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Superhydrophobic conjugated microporous polymers for separation and adsorption†

An Li,^{*ab} Han-Xue Sun,^a Da-Zhi Tan,^{bc} Wen-Jie Fan,^b Shu-Hao Wen,^b Xiao-Juan Qing,^a Gui-Xian Li,^a Shi-You Li^a and Wei-Qiao Deng^{*b}

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Superhydrophobic conjugated microporous polymers show good selectivity, fast adsorption kinetics, excellent recyclability and absorbencies for a wide range of organic solvents and oils, which make them the promising candidates for potential applications, including liquid–liquid separation, water treatment and so on.

Superhydrophobic surfaces (water contact angle (CA) larger than 150°) have generated extensive commercial and academic interest.^{1–7} In recent years, there has been an increased interest in generation and utilization of the surface superhydrophobicity of a solid for direct separation or selective adsorption of oil or hydrophobic organic solvents from water. The first example for oil–water separation by using superhydrophobic and superoleophilic coating mesh has been reported by Jiang *et al.*⁸ Along this line, more recently, the creation of nanometre- or micrometre-sized porous materials with excellent

surface superhydrophobicity has been reported and successfully used for separation and adsorption of oils or organic solvents from water. For example, Yuan *et al.* reported the selective adsorption of oil from water by a superwetting nanowire membrane.⁹ Similar selective adsorption performance has also been reported by Zhang *et al.* using superhydrophobic nanoporous polydivinylbenzene.¹⁰ Due to their excellent selective adsorption performance, fast adsorption kinetics, good working capacity and recyclable use performance, these materials have great advantages over those traditional absorbent materials such as active carbons,^{11,12} which suffer from a number of drawbacks, including slow adsorption kinetics, poor selectivity and limited working capacity. Owing to the global scale of severe water pollution arising from oil spills and industrial organic pollutants, the creation of efficient absorbent materials for separation and removal of oils or organic pollutants from water should be of great importance to address environmental issues.^{9,13} Though many efficient absorbents, including silicas,¹⁴ carbon nanotubes,^{15–19} organic–inorganic hybrids,^{20,21} functionalized polymers and resins,^{22–26} *etc.* have been developed for adsorption or removal of organic pollutants from water, only a few experiments involving hydrophobic microporous polymer absorbents^{27–29} or superhydrophobic absorbents^{9,10} have been reported to date. From a materials science standpoint, the development of superhydrophobic absorbents with open pore structures, good stabilities and large surface areas that can adsorb a wide range of organic compounds is of special interest.

Recently, conjugated microporous polymers (CMP) have received considerable research interest because of their fine tuned

^aState Key Laboratory of Gansu Advanced Non-ferrous Metal Materials, Key Laboratory of Non-ferrous Metal Alloys and Processing, Ministry of Education, College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou, 730050, PR China. E-mail: lian2010@lut.cn; Tel: +86-931-2973305

^bState Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, PR China. E-mail: dengwq@dicp.ac.cn

^cExperiment Center of Chemistry, Dalian University of Technology, Dalian, 116023, PR China

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Broader context

Owing to the global scale of severe water pollution arising from oil spills and industrial organic pollutants, the creation of efficient absorbent materials for separation and removal of oils or organic pollutants from water should be of great importance to address environmental issues. Here we report for the first time the surface superhydrophobicity of the conjugated microporous polymers (CMP) as well as their excellent adsorption performance for oils and organic solvents. Due to their open pore structures and excellent surface superhydrophobicity, oils or non-polar organic solvents can be easily absorbed and separated from water by the CMP without adsorption of water. The CMP also show excellent adsorption performance for those polar organic solvents and toxic organic solvents with the absorbencies ranging approximately from 700 wt% to 1500 wt% for the **HCMP-1** and 600 wt% to 2300 wt% for the **HCMP-2**, respectively. By loading the CMP, the hydrophilic sponge can be changed to be oleophilic to oil. With a loading of 7.0 mg cm⁻³ of the **HCMP-1** in sponge, the as-treated sponge shows an absorbency of 2300 wt% for octane and 3300 wt% for nitrobenzene, which have great potentials for large-scale removal of toxic organic contaminants or oil spills from water.

microporosity, large surface areas and good stability.^{30–38} Their particular physicochemical properties make them ideal absorbents for gas adsorption,^{30–33,35–38} however, no studies involving either their surface wettabilities or their adsorption performance for organic solvents have been reported to date. In a continuation of our previous studies on absorbent materials,^{38–40} in this work we report for the first time the surface superhydrophobicity and strong oleophilicity of the CMP as well as their excellent adsorption performance for organic solvents. The CMP not only show good selectivity, fast adsorption kinetics, excellent recyclability and excellent absorbencies for oils and nonpolar organic solvents but also exhibit good absorbencies for those toxic or polar organic solvents, which make them the promising candidates as efficient absorbents for a wide range of potential applications, including liquid–liquid separation, water treatment and so on.

We synthesized the CMP *via* Pd(II)/Cu(I)-catalyzed homocoupling polymerization of 1,3,5-triethynylbenzene (named as **HCMP-1**) according to previous studies.^{27,29} Computational simulation shows that the **HCMP-1** has a porous three-dimensional network structure arising from the three-pronged butadiynylene linkages (Fig. 1a). The scanning electron microscopy (SEM) image (Fig. 1b) shows that the **HCMP-1** is composed of agglomerated microgel particles with a size of approximately 60–120 nm in diameter. The transmission electron micrograph (TEM) of the **HCMP-1** shows the presence of nanometre-sized honeycomb-like pores on the surface of the **HCMP-1** (Fig. 1c). The porous properties of the **HCMP-1** were evaluated by nitrogen adsorption analyses at 77 K and details are presented in the ESI†. The **HCMP-1** prepared under our experimental conditions exhibits a BET surface area of 955 m² g⁻¹. The porous properties analyses show that the **HCMP-1** is consisted of both micropores (pore sizes less than 2 nm) and mesopores (pore sizes larger than 2 nm). Thermogravimetric analysis (TGA) shows the **HCMP-1** has good thermal stability with a thermal decomposition temperature

over 300 °C (Fig. S1†, ESI). For comparison purpose, in this work we also synthesized an analogue of the **HCMP-1**, which was produced from 1,3,5-triethynylbenzene and 1,4-diethynylbenzene (named as **HCMP-2**) by employing the same synthesis method (ESI†).

The water CA measurement was performed to investigate the surface wettability of the **HCMP-1** and the **HCMP-2**. It was observed that the **HCMP-1** exhibits surface superhydrophobicity with a water CA of 167° (Fig. 1d). Such significant surface superhydrophobicity should be attributed to the cooperation of both microporous morphological structures and strongly hydrophobic chemical compositions (only consist of hydrophobic aromatic rings and conjugated carbon carbon triple bonds) of the **HCMP-1** microgel particles, which are two well-known key factors for the surface superhydrophobicity.^{1–7} Similar observation is also found in the surface water CA measurement for the **HCMP-2**, which exhibits surface superhydrophobicity with a water CA of 157° (Fig. S5†, ESI). The sliding angles of water droplets were measured to be 2.1° and 2.8° for **HCMP-1** and **HCMP-2**, respectively. In contrast to superhydrophobic wettability to water, interestingly, both the **HCMP-1** and the **HCMP-2** show strong oleophilic properties to oil. For example, when a diesel oil droplet was placed on the surface of the **HCMP-1**, it can be quickly absorbed into the **HCMP-1** and a CA with oil of nearly 0° was obtained (Fig. 1e). To the best of our knowledge, such unique surface superhydrophobicity and strong oleophilicity for the CMP has never been reported. Taking advantages of both superhydrophobicity and oleophilicity as well as their microporous features, the CMP would be ideal candidates as absorbents for oil–water separation or removal of organic solvents from water.

Due to their open pore structures and excellent surface superhydrophobicity, oils or non-polar organic solvents can be easily removed from water by the **HCMP-1** without adsorption of water, implying an excellent selective adsorption. As shown in Fig. S6† (ESI), when a small piece of the **HCMP-1** (10 mg) was placed on the surface of an octane–water mixture in a glass dish, the red-colored octane can be absorbed by the **HCMP-1** in several minutes by slightly shaking the dish. Such fast adsorption kinetics should be attributed to strong oleophilic nature of the **HCMP-1** combining with its microporous features where absorbing of octane by capillary action of its surface nanometre-pores may occur as well.⁹ Due to its light density and superhydrophobic nature, the **HCMP-1** is floating on the surface of water before and after collecting all of octane from water. Thus, the octane can be easily removed from water only by filtration, which is greatly of technological significance for practical use especially for spills cleanup. The absorbed octane can be recollected from the **HCMP-1** by treatment of filtrates under low-pressure distillation (Fig. S7†, ESI). Also, the **HCMP-1** can be regenerated after use by ultrasonic washing with organic solvents which make them recyclable absorbent materials. We found that, in the case of removal of octane from water, the absorbency of the **HCMP-1** remains nearly unchanged even after 20 cycles of adsorption/desorption. Similar observations were also found in the systems of superwetting nanowire membrane⁹ and carbon nanotube sponges.¹⁹

To investigate the absorbencies of the **HCMP-1** and the **HCMP-2**, various non-polar organic solvents and oils were employed in this work. As shown in Fig. 2, the **HCMP-1** shows absorbencies in the range from 700 wt% to 1000 wt% and the maximum absorbency reaches up to 10 times its weight. In the case of the **HCMP-2**, the absorbency varies from 600 wt% to 1000 wt%. The average

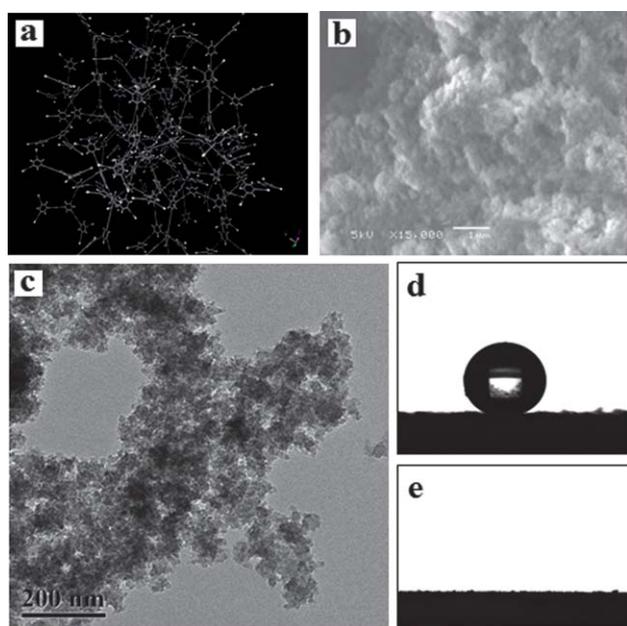


Fig. 1 a) Simulation structure of the **HCMP-1** (Materials Studio, polymer builder). (b) SEM image of the **HCMP-1**, scale bar: 1 μm. (c) TEM image of the **HCMP-1**, scale bar: 200 nm. (d) The measurement of contact angle with water and (e) with diesel oil for the **HCMP-1**.

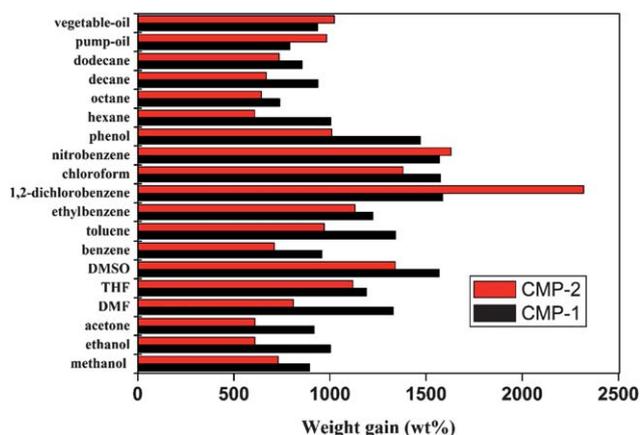


Fig. 2 The absorbencies of the **HCMP-1** and the **HCMP-2** for various organic solvents and oils with different densities, including methanol (0.79 g cm^{-3}), ethanol (0.79 g cm^{-3}), acetone (0.78 g cm^{-3}), DMF (0.94 g cm^{-3}), THF (0.89 g cm^{-3}), DMSO (1.10 g cm^{-3}), benzene (0.88 g cm^{-3}), toluene (0.87 g cm^{-3}), ethylbenzene (0.87 g cm^{-3}), 1,2-dichlorobenzene (1.30 g cm^{-3}), chloroform (1.48 g cm^{-3}), nitrobenzene (1.21 g cm^{-3}), phenol (1.07 g cm^{-3}), hexane (0.66 g cm^{-3}), octane (0.70 g cm^{-3}), decane (0.73 g cm^{-3}), dodecane (0.75 g cm^{-3}), pump-oil (0.96 g cm^{-3}) and vegetable oil (0.77 g cm^{-3}).

absorbency for the **HCMP-1** is slightly greater than that of the **HCMP-2**, which may be due to the fact that the **HCMP-1** possesses a large total pore volume of 1.58 g cm^{-3} and a surface area of $955 \text{ m}^2 \text{ g}^{-1}$ (the total pore volume and BET surface area of **HCMP-2** were measured to be 1.27 g cm^{-3} and $928 \text{ m}^2 \text{ g}^{-1}$, Fig. S3†, ESI). Viewing the recent development in the field of the CMP reported by Cooper *et al.*,^{35–37} further improvement in oils absorbency for the CMP can be anticipated because the surface areas and pore volumes of the CMP could be tuned by employing different monomers with various molecule lengths.

In addition to those non-polar organic solvents, both the **HCMP-1** and the **HCMP-2** also show excellent absorbencies for polar organic solvents. As shown in Fig. 2, the absorbencies for these organic solvents range approximately from 700 wt% to 1500 wt% and 600 wt% to 2300 wt% for the **HCMP-1** and the **HCMP-2**, respectively. Because the CMP are mainly composed of micropores (1–2 nm) and mesopores (> 2 nm),^{36,38} which are larger than the molecular length of all of the selected organic solvents. So, it is concluded that the organic solvents can be absorbed into both micropores and mesopores. Therefore, the changes in absorbency may mainly be depended on the density of organic solvents as well as total pore volumes and surface areas of the CMP. In fact, the more interesting finding of this study is that both the **HCMP-1** and the **HCMP-2** show good absorbencies for those toxic organic solvents such as nitrobenzene, dichlorobenzene and phenol, which are well known as toxic organic contaminants in water treatment.^{13,41,42} For instance, the absorbency of nitrobenzene, 1,2-dichlorobenzene and phenol for the **HCMP-1** is 1569 wt%, 1586 wt% and 1470 wt%, respectively. As reported previously,³⁶ the CMP show excellent chemical stability and are totally insoluble in all organic solvents. Based on this unique physicochemical property, it would be natural to assume that the CMP can be used as absorbents for any kinds of organic solvents. Though the remarkable absorbencies for organic solvents were reported by recently developed absorbents such as superwetting nanowire membrane⁹ and

functionalized polyelectrolyte gels,^{22,23} those materials only show excellent absorbencies for non-polar organic solvents. Our materials show superior absorbencies for both non-polar and polar organic solvents, which have great potentials for the removal of toxic organic contaminants or oil spills from water. Moreover, quite from those traditional absorbents, there are active sites (carbon carbon triple bond) in the backbone of the **HCMP-1** network which are capable of binding metallic ions,^{36,38} making the **HCMP-1** also a possible candidate as an absorbent for metallic ions. The work in this direction is currently under the way.

Most interestingly, in this study we found that the **HCMP-1** microgel particles can be loaded on a porous substrate even with hydrophilic property for facile production of low cost and efficient absorbents. For example, the sponge is a kind of cheap and commercial available hydrophilic porous material, usually it can absorb both water and oils or organic solvents, which makes it impractical for removal of oil from water due to its poor selectivity. Immersing of the sponge into a homogeneous mixture of the **HCMP-1** in chloroform solution, the **HCMP-1** microgel particles can be physically coated in the pores both inside and outside of sponges after removal of chloroform under low-pressure distillation (Fig. 3a and b), which makes the sponges hydrophobic to water while oleophilic to oil. As shown in Fig. 3c–e, when a piece of the sponge and the **HCMP-1** treated sponge were placed in a water bath, the sponge absorbed water and sank to below the surface level while the

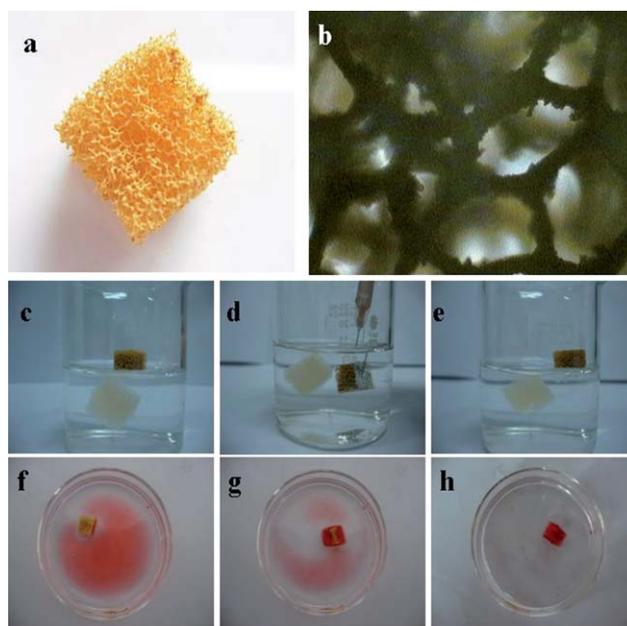


Fig. 3 (a) Camera image of the **HCMP-1** treated sponge. (b) Optical microscopy image of the **HCMP-1** treated sponge, showing the **HCMP-1** microgel particles coated on the surface of sponge backbone. (c) When a piece of the sponge and the **HCMP-1** treated sponge were placed in a water bath, the sponge absorbed water and sank to below the surface level while the **HCMP-1** treated sponge was floating on the water surface. (d) When the **HCMP-1** treated sponge was pressed below the water surface under pressure, (e) it immediately floats on the surface of water after release of the pressure and no water uptake was observed during the procedure. (f–h) Snapshots showing the adsorption of a 12 cm^2 red colored octane film (dyed with red oil o) distributed on a water bath by a piece of the **HCMP-1** treated sponge ($0.6 \times 0.6 \times 0.6 \text{ cm}$).

HCMP-1 treated sponge was floating on the water surface. Even when the **HCMP-1** treated sponge was pressed below the water surface under pressure, it immediately floats on the top of the water surface after release of the pressure and no water uptake was observed during the procedure by weighing the **HCMP-1** treated sponge. Similar to that of the **HCMP-1**, the **HCMP-1** treated sponge also shows excellent ability for removal of octane from water (Fig. 3f–h) and the octane can be easily separated from water only by taking out the as-treated sponge from water without further process. With a loading of 7.0 mg cm^{-3} of the **HCMP-1** in sponge, the absorbency of octane for the **HCMP-1** treated sponge is measured to be 2300 wt%. For a high density organic solvent such as nitrobenzene, its absorbency reaches 3300 wt%. Given the light density of the **HCMP-1** treated sponge, in this case is 0.027 g cm^{-3} , specifically, the absorbencies for such **HCMP-1** treated sponges reach up to 0.6 t m^{-3} for octane and 0.9 t m^{-3} for nitrobenzene, respectively. Compared with the carbon nanotube sponges,¹⁹ the **HCMP-1** treated sponge is more easy to prepare and handle for practical use, which has great potentials for the removal of toxic organic contaminants or oil spills from water. A more immediate application for these **HCMP-1** coated sponges will be in the large-scale removal of oils or organic solvents from water, which may open an opportunity to address the environmental issues especially for the global scale of severe water pollution arising from oil spills and industrial organic pollutants.

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