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A novel approach toward fabrication of porous molecularly imprinted nanocomposites with bioinspired multilevel internal domains: Application to selective adsorption and separation membrane

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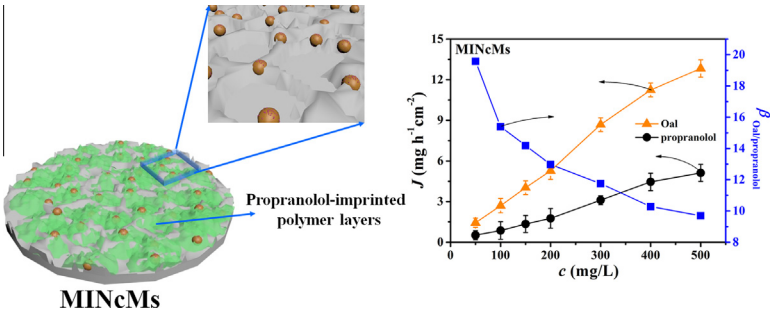
HIGHLIGHTS

- A bioinspired propranolol-imprinted nanocomposite membrane was first prepared.
- An optically and thermally responsive MIMs methodology was proposed.
- Photoinitiated ATRP was first used for synthesizing molecularly imprinted membrane.
- Efficient light-dependent permeability toward template molecule could be obtained reversibly.

GRAPHICAL ABSTRACT

A bioinspired porous molecularly imprinted nanocomposite membrane was developed for selective recognition and separation of propranolol.



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ABSTRACT

The development of membrane-associated molecularly imprinted materials that can rapidly adsorb and separate specific compound has broad technological applications for areas ranging from sewage treatments to biomedical devices. However, issues such as low permselectivity and unstable composite structures are restricting it from developing stage to a higher level. Here, inspired by the bioadhesive technology of polydopamine (pDA), we present a novel molecular imprinting strategy to integrate multilevel nanocomposites (Br-Ag-pDA@SiO_2) into the porous membrane structure. The molecularly imprinted nanocomposite membranes (MINcMs) were then obtained through an in situ photoinitiated ATRP method by using propranolol as the template molecule, which was one of the pharmaceutically active compounds (PhACs). In this work, largely enhanced specific rebinding capacity (48.53 mg/g) and permselectivity (the permeability factor β values were also more than 9.6) had been successfully achieved, which should be attributing to the creation of high-stability and uniform growth of propranolol-imprinted polymer layers onto the nanoparticle-integrated nanocomposite membrane surfaces. Specifically, the as-prepared MINcMs not only exhibited rapid adsorption dynamics of template molecule, but also possessed excellent regeneration performance. Moreover, when the other PhACs were respectively imprinted, similar recognition selectivity could be observed dependent on the template molecule. Importantly in this case, all synthesis methods were conducted in aqueous at ambient temperature, which was environmental friendly for scaling up without causing pollution.

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1. Introduction

With the increasingly serious water contamination accompanying the development of pharmaceutically active compounds (PhACs), they are recently behaving as persistent organic micropollutants because of the continuous accumulation and input into the environment [1]. Of special concern are those PhACs (including antiepileptics, antibiotics, analgesics, and contrast media agents et al.), which provoke toxic effects on living organisms, can now resist traditional treatment processes and, meanwhile, are detected in sewage, groundwater, and drinking water [2]. Consequently, these micropollutants will pose a serious threat to the quality of water resources, and thus lead to the deterioration of natural environment. Although several advanced technologies such as application of ozonation, photocatalysis, and UV are evidenced to effectively treat the PhACs, the high-demanding energy costs, maintenance, and construction largely limit the applicability [3–5]. In addition, as the PhACs elimination by conventional materials or processes is often non-selective and non-intelligent, PhACs cannot be reused and recycled after the treatments. Therefore, it is necessary to develop a recyclable, durable, and selective separation methodology to improve the PhACs purification efficiency from water.

Nowadays, membrane-based separation techniques (MST) with better anti-fouling property and stability have been widely and extensively used in many fields like solid-phase extractions, water treatment, oil refinement, gas separation, and most recently, drugs purification. Meanwhile, development of synthetic/artificial membrane which rivals biological membrane in selectivity is now a significant issue in environmental and bioorganic chemistry [6–8]. As is well-known, molecular imprinting technique (MIT) has been regarded as an efficient strategy of mimicking the specificity of molecular recognition capability by biological structures such as antibody [9–12]. And development of molecularly imprinted polymers (MIPs) has already made tremendous advance in the field of selectively separating and purifying natural products. Thereinto, research into combinations of MIT and MST for separation and purification of specific compound is very appealing [13]. Molecularly imprinted membranes (MIMs) are membranes composed of MIPs or containing MIPs, which can lead to the formation of tailor-made recognition sites (sterically complementary cavities to original template molecules) in membranes during copolymerization procedure. This simple method, however, often leads to MIMs showing relatively low specificity and permeability [14–17]. In addition, among a wide range of PhACs treatment methods, MIMs also have unique combinations of flexible design, high reliability, and anti-fouling ability, which make them ideal candidates for further sophisticated purification process. However, there are still some challenges, such as low accessibility of recognition sites, aggregation of nanomaterials, and poor structural durability, that limit the commercial viability and efficiency of MIMs.

It goes without saying that an ideal molecularly imprinted membrane should be capable of having high-pollution resistant properties, and excellent perm-selectivity and chemical stability [6–7]. However, unlike common recognition systems, most of the imprinted cavities are distributed inside bulk MIPs, it is difficult to form tailored and successive channel structures in MIMs. For instance, the major issue of an imprinted membrane material is to create well-defined recognition sites and selective transmembrane transport pathways simultaneously. Porous polymer membranes with integrated internal domains and multi-layered nanostructures (SiO_2/TiO_2/Ag/Pd) can provide additional avenues for improved chemical stability, hydrophilicity, and anti-pollution property [18–19]. In addition, the internally formed nanostructures can also effectively decrease the blocking probability of macromolecular-based polymers in membranes. Meanwhile, as to the innovative principles for preparation of high performance surfaces, a bio-inspired polydopamine (pDA) self-assembled strategy has been developed to introduce the versatile secondary platform for further modification procedure, called pDA-assisted inorganic film formation (pIFF, Fig. S1) [20]. This methodology not only allows for the large improvement of anti-fouling performance and chemical stability, but also provides a versatile surface for the further functionalization of tightly and uniformly formed composite organic/inorganic nano-layers. At present, a great deal of research interests have been devoted toward the manufacture and optimization of pIFF-based internally formed nanostructures to obtain the high comprehensive membranes [15].

Herein, for the first time, by utilizing pIFF-inspired Ag@pDA@SiO_2 nanostructures as the highly adjustable active domains, we present a novel yet efficient strategy for developing molecularly imprinted nanocomposite membranes (MINcMs) with excellent perm-selectivity and recognition capacity of PhACs. Importantly, instead of constructing multi-functional MIPs layer by layer on membrane surfaces, an integration method of Ag@pDA@SiO_2 nanoparticles into porous polyvinylidene fluoride membrane (PVDF) structures was performed to obtain the high performance membranes. After that, the MINcMs were finally synthesized using propranolol as the template molecule, at low temperature, through an in situ photoinitiated atom transfer radical polymerization (ATRP) by using fac-[Ir(ppy)$_3$] (ppy = 2-phenylpridine) as the ATRP photoredox catalyst (Fig. S2) [21]. This photoinitiated polymerization technique not only enables the initiation of the reaction at room temperature by visible light, but because of inexistence of metal catalyst it also exhibits extremely tolerant to acidic moieties [22]. Specifically, the methacrylic acid (MAA), which is inherent incompatible with traditional ATRP, was used as functional monomer in this work. Meanwhile, the optimized recognition capacity of propranolol was obtained and investigated in detail by adjusting the polymerization time. In addition, the chemical composite processes during different modification stages were investigated by X-ray photoelectron spectroscopy (XPS) tests, and the morphologies of various nanostructures and hybrid membranes were evaluated with atomic force microscopy (AFM) and scanning electron microscope (SEM). As evidenced by the obtained results, this novel developed bio-functionalized method for the preparation of MIMs can also effectively enhanced the membrane performance such as binding capacity, perm-selectivity, anti-fouling property, and most importantly, regeneration stability. That is to say, this novel developed strategy would work very well for selective recognition and purification of propranolol in complex systems. Finally, the whole synthesis process were all conducted in aqueous solution at room temperature, which is potential for scaling up without causing pollution.

2. Experimental section

2.1. Materials

Commercial PVDF powder was purchased from French company Arkema. Propranolol, O-pivaloylpropranolol (Opl) and O-acetylpropranolol (Oal), acrylamide (Am, dopamine, silver nitrate ($AgNO_3$), methylene bisacrylamide (MBAA), fac-[Ir(ppy)$_3$] (ppy = 2-phenylpridine), and tris(hydroxymethyl) aminomethane (Tris-HCl), were purchased from Aladdin Reagent (Shanghai, China). Polyvinylpyrrolidone (PVP), N-methylpyrrolidone (NMP), CuBr, 2-bromoisobutyryl bromide (2-BIB), triethylamine (TEA, AR), HPLC grade water and methanol were supplied by Sinopharm Chemical Reagent (Shanghai, China). CuBr was purified with etha-