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Full Length Article

Facile preparation of polymer microspheres and fibers with a hollow core and porous shell for oil adsorption and oil/water separation

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ABSTRACT

Non-solvent assisted electrospinning was proposed for fabricating Polymethylmethacrylate (PMMA) microspheres and fibers with a hollow core and porous shell, which could be used for oil adsorption and oil/water separation. Propanediol was chosen as the non-solvent because of its high surface tension and viscosity as well as large phase separation tendency with polymer, which was beneficial to the formation of both the hollow core and porous shell during the electrospinning. With the increase of the polymer solution concentration, the microsphere gradually evolved to the bead-on-string geometry and finally to a continuous fiber form, indicating the transition from electro-spraying to electrospinning. The hollow core and dense surface pores enhanced the hydrophobicity, oleophilicity, permeability, and specific surface area of the fibers, and hence imparted the fibrous mat a high oil adsorption capacity. When the porous hollow microspheres were electro-sprayed onto the stainless steel mesh followed by the PDMS modification, the modified mesh became super-hydrophobic and super-oleophilic with the contact angle of 153° and sliding angle of 4°. The as-prepared mesh showed rapid oil/water separation with high efficiency and excellent recycling performance. The flux for separation of oil/water mixture could reach as high as 11,000 L m^{-2} h^{-1}. This facile non-solvent assisted electrospinning method provides a new avenue for preparation of multifunctional porous materials which possess potential applications in large-scale oil/water separation.

1. Introduction

Oil spill has now become an emerging threat to the marine environment and aquatic ecosystem [1,2]. Materials with special wettability have been developed for the oil removal from the waste water [3–7]. Porous materials with super-hydrophobicity and super-oleophilicity are good candidates, because they can selectively filter or absorb oil from the oil/water mixtures [8–10]. One of these materials is derived from metal meshes, textiles, sponges/-foams, etc., which usually experienced the roughening of their skeletons/surfaces, followed by the hydrophobization [11–14]. When they are used as the filter for oil/water separation, the oil is able to go through the membrane quickly because of their super-oleophilicity, while the water can only stay on the top surface of the super-hydrophobic materials. Various techniques, including nanoparticle decoration [15–18], carbon-based coating [19–21], chemical etching [22,23], and chemical vapor deposition [24,25], have been explored to construct the hierarchical micro/-nano structures, in order to improve the surface roughness and thus super-hydrophobic and super-oleophilic properties. For example, Shang et al. introduced polydopamine (PDA) particles into different porous materials including the stainless steel mesh, nylon netting and cotton cloth by the self-polymerization of the DA, which significantly increased the surface roughness of the steel mesh or the fabrics, and the subsequent decoration with fluorine containing thiol featured the surface super-hydrophobic and super-oleophilic. The as-prepared super-hydrophobic materials displayed excellent oil/water separation performances as well as good recyclability [26]. However, the above mentioned methods are usually complicated, and multistep reaction and delicate manipulation are required. Additionally, in many cases, the fluorine- containing reagent is chosen for the chemical modification to decrease the surface energy of the materials, which brings underlying harm to the environment.

Oil/water separation could also be achieved by the adsorption route, that is, oil is captured by the absorbents. Scientists have developed a great number of absorbent materials for oil adsorption, among which electrospun polymer fiber mat is a good

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candidate, due to its porous structure, lightweight, etc. [27–29]. Porous or hollow structure is usually introduced into the fibers to increase the permeability and the specific surface area and hence the oil adsorption capacity [30,31]. A typical example is the porous polystyrene (PS) fibers, and the pores can be located on the fiber surface and/or inside the fibers by choosing the proper solvent for electrospinning. The pore formation is ascribed to the vapor induced phase separation and breath figure effect [32,33]. The electrospun fiber with a hollow core can be achieved by a coaxial-electrospinning [34], phase separation [35], and template method [36]. In fact, the combination of the two structures, namely the hollow core and porous shell, is desirable, because it can further increase the specific surface area as well as the permeability while decrease material density, which would increase not only the capacity but also the rate for the oil adsorption. However, up to now, it is still a challenge to develop a simple but effective method to obtain polymer fibers with such a hierarchical structure.

Here, a facile one-step method, *i.e.*, non-solvent assisted electro-spraying or electrospinning, is proposed to prepare the microspheres or fibers with a hollow core and porous shell. The morphology evolution from the microsphere to fiber is easily achieved by controlling the polymer solution concentration for electrospinning. The unique porous and hollow microstructure, which was formed by the non-solvent induced phase separation, could not only increase the surface roughness of the microspheres or fibers and hence their hydrophobicity, but also significantly improve the permeability of the obtained materials, which is beneficial to the oil wetting and subsequent adsorption. When the commercially available stainless steel was deposited with the electro-sprayed porous microspheres, followed by the PDMS modification, it became super-hydrophobic and super-oleophilic with the contact angle of 153° and sliding angle of 4°. The as-prepared mesh showed rapid oil/water separation with high efficiency and excellent recycling performance. The flux for separation of oil/water mixture could reach as high as 11,000 L m^{-2} h^{-1}.

2. Experimental section

2.1. Materials

Poly(methylmethacrylate) (PMMA, Mw = 112,000) is a commercial product, which was purchased from Chi Mei company. Dichloromethane (DCM, the solvent), non-solvent including 1,2-propanediol, butanol and hexanol, and oily liquid used for oil/water separation such as hexane, hexadecane, and xylene, were purchased from Sinopharm Chemical Reagent Co., Ltd., P.R. China. PDMS prepolymer (Sylgard 184A) and the curing agent (Sylgard 184B) were received from Dow Corning Corporation, America. Diesel and petroleum ether were obtained from local stores. All materials and reagents were used without further purification. The physical properties [37] of polymer, solvent and non-solvent are listed in Table. 1.

2.2. Electrospining and electro-spraying

Non-solvent (propanediol) was first mixed with DCM, and then a certain amount of PMMA was dissolved into the mixed solvent/non-solvent solution, which was subsequently subject to magnetic stirring for 4 h. When the weight ratio between the propanediol and PMMA (W_R) was fixed at 2:1 and the PMMA concentration was 3 wt%, 5 wt%, 7.5 wt%, 10 wt%, and 15 wt%, the obtained microspheres or fibers were represented by PF3, PF5, PF7.5, PF10, PF15-1, respectively. At a solution concentration of 15 wt%, the fibers were named as PF15-2, and PF15-3 with W_R of 1:1 and 1:2. For electrospinning, the feed rate was 1 mL·h^{-1}, the applied voltage was 12 kV, and the distance between the metallic needle and the stainless steel drum (the collector) was 12 cm. During electrospinning, fibers or microspheres were collected on an aluminum foil attached on the rotating drum.

2.3. Modification of stainless steel mesh for oil/water separation

As a typical preparation, PF5 (microspheres) with a hollow core and porous shell were electro-sprayed onto a piece of stainless steel mesh. The obtained microsphere coated mesh was then immersed into a hexane solution containing 1 wt% PDMS prepolymer and 0.1 wt% curing agent for 3 h, and subsequently subject to curing at 80 °C for 3 h.

2.4. Morphology characterization

The surface morphology of the gold-sputtered fibers or microspheres were examined by a scanning electron microscopy (SEM, Zeiss_Supra55, Germany) operated at 5 kV. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and energy dispersive spectrometry (EDS) mapping of the PDMS modified microspheres were obtained on a FEI Tecnai G2 F30 field emission transmission electron microscopy with an accelerating voltage of 300 kV and equipped with energy dispersive spectrometry. Fourier-transform infrared (FTIR) spectra of the PMMA microspheres and PDMS modified microspheres were recorded in the range of 400–4000 cm^{-1} using FTIR spectroscopy (Cary 670, Varian, USA). The diameter of the surface pores for the microspheres or fibers was measured from the SEM images by using the software of Nano measurer, and at least 50 surface pores were selected for the measurement.

2.5. Contact angle (CA) measurement

Static contact angles were carried out on an optical contact angle measuring device (OCA40, Germany) at an ambient temperature. 5 μL of deionized water was dropped onto the microsphere coated surface or fiber surface, and the CA values were determined by averaging at least four separate runs. The sliding angle was determined by the angle between the modified mesh and the horizontal plane, at which the water droplets began to roll off the mesh surface.

Table 1
Physical properties of solvent and nonsolvent used in the experiment.

Materials	Boiling point (°C)	Viscosity (mPa·s)	Solubility parameter (cal·cm^{-3})	Surface tension (mN·m^{-1})
DCM	39.8	0.43	9.7	26.5
PMMA	NA	NA	9.3	40
Propanediol	188	60.5	14.8	38
Butanol	117	2.05	11.4	24.6
Hexanol	157	5.2	10.7	27.9