# Molecular imprinting in ultra-thin titanium oxide films

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Molecular imprinting (MI) is one of the most promising approaches to achieve precise molecular recognition. Variety of structures, from the smallest molecules to proteins, viruses or cells can be the subject of imprinting in different matrices [1]. The whole approach can be conditionally divided into two branches – imprinting in organic polymers (prevailing) and imprinting in inorganic materials such as silica or metal oxides.

Imprinting in titanium dioxide ($TiO_2$, titania) was first introduced by Kunitake group in late 1990s and since then it was used for imprinting variety of the templates such as carboxylic or amino acids, peptides, sugars, macrocyclic compounds such as porphyrins or phthalocyanines, polymers, ions, etc. Bulk imprinted materials are however associated with some drawbacks such as complex fabrication procedure, low binding efficiency, and slow binding process, since the imprinted sites are far from the surface leading to very slow diffusion and low reversible binding.

Alternatively, the molecular imprinting technique in the form of ultrathin films attracts more practical interests because of its improved efficiency. In particular, imprinted inorganic thin films have been applied to sensor transducers owing to their simple deposition onto the surface. Variety of approaches can be used for MI-$TiO_2$ film preparation such as metal oxide precursor spin coating, liquid phase deposition, surface sol-gel process, etc, while imprinting efficiency can be estimated by spectroscopic methods.

In this report I will demonstrate previous accomplishments in the field of MI in $TiO_2$ such as enantiomers imprinting and tools for selectivity improvement [2], imprinting of the macrocycle compounds using surface sol-gel process [3]. Other interesting properties of the titania is the ability to form the regular phase-separated structures of $TiO_2$ with hydrophobic organic polymers. Using the effect of phase separation we have demonstrated the phenomena of nanosandwich self-supporting film formation when $TiO_2$ precursor was mixed with the polystyrene (PS) [4]. In the most recent work the usage of PS/$TiO_2$ interface was used for the new type of imprinting where hydrophobic interaction of template with PS was utilized to improve the binding of the template [5].

In current study we are trying to apply the concept of the molecular imprinting in the ultrathin inorganic films for the design of the gas separation membranes. We believe that: 1) ideal and uniform metal oxide film can provide the sufficient gas barrier needed for membrane on the first stage of preparation 2) molecular imprinting / molecular templating can be used to create the selective sites or selective channels for the carbon dioxide penetration (Fig.1).

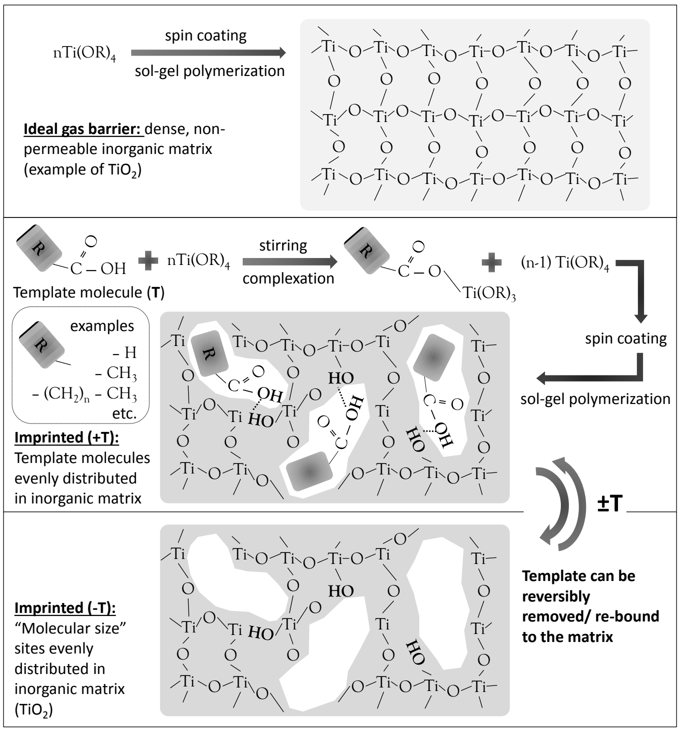


**Fig. 1** Schematic illustration of the MI of carboxylic acid in $TiO_2$ as a method of the membrane selectivity tuning.

**Previous works**:


1) Lee, S.-W., Korposh, S., Selyanchyn, R., Kunitake, T. Fundamentals and perspectives of molecular imprinting in sensor applications **(2012)** Handbook of Molecular Imprinting: Advanced Sensor Applications, pp. 3-62
2) Mizutani, N., Yang, D.-H., Selyanchyn, R., Korposh, S., Lee, S.-W., Kunitake, T. **(2011)** *Analytica Chimica Acta*, 694 (1-2), pp. 142-150.
3) Araki, K., Yang, D.-H., Wang, T., Selyanchyn, R., Lee, S.-W., Kunitake, T. **(2013)** *Analytica Chimica Acta*, 779, pp. 72-81.
4) Mizutani, N., Korposh, S., Selyanchyn, R., Yang, D.-H., Lee, C.-S., Lee, S.-W., Kunitake, T. **(2012)** *Chemistry Letters*, 41 (5), pp. 552-554.
5) Selyanchyn, R., Lee, S.-W. **(2013)** *Microchimica Acta*, 180 (15-16), pp. 1443-1452.