Switching Ceramic Surface Chemistry from Oxide to Non-Oxide Using Thermal ALD - Evaluation of BN/α-Al_2O_3 MF Membranes

A. Julbe*, C. Mansas, S. Masson, M. Weber, M. Drobek, P. Miele and M. Bechelany
Institut Européen des Membranes, CNRS, University of Montpellier, France
* anne.julbe@umontpellier.fr

Abstract

Controlling the fluid-solid interface of membranes is a key to improving their filtration/separation performance [1]. Tremendous progress has been made recently in the rational design of membrane surfaces and interfaces, supported by the emergence of a wide diversity of new materials and surface modification methods. Exciting developments in the field of water treatment and purification have been reported, mainly based on the performance of new inorganic, hybrid and composite membrane materials. In this area, non-oxide ceramic membranes are promised to a bright future, thanks to their specific surface charges and their antifouling properties.

As a typical example, silicon carbide (SiC) offers decisive advantages over conventional oxide ceramic membranes in industrial water filtration processes, including oily water treatment. In fact, its low zeta potential (similar to silica) and high surface hydrophilicity could be responsible for enhanced resistance to fouling, although a slippage effect [2] due to a tightly bound water film on the native silica has been reported to contribute to high measured water fluxes. On the other hand compared to conventional oxides, the manufacturing process for these high-performance SiC membranes (requiring typically recrystallization above 1500°C in the total absence of oxygen), is quite expensive and generates a large pore size distribution, with nominal value hardly less than 100 nm. Pore size control and post-modification of SiC membranes are thus the subject of intensive research [3]. In parallel, an alternative option to produce low-fouling membranes with smaller pores has been proposed by the modification of cheaper alumina supports with (amorphous) SiC layers prepared by low-pressure CVD [4].
Indeed, modifying the surface of commercial oxide supports by deposition of a thin layer of a non-oxide material is clearly a relevant strategy for adjusting membrane pore size and surface chemistry. Among the diversity of surface modification techniques, Atomic Layer Deposition (ALD) is particularly studied in our group as it allows the preparation of thin films of high quality materials (oxides, metals, non-oxides, hybrids and composites) on substrates with a high aspect ratio, precise thickness control, high uniformity and excellent conformality. It is therefore very well suited for controlling membrane pore size as well as the chemistry of surfaces/interfaces at large scale [5]. The ALD process is extremely challenging for the conformal deposition of carbide materials like SiC, but it is commonly used for the deposition of other non-oxides materials such as sulfides and nitrides. Using thermal ALD, we successfully deposited boron nitride (BN) on anodized aluminum disks (ANOTEC) to adjust their surface properties and reduce the size of capillary pores from 100 nm to a few nm [6]. Just like SiC, BN is an attractive non-oxide material for membrane applications. It is a slightly polar material, with a moderate surface energy of about 40 mJ/m^2, close to that of carbon, and 15 to 7 times lower than those of alumina and SiC, respectively. It is already negatively charged at pH 4 and is rather hydrophilic. Several BN morphologies with large specific surface areas (nanotubes, nanosheets) have already been integrated into membranes to study the separation of molecules and the depollution of water at lab scale [7,8].

In this work, the ALD process has been used to modify the surface properties of commercial tubular α-alumina microfiltration (MF) membranes. Conformal ultrathin layers of BN were deposited to uniformly cover the oxide grains. The objective was to generate BN-coated membranes with improved performance (water flux and fouling resistance) for the filtration of acidic surface water (i.e. pH 5-6, in the presence of humic acid). Thermal ALD at 750°C using BBr_3 and NH_3 as precursors was found to be an efficient strategy to control the growth of conformal and adherent BN layers with thickness in the range 5-20 nm on the alumina support grains. The physicochemical characteristics of the BN-coated alumina membranes will be described and their performance (increased water flux and antifouling behaviour) will be discussed, in comparison with those of their ceramic oxide counterparts.

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