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Hydrophobicity control by a supercritical drying technique in a sol–gel process with hybrid materials

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ABSTRACT

We successfully synthesized one type of cheap super-hydrophobic hybrid porous materials in a sol–gel process. In this route, hydrophilic polymers and TEOS-base sol are used as precursors, the ultraviolet ray-initiated polymerization and supercritical fluid drying techniques are combined together to fulfill this task. All fabricated samples exhibit lotus-leaf-like surface structures with super-hydrophobicity. The underlying mechanisms are carefully investigated using a field-emission scanning electron microscopy (FESEM) and an X-ray photoelectron spectroscopy (XPS). We found that a well-controlled drying process is crucial to the formation of such super-hydrophobic surfaces. As high as 90% production rate is obtained in our route and thus, it might provide a cost-effective way to produce super-hydrophobic hybrid materials for industry applications.

1. Introduction

A cheap, self-cleaning material used for windows [1], building surfaces [2], automobiles [3], etc. is always desired in our daily lives. The presence of such a material could not only keep the surfaces clean but also could reduce maintenance costs, providing economic and safe solutions to above mentioned applications. Porous materials with super-hydrophobicity might meet these needs, due to their excellent water-repellant properties, super thermal insulation, as well as absorption properties [4,5]. Generally speaking, a so-called super-hydrophobic surface is the surface with a water contact angle (WCA) larger than 150° [6], and it is believed that the wettability of a surface is governed by the chemical circumstances and geometrical configurations of solid surfaces [7].

From the viewpoints of chemical synthesis, one can obtain such a super-hydrophobic surface by replacing the —OH groups on the surfaces with the $—CH_3$,$—CF_3$ functional groups or other low surface energy substances [8]. In a sol–gel process, some reagents, such as chlorotrimethylsilane (TMCS), hexamethyldisilylamine (HMDSA), with methyl or other alkyl groups molecules can be introduced into the system and branched with the surface OH group [9]. In porous materials, low-surface-energy groups such as fluorinate, silicon, and fluoroalkyl silane or expensive materials like carbon nanotubes are usually employed to make super-hydrophobic surfaces [10]. Also, polymers are used to create super-hydrophobic surfaces, such as template synthesis [11], solution method [12] and solvent-induced crystallization [13], phase separation [14], plasma polymerization or etching [15], electro-hydrodynamic techniques [16] and mechanical treatment [17], etc. Although great progress has been made on the fabrications of such surfaces, the preparation of super-hydrophobic materials from low cost hydrophobic material without introducing any expensive low-surface-energy reagents by a simple and fast procedure is still technically or commercially challenging.

Also, via structural tuning on surfaces [18,19], the lotus-leaf-like hydrophobic and super-hydrophobic surfaces can be obtained. The artificial microstructures synthesized from labs can have similar hydrophobic properties as natural lotus leaves without changing the chemical environment of the surfaces. Nevertheless, the key obstacle to construct the artificial super-hydrophobic surfaces in labs is the replication of the lotus structures and their original functionalities [19]. Recent studies show that the surface roughness plays a dominant role on the hydrophobicity even for a low energy surface [20]. It should be pointed out that the fabrications of micro- and nano-structure with super-hydrophobic surfaces or bulk materials from hydrophilic materials, especially with low cost ones, are still restricted.

In this work, we present a facile method to fabricate super-hydrophobic porous materials from hydrophilic polymer (monomers) and silica colloidal particles polymerized by exposing to UV light, and a CO_2 supercritical drying (SCD) process. No surface

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modification with low-surface-energy materials such as fluorides or silanes is used. All SCD samples exhibit super-hydrophobicity. Our investigations might provide an efficient way to fabricate super-hydrophobic surfaces from broad hydrophilic polymer and metal oxide colloidal hybrid porous materials.

2. Experimental details

2.1. Sample preparation

All reagents are purchased from Chengdu Chemical Co. (China) and used as received. A mixture of tetraethyl orthosilicate (TEOS, AR), 3-(trimethoxysilyl)propyl methacrylate (MPMS), alcohol, deionic water, and nitric acid aqueous is vigorously stirred to pre-hydrolyze the silica precursor. The molar ratio of TEOS, MPMS, H_2O, and HNO_3 is 1:0.1:2:10^{-4}. The resultant mixture solution is stirred at room temperature for three days to allow an adequate sol–gel reaction of siloxanes. The mixture is exposed to vacuum at 45 °C, so that the produced ethanol and methanol (due to the co-hydrolysis of TEOS and MPMS) can be removed. Afterwards, the resin-like mixture is dissolved in methyl methacrylate (MMA, AR) to form a 15 wt% solution, labeled as MS; MS and trimethylolpropane triacrylate (TMPTA, AR, Tokyo Kasei Kogyo Co., Ltd., Japan) are dissolved in alcohol. The resultant solution is then exposed to UV light (UV Rolence 100, 450 mW/m^2) until the gels are formed in beakers. After then, the gels are placed in a Speed SFE autoclave to extract the organic solvent (i.e., the alcohol or acetone) with a supercritical (SC) CO_2 fluid. After drying process, all samples are stored in a dryer chamber for 24 h, and then taken out for characterization. To make our experiments reproducible, we fabricated at least three samples for each set and evaluated the performance. The sample preparation conditions are listed in Table 1.

2.2. Characterization

The surface morphology is examined by a field-emission scanning electron microscopy (SEM, FEI Sirion 200). The X-ray photoelectron spectroscopy (XPS) measurements are performed on an ESCALAB-MK II instrument at room temperature. The XPS samples are with a dimension of 10 mm × 10 mm × 3 mm (length × width × thickness). The WCA is measured by using a contact angle measurement system. AFM (Atomic Force Microscopy) measurements are implemented on a Bruker Dimension Edge AFM.

2.3. Drying process

The SCD procedure is shown in Fig. 1. Initially, CO_2 gas is injected into the reactor that assembled with samples. The system pressure is increased to 10 MPa in 20 min by the booster pump. Then, the reactor is sealed and the pressure is kept at 10 MPa for 4 h to ensure adequate and complete solvent exchanges. Afterwards, the system temperature is elevated to 55 °C at a rate of 0.5 °C/min. In this stage, the pressure is kept at 12 MPa; the solvent exchanges will last for 4 h at 55 °C. Then, the CO_2 let-in is shut down, the depressurization rate is set as 6 MPa to release CO_2. Once CO_2 is piped off, the valve is closed and the heating system is stopped. When the reactor temperature is naturally cooled down to room temperature, the samples are then taken out for characterizing.

Table 1
Summary of sample preparation conditions.

No.	MS (ml)	TMPTA (ml)	Alcohol (ml)	Exposure time (s)	Drying method
S-1	5	5	15	180	SCD
S-2	5	10	15	180	SCD
S-3	5	15	15	180	SCD
T-1	5	10	15	180	TD

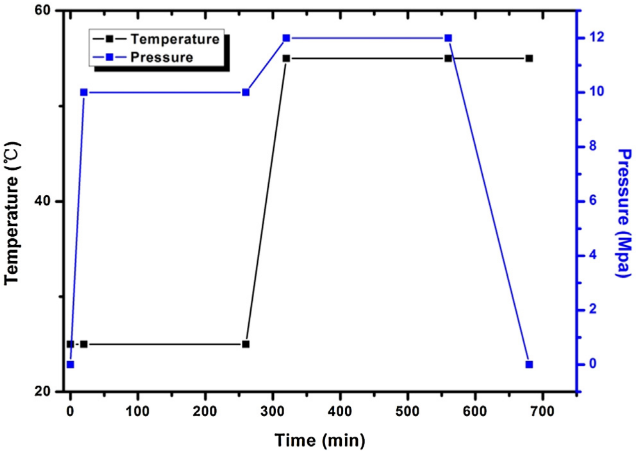

Fig. 1. SCD process used in this work.

The thermal drying (TD) process is done by directly heating the samples to 55 °C in the oven.

3. Results and discussion

3.1. Microstructures

Four sets of samples are synthesized. Namely, the SCD (Samples S-1, S-2, and S-3) and TD (Sample T-1, note that the pore structure will collapse during TD, and therefore only one TD sample is selected here for comparison). Fig. 2 shows the typical FESEM images of those samples. It is evident that the hybrid gels in the supercritical CO_2 fluid will form micro/nano structures after drying. The dimensions of the aggregated spheres are in the range of 300–600 nm. Each aggregated sphere consists of numerous papillae with diameter about 10–30 nm (Fig. 2(a)). With the increase of silica concentration (i.e., from 5 to 10 ml), the papillae and the aggregated spheres increase to 30–50 nm and 800–1300 nm, respectively (Fig. 2(b)), indicating that larger silica concentration would lead to larger particle aggregations under SCD. When getting a closer look at the aggregation (Fig. 2(c)), one can observe the binary-hierarchical structures on the sphere surface with a lotus-leaf-like or strawberry-like shape [20]. In addition, by carefully selecting the silica concentration and controlling drying conditions (i.e., the TMPTA is 10 ml and at a temperature ramp rate of 0.5 °C/min), we can easily tune the sizes of papillae. Furthermore, to demonstrate the reproducibility of our route, we also prepared several sets of samples with SCD and similar artificial structures are found for all samples. We then discuss the possible formation mechanisms of the lotus-leaf-like surface structures in the following.

We know that silica particles are insoluble in SC CO_2 and the spaces between polymer chains can be penetrated by SC CO_2. Therefore, the mobility and free volume of polymer matrix will be altered [20]. As a consequence, in the SC CO_2 system, the PMMA chains on the surface of the silica particle cores and the PMMA-rich domain will be stretched [21]. With the venting of SC CO_2, a soluble chain of the PMMA domains will shrink and condense around the silica cores or the cross-linked PTMPA intersection point with PMMA. These condensed PMMA chains are hardly able to interpenetrate into the PMMA chains of other cores and form a skin-like layer on the surface of aggregations. In this way, to