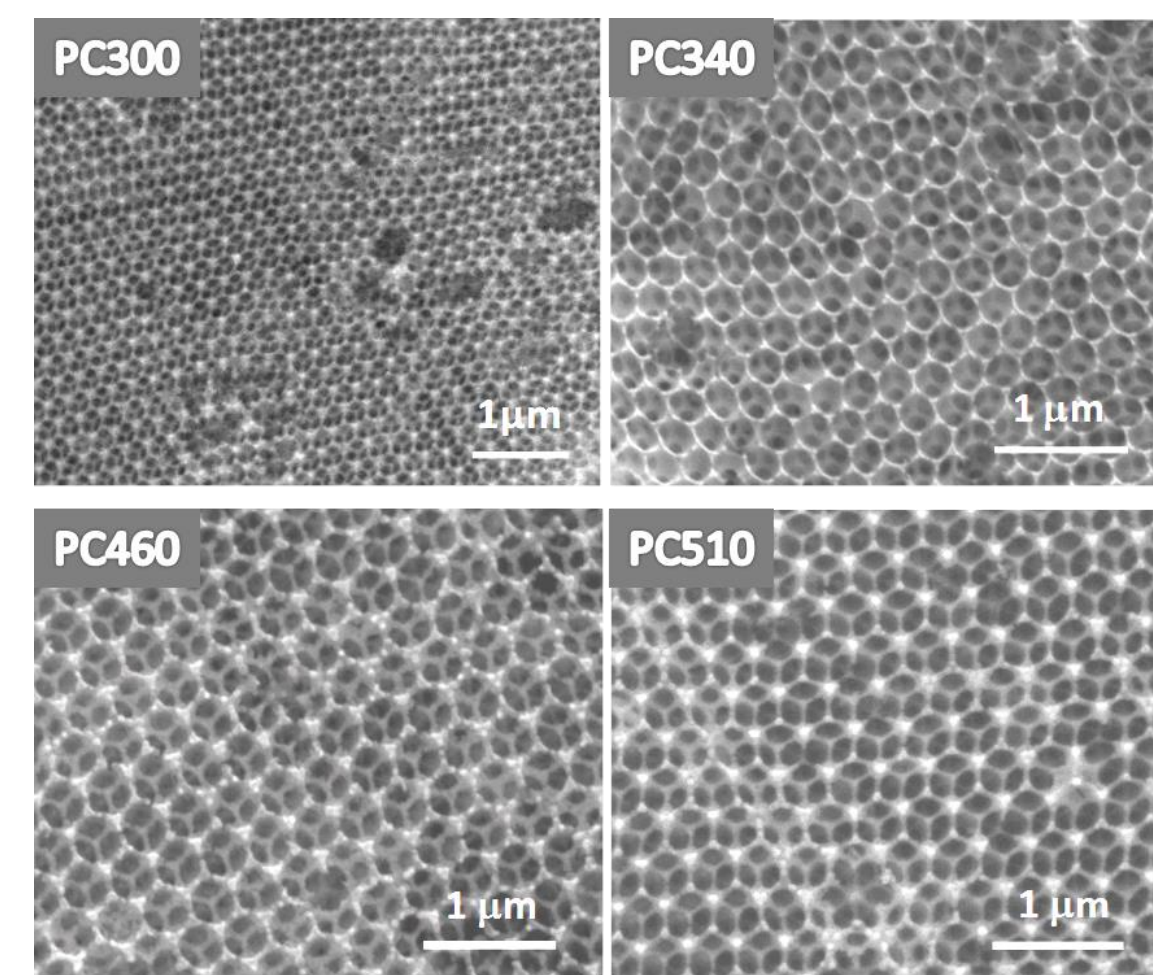


The PC films chemical composition consisting of the Bi, V and O elements was verified by TEM-EDX mapping. The (121) and (011) planes with the characteristic d-spacings of the monoclinic phase were identified in the fast Fourier transform (FFT) patterns of high-resolution TEM images for the nanocrystalline inverse opal skeleton.

Slow photon tuning



Sample	D _{SEM} (nm)	λ _{exp} (15°) (air)	n _{eff} (air)	1-f	λ(0°) (air)	n _{eff} (H ₂ O)	λ(0°) (H ₂ O)
PC300	200	460	1.43	0.221	468	1.63	532
PC340	210	480	1.42	0.216	488	1.62	556
PC418	260	534	1.28	0.136	545	1.52	646
PC460	280	547	1.22	0.105	560	1.48	676
PC510	300	601	1.25	0.120	614	1.50	735

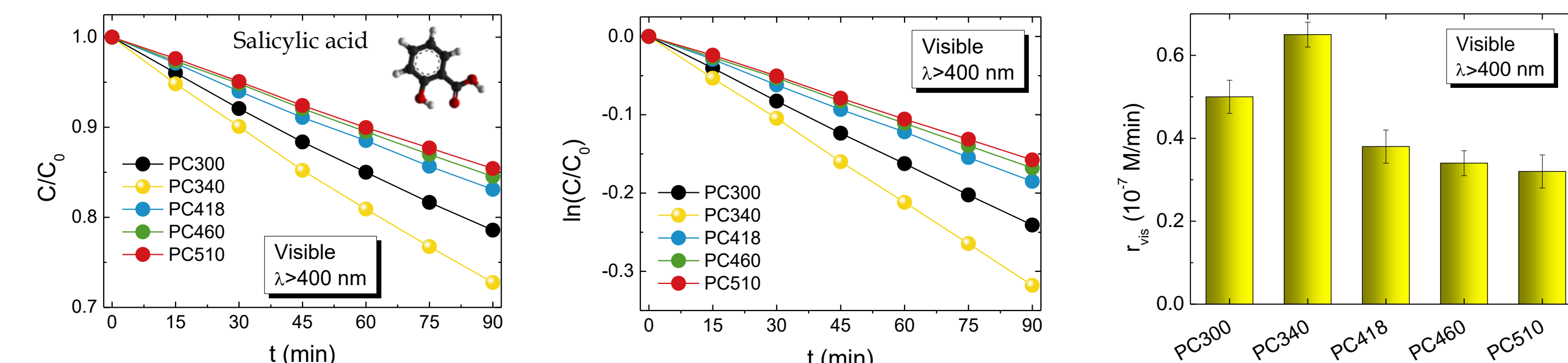


D = macropore diameter of the PC films determined by SEM
λ_{exp} = stop band determined from 15° incidence R% spectra
λ(0°) = stop band predicted from modified Bragg law

- [1] Likodimos, V. Photonic crystal-assisted visible light activated TiO₂ photocatalysis, *Appl. Catal. B.* **2018**, 230, 269-303.
[2] Kim, J.; Lee, J. S. Elaborately modified BiVO₄ photoanodes for solar water splitting, *Adv. Mater.* **2019**, 31, 1806938.
[3] Zhou, M. et al. Photoelectrodes based upon Mo:BiVO₄ inverse opals for water splitting, *ACS Nano* **2014**, 8, 7088-7098.
[4] Abdi, F.F. et al. Photoelectrochemical Solar Fuel Production, *t ed. by S. Gimnez, J. Bisquer, Springer*, **2016**, p.355

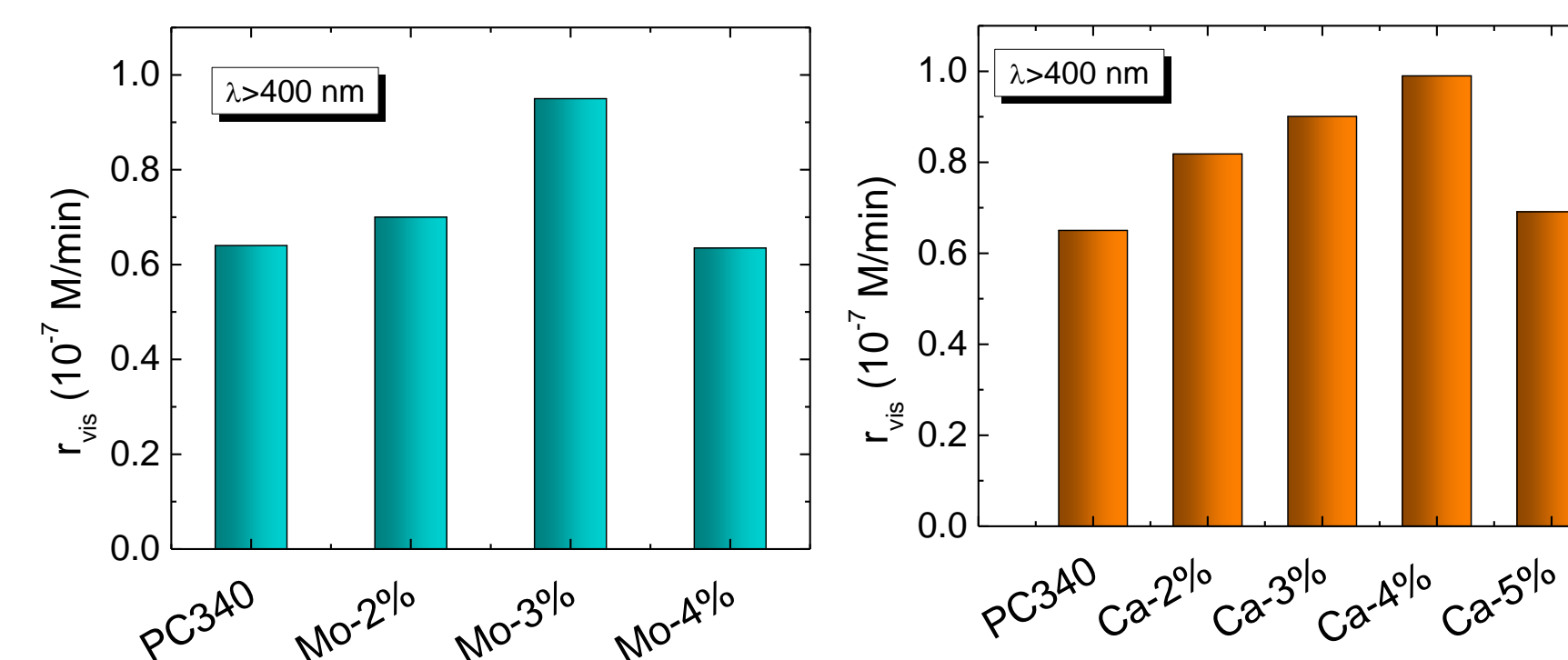
Slow photon enhancement

The photocatalytic activity of the BiVO₄ photonic films was evaluated on the aqueous phase degradation of salicylic acid (SA), a colorless water pollutant, under visible light using 3 ml of 30 μM SA aqueous solution at pH=3 under stirring and incident power density of 70 mW/cm² (150 W Xe). PC340 presented the highest performance due to the optimal overlap of blue slow photons with BiVO₄ absorbance edge.

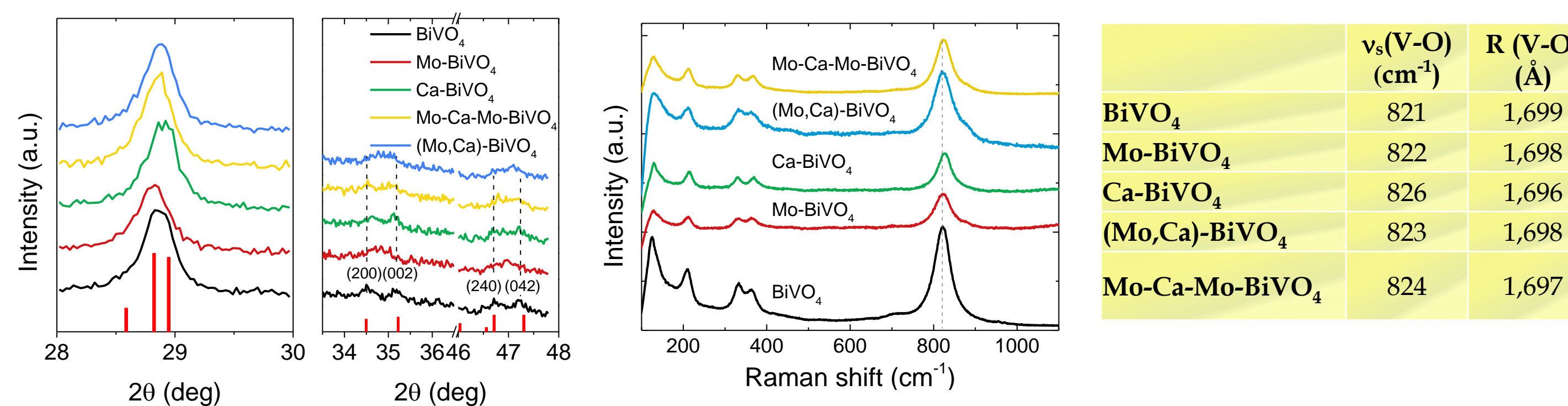


Single metal-doping optimization

Optimization of metal doping by Mo and Ca ions based on the films photocatalytic activity on SA degradation showed that the optimum concentrations were 3% Mo and 4% Ca. These levels were used for co-doping (Mo,Ca)-BiVO₄ and the successive deposition of Mo-BiVO₄/Ca-BiVO₄/Mo-BiVO₄ nanoscale homojunctions.

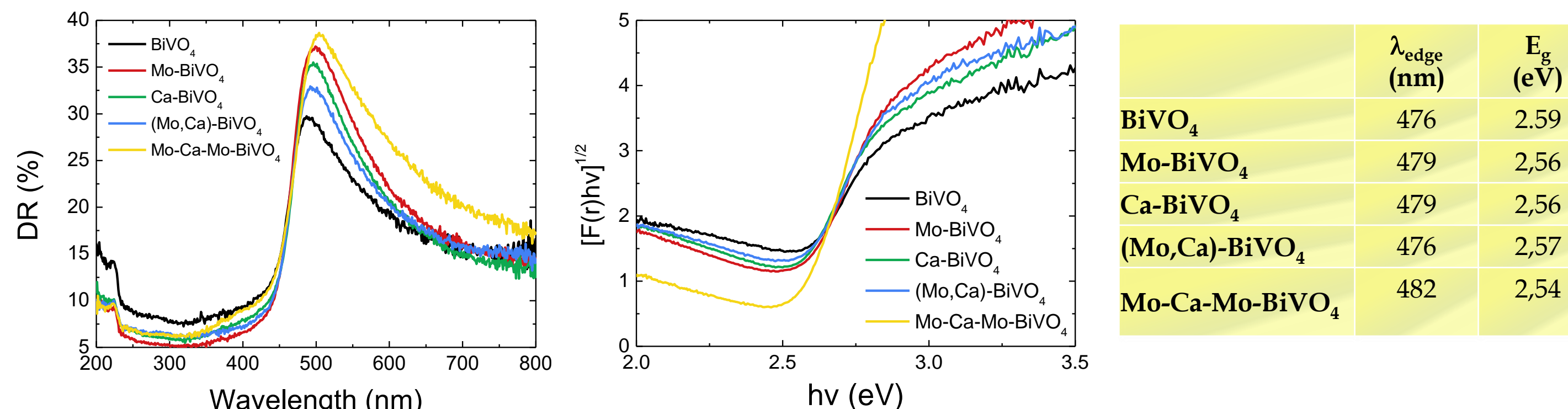


Structural properties of doped BiVO₄ photonic films



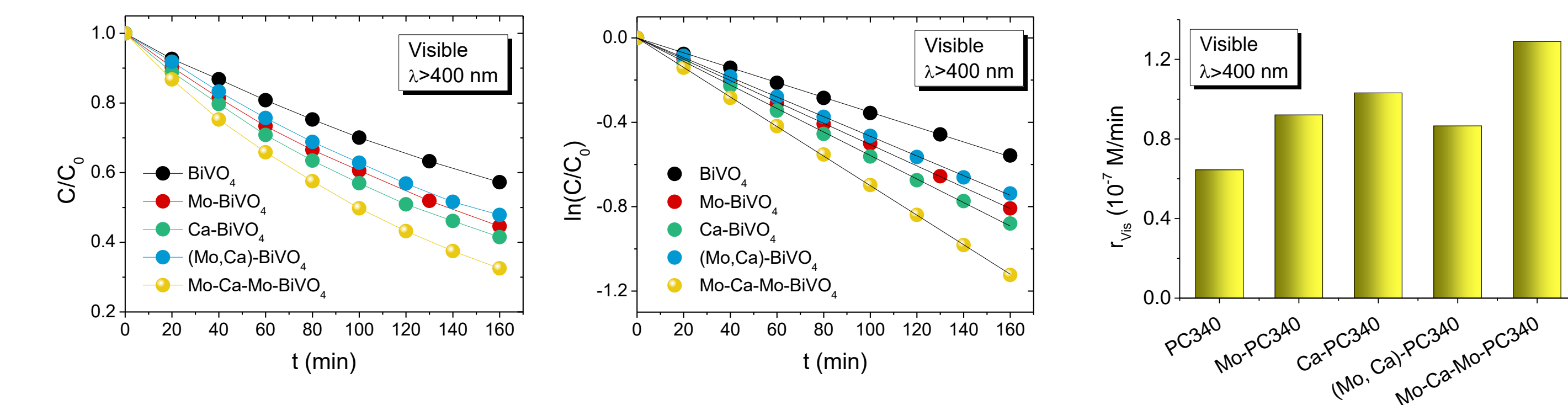
XRD and Raman indicate that Mo, Ca doping introduces disorder and causes deformation towards to the tetragonal scheelite structure.

Optical properties of doped BiVO₄ photonic films

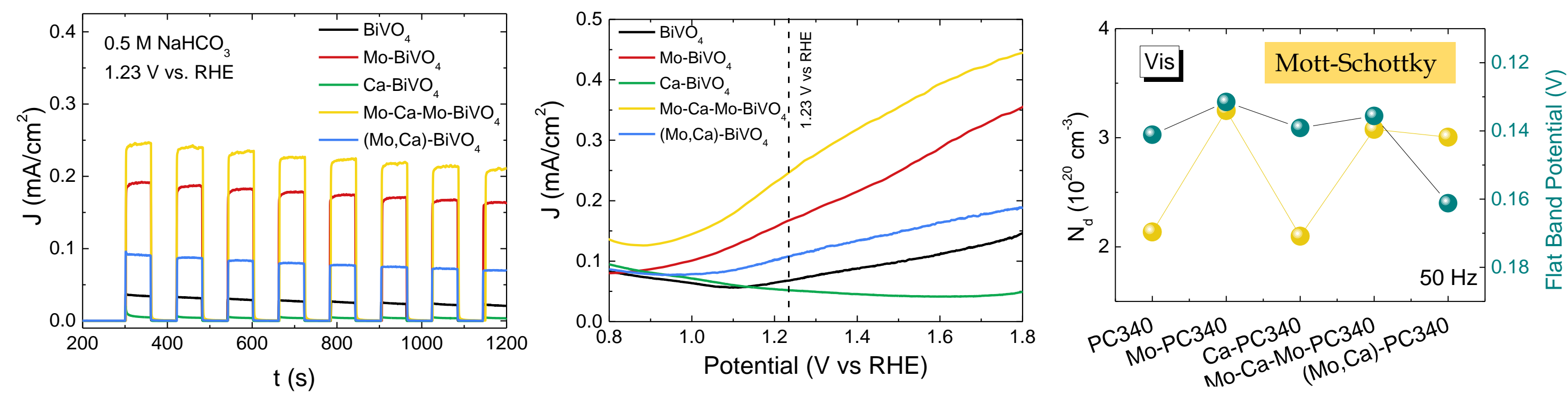


Doping of BiVO₄ results in slight narrowing of the energy band gap complying with the introduction of shallow Mo⁶⁺ (0.62 Å) donors and Ca²⁺ (0.99 Å) acceptors at the V⁵⁺ (0.52 Å) the Bi³⁺ (1.11 Å) lattice sites, respectively.

Photocatalytic activity



Electrochemical performance



Performance evaluation showed that the Mo-Ca-Mo-BiVO₄ PC films present the highest activity compared to their individual constituents, reaching a two-fold and nearly ten-fold enhancement of the SA degradation rate and photocurrent density, respectively, compared to the bare BiVO₄ under visible light (λ>400 nm). This marked improvement is related to the formation of numerous homojunctions between Mo-BiVO₄ and Ca-BiVO₄ nanoparticles that boost charge separation in synergy with optimal light trapping by the photonic films.

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