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Analysing Mesoporous Thin Films Electrodes by Glancing-Incidence XRD-Application to Photorechargeable Li-ion Batteries

Olivier Nguyen, Natacha Krins, Gianguido Baldinozzi, Christel
Laberty-Robert

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Outline

Photo-rechargeable lithium-ion batteries, which are able to both harvest and store solar energy within electrodes, are a promising technology for a more efficient use of intermittent solar radiation [1]. However, there is a lack of understanding on how the light-induced lithium extraction reaction occurs within the electrode host lattice. In fact, this technology is based on bifunctional nanostructured electrodes, which undergo simultaneous complex modifications: structural reorganization through lithium-ion insertion and photo-excited charges creation through solar illumination.

In order to get more insight on the mechanism governing the photo-recharge of a single device based on a TiO₂ thin film electrode made of mesoporous anatase, we perform ex-situ glancing-incidence XRD experiments. Using laboratory glancing incidence diffraction, and implementing proper corrections for the instrumental broadening of this diffraction geometry in the Rietveld refinement software XND, it was possible to extract quantitative information about the structure (lattice, strain, and atomic positions) and the microstructure (crystallite size and micro-strain), selectively probing the material on a depth of few nanometers.

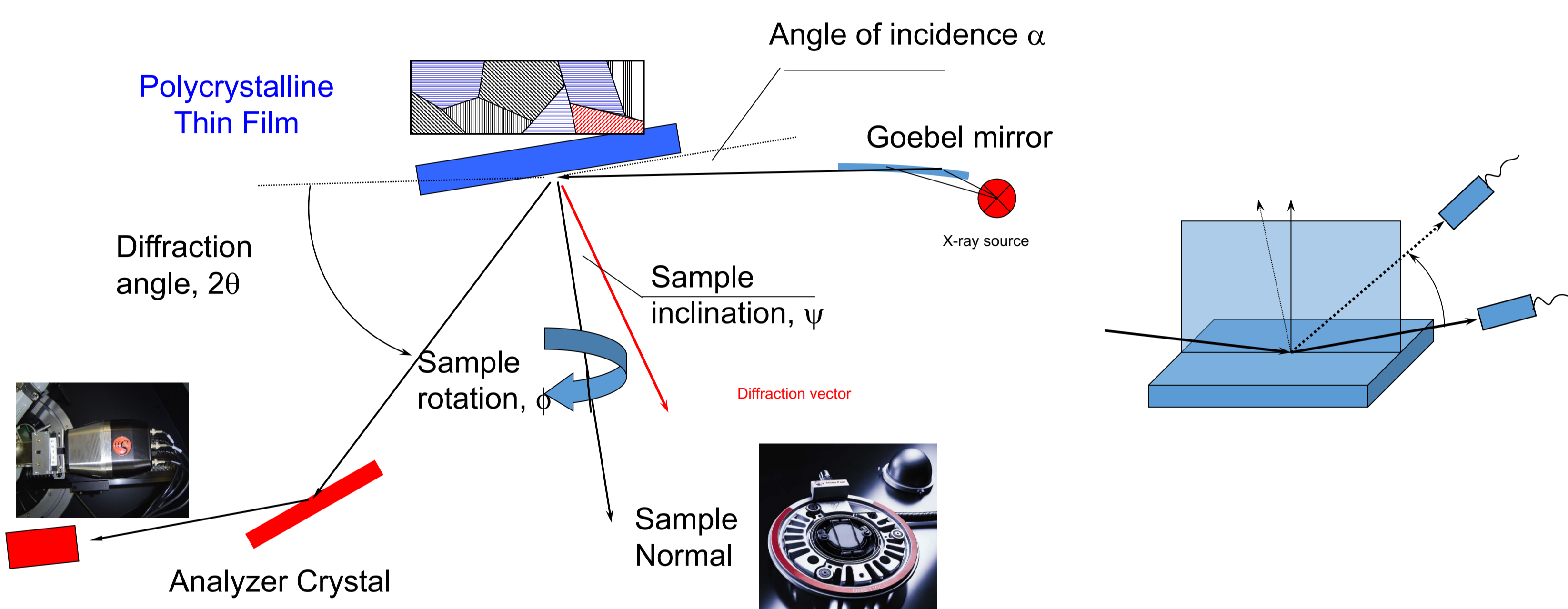
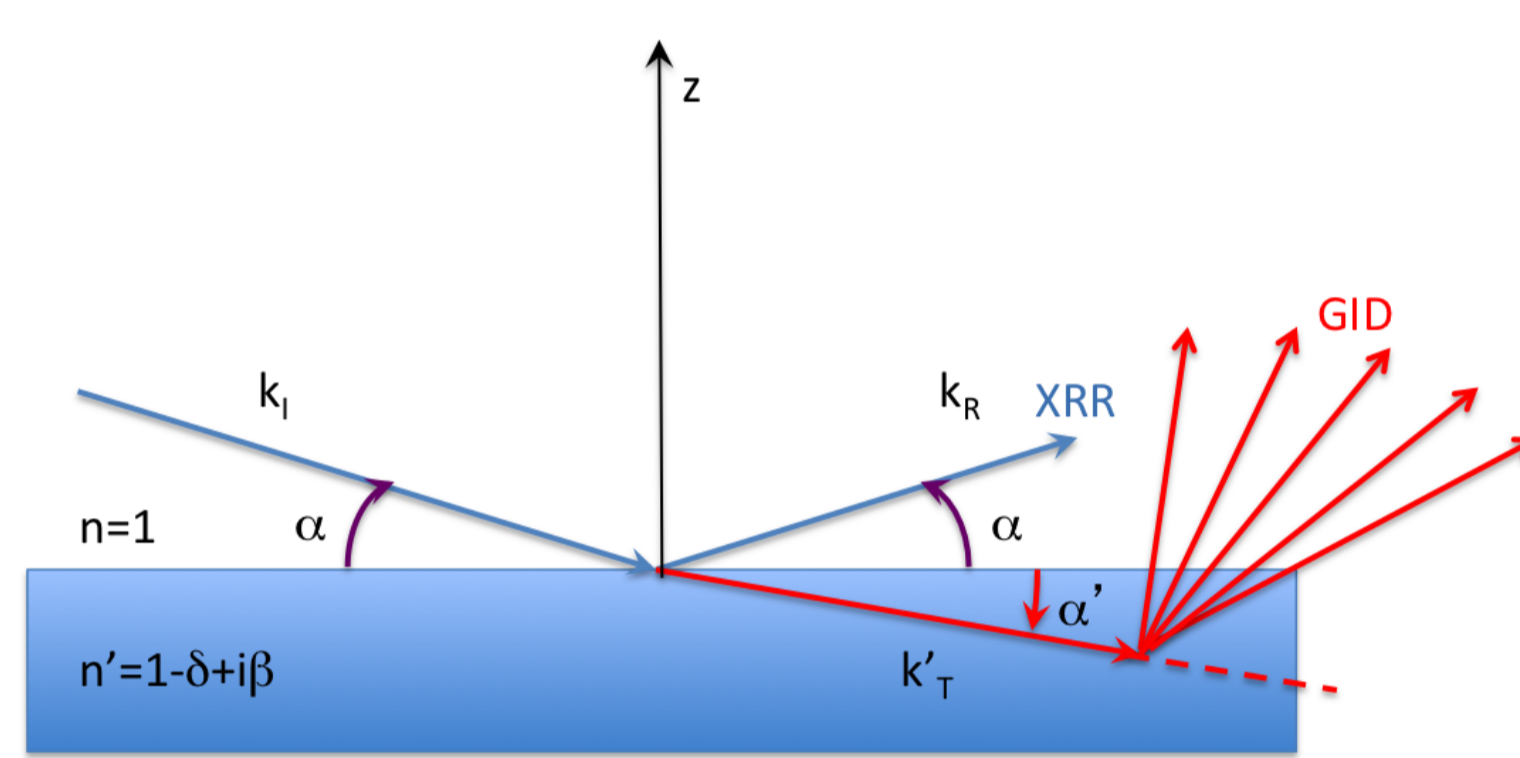
Glancing Incidence XRD [2]

$$\begin{cases} n \cos \alpha' = \cos \alpha \\ (a_i + a_r) n \sin \alpha' = (a_i - a_r) \sin \alpha \end{cases}$$

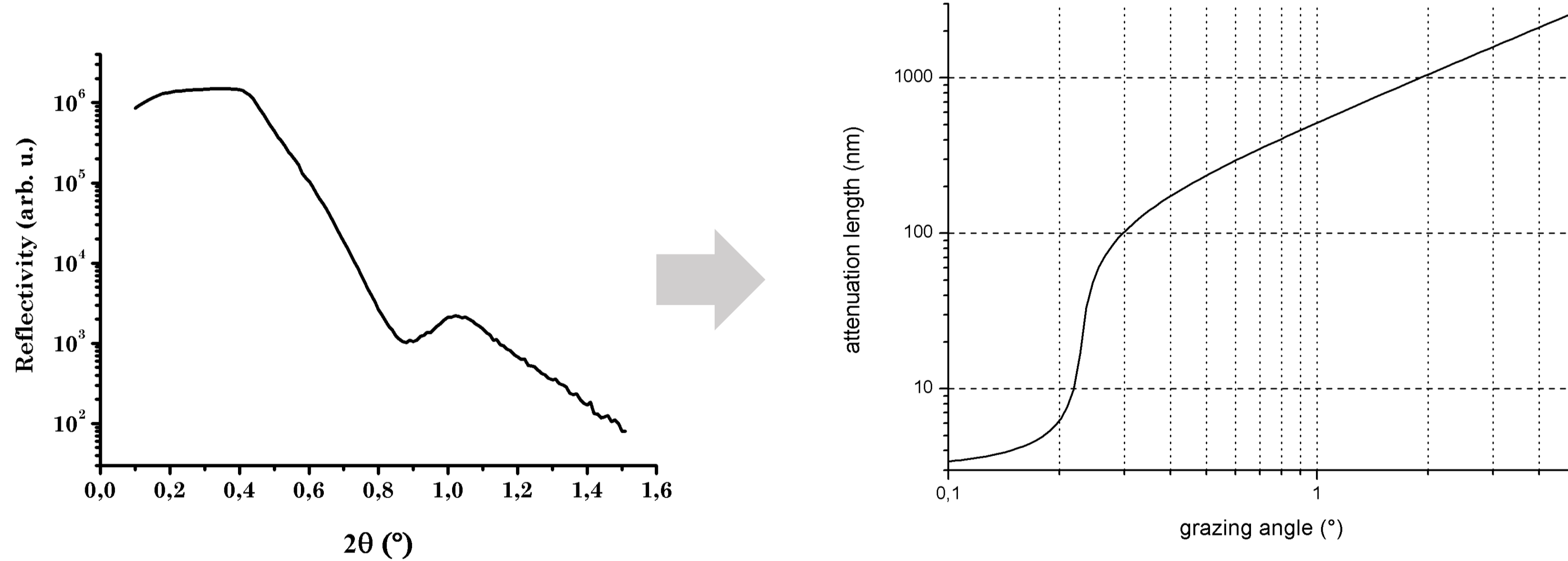
$$n = 1 - \delta + i\beta \approx 1 - \frac{\alpha_c^2}{2} + i\beta; \alpha_c^2 \equiv \left(\frac{4\pi}{k^2}\right) \rho; \beta = \frac{\mu}{2k}$$

$$\begin{cases} \left(1 - \frac{\alpha_c^2}{2} + i\beta\right) \left(1 - \frac{\alpha'^2}{2}\right) = \left(1 - \frac{\alpha^2}{2}\right) \rightarrow \alpha'^2 = \alpha^2 - \alpha_c^2 + 2i\beta \\ \left(1 + \frac{a_r}{a_i}\right) \alpha' = \left(1 - \frac{a_r}{a_i}\right) \alpha \rightarrow R \equiv \frac{a_r}{a_i} = \frac{\alpha - \alpha'}{\alpha + \alpha'} \end{cases}$$

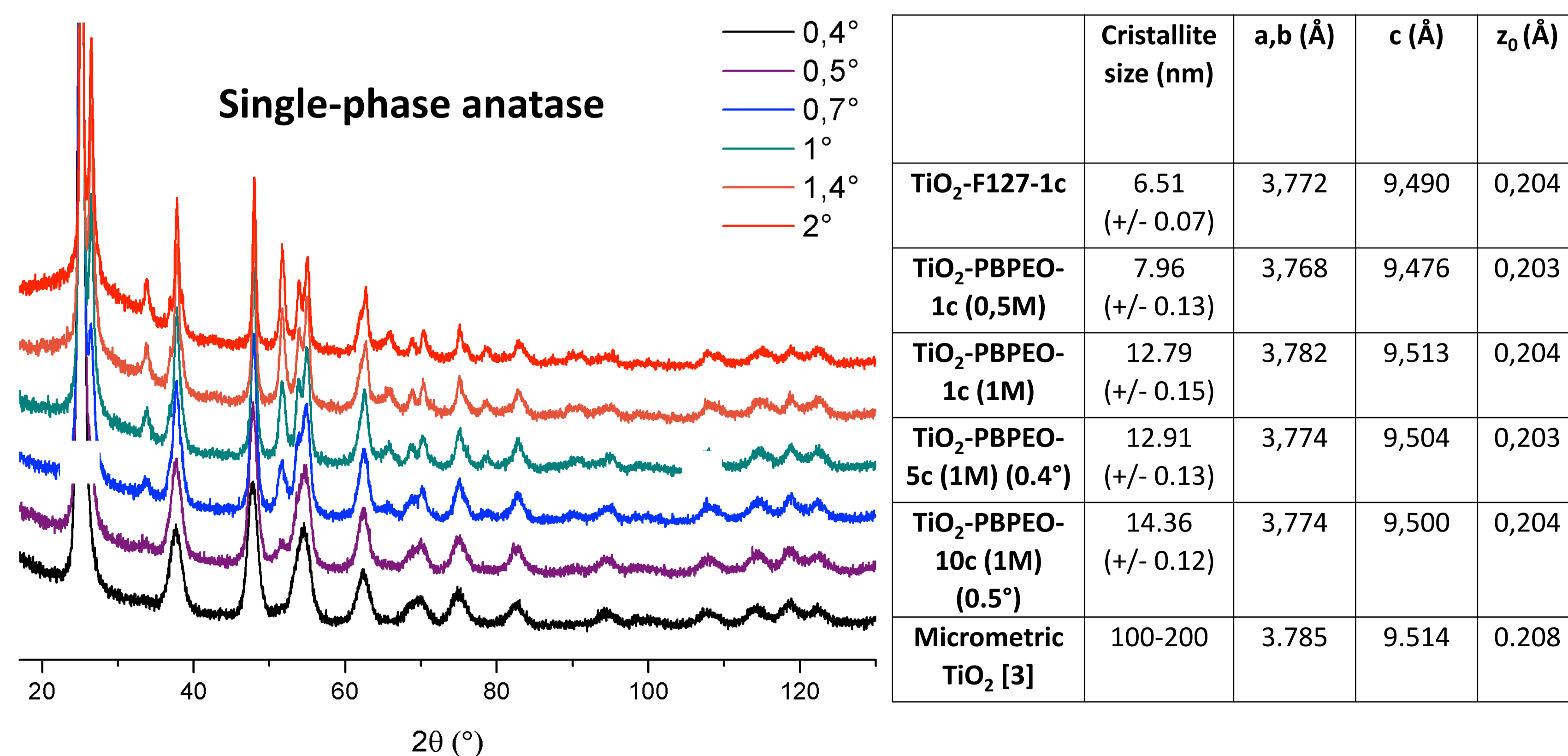
Snell, Fresnel and XRD



Mesoporous TiO₂ Anatase thin film dipped on FTO/glass



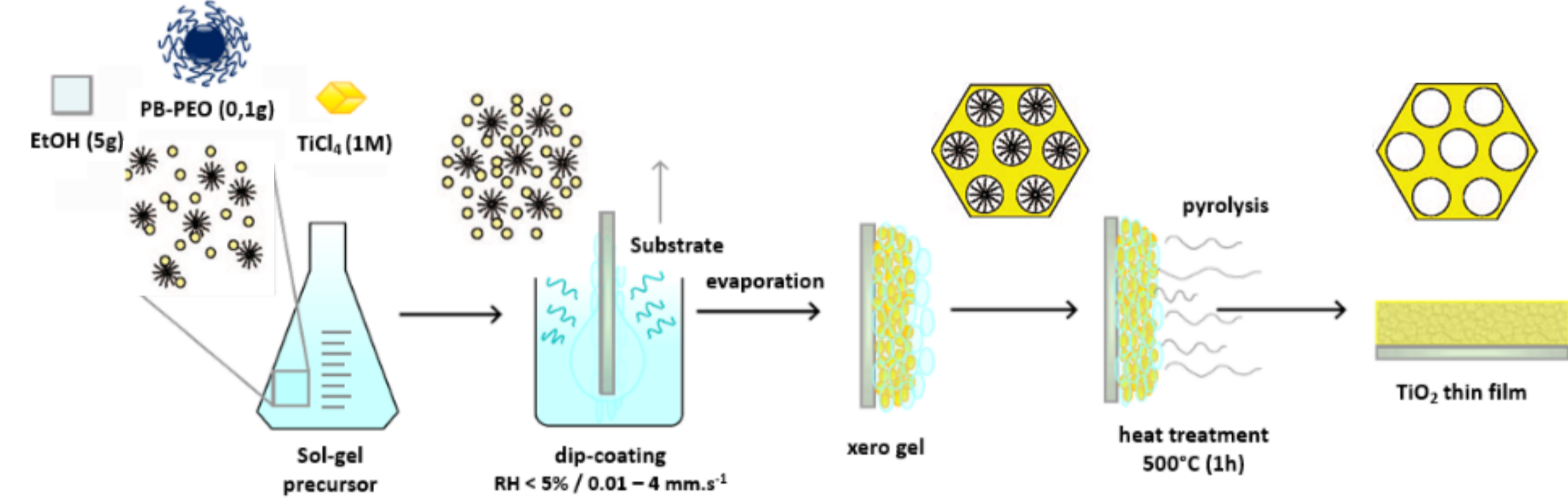
Single-phase anatase



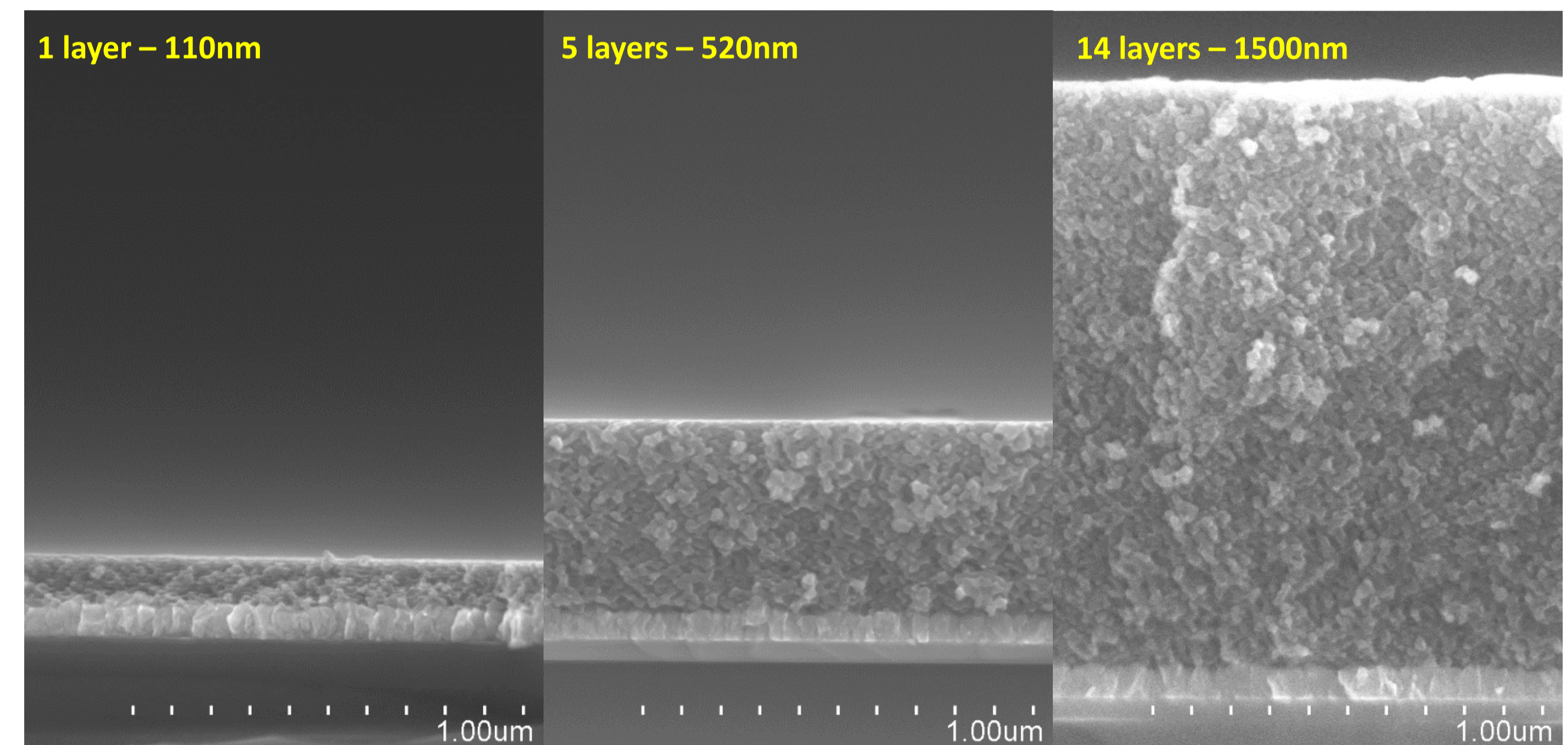
Conclusion

- The characteristics of architected mesoporous TiO₂ thin films, produced by dip-coating on a FTO/glass substrate, can be studied across their thickness.
- Probing the films at multiple glancing angles shows evidence of single-phase nanocrystalline anatase with a same structure and microstructure across the entire film thickness, a result in very good correlation with SEM-FEG and TEM analyses that involve the destruction of the sample.

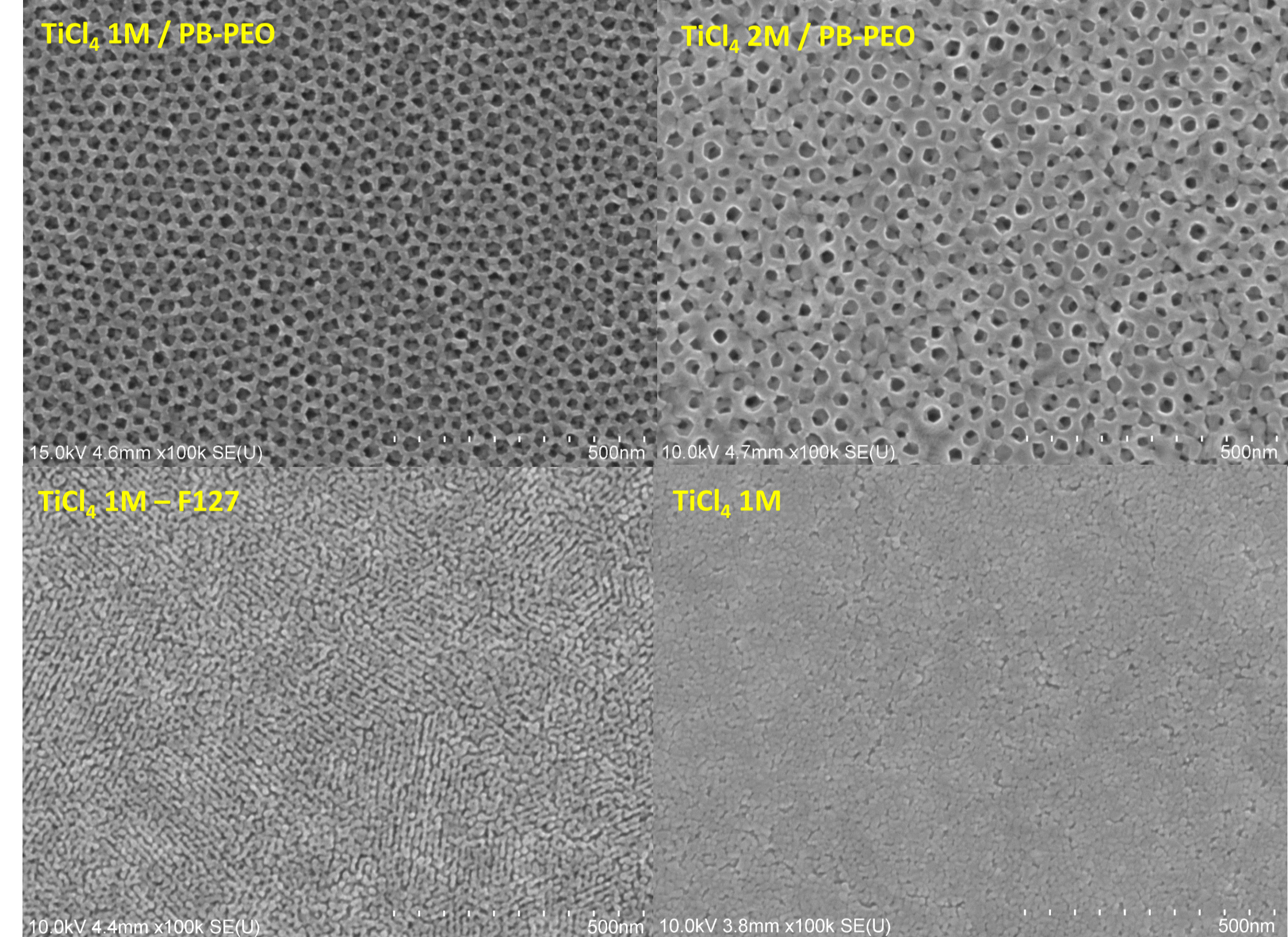
Thin Film Electrode Synthesis



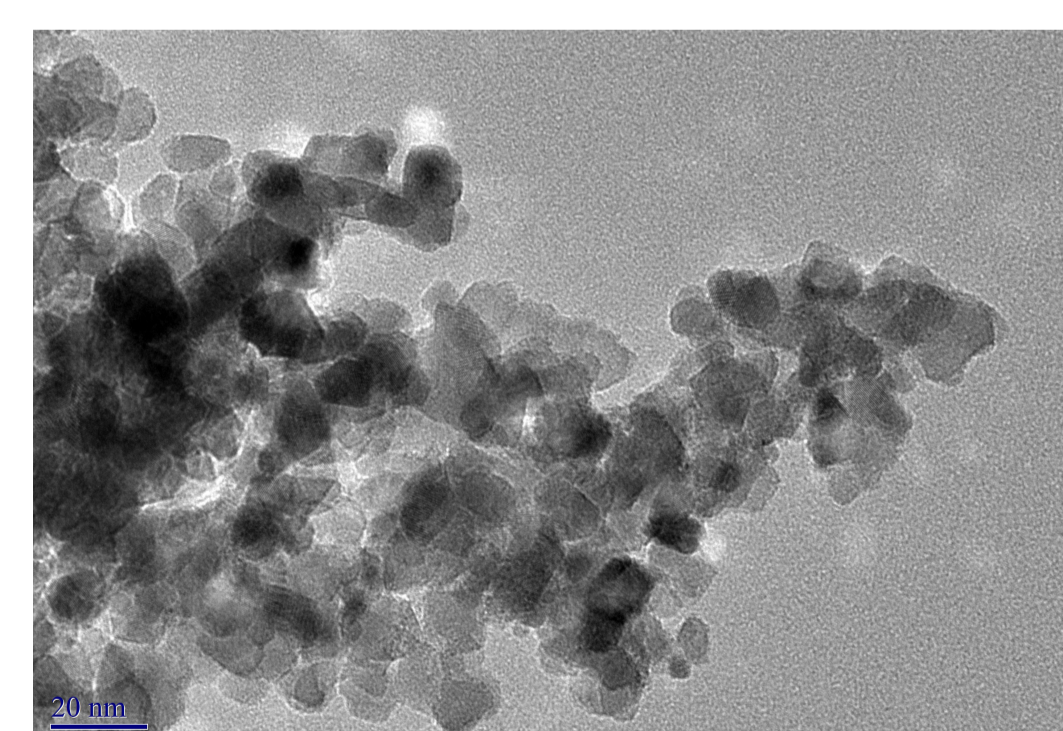
Tunable Electrode Architecture



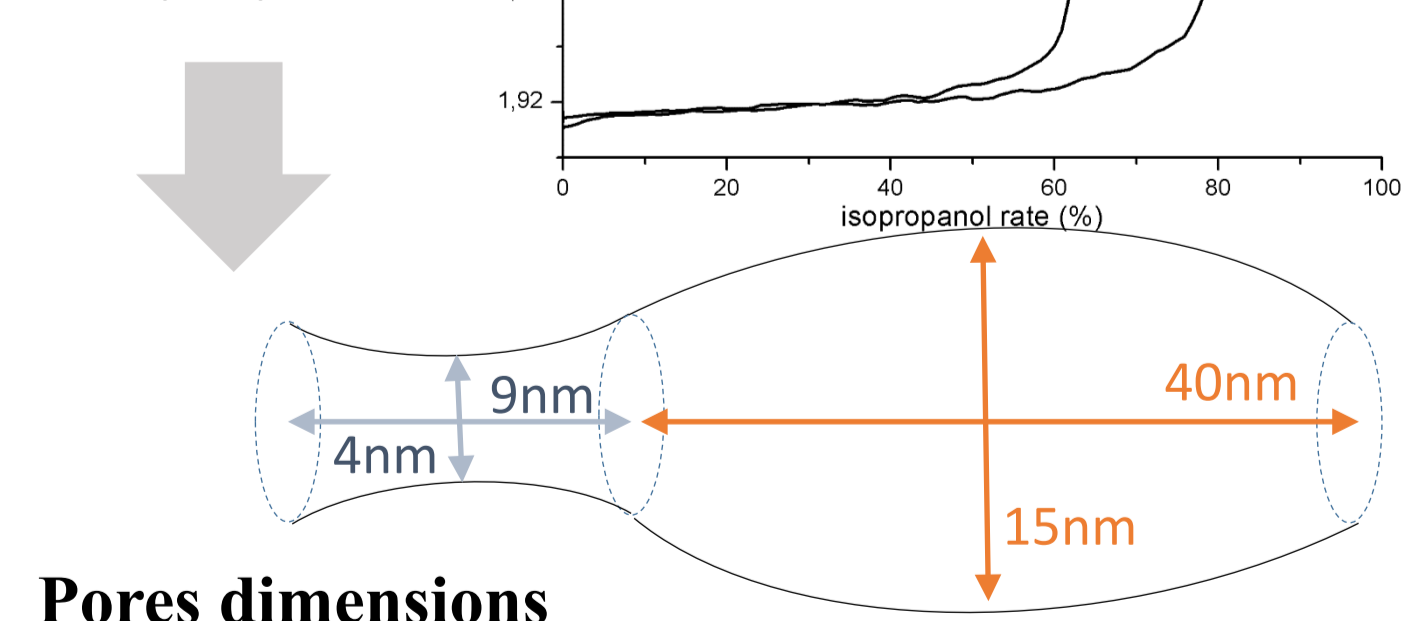
SEM FEG



TEM



Ellipsometry porosimetry (Isopropanol)



Pores dimensions

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