Nanoporous anodic aluminium oxide membranes with layered surface chemistry†

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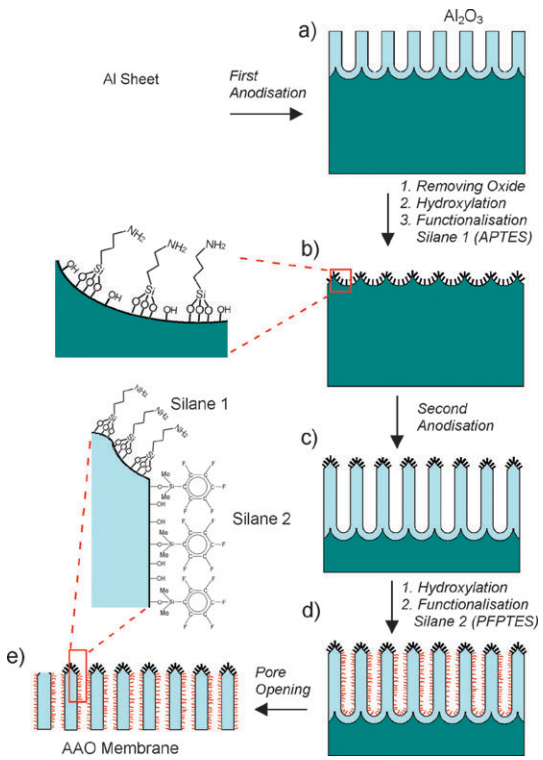
A new and facile method is described to prepare Janus-like nanoporous anodic aluminium oxide (AAO) membranes with distinctly different internal and external surface chemistry.

In recent years, nanoporous anodic aluminium oxide (AAO) membranes have become popular and attractive materials for a diverse range of applications including molecular separation,[1] catalysis,[2] energy storage,[3] drug delivery,[4] biosensing,[5] and template synthesis.[6] This profound interest is due to the salient features of this nanostructured material. First, AAO membranes can be easily fabricated with monodisperse, geometrically regular and self-organised pore structures. Furthermore, such membranes have a high surface area (180–250 $m^2\ g^{-1}$), high porosity (10^{10} pores cm^{-1}), are robust and biocompatible.[7,8]

AAO membranes have been used in a range of sophisticated molecular separation tasks including the separation of enantiomers,[4] amino acids,[9] proteins,[10] nucleic acids,[11] as well as for controlled molecular release.[12] These examples rely heavily on the appropriate chemical functionality at the AAO pore surface. A common approach to AAO surface functionalisation involves gold layer deposition for fabricating self-assembled monolayers of alkanethiols.[13,14] A more straightforward approach for surface modification of AAO membranes involves silane chemistry.[15] A wide selection of silanes offering different functional groups, charge and interfacial properties are commercially available. Using silanised AAO membranes, manipulation of electro-osmotic flow,[16] label-free detection of DNA,[17] and ligand-gated ion channelling has been achieved.[18]

However, in order to impart multi-functionality in AAO membranes, an approach that generates distinct layers of differing surface chemistries or discriminating between the pore opening and the inside of the membrane is desirable.[19] This would permit new methods for tailoring molecular transport properties, molecular selectivity and perhaps increase biocompatibility.[20,21] Two-faced or layered hydrophobic and hydrophilic surface chemistry would aid the design of suspended lipid bilayers and drug-delivery devices.[22,23] Unfortunately, reports of such structures are rare, and to our knowledge none involve silane chemistry. AAO membranes with a hydrophilic side and a hydrophobic side functionalised by plasma polymerisation of a fluorocarbon layer have been reported.[24] However, this process not only significantly altered the diameter of the pore openings but failed to functionalise the internal pore walls. Link and Sailor prepared two-layered porous silicon membranes where an anodised first layer was hydrosilylated with a hydrophobic alkene, and a subsequent etch provided a second layer which was oxidised imparting hydrophilic character.[25] Recently, a mesoporous silicon film was differentially functionalised in an approach that exploits both surface tension and capillary action to prevent or encourage entry of reagents into the porous layer.[26]



Scheme 1 Producing layered surface chemistries in AAO membranes. Membranes after (a) first anodisation, (b) removal of the sacrificial layer and functionalisation with APTES, (c) second anodisation, (d) second silanisation with PFPTES and (e) pore opening at the membrane bottom.

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In this communication, we report a new approach for controlling surface architecture of AAO membranes that generates layered, silane-based surface chemistries and yields distinctly different functionalities on the pore openings and the internal pore surfaces (Scheme 1).‡ Our approach is predicated on the remarkable stability of the silanised AAO surface during anodisation. After a first short anodisation and removal of most of the generated porous alumina, the remaining thin (70–90 nm) porous layer was treated with 3-aminopropyltriethoxysilane (APTES). A longer subsequent anodisation was initiated at the bottom of the first porous layer and resulted in the formation of an increased internal pore volume. The newly generated pores were then functionalised with hydrophobic pentafluorophenyldimethylchlorosilane (PFPTES) with distinctly different properties than the APTES present in the pore openings. A free-standing membrane was finally prepared by dissolution of the remaining substrate, followed by pore opening at the membrane bottom.

The morphologies of the formed structures and patterns of nanoporous AAO membranes were characterised by scanning electron microscopy (SEM). Fig. 1 shows a series of SEM images of AAO membranes prepared by our approach. The AAO surface after first anodisation, stripping and APTES treatment is depicted in Fig. 1a. This pretextured surface assists the formation of ordered pore structures during second anodisation. SEM analysis did not reveal a morphological difference before and after APTES treatment.

Fig. 1b is a top view of the membrane after the second anodisation. The pores are hexagonally aligned with a mean pore diameter of about 30 nm and an interpore distance of approximately 80 nm. This result confirms that anodisation is possible on a silane-modified AAO surface. The bottom surface of a free-standing membrane (Fig. 1c) shows a hexagonal array of pores with an average diameter and interpore distance of 30–45 nm and 100 nm, respectively. A typical cross-sectional view (Fig. 1d) of the membranes shows the typical non-intercrossing, straight and cylindrical pores of AAO.

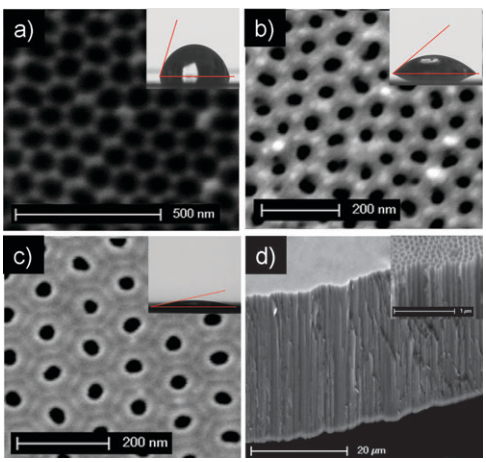

Fig. 1 SEM images of fabricated AAO membranes with different internal and external surface chemistry. (a) AAO surface after first anodisation, stripping and APTES modification. (inset: image of water droplet on APTES modified surface), (b) top surface after second anodisation (inset: image of water droplet on this surface), (c) bottom membrane surface after second anodisation and pore opening process (inset: image of water droplet on this surface), (d) membrane cross-section (inset: zoom-in).

Water contact angle measurements were performed to determine the wettability of the membranes. Substrates treated with APTES after first anodisation display a water contact angle of 86 ± 1.2° (inset of Fig. 1a). The water contact angle changed to 55 ± 0.9° after completing the second anodisation (inset Fig. 1b). Rather than the destruction of the initial APTES layer (as confirmed by XPS), we attributed this increase in wettability to the change of surface topography.[27,28] After the second anodisation, the initial AAO pores with 100 nm diameter (Fig. 1a) were converted into narrower pores with 40 nm average diameter (Fig. 1b). On AAO, the contact angle is known to increase monotonically with pore diameter.[29] The water contact angle after the second anodisation is still significantly higher than that of the bare AAO membrane (<20°). In contrast, the bottom part of the membrane, after detaching from the Al substrate and pore opening, indeed shows a water contact angle of 15° (Fig. 1c, inset). X-Ray photoelectron spectroscopy (XPS) (ESI† Fig. S1) on the membranes confirmed that APTES attachment indeed survived the second anodisation. Survey scans of the APTES-modified surfaces showed a silicon peak, and high-resolution C1s spectra show carbon peaks with binding energies of 286.4 and 287.7 eV, which we assigned to C–N (amine) and C–O (alkoxy) groups, respectively.

When the internal surface of the APTES-capped AAO membranes was functionalised with PFPTES. The water contact angle of the top membrane surface remains stable at 53 ± 1.5°. This is in stark contrast to a control bare membrane sample treated with PFPTES, which gave a water contact angle of 119 ± 1.1°. These results provide strong evidence that PFPTES attachment under our experimental conditions is successful and that the APTES is not displaced from the exterior surface. To further confirm the attachment of PFPTES inside of the membrane, energy-dispersive X-ray spectroscopy (EDX) analysis of a membrane cross-section was performed. EDX spectra revealed the presence of fluorine, silicon and carbon peaks attributed to PFPTES (ESI† Fig. S2).

To verify that the amine groups on the top of the membrane are still functional for attachment of molecules, an important prerequisite for tailorable membranes, the membrane was treated with fluorescein isothiocyanate (FITC). The APTES-capped top surface indeed showed strong green fluorescence

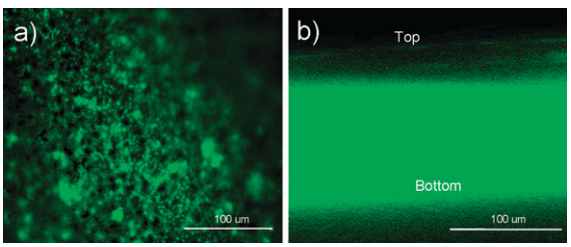

Fig. 2 Fluorescence microscopy images of (a) APTES (top) and PFPTES (inside) functionalised AAO membrane and (b) cross-section of a membrane functionalised with PFPTES on the upper layer and APTES on the layer beneath after treatment with FITC.

(Fig. 2a), whilst a bare membrane treated with FITC did not fluoresce.

This last result underlines the success of our approach to prepare membranes with distinctly different surface chemistries. To further demonstrate the versatility of our surface modification, we fabricated a thicker top membrane layer (approx. 20 μm) and switched the functionalisation sequence by reacting the top layer with PFPTES and treated the new porous layer (80 μm thick) generated after further anodisation with APTES. Fig. 2b is a fluorescence microscopy image of a membrane cross-section after reaction with FITC showing strong green fluorescence inside the membrane and weak fluorescence of the top layer.

We should point out that the bottom part of the AAO membranes after detachment from the support and pore opening is potentially available for a third silanisation. Alternatively, before lifting the membrane of the support, additional anodisation steps could be employed in series, after each of which the new porous area could be silanised, generating a multilayered chemistry inside of the pores. Many other silanes could substitute the ones we have employed here to prove the concept.

In summary, our simple and inexpensive surface modification approach combines serial anodisations and silane chemistry to generate Janus-like membranes displaying a sharp contrast in surface chemistry. These membranes with layered surface chemistry have multifunctional and tailorable properties, which can be harnessed for complex and advanced molecular separation applications, targeted drug release and biosensing.

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Notes and references

‡ High purity Al sheets (99.99 wt%, Alfa Aesar) with a thickness of 100 μm were degreased in acetone and sonicated for 30 min followed by dipping in aqueous sodium hydroxide solution (5%) for a few seconds. The cleaned sheets were thoroughly rinsed with MilliQ water, dried and then electrochemically polished with (1 : 4 v/v $HClO_4$–EtOH) for 1 min at a constant voltage 25 V in a custom-built etching cell. AAO membranes were fabricated through a typical two-step anodisation process following previous reported procedures.[30] The first anodisation was performed for 4 h under a constant voltage of 40 V and an electrolyte temperature of 1 °C in 0.3 M oxalic acid and 1% surfactant NCW 1001 (Wako). The resulting alumina layer was then stripped off and the surface was hydroxylated in 30% H_2O_2 for 30 min and subsequently treated with APTES (Aldrich) by chemical vapor deposition.[31] A second anodisation was then performed for 25 h using the same etching conditions as described above. The newly generated surface was modified using neat PFPTES (Aldrich) at 80 °C for 2 h. To prepare a free-standing AAO membrane, the remaining Al was removed by $CuCl_2$–HCl solution and pores were opened by treatment with 0.1 M H_3PO_4 at room temperature for 2 h. Water contact angle measurements were performed with a Panasonic SuperDynamic WV-BP550/G camera equipped with a macrolens. XPS analysis of the samples was carried out using an Axis Ultra spectrometer (Kratos Analytical Ltd, GB) with a monochromatic Al Kα source. SEM images and EDX spectra were collected on a Philips XL 30 FEGSEM and EDAX Genesis, respectively. Fluorescence labelling was performed by treating the membranes with 200 μg mL^{-1} of fluorescein isothiocyanate (FITC) in phosphate buffered saline (PBS) buffer (pH 7.4) for 2 h at room temperature and subsequent washes in PBS buffer to remove unbound dye. Fluorescence images were captured with an Olympus IX81 inverted microscope.

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