



Preparation of DOPA-TA coated novel membrane for multifunctional water decontamination



Tzungyu Shih^{a,1}, Na Liu^{b,1}, Qingdong Zhang^a, Yuning Chen^a, Weifeng Zhang^a, Yanan Liu^a, Ruixiang Qu^a, Yen Wei^a, Lin Feng^{a,*}

^a Department of Chemistry, Tsinghua University, Beijing, 100084, PR China

^b Institute of Materials for Energy and Environment, School of Materials Science and Engineering, Qingdao University, Qingdao 266071, PR China

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ABSTRACT

Multifunctional microfiltration membrane for water decontamination is prepared via one-step assembly coating of dopamine (DOPA) and tannic acid (TA). The DOPA-TA coated membrane with superhydrophilicity and superoleophobicity is capable of emulsion separation and simultaneous heavy metal ions as well as non-metal ions adsorption. Such a facile approach, is the first example for dealing with the complicated contaminants polluted wastewater and has great potential in practical water remediation.

1. Introduction

The fresh water supply throughout the world is severely scarce because of growing population and increasing industrial pollution [1,2]. Oil and water mixtures, particularly the stable emulsions are harmful to ecosystem especially drinking water because of toxic and hazardous substances and lacking oxygen [3–5]. Membranes with special wettability have attained widespread attention because of their effective application prospects in oil/water separation [6–23]. How to deal with the oil contaminated water has been a very important and urgent issue, and experts in different fields are committed to solving this problem to enhance the availability of freshwater. However, there are always not only oils but also many pollutants such as pesticides, dyes, organic contaminants, anions and heavy metal ions make great harm to human health [24–27]. Therefore, it is necessary to develop a multifunctional membrane for more efficient water purification.

Heavy metal ions are directly discharged into rivers, lakes or oceans without proper treatment. These heavy metal pollutants into the environment cannot be self-biodegraded by the environment [28]. Although heavy metals such as manganese, copper and zinc are essential trace elements for life activities, most of the heavy metals such as mercury and lead, are not necessary, and over a certain concentration of heavy metals are toxic to the human body. For example, lead can damage human brain cells and cause cancer, while mercury will cause neuropsychiatric symptoms if ingested. Besides metal ions, anionic contamination should be also treated due to environmental damage.

For instance, phosphorus existing in pesticides is widely used in agricultural production, which caused more serious water pollution and eutrophication that severely destroyed the ecosystem balance.

Tannic acid (TA) is prolific in the nature and broadly applied in medical and food industrial fields because of its nontoxicity and antioxidant properties [29], and three galloyl groups from TA can react with the Fe (III) ion to form a stable octahedral complex [30]. Caruso et al. reported the assembly of metal-polyphenol complex (MPC) films and capsules via the sequential deposition of iron ions (Fe (III)) and TA driven by metal-ligand coordination [31,32]. Ejima et al. reported the formulation of thin polyphenol coating by a one-step assembly method using the TA and iron ion (Fe (III)). Considering the TA molecules can chelate ferric ions to form coordination complexes, we try to apply it further on other ions [33,34].

In our group, some works about in situ dual-function oil removal and photo degradation of dyes have been reported previously for treating the complicated sewage system [35,36]. Herein, we designed the dopamine and tannic acid coated membrane via one-step immersion method for multifunctional water decontamination involves simultaneous adsorption of heavy metal ions and anions as well as in situ emulsion separation. There is no competition between the different ions, and all have very high efficiency at low doses. Furthermore, repeated experiments show that they are capable of recycling. The advantages of time-saving and cost-effective make this method has some practical value in wastewater treatment.

* Corresponding author.

E-mail address: fl@mails.tsinghua.edu.cn (L. Feng).

¹ These authors contributed equally.

2. Experimental section

2.1. Materials and measurements

Dopamine hydrochloride (Sangon Biotech Co. Ltd., Shanghai, China) and tannic acid (InnoChem Science & Technology Co. Ltd, Beijing, China) were used as purchased. Other reagents from Sinopharm Chemical Reagents are of analytical grade and used without further purification.

2.2. Fabrication of DOPA-TA deposited membranes

Tannic acid (4.0 mg/mL) was dissolved in 50 mL of deionized water and sonicated to ensure homogeneity. A piece of mixed cellulose ester (MCE) microfiltration membrane was immersed in the solution, then 50 mL of dopamine (4.0 mg/mL) was added. The mixture was placed for 48 h after the solution of Tris (30 mmol/L, pH = 8.5) was dropwise added. The as-obtained membrane was taken out, washed thoroughly with deionized water.

2.3. Preparation of oil-in-water emulsions

Oil phase (toluene, n-octane and diesel) and water phase (deionized water) were mixed in conical flasks at the ratio of 1:100 (v/v) with addition of surfactant (0.5 g/L Tween 20). The emulsions were obtained after vigorously stirring for 12 h.

2.4. Instruments and characterization

FESEM images were obtained on a field emission scanning electron microscope (SU-8010, Hitachi Limited, Japan). FTIR spectra were recorded using a Fourier Infrared Spectrometer (NICOLET6700, Thermo Co-operation, USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo escalab 250 Xi spectrometer using an Al K α X-ray source (1486.6 eV). Contact angles were measured on a contact angle measurement machine (OCA 15 machine, Data-Physics, Germany). The ions content in the filtrate was measured with infrared spectrometer oil content analyzer (Oil480, Beijing Chinainvent Instrument Tech. Co. Ltd., China). Emulsion separation experiment of the DOPA-TA membrane: the as-prepared membrane was fixed between two Teflon fixtures. Both of the fixtures were attached with a glass tube and placed. The diameter of the glass tube was 30 mm. The emulsion mixtures (1 v/v%) were poured onto the membrane. The separation was achieved by the force of gravity.

3. Results and discussion

The DOPA-TA coated membrane is prepared by soaking mixed cellulose esters (MCE) membrane in the mixed solution of tannic acid (TA, 2 mg/mL) and dopamine hydrochloride (DOPA, 2 mg/mL) with a basic buffered solution (2-amino-2-(hydroxymethyl) propane-1,3-diol). Fig. 1a and b are the typical images of the white MCE membrane substrate with an average pore size of approximately 0.22 μ m in diameter. After reacting for 48 h, TA has been successfully grafted onto the film evenly due to the strong binding of DOPA with the porous substrate through covalent and noncovalent interactions. As shown in Fig. 1c, the surface morphology has changed obviously compared with the original one. From the inset and Fig. 1d, the color of the initial membrane changed from white to brown and lots of papillae could be observed, indicating the successful construction of a composite coating layer of DOPA-TA on the membrane surface. For comparison, the initial MCE polymeric membrane was also decorated with polydopamine via DOPA self-polymerization. Fig. S1a (Supplementary material) showed that the

thickness of the initial membrane framework was relatively enhanced after one-step soaking method, while its morphology was quite different from that obtained in the mixed solution of dopamine hydrochloride and tannic acid. Fourier Transform infrared spectroscopy (FTIR) was further conducted to testify the existing TA on the as-prepared membrane surface. The strong adsorption peak at 3300 cm^{-1} that attributed to hydroxyl groups in Fig. S1b (Supplementary material) illustrated the presence of TA. The C1s core level spectra of DOPA coated membrane by X-ray photoelectron spectroscopy (XPS) was shown in Fig. S2a (Supplementary material) and could be deconvoluted into three peaks components with binding energies at about 284.6, 286.7 and 287.7 eV, attributable to the C–C, C–C–O, C–ONO₂, respectively. Although the C1s spectrum of DOPA-TA coated membrane also exhibited the majority of the same peaks (Fig. S2b (Supplementary material)), the marked appearance of the C–N component at 286.1 eV indicated the successful formation of DOPA-TA composite through Michael addition reaction.

The unique hierarchical structure endowed the DOPA-TA coated membrane with special wettability. The as-prepared membrane exhibited superamphiphilicity and the wetting behavior of water and oil droplets on the membrane surface were shown in Fig. 2a and b. When the water droplet in the air contacted with the membrane surface, it propagated instantaneously in a short time and the water contact angle (WCA) was close to zero. When the droplet of the 1,2-dichloroethane was placed underwater, the membrane exhibited superoleophobicity and the average oil contact angle (OCA) was 156.3°. These results clarified that the as-prepared membrane had the potential in separating oil and water mixtures.

Given that the DOPA-TA composite coated membrane was super-hydrophilic and underwater superoleophobic, three types of oil-in-water emulsions were prepared freshly to test its capacity of emulsion separation. The stabilized emulsions containing nearly 1% volume of oil including toluene, n-octane and diesel, respectively, were stirred for 12 h with adding of surfactant. The membrane was fixed in the separation apparatus and the milky emulsion was poured onto the surface of the membrane. Here, the toluene-in-water emulsion was chosen as an example. After separation driven by gravity solely, the transparent filtrate was collected. Aside from toluene, the composite coated membrane could also effectively separate various stabilized emulsions composed of a range of oils such as n-octane, diesel (Fig. 2c). Integrated the microscale pore size with the underwater superoleophobic property of the resultant membrane, when the emulsion contacts with the surface, it enables to capture the dispersed micro-oil droplets while permitting water penetrating through itself, thus realizing the emulsion separation process. All the separation efficiency towards these three kinds of emulsions repeated for three times, respectively, was higher than 99%. With regard to practicality, the performance of the membranes for chemical inertness was also examined via being immersed in aqueous solutions over the pH range from 1 to 11 for 3.5 h, respectively. The surface maintained robust superoleophobicity with the oil contact angle above 145° for all pH ranges (Fig. S3 (Supplementary material)).

One of the biggest goals for purifying wastewater is to adsorb heavy metal ions. In this work, copper, mercury, and lead ions were chosen as the simulated heavy metal pollutants. 10 mL of Cu²⁺ (63.5 mg/mL), Hg²⁺ (29.8 mg/mL) and Pb²⁺ (20.1 mg/mL) solutions were allowed to pass through the DOPA-TA coated membranes and the corresponding filtrate was detected, respectively. As shown in Fig. 3a–c, energy dispersive X-ray spectroscopy (EDX) displayed that the ions were all captured by the membrane after permeation. The mapping results also confirmed that the target metal ions have been detected on the membrane surface (Fig. S4 (Supplementary material)). In addition, the quantitative adsorption capacity of the as-prepared membrane has shown in Fig. 3d, in which all the adsorption capacity was larger than

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