# Facile Preparation of Flexible, Optically Transparent Superhydrophobic Surfaces by Conjugated Microporous Polymer

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**Abstract.** Creation of optically transparent superhydrophobic surfaces has increased extensive attention in the self-cleaning area. In this work, flexible, optically transparent superhydrophobic surfaces were fabricated by coating the conjugated microporous polymer on poly(dimethylsiloxane) (PDMS) substrate over large areas without using any expensive or complicated techniques. Result shows that the as-treated PDMS films exhibit super water repellence with a water CA of 163$^{o}$. The surface superhydrophobicity should be contributed to both the strong hydrophobic surface chemical compositions and the micoporous morphological structures of the polymer microgel particles. The as-treated PDMS film also exhibits excellent optical transparency. Our study could not only prove to be a route to superhydrophobic surfaces but also may pave the way for large-scale, commercial production of flexible, optically transparent superhydrophobic surfaces, which is greatly technological significance for large-scale fabrication of self cleaning surfaces, anti-fogging coatings, etc..

## Introduction

The creation of superhydrophobic surface (water contact angle (CA) larger than 150$^{o}$) has attracted intensive research interest both in academy and industry [1]. Extensive studies have revealed that the superhydrophobicity of a solid surface is controlled by the surface free energy and roughness and it is usually enhanced by surface roughness [2]. Understanding the complementary roles of these two key parameters, to date a number of artificial superhydrophobic surfaces have been developed by controlling the surface chemistry and surface roughness [3]. In recent years, there has been an increased interest in the creation of optically transparent superhydrophobic surfaces due to their potential optical applications such as solar panels, automobile windows, lenses and other optical instruments that have to stay clean [4]. However, there are only a few reports of optically transparent superhydrophobic surfaces [5]. More recently, though flexible and transparent superhydrophobic surfaces created on poly(dimethylsiloxane) (PDMS) substrates have been reported [6,7], these methods have limitations for large-scale production caused by either the need of expensive or complicated fabrication techniques or limitations in substrates size. From a standpoint of material science, the seeking of efficient approaches for the creation of flexible and transparent superhydrophobic surfaces on a large scale only by a facile process should be a priority and would be of great importance especially for practical applications. In this work, we report a novel, “grafting” approach for the creation of flexible, optically transparent superhydrophobic surfaces by coating of the conjugated microporous polymer (CMP) microgel particles on the surface of PDMS films. This work does not need any expensive or complicated techniques and the superhydrophobic surface can be simply constructed over large areas without limitations in shape or size of PDMS substrates, which is greatly technological significance and may have great potentials for large-scale fabrication of flexible, optically transparent self-cleaning surfaces, anti-fog coatings, etc.

## Results and discussion

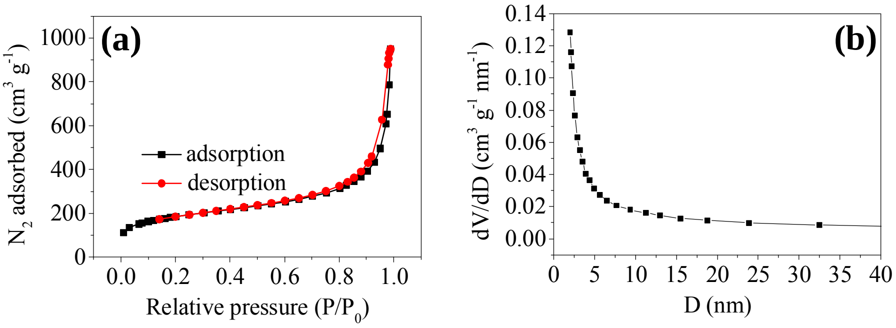

**Fig. 1.** (a) Nitrogen adsorption and desorption isotherms of the CMP. (b) Pore size distribution of the CMP.

The CMP was synthesized from 1,3,5-triethynylbenzene via a facile Pd(II)/Cu(I)-catalyzed homocoupling polymerization according to literatures [8] or our previous studies [9,10]. In this work, we used intrinsic superhydrophobic CMP as the coating material for fabrication of optically transparent self-cleaning surfaces. The nitrogen adsorption and desorption isotherms of the CMP at 77K were measured to evaluate the porosity of the CMP. As seen in Fig. 1a, according to the International Union of Pure and Applied Chemistry classification, the synthesized CMP displays mixed II/IV adsorption isotherm, with obvious hysteresis loop character in the relative pressure range 0.4-0.9 and strong $N_2$ adsorption at lower (<0.1) and higher pressure (>0.9), indicating the coexisting of micropores, mesopores and macropores. The Brunauer-Emmett-Teller (BET) surface area and micropore area was calculated to be 655 $m^2$ $g^{-1}$ and 173 $m^2$ $g^{-1}$. The CMP exhibited a narrow pore size distribution in the range of 2-8 nm (Fig.1b). The total pore volume was measured to be 0.94 $cm^3$ $g^{-1}$ ($P/P_0$=0.969) using the Barrett-Joyner-Halenda method.

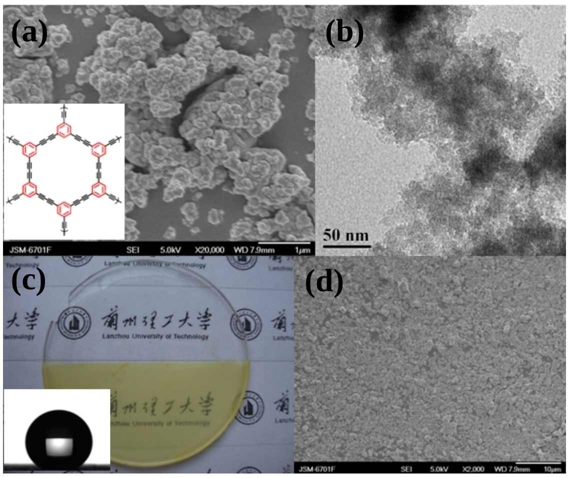

**Fig. 2** (a) SEM image of CMP. Inset is the structure chart of CMP. (b) TEM image of CMP. Scale bar: 50 nm. (c) Camera image of the PDMS film of one half coated with the CMP (yellow part) and the other half without coating (colorless part). Inset is the water CA mesurment for CMP coated PDMS film. (d) SEM image of the CMP coated PDMS film. Scale bar: 10 µm. Scale bar: (a) 1 µm, (b) 50 nm, (c) 10 µm.

SEM was preformed to evaluate the morphology of the as-prepared CMP, as shown in Fig. 2a, the CMP is composed of agglomerated microgel particles with a size of approximately 60-120 nm in diameter. The structure chart (Fig. 2a inset) exhibits that the CMP can form a porous three-dimensional network structure which arises from three-pronged butadiynylene linkages. TEM image shows there are nanometer-sized, honeycomb-like pores on the surface of the microgel particles (Fig. 2b), which is in good agreement with the results of the porosity analysis. Such unique hierarchical structures of the CMP microgel particles are similar to that of micrometer-sized papillae of lotus leaves which is well known to be responsible for the surface superhydrophobicity of lotus leaf by the combination of their hydrophobic cuticular waxes. In view of both the strong hydrophobic chemical compositions (only consist of aromatic rings and conjugated carbon carbon triple bonds) and the micoporous morphological structures of the CMP microgel particles, this material would be an ideal candidate for creation of lotus leaf-like superhydrophobic surfaces.

Inspired by the observation that fine particles can readily attach on a solid surface to form a particle layer by so-called fine particle adhesion [11], in this work we have succeeded in creation of superhydrophobic surfaces by coating the CMP microgel particles on PDMS films in the same way. Painting fine microgel particles (particle sizes smaller than 10 μm) of the CMP on PDMS surfaces by a brush, then removal of those loosely attached particles by air flush followed by rubbing the particles layer by a cloth, we obtained a stable, macroscopically homogeneous particles layer on PDMS surfaces (Fig. 2c and d), which is similar to various artificial superhydrophobic surfaces, such as polyelectrolyte multilayer surface coated with silica nanoparticles [12], electrodeposited cauliflower-like poly(fluorinated thiophene) films on ITO electrode [13] and electrochemical deposited gold clusters on polyelectrolyte multilayer modified ITO electrode [3]. During rubbing process, we found that the microgel particles of the CMP can be pressed to insert into the surface of PDMS substrate due to the rigid and porous structure of the CMP microgel particles and soft nature of the PDMS, giving a stronger adhesive force between the CMP particles and substrates. In fact, even without rubbing process, the CMP microgel particles show strongly, spontaneously adhesive force to PDMS substrates and can hardly be removed by mechanical rubbing. Such insertion of the CMP particles into PDMS substrates can also be easily achieved by direct mechanical squeezing the as-treated PDMS substrates using a smooth substrate, for example, glass slide or silica wafer.

The water CA measurement was performed to investigate the surface wettability of the CMP coated PDMS films under room temperature. The as-treated PDMS films exhibit super water repellence with a water CA of 163$^o$ (Fig. 2c inset). When water droplets are placed on the surface of the CMP treated PDMS, water droplets are almost spherical. The millimeter-sized water droplets can be suspended on top of the surface of the as-treated PDMS film and roll off easily. The sliding angle of water droplets on the CMP treated substrate was measured to be ca. 3.6$^o$. For comparison purpose, the surface water CA for untreated PDMS film was measured to be in the range of 98$^o$-102$^o$, indicating that the surface superhydrophobicity of as-treated PDMS films are indeed generated from the CMP microgel particles instead of the substrates. Such significant surface superhydrophobicity should be attributed to the combination of both micoporous morphological structures and strongly hydrophobic chemical compositions (only consist of aromatic rings and conjugated carbon carbon triple bonds) of the CMP micorgel particles, which are two key factors for the creation of superhydrophobic surfaces. The temporal stability of the as-treated PDMS surface in terms of water CA was also measured. Only a slight decrease of 2.0$^o$ in water CA was observed after 30 min duration. Owing to the high chemical (totally insoluble in all organic solvents) and thermal stability of the CMP (the thermal decomposition temperature is greater than 300 $^o$C), the water CA of the CMP treated PDMS surface remains nearly unchanged after treatment of the CMP with the usual organic solutions and a treatment temperature of up to 220 $^o$C for 1h in air.

The surface superhydrophobicity of the CMP coated substrates show high reproducibility in terms of the water CA. We carried out many experiments and the surface wettability based on each batch of the CMP product exhibit a similar water CA, though there is a slight change in BET surface areas and porous properties of the CMP. These results indicate a well-controlled porous morphology of the CMP microgel particles, which is dominated by inherent geometrical structures of the CMP. Quite different from those artificial superhydrophobic surfaces constructed by controlling the surface morphological features where surface wettability is greatly influenced by experimental conditions or techniques adopted, our strategy takes advantage of inherentmchemistry of conjugated microporous polymers which allows both strong hydrophobic chemical compositions and well-defined microporous characteristics are easily obtained at the same time to create a superhydrophobic surface only through a facile synthesis and a painting process without using any complicated techniques.

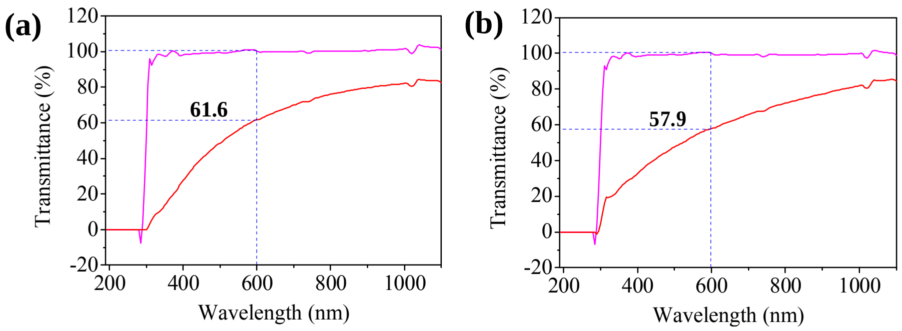

**Fig. 3** Light transmittance of the PDMS film with a thickness of (a) 0.2 mm and (b) 0.3 mm before (blue curve) and after coating (red curve).

Interestingly, such the CMP coated PDMS exhibits excellent optical transparency. Given a PDMS film thickness of 0.2 mm and CMP microgel particles sizes less than 10 μm, the light transmittance of the as-prepared PDMS film reaches 61.6 % and 70.0 % at a wavelength of 600 nm and 700 nm, respectively (Fig. 3a). Such the CMP treated PDMS film is more than like a flexible, optically transparent artificial “lotus leaf”. On the other hand, we found that the light transmittance of the as-treated PDMS film decreases with the increase of the thickness of both the CMP particle layer and PDMS film. For instance, under the same preparation conditions, the light transmittance of the as-treated PDMS film with a thickness of 0.3 mm was measured to be 57.9 % and 65.7 % at a wavelength of 600 nm and 700 nm, respectively (Fig. 3b). Therefore, by fine controlling of both the thickness of PDMS films and the size of the CMP microgel particles, further improvement in the transparency of the resulting PDMS films can be anticipated, which may have great potentials for large-scale fabrication of flexible, optically transparent self-cleaning surfaces, anti-fogging coatings, etc. In addition to facile fabrication, our approach offers several special advantages for creation of superhydophobic surface on PDMS films. For instance, the elastomer nature of PDMS allows the CMP coated PDMS capable of bending or folding for special use. Most importantly, due to the readily deformability of PDMS precursor as well as its ease formation of thin film on other solid substrates, the superhydrophobic surfaces can be simply created by coating of the CMP microgel particles on those PDMS covered substrates without limitations in shape or size.

## Conclusions

In summary, we demonstrated a novel, “grafting” approach for the construction of flexible, optically transparent superhydrophobic surfaces by coating of the conjugated microporous polymer microgel particles on the surface of PDMS films without using any expensive or complicated techniques. Our approach proved to be simple, efficient and highly reproducible. Based on our approach, the superhydrophobic surface can be simply constructed on PDMS films over large areas without limitations in shape or size of the substrates, which could not only prove to be a promising route to superhydrophobic surfaces but also may pave the way for large-scale, commercial production of flexible, optically transparent superhydrophobic surfaces.

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