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Robust multifunctional superhydrophobic organic–inorganic hybrid macroporous coatings and films

Song Hee Koo [a,1], Seung Goo Lee [b,1], Hyojin Bong [b], Young-Je Kwark [a], Kilwon Cho [b], Ho Sun Lim [c,*], Jeong Ho Cho [d,*]

[a] Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul 156-743, Republic of Korea
[b] Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
[c] Electronic Materials and Device Research Center, Korea Electronics Technology Institute, Gyeonggi-do 463-816, Republic of Korea
[d] SKKU Advanced Institute of Nanotechnology (SAINT) and Center for Human Interface Nano Technology (HINT), School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

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ABSTRACT

We demonstrate a facile and efficient method for fabricating multifunctional superhydrophobic organic–inorganic hybrid macroporous coatings and films with robust environmental stabilities involving the electrospinning of phenylsilsesquiazane (PhSSQZ) in the presence of polystyrene (PS). The resulting freestanding PhSSQZ/PS webs, which featured hierarchical fibrous structures with the unique chemical properties of PhSSQZ, provided a practical material with potential uses in many applications including structural coatings, oil–water separation membranes, and high-performance air filters. The materials maintained their fibrous structures and superhydrophobicity even after heat treatment at 600 °C under an ambient atmosphere, which is among the highest level reported up to date for solution-processed superhydrophobic surfaces with soft materials. The solvent resistance and mechanical strength of the PhSSQZ/PS webs were significantly enhanced through the structured siloxane network due to thermally induced hydrolysis of PhSSQZ and condensation of the resulting silanols. The properties of this novel material suggest that the present approach will advance our knowledge and capability to design and develop multifunctional smart materials with robust superhydrophobicity and macroporosity.

1. Introduction

Superhydrophobic surfaces with water contact angles greater than 150° have attracted great interest for numerous attractive features that include self-cleaning [1,2], anti-icing [3,4], buoyancy [5,6], and drag reduction [7,8]. These superhydrophobic surfaces have been prepared through the control of the chemical composition and the topographical structure [1–24]. Traditional superhydrophobic surfaces are used in waterproof and protective coating applications. Advanced superhydrophobic surfaces demand multiple functionalities, including optical transparency [14–21], conductivity [19], or tunable wettability [20]. Above all, simple low-cost fabrication techniques and robust environmental stability are preferential qualities for practical applications of superhydrophobic surfaces [21–24].

Electrospinning is an efficient and simple tool for fabricating microscale-to-nanoscale fibers over large areas [23–32]. Electrospinning enables the fabrication of superhydrophobic webs from polymers with low surface energies such as polystyrene [29], poly(styrene-block-dimethylsiloxane) [30], polyacrylonitrile, [31] and polypropylene [32]. However, the low thermal and chemical stability of these polymers has restricted their practical applications under harsh conditions. In contrast, organic–inorganic hybrid materials show superior properties (including environmental stability, flexibility, and processability) compared with their pure counterparts because organic and inorganic components are homogeneously distributed on the molecular or nanometer level [33–35]. Organopolysilazane is a fascinating organic–inorganic hybrid material, which displays good mechanical strength and contain functional organic groups and polar reactive silazane groups [36]. Polysilazane, which is a silicon–nitrogen backbone polymer, can be converted to polysiloxane, which contains the chemically and thermally inert silicon-oxide bonds, in the presence of water or the application of heat (Fig. 1a) [37,38]. Thus, combining the advantages of both the organic–inorganic hybrid material and the

* Corresponding authors.
E-mail addresses: hslim@keti.re.kr (H.S. Lim), jhcho94@skku.edu (J.H. Cho).
[1] S. H. Koo and S. G. Lee contributed equally to this work.

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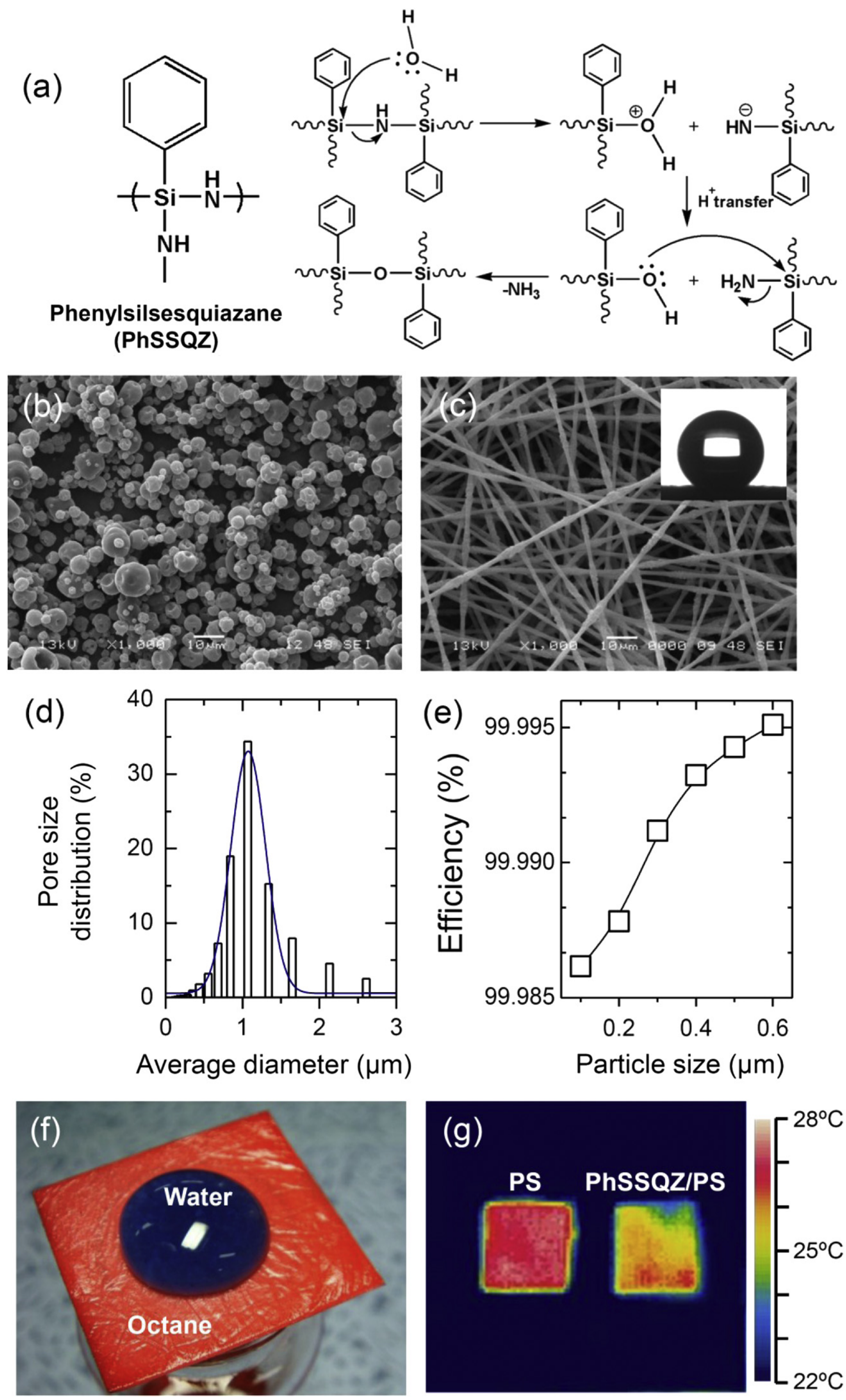

Fig. 1. a) Chemical structure and hydrolysis scheme of phenylsilsesquiazane (PhSSQZ). b, c) SEM images of the electrospun PhSSQZ (b) and PhSSQZ/PS (c) surfaces. The inset shows water contact angle measurements of the PhSSQZ/PS fibrous web. d) Pore size distribution of the electrospun PhSSQZ/PS fibrous web. e) Fractional efficiency of particle removal by the PhSSQZ/PS webs loaded with polydisperse NaCl particles. f) Water droplet profile on a PhSSQZ/PS web prepared for use in the separation of water (colored with methylene blue) from octane (colored with Oil Red O). g) Infrared thermal images of the electrospun PS web (left) and the electrospun PhSSQZ/PS web (right) mounted on a heating stage heated at 35 °C.

electrospinning processing technique allows the fabrication of continuous fibrous webs with versatile properties such as improved flexibility and thermal, chemical, and mechanical resistance.

Here, we developed a set of robust water-repellant macroporous coatings and films based on phenylsilsesquiazane (PhSSQZ), a branched form of organopolysilazane, for use in multifunctional fibrous webs for highly efficient air filtration, oil/water separation, and thermal insulation applications. The freestanding PhSSQZ-based fibrous webs exhibited extreme water repellency with water contact angles exceeding 150° due to a combination of the hierarchical fibrous structure and the low surface energy of the phenyl groups in PhSSQZ. Interestingly, our as-prepared webs maintained their fibrous structures and superhydrophobicity even after heat treatment at 600 °C under an ambient atmosphere. This level of resistance to thermal degradation is the highest level