

Functional oxide nanomaterials - infiltration synthesis using block copolymers and organometallic transition metal compounds

By slicing a tomato on a white polyethylene board, we inevitably soil it with its remains. Then we try to wash it either in a dishwasher or by hand with dishwashing liquid. Both ways, despite their repetition, do not change the result - a red tint remains on the board (this dye is lycopene) in the place of soiling with tomato leftovers.

The above example from everyday life perfectly illustrates the existence of free volume in the porous structure of polymers. In the case of a tomato, the dye particles have been physically trapped inside the structure and their release is not possible without destroying it. In my project I would like to examine in a similar way, by means of a chemical reaction, the process and depth of penetration of complex molecules of compounds of selected transition metals inside a polymer. Understanding it will allow me to develop a universal way of dealing with the deposition of more metal oxides, currently unattainable for this technique.

Block copolymers are polymers, i.e. macromolecular compounds, made up of at least two different blocks. One block consists of n the same molecules (mers) connected by chemical bonds to each other. The second of them form different kinds of molecules, equally grouped, in the number m . Due to the covalent bond between these blocks, block copolymers are characterized by a "chemical incompatibility". It causes an unusual phenomenon of self-assembly. Copolymers heated above a certain specific temperature arrange themselves into shapes that can be predicted in advance by modifying the copolymer composition. Inside these types of polymers, similarly to the example with a board and a tomato, the penetration of chemical particles containing metal is possible. This can be achieved by performing the so-called infiltration synthesis process in a specially designed chemical reactor. Due to the chemical differences between the blocks, the metal-containing molecules selectively deposit only in the one distinct polymer block. This type of process is carried out in mass in electronic component factories, where the optical devices create patterned templates. The use of copolymers and the proposed infiltration method for the production of microelectronic systems would reduce production costs and speed up fabrication time. The key factor inhibiting the development of the polymeric method is insufficient knowledge of the controlled way of polymer formation and the process of penetration leading to a final chemical reaction inside the polymer.

Small metal-containing molecules penetrate the polymer pores relatively quickly and deeply, where they easily adsorb. Unfortunately, for selected transition metals, the synthesis of chemically similar small compounds is impossible due to their decomposition at room temperature. The solution is to create compounds of these metals that are stable at room temperature. Such compounds exist, however, due to their size, these molecules have a limited depth of penetration into the polymer. This significantly hinders the development of block copolymers in using them as a template for the synthesis of oxide nanomaterials of a given shape. I would like to fill this gap, so in this project I would like to thoroughly investigate this process by infiltrating polymers that have different chemical groups in their structure with previously unused larger metal particles. In my work I will use optical techniques, utilizing X-ray radiation as well as electrons to determine the necessary physicochemical parameters to get a full image of the laws governing the process.

The information gathered from the conducted experiments will contribute to the development of knowledge about the governing mechanisms of reactions of low-volatile large-molecule precursors. The successful project outcomes will open new perspectives related to the synthesis of functional oxide nanostructures of elements not yet obtained by this method. Applications for such 3D hybrid nanomaterials are in the area of chemical sensors, catalytic coatings, durable dental fillings or ion exchange membranes utilized in water purification.