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Bioinspired synthesis of pDA@GO-based molecularly imprinted nanocomposite membranes assembled with dendrites-like Ag microspheres for high-selective adsorption and separation of ibuprofen

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ABSTRACT

Inspired from the highly bioadhesive performance of polydopamine (pDA)-based layers, a facile method was developed to modify GO nanosheets with pDA (pDA@GO). The key design of the molecularly imprinted nanocomposite membranes (MINMs) was integrated pDA@GO nanosheets into the porous PVDF membranes as the highly adjustable active domains. Dendrites-like 3D Ag microspheres were obtained on the surface of nanosheets-infiltrated nanocomposite membranes (NS-NMs) to obtain high performance membranes. The as-prepared pDA coating layers not only modified GO nanosheets, but also could be used as a versatile platform for the further immobilizing dendrites-like 3D Ag microspheres on the surface of NS-NMs to improve anti-fouling property. Attribute to the highly adjustable active domains and dendrites-like 3D Ag microspheres, the as-prepared MINMs revealed an outstanding adsorption amount ($61.55\ mg\ g^{-1}$), a better hydrophilicity and regenerability. Most importantly, excellent perm-selectivity performance ($\beta_{ketoprofen/ibuprofen}$ and $\beta_{naproxen\ sodium/ibuprofen}$ were 6.55 and 6.63, respectively) could be also achieved, which is beneficial to adsorb and separate of ibuprofen.

1. Introduction

Molecularly imprinted polymers (MIPs) were called as “antibody mimics”, because they attempted to imitate the interactions of the natural recognition materials (enzymes and substrate, hormone and receptors, antigens and antibodies), which have made great progress in the fields of selective separation and purification of natural products due to its intrinsic stability, ease preparation, low cost, and longtime life [1,2]. Particularly, molecularly imprinted membranes (MIMs) combined the advantages of membrane separation technique and MIPs could offer membrane-based high selective separation for target molecules with less energy consumption [3]. Therefore, MIMs were believed to be one of the most promising materials in the fields of separation and purification of specific target molecules [4,5].

The main method for the synthesis of MIMs was casting imprinting polymer layers at the surface of membranes materials. Meanwhile, the membranes materials have better permeability and regenerability, which could be served as support polymer [6]. Polyvinylidene fluoride (PVDF) was widely used in scientific researches because of its high mechanical strength, excellent thermostability, and good membrane forming characteristics [7–9]. However, the hydrophobic of PVDF membranes leaded to serious pollution on the surface of membrane materials, which restricted its further industrial application [3]. Therefore, researchers committed to study advanced methods to enhance the comprehensive properties of PVDF membrane. In the past few years, adopted nanoparticles into the membrane materials to prepare nanocomposite membranes exhibited remarkable performance has attracted considerable attention [10], which including inorganic nanoparticles (SiO_2, TiO_2, Al_2O_3) [11,12], however the methods were still immature due to the weak binding force between the nano-level materials and membranes materials. Recently, graphene oxide (GO) nanosheets were considered as one of the most promising organic materials to modify membrane materials, which had attracted great interest due to its abundance of oxygen-containing functional groups, extremely high specific surface area, unique single atomic thickness, two-dimensional structure, and easy surface functionalization [13–15]. Correspondingly, GO-based composite membranes showing good hydrophilic had become a research hotspot. Zhang et al. concluded that tensile

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strength, hydrophilicity and elongations were all well improved when added GO nanosheets into the pristine PVDF membrane [16]. Sun confirmed that the as-prepared GO-AgNPs/CA membranes produced higher antimicrobial membrane surface than the CA membranes [17]. Ganesh et al. stated that water flux, hydrophilicity, and salt rejection of GO/PSF membranes were enhanced significantly compared with the pristine PSF membranes [18]. Therefore, GO nanosheet is an excellent candidate as the membrane forming materials may make a contribution to improve adsorption capacity and perm-selectivity performance of MIMs. Not merely because GO nanosheets have a huge surface area and an abundant π-electron conjugated system, which will intensively adsorb the aromatic molecule compounds [19,20]. Moreover, its two-dimensional plane assists simultaneous adsorption of target molecules [21].

Previous studies have found that GO nanosheets had strong tendency of agglomeration, which would weaken the mechanical strength of the membrane materials [10]. Nevertheless, a major challenge is to develop a facial and effective method to modify GO nanosheets in order to keep its monodispersity. In recent years, dopamine (DA) has been widely reported due to its strong bioadhesive performance and good biocompatible layer on the substrate on which it is grown, which acted as a wonderful surface adherent material for multifunctional surface coating [22]. Meanwhile, DA could be self-polymerized to form polydopamine (pDA). Hence, pDA could not only modify GO nanosheets, but also severed as the versatile platform for Ag microspheres immobilization.

Herein, by using pDA-inspired pDA@GO nanosheets as the highly adjustable active domains, rather than building layer by layer multifunctional MIPs on the surface of membrane materials, an integration method of pDA@GO nanosheets into the porous PVDF membranes was performed to obtain nanosheets-infiltrated nanocomposite membranes (NS-NMs). Then, by reducing silver nitrate on the surface of NS-NMs, dendrites-like Ag microspheres were formed to obtain high performance membranes. Molecularly imprinted nanocomposite membranes (MINMs) were finally synthesized by a sol-gel imprinting process using ibuprofen as template molecules, which was a pharmaceutically active compound. Due to the unique structure of MINMs, hydrophilicity, adsorption capacity and regenerability were greatly improved. Importantly, the perm-selectivity was also achieved in this work. Moreover, all the synthesis processes were carried out in aqueous solution, which was environment-friendly for large-scale applications.

2. Experimental

2.1. Chemicals

PVDF powders were purchased from French company Arkema. Concentrated sulfuric acid (H_2SO_4, 98%), natural graphite power, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 36.0–38.0%), methanol (AR), ethanol (AR), and acetic acid (AR) were acquired from Shanghai Sinopharm Chemical Reagent Co. LTD (China). Tris (hydroxymethyl) aminomethane (Tris-HCl), dopamine (DA, 98%) N-methyl pyrrolidone (NMP), silver nitrate ($AgNO_3$), potassium biphthalate, ascorbic acid, ibuprofen, ketoprofen, naproxen sodium, and sodium hydroxide (NaOH) were supplied by Aldrich-reagent (Shanghai). All of the above reagents were analytical grade or better. Doubly distilled water was used for preparing all the aqueous solutions and cleaning processes.

2.2. Characterizations

The morphological evolutions of various membranes were observed by field emission scanning electron microscopy (SEM, S-4800 instrument). Transmission electron microscopy (TEM, JEM-2100 instrument, Japan Jeol) has a 200 kV accelerating voltage was used to characterize the more elaborate structure of nanosheets. The surface roughness of various membranes was investigated by AFM (Solver P47 Atomic Force Microscopy, Russia). The surface chemical composition of various membranes was further investigated by X-ray photoelectron spectroscopy (XPS) with an Omicron ESCA probe spectrometer. Fourier-transform infrared spectrometer (FT-IR) for the nanosheets was examined by a Nicolet-560 FT-IR apparatus (United States). UV–vis spectrophotometer (UV–vis, U-3600 plus instrument, Japan Shimadzu) was used for determination ibuprofen, ketoprofen and naproxen sodium at 264 nm, 261 nm, and 262 nm, respectively.

2.3. Preparation of GO nanosheets

GO nanosheets were prepared using modified Hummers' method [18]. Briefly, 1.0 g natural graphite power, 2.5 g $NaNO_3$, and 4.0 g $KMnO_4$ were added slowly into H_2SO_4 (30 ml) solution in an ice bath with continuously stirring for 2 h, then the mixed solution turned into dark green. Raised the temperature to 35 °C and began to reflux. 40 ml deionized water was slowly added, a bright yellow mixed solution was obtained after raising the temperature to 98 °C for 40 min. Subsequently, 30% H_2O_2 (10 ml) was added drop by drop and kept for 5 min. The above mixture was poured into 50 °C (140 ml) deionized water. Finally, GO nanosheets were obtained after washed fully with 5% HCL until the pH of the supernatant was neutral.

2.4. Preparation of pDA@GO nanosheets

The typical pDA modified process as follows: 0.5 g GO nanosheets were preprocessed with Tris-HCl (pH = 8.5) aqueous solution for 10 min. Dissolving dopamine into Tris–HCl (pH = 8.5) aqueous solution to prepare 2 mg ml^{-1} of dopamine solution (100 ml). The preprocessed GO nanosheets were dispersed evenly into above dopamine solution. The resulting mixture was stirred continuously for 3 h at room temperature. After the reaction, centrifugation for 3 min (10,000 r min^{-1}), and the product was washed with deionized water to remove redundant pDA particles and unreacted DA. Finally, the pDA@GO nanosheets were obtained after drying to constant weight.

2.5. Synthesis of ibuprofen-based imprinted nanocomposite membranes (MINMs)

Firstly, pDA@GO nanosheets-infiltrated nanocomposite membranes (NS-NMs) synthesized process as follows: the predetermined amount of pDA@GO nanosheets and corresponding amount of PVDF powder were added into 20 ml NMP, the mixture was sealed and mechanical stirred at 50 °C for 24 h to prepare casting solution. After fully degassing, the as-prepared solution without bubbles was cast on a glass plate using a doctor knife, the as-prepared NS-NMs were promptly immersed into a coagulation bath containing pure water to go through a phase inversion process. After completely coagulated, the NS-NMs were placed in deionized water before usage. The detailed preparation parameters for the various membranes were listed in Table 1.

Subsequently, the synthesis of the dendrites-like Ag microspheres based NS-NMs (Ag@NS-NMs) as follows: 1.0 mmol $AgNO_3$ dissolved in deionized water (10 ml) with magnetic stirring until a transparent solution formed. Then, 0.0125 M potassium biphthalate (20 ml) was

Table 1
Composition of various NS-NMs solutions.

Membranes	pDA@GO (g)	PVDF (g)	NMP (ml)
M-0	0	4.0	20
M-1	0.1	3.9	20
M-3	0.3	3.7	20
M-5	0.5	3.5	20
M-7	0.7	3.3	20