Highly Ordered Nano-Arrays of Titania-Based Nanohybrids

Titanium oxide (TiO$_2$, titania) is well-known as an important ceramic material. Due to its versatile optical, electrical and photochemical properties, it has found extensive applications in high-refractive index devices, optical waveguides, photo-catalysts and photovoltaic cells. Particularly, in the form of very fine particles on the scale of ten to hundreds of nanometers, TiO$_2$, along with other functional nanomaterials, has been the subject of extensive investigation and close scrutiny among scientists and engineers for the past decade. In the following, we describe a very recent, exciting development with nanocrystalline TiO$_2$: titania-based nanohybrids.

As the name suggests, the nanohybrids typically consist of titania nanoparticles that are purposely embedded in a polymeric matrix. The beauty of such nanohybrids is that they can effectively couple the unique optical and electronic characteristics of TiO$_2$ with distinctly different functional properties of the organic matrix. This leads to uniquely different optical properties such as an ultra-fast nonlinear response time and a very high nonlinear optical coefficient, which promise a wide range of applications in optical switching and filtering devices. In this connection, our laboratory has successfully synthesized nanohybrids consisting of 3-5 nm TiO$_2$ nanoparticles embedded in a poly (methylmethacrylate) (PMMA) matrix via an in situ sol-gel and polymerization technique (Figure 1). The resulting nanohybrid thin films yielded a third-order nonlinear optical susceptibility ($\chi^{(3)}$) up to 1.93 x 10$^{-9}$ esu, which is about two orders of magnitude higher than that of bulk titania.
Based on TEM studies, however, it was realized that the current synthesis route still leads to non-uniformity in the inorganic-organic nanostructures. This is mainly due to the nature of the condensation process of hydrolyzed TiO2 precursor, which takes place in random locations in the polymer matrix. Therefore, it is of considerable interest to synthesize nanohybrids where the formation sites for TiO2 nanoparticles in the PMMA matrix can be controlled. For this purpose, the polymer matrix needs to have particular compartments which can selectively uptake the inorganic precursor. To realize this, we make use of poly(methylmethacrylate)-polyethylene oxide (PMMA-PEO) di block copolymer as a template. The uniqueness of this copolymer is that it contains two chemically dissimilar polymer chains which have different affinity towards water. One building block loves water (hydrophilic) and the other one hates it (hydrophobic). Due to their immiscibility in a selective solvent, the constituent blocks can form a variety of ordered nanoscale morphologies such as spheres, cylinders, or lamellae, etc.

Taking a cue from this phenomenon, our synthesis technique involves the formation of micelles consisting of hydrophilic PEO corona and hydrophobic PMMA core by
dissolving this copolymer in a mixture of tetrahydrofuran (THF) and water (Figure 2a). This is followed by a thorough incorporation of titanium alkoxide as the inorganic precursor into the PEO sites. The synthesis challenge lies in trading off two contradicting aspects, i.e. huge amount of water in the mixture solvent, which is essential for micellization of PMMA-PEO blocks to occur, and the highly water-sensitive nature of titanium alkoxide. We overcome this problem by adding the proper amount of hydrochloric acid into the solution. The presence of this acid also assists the selective uptake of titanium alkoxide precursor into the PEO domains. Under a controlled annealing process, the resulting nanohybrid thin film shows a highly dense and regular pattern of long-range hexagonally ordered PMMA domains surrounded by very fine titania nanoparticles, estimated to be less than 2 nm (Figure 2b). Increasing the heating rate in the annealing schedule enabled the conversion of hierarchical structural configuration into cubical patterns, accompanied by a significant increase in the size of titania nanoparticles up to about 7-10 nm (Figure 2c).

![Diagram](image)

**Figure 2**: (a) Schematic representation of formation of TiO2 nanoparticles in a highly ordered array by using PMMA-PEO diblock copolymer templating. HRTEM images of the resulting thin films show: (b) long-range hexagonally ordered PMMA domains surrounded by very fine titania nanoparticles of about 2 nm, (c) a cubical pattern of titania nanoparticles of about 7-10 nm, resulting from annealing with a faster heating rate.
In conclusion, we have successfully devised a novel templating synthesis route using PMMA-PEO block copolymer to prepare nanohybrid thin film containing highly ordered arrays of TiO2 nanoparticles in PMMA matrix. Such bottom-up fabrication techniques are attractive for generating patterns which are smaller in size than those produced by lithography techniques. Besides, the technique is also simple and cost-effective.

Contact Person : Prof J Wang

E-mail: msewangj@nus.edu.sg

Tel : 6516 1268
Fax: 6776 3604