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Regular Article

Bioinspired synthesis of multiple-functional nanocomposite platform showing optically and thermally responsive affinity: Application to environmentally responsive separation membrane

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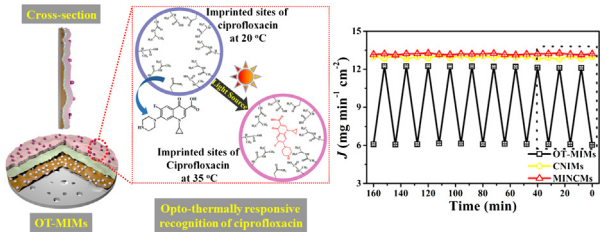
GRAPHICAL ABSTRACT

Bioinspired synthesis of molecularly imprinted membranes showing optically and thermally responsive affinity for reversibly controlling the selective recognition and separation performance.



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ABSTRACT

A tremendous effort has been made for the synthesis and multifunction of environmentally responsive and selective separation membranes. With the bioinspired design of polydopamine (pDA)-assisted inorganic film, we proposed a simple, yet efficient, thermo-responsive cell culture substrate. Herein, a Ag/TiO_2/pDA-based nanocomposite structure was initially obtained, and the ciprofloxacin-imprinted membranes (MINCMs) with thermo-responsive recognition sites were then synthesized by using NIPAm as backbone monomer. The opto-thermally responsive molecularly imprinted membranes (OT-MIMs) were obtained through in situ reduction of $HAuCl_4$ on membrane surfaces, Au nanoparticles were used as the light-heat converters. The light-switching principle was elaborated as well as the energy conversions that took place in this system. These conformational changes finally allowed the constructions or destructions of ciprofloxacin-imprinted sites. Due to the formation of the opto-thermally responsive ciprofloxacin-imprinted sites, rapid adsorption dynamics and opto-thermally responsive perm-selectivity toward templates were both achieved. Therefore, 58.65 mg/g of adsorption capacity and 4.91 of permselectivity factor from OT-MIMs were successfully obtained. Importantly, the as-designed bioinspired strategy led to a state-of-the-art design that was capable of reversibly controlling the flow rate (J) of ciprofloxacin from 12.10 to 4.93 mg min^{-1} cm^{-2} in less than a few minutes using light.

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1. Introduction

Development of stimuli responsive nanocomposite membranes (SRNMs), which would transform the surface physicochemical structures by external stimulus, has attracted a great attention in intelligent membrane separation field [1–4]. Thereinto, SRNMs with response-type performance could be engineered and synthesized through the modification and functionalization of various environmental responsive polymers onto porous membrane materials. This methodology can allow for fast flow and on-off controls due to the combination of membrane separation technique (MST) and response-type polymer materials. Recently, poly(N-isopropylacrylamide) (PNIPAm)-functionalized membranes with reversible collapsed-expanded conformation transformation, which is varying with the temperature around lower critical solution temperature (LCST), have been widely used in intelligent membrane separation system [5–7]. However, in spite of numerous studies in intelligent membrane separation, SRNMs technique is still restricted to the challenges such as non-selectivity and low flux [8–10].

Firstly, because of the inexistence of specific recognition sites from normal SRNMs, non-selectivity and low flux still remain challenges. Secondly, considering the timeliness and high-durability requirements of membrane systems, it is now described as a 'mammoth task' to achieve rapid response times in permselectivity without changing any environmental conditions of the entire system [11–13]. To conquer these long-standing problems, the selective separation technique of molecularly imprinted membranes (MIMs) has been developed through the combination of membrane separation technique (MST) and molecularly imprinted polymers (MIPs) [14–16]. Therefore, tailor-made imprinted sites and intrinsic layered membrane structure could be obtained during the membrane imprinting processes. Therefore, temperature-responsive MIPs with reversible recognition sites have also been successfully synthesized by using NIPAm molecules as the functional monomers [17–22]. Nonetheless, further separation applications of MIMs were still plagued with weak regeneration stability, low-affinity adsorption, low-permeability performance. And above all, the invasive modulating procedures, current attempts at getting over the above challenges and improving the efficiency of 'smart' membrane separation systems still face a dilemma.

However, the crucial adjective problem, which limits the further applications of MIMs, is the simultaneous optimization of specific adsorption efficiency and permselectivity. Membrane-based nanocomposite porous structures with uniformly and tightly modified inorganic nanoparticles have been regarded as the crucial factors for synthesizing high-performance membranes [23–24]. Recently, a bioinspired membrane-functionalized strategy of dopamine self-assembled principle has been in-depth studied for the formation of versatile secondary reaction platforms, the polydopamine (pDA) could be easily obtained through the self-polymerization of dopamine (Fig. S1). Most of all, highly anti-fouling and constitutionally stable surfaces can be easily achieved by the pDA-modified strategy. Meanwhile, a versatile membrane platform, which can be used for the further functionalization of inorganic nanoparticles, is also obtained [25–27].

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.07.033.

Ideas in material synthesis which describe inspiration from nature have generated impressive collections of great developments [28–29]. The transformation of optical energy into other forms of energy can be easily achieved through chlorophore or photoreceptor in natural systems (Fig. S2). Importantly, light energy transformation systems which sustain photomodulation reactions are recently prime to various biomedical and biological applications. With this strategy in mind, Au nanomaterials with excellent biocompatibility could be coupled to the PNIPAm-based surfaces for the construction of sensitive light-heat converters, which will rapidly undergo transformation in their physical conformations around LCST [30–31].

This work reported the design and construction of the optically and thermally responsive MIMs (OT-MIMs), which used light at specific wavelength for the controllable regulation of selective adsorption and permselectivity toward templates (Scheme 1). Ciprofloxacin, the established broad-spectrum fluoroquinolone antibiotics, was used as template molecule in this case, which could be used for the exacerbation treatments in the parenteral and oral dosage pattern [32–33]. Specifically, inspired by this polydopamine-assisted inorganic film formation (pIFF) based strategy, a versatile bio-functionalization surface was initially achieved through a self-polymerization procedure of bionic pDA, followed by a growth process of well-defined TiO_2/Ag nanocomposite layer on the regenerated cellulose membrane (RC). After that, the molecularly imprinted nanocomposite membranes (MINCMs) with thermo-responsive recognition sites were synthesized through a photoinitiated atom transfer radical polymerization (pATRP, Fig. S3) by using NIPAm as backbone monomer, acrylamide (AAm)/methacrylic acid (MAA), methylene bisacrylamide (MBAA), N-[3-(dimethylamino)propyl]methacrylamide (DMAPMA), as hydrogen-bonding monomers, crosslinker and positively charged monomers, respectively. After the in situ reductions $HAuCl_4$ on membranes, a sensitive photoswitching system could be achieved to control the adsorption/desorption of ciprofloxacin molecules in response to light (Scheme 1). To the best of our knowledge, although SRNMs have exhibited some expanded separation and sensors applications, this study is the first demonstration of ciprofloxacin-imprinted membranes as the methodology for harvesting light-triggered recognition and separation system.

2. Experimental section

2.1. Materials

All solvents and reagents were commercially available used as received without any purifications.

2.2. Characterizations

Micromorphologies of various membrane materials were studied by field emission scanning electron microscopy (SEM, S-4800, Japan). Atomic Force Microscopy (AFM, Solver P47, Russia) was used for the characterization of membrane surface roughness and morphology. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra for synthesized membrane materials were collected on an FT-IR Nicolet560 (Nicol, U.S.). Surface chemical compositions of different synthesized materials were studied by X-ray photoelectron spectroscopy (XPS). High performance liquid chromatography (HPLC) (Agilent 1200 series, U.S.A.) was used for the determination of ciprofloxacin, moxifloxacin (MOFX), and ciprofloxacin lactate (CPFL). The mobile phase was 0.05 mmol/L citric acid/acetonitrile (82/18, v/v) mobile phase. The HPLC was set to a flow rate of 1 mL/min and injection volume of 100 μL resulting in a retention time of 4 min. In addition, the detection wavelength was 277 nm and column temperature was set at 25 °C.

2.3. Preparation of pDA@RC followed by the modification of nano-sized TiO_2 layers

Initially, RC membranes were then added to solution containing dopamine (2 mg/mL) and 10 mM Tris-HCl (pH 8.5)