Ultrathin nanofilm with tailored pore size fabricated by metal-phenolic network for precise molecular separation

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Abstract:

The nanofilms with tailored pore sizes are desirable for precise molecular separation. In this study, the nanofilm fabricated by tannic acid (TA) and ferric ions (Fe^{3+}) has an ultrathin thickness of 5 nm and is probably the thinnest nanofilm used for liquid separation. The pore size of TA/Fe^{3+} nanofilm is approximately 0.7 nm, which is consistent with the result obtained by molecular simulation. These results confirm our hypothesis that the pore size of the nanofilm is related to the TA molecular structure and the pore size is smaller than 1.5 nm. Thus, the nanofilms with fine-tuned pore sizes can be produced using molecules with various structures. Furthermore, with a narrow pore size distribution, the TA/Fe^{3+} nanofilm can separate molecules that are close in size.

Introduction

Nanofilms have been of great interest in many conventional gas and liquid separation processes due to their less energy consumption.[1] With the development of nanotechnology, the study of micro pores on nanofilms has shifted from the empirical-based structures into the tailor-made structures that are useful for precise separation. Amorphous materials are supposed to form the ultrathin nanofilms without defects. The emerging metal-phenolic networks (MPN), simply prepared from phenolic ligands and metal ions, are amorphous materials as a result of the asymmetric structure of the phenolic ligands. [2] Moreover, attributed to the versatile nature of the assembly process, the MPNs are tunable and functional materials that have attracted significant interests.

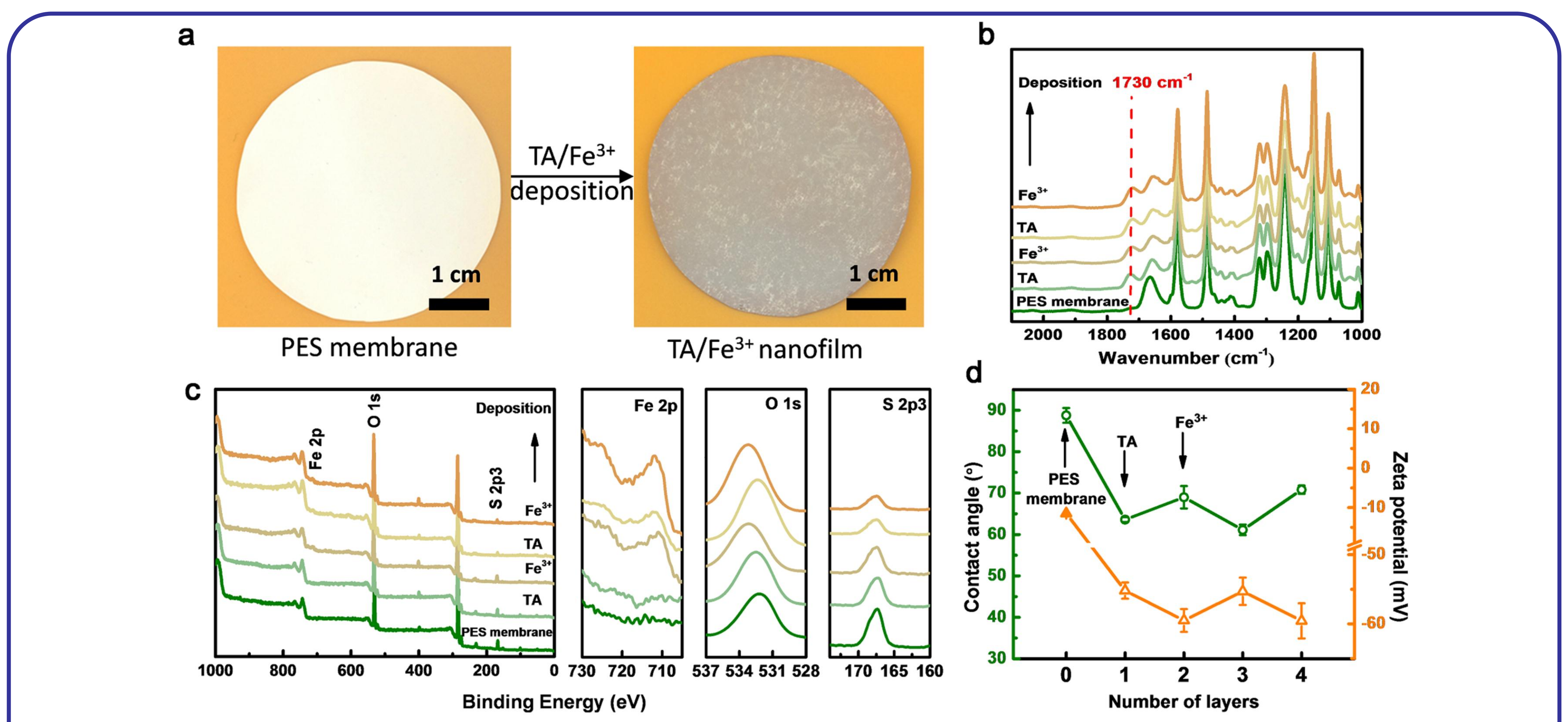

Fig.1. Chemical characterization of the TA/Fe3+ nanofilm. a) Optical photographs of the polyether sulfone membrane (left) and the nanofilm on the substrate (right). b) FTIR-ATR spectra of the PES substrate and nanofilms as the layers grow. c) XPS spectra of PES substrate and nanofilms as the layers build up. d) Water contact angle and zeta potential for the PES substrate and nanofilms as the layers build up.

Fourier transform infrared spectrophotometry by attenuated total reflectance (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS) demonstrated the successful deposition of the TA/Fe^{3+} complex on the PES membrane.

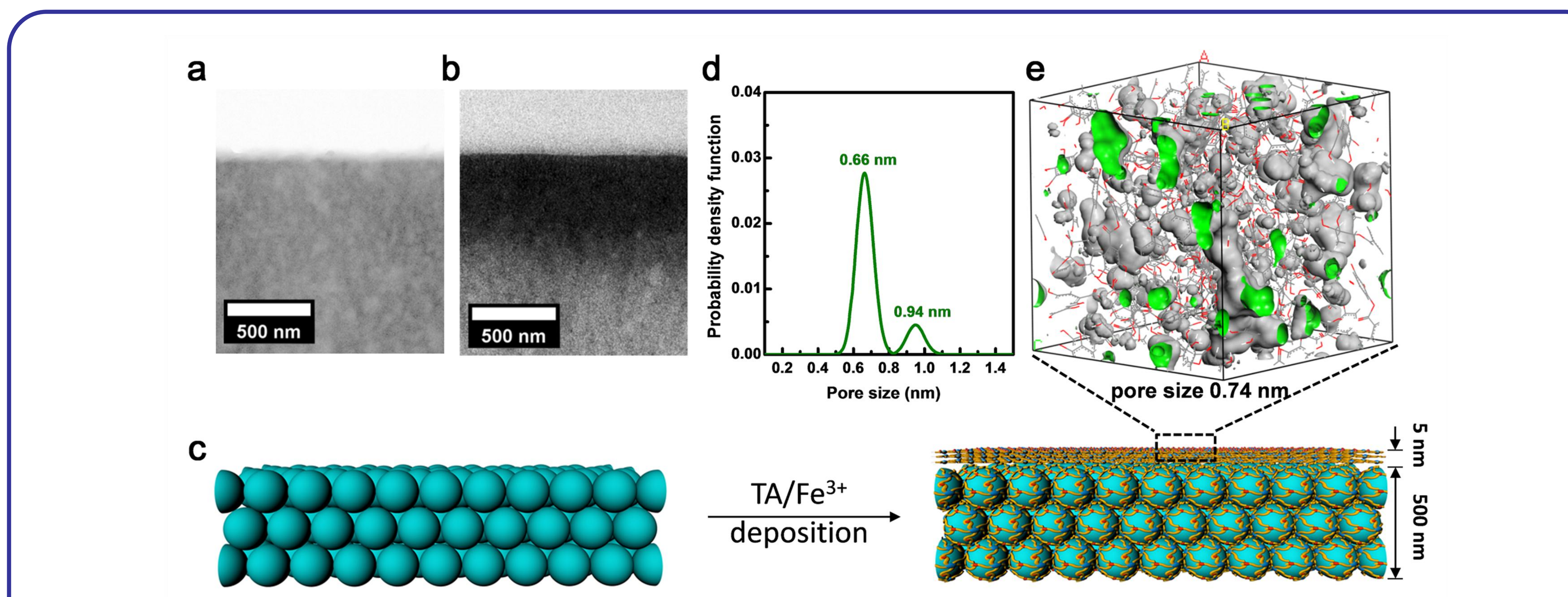

Fig. 2. Thickness and pore structures of the TA/Fe3+ nanofilm. TEM images of the cross section of a) the PES membrane and b) TA/Fe3+ nanofilm, respectively. c) Schematic illustration of TA/Fe3+ nanofilm formed on the PES membrane. d) Pore size and pore size distribution of the TA/Fe3+ nanofilm detected by PALS method. e) Molecular simulation of the pore structure of the TA/Fe3+ nanofilm. Cell size: 26.4 × 26.4 × 26.4 Å.

The nanofilm has an ultrathin thickness of 5 nm and is probably the thinnest nanofilm used for liquid separation. The average pore size of the TA/Fe^{3+} nanofilm obtained by PALS was about 0.7 nm, which was consistent with the results from molecular simulations.

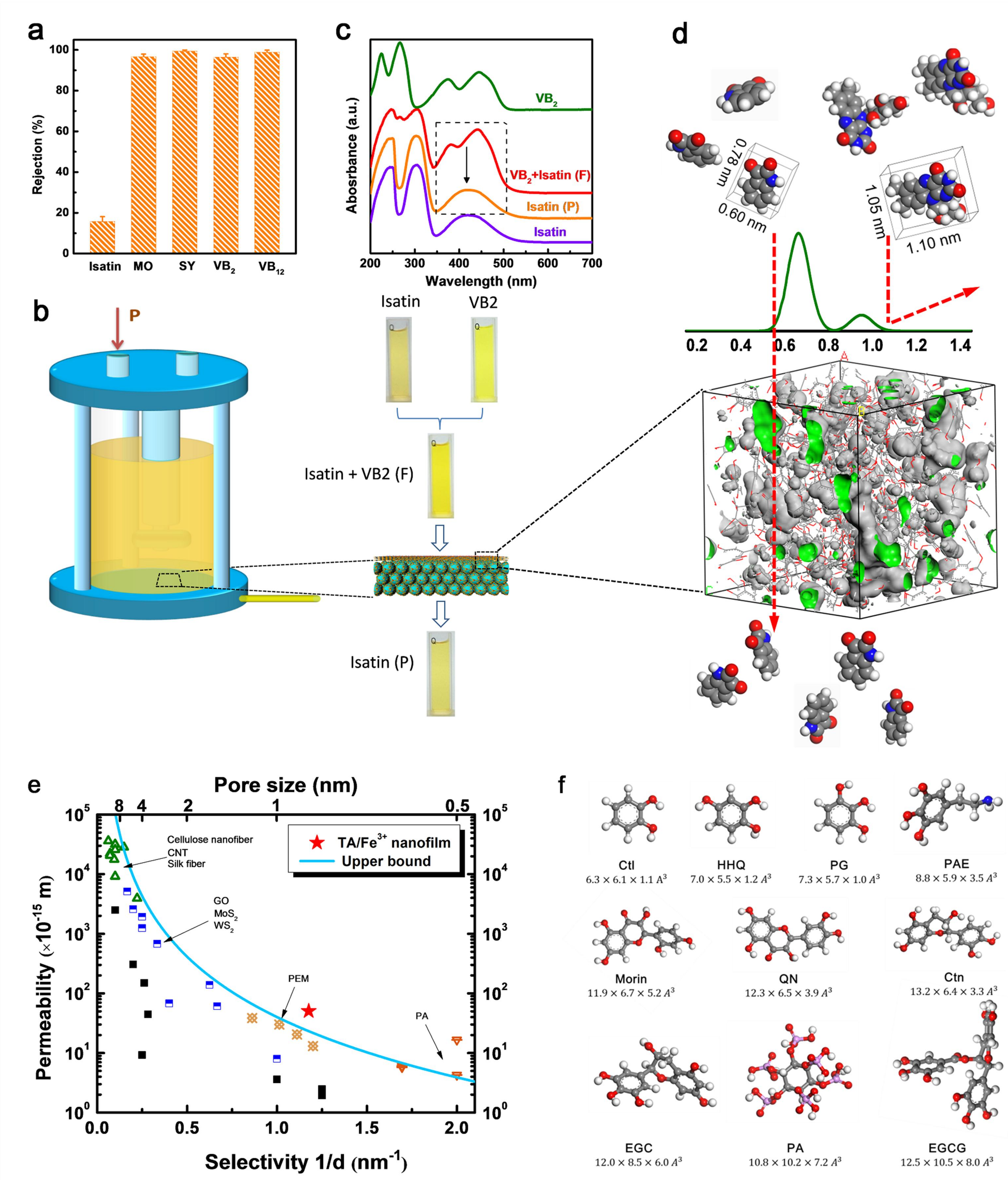

Fig. 3. Filtration results of the TA/Fe3+ nanofilm. a) Rejections of the TA/Fe3+ nanofilm for various molecules [Isatin, methyl orange (MO), sunset yellow (SY), vitamin B2 (VB2), and vitamin B12 (VB12)]. b) Schematic diagram of the molecular separation of Isatin from a mixture of Isatin and vitamin B2 (VB2), ("F" stands for feed and "P" represents permeate). c) UV-vis spectra of the dye solutions in the molecular separation. d) Schematic diagram of the molecular separation mechanism of the TA/Fe3+ nanofilm. e) Comparison of the selectivity-permeability between the TA/Fe3+ nanofilm and other nanofilms in the literatures. f) 3D structure of some molecules that can be used to fabricate nanofilms with various pore structures.

To study the pore size effect on molecular separation, a mixture solution of Isatin and VB2, both of which were neutral solutes, was filtrated under the same test conditions. The nanofilm effectively separated these two molecules by selectively allowing the passage of Isatin. This was further confirmed by UV-vis spectroscopy. It is interesting that the TA/Fe^{3+} nanofilm could precisely separate molecules with slight differences in sizes. Compared with the reported nanofilms, the TA/Fe^{3+} nanofilm with ultrathin thickness and a narrow pore size distribution shows outstanding selectivity-permeability by exceeding the upper bound. Since the pore structure depends on the molecular structure, these molecules are expected to form a series of nanofilms with various pore sizes.

Conclusions

In summary, the TA/Fe^{3+} nanofilm with tailored pore size was successfully fabricated by the alternate deposition of TA and Fe^{3+} on a PES membrane. The nanofilm has an ultrathin thickness of 5 nm and is probably the thinnest nanofilm used for liquid separation. The average pore size of the TA/Fe^{3+} nanofilm obtained by PALS was about 0.7 nm, which was consistent with the results from molecular simulations. These results confirmed our hypothesis that the pore structure of the nanofilm was mainly determined by the TA molecular structure and the pore size was smaller than 1.5. This work provides a novel approach for nanofilm fabrication with a molecular-level design and through the manipulation of the nanoscale pore structure. By choosing molecules with various structures, a series of nanofilms with fine-tuned pore sizes and narrow pore size distributions can be produced.

Acknowledgement

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References

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