

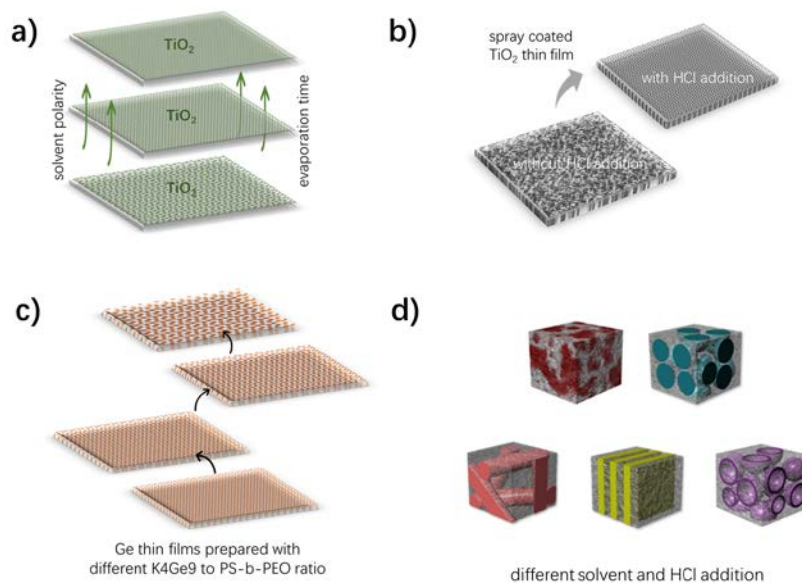
## Mesoporous metal oxide thin films

During the past decades, nanostructured inorganic thin films, such as  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and Ge thin films, have been widely studied due to their attractive properties. Main fields of applications of these inorganic thin films involve solar cells, gas sensing, lithium/sodium ion batteries, and photocatalysis. When used as the anode material of lithium/sodium ion batteries, the high surface-to-volume ratio of these inorganic thin films facilitates penetration of electrolyte and intercalation of lithium or sodium ions. In the case of organic-inorganic hybrid solar cells, the exciton diffusion length within typical backfilling materials is typically less than 20 nm. The existence of the mesoporous structures provide an excellent basis to suppress recombination losses of excitons. Among plenty of preparation routes to porous inorganic nanostructures, amphiphilic block copolymer assisted sol-gel chemistry features a low cost, operation compatibility with ambient atmosphere and easy one-pot processing route, and therefore has been confirmed as a particularly promising approach.<sup>1</sup>

With the assistance of amphiphilic block copolymers, various nanostructured inorganic thin films are prepared in our group during the past several years. Typical examples are the  $\text{TiO}_2$  and Ge thin films prepared by Hohn et al. and the  $\text{TiO}_2$  thin films prepared by Rawolle and Yin et al..<sup>2-5</sup>

Hohn et al. studied the changing of the solvent evaporation time, polarity of the immersion solvent, addition of HCl catalyst and molar mixing ratio of the raw material on the final thin film morphologies. Specifically, by analyzing the effect of solvent evaporation time and the composition of the immersion solvent on the final  $\text{TiO}_2$  film morphologies, the interdependence of mobility and polarity upon the formation of porous titania thin films is illustrated (**figure 1a**)<sup>5</sup>. With the in-situ grazing incidence small-angle X-ray scattering (GISAXS) measurements, the structure evolution kinetics of the PS-b-PEO templated  $\text{TiO}_2$  thin films along with the HCl addition was systematically studied. It was found that templating effect of the employed diblock copolymer can be significantly improved with in the presence of HCl.(figure 1b)<sup>3</sup>. Apart from the studies on  $\text{TiO}_2$  thin film preparation, mesoporous Ge thin films were also prepared by using amphiphilic diblock copolymer polystyrene-b-polyethylene oxide as structure directing agent. It is found that the size of the predominant foam-like structures inside the Ge-based thin film can be systemically tuned from an average radius of 6.7 nm up to 12.7 nm by simply changing of the molar mixing ratio between polymer template and Ge precursor (figure 1c).<sup>2</sup>

The emphasis of Yin et al.'s study was primarily on the different solvent categories and the amount of available hydrochloric acid catalyst employed during the gelation process. Figure 1d shows the TiO<sub>2</sub> nanostructures formed by changing the solvent category and HCl catalyst content. It was found that the formation of different nanostructures is mainly governed by the following three factors: the surface energy between PS blocks and surrounding solvent, the aggregation behavior of the titania nanoparticles, and the block specific selectivity of the used solvent.<sup>4</sup>



**Figure 1.** TiO<sub>2</sub> thin films prepared by (a) changing the solvent evaporation time prior to poor solvent immersion and (b) influence of HCl addition on the PS-b-PEO templated TiO<sub>2</sub> thin film morphologies. (c) Foam-like Ge-based thin films prepared by changing the molar mixing ratio between polymer template and Ge precursor. (d) TiO<sub>2</sub> nanostructures formed by changing the solvent category and HCl catalyst content.

Based on the studies performed in our group, further investigation on the development of new preparation methods of nanostructured inorganic thin films and their corresponding device performance are foreseen in the near future.

## References

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