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Superhydrophobic hybrid films prepared from silica nanoparticles and ionic liquids *via* layer-by-layer self-assembly

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ABSTRACT

The construction of superhydrophobic surfaces is of great interest in the fields of materials science and engineering. In this work, a class of hybrid thin films with controlled wetting property was prepared from silica nanoparticles and an ionic liquid *via* layer-by-layer self-assembly. Positively charged ionic liquid 1-dodecyl-3-methylimidazoliumbromide ([C_{12}mim]Br) and negatively charged silica nanoparticles were alternatively adsorbed onto glass substrates. The silica nanoparticles were characterized by transmission electron microscopy, and the hybrid films were characterized by scanning electron microscope and X-ray photoelectron spectroscopy. The wetting property of the bulk films was examined by water contact angle measurements. The hydrophobicity of surfaces originated from the formation of nanostructure and the hydrophobic property of the ionic liquid. The change in the layer numbers, concentration of $NH_3 \cdot H_2O$ and the type of silica precursor (tetramethoxysilane and tetraethoxysilane) could control the wettability. Under the optimum layer numbers and size of SiO_2, a superhydrophobic (SiO_2/[C_{12}mim]Br)$_{13}$ hybrid film with a contact angle of 152.3 ± 5.0° was obtained.

1. Introduction

With the development of material chemistry, organic–inorganic hybrid materials have drawn great attention [1,2]. They combine the advantages of inorganic materials and organic compounds, and the synergistic action of moieties will result in special functions. Silica nanoparticles (SiO_2 NPs) have been very important functional materials in many fields due to their advanced properties (*e.g.*, stability, large specific surface areas, ordered pore systems, and well-defined pore radius distributions) [3]. Meanwhile, ionic liquids (ILs), particularly imidazolium-based ILs have been central to many areas of chemistry. The special structure and interaction of ions determine their unique physicochemical properties, such as negligible vapor pressure, chemical, thermal and photocatalytic stability, nonflammability, relatively high ionic conductivity, and a wide electrochemical potential window [4–7]. The facile designability and functionalization of SiO_2 or ILs give many SiO_2-based or IL-based hybrid materials, which have attracted substantial academic and industrial interest. For example, silica-based hybrid materials, such as SiO_2/polymer and SiO_2/organic compound, have been used in electrochemistry, surface chemistry and pharmaceutical chemistry [8,9]. And much effort has been devoted to the study of IL-mediated hybrid materials in catalytic reaction, surface science and other fields [10,11]. In the parallel dramatic development of SiO_2 NPs and ILs for material chemistry, hybrid materials composed of SiO_2 and ILs are widely studied [12–14], and show a promising electrochemical property, catalytic activity, and lubricating function, which are mainly investigated in electrodes [3], catalytic chemistry [15], lubrication [16,17] and so on. Among these studies, diverse fabricating strategies have been adopted, including blending each other, grafting *via* covalent bonds, sol–gel process, and *in situ* polymerization [18–21].

Wettability of a solid surface is an important property, which is governed by surface chemistry and morphology. Superhydrophobic surface, referring to the surface with contact angles (CAs) larger than 150°, is one of the most important functional material in both fundamental research and practical applications [22–24], and a variety of inorganic oxides and organic compounds have been used as superhydrophobic materials. Silica-based hybrids with hierarchical structures are viewed as being ideal superhydrophobic materials due to their ultraviolet-durable superhydrophobic property and promising antireflection, *etc.* [25–28]. Similarly, the intrinsic low surface tension [29] and tunable property [30–32] of ILs drive them to be wettability controlling agents. Nowadays, the wettability of ILs has been an important issue in surface chemistry.

Considering the unique wetting behavior of both SiO_2 and ILs, SiO_2/IL hybrid films will be highlighted in superhydrophobic domain. Among various techniques to fabricate thin films, layer-by-layer (LbL) assembly is a simple and inexpensive method which initially is developed for pairs of oppositely charged polyelectrolytes, in which both SiO_2 and ILs are ideal species to the LbL technique [33–35]. Therefore, in this work, we developed a class of (SiO_2/IL)$_n$ hybrid thin films *via* alternatively adsorbing positively charged 1-dodecyl-3-methylimidazoliumbromide ([C_{12}mim]Br) and negatively charged SiO_2 NPs on glass surfaces using the LbL technique, and investigated their hydrophobicity. Under the

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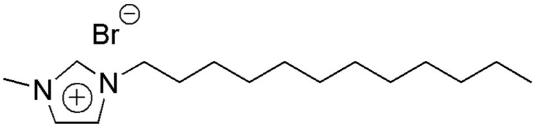


Scheme 1. Structural formula of [C_{12}mim]Br.

optimal number of bilayers, superhydrophobic hybrid films with CAs of 152.3 ± 5.0° were obtained from SiO_2 and ILs, combining the formed surface nanostructure and the low surface energy of ILs.

2. Experimental methods

2.1. Chemicals

Microscopic glass slides (25.4 × 63.5 mm) were used as the substrates. *n*-Dodecyl bromide and silicon alkoxides, including tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) were purchased from Alfa Aesar and were used without further purification. Methylimidazole was purchased from Gelest Inc., Shanghai, China, and $NH_3 \cdot H_2O$ (25%) was purchased from Tianjin North Tianyi Chemical Reagent Factory. [C_{12}mim]Br was synthesized according to the literature [36], and its structural formula was shown in Scheme 1. All aqueous solutions were prepared with deionized water.

2.2. Cleanness of glass substrates

Microscopic glass slides were cut into 1 cm × 1 cm pieces. Then they were sonicated in soapy water for 30 min, rinsed with deionized water, and sonicated with ethanol, acetone for 15 min, respectively. Subsequently, they were cleaned using a freshly prepared "piranha" solution (3:7 by volume of 30% H_2O_2 and H_2SO_4; *Caution! piranha solution reacts violently with most organic materials and must be handled with extreme care*) at 90 °C for 1 h to clean the surfaces, rinsed with deionized water, ethanol and dried under a stream of nitrogen. Then the glass substrates were immersed in the H_2O–H_2O_2–NH_4OH solution at 70 °C for another 30 min. After being dried in a nitrogen stream, the clean substrates with negatively charged surface were obtained.

2.3. Preparation of negatively charged SiO_2 colloid using the Stöber method [37]

A 9 mL of H_2O, 84.6 mL of ethanol and indicated amount of $NH_3 \cdot H_2O$ (25%) were first mixed thoroughly under stirring, and then 3.2 mL of TMOS or TEOS as silica precursors was added drop-wise to the solution. After all of silica precursor was added, the mixture was stirred continuously for 3 h at ambient temperature. The white precipitate was centrifuged (4000 rpm, 20 min), and wet solid SiO_2 spheres were obtained finally. After being exhaustively rinsed with ethanol to neutrality, SiO_2 spheres were dispersed with deionized water to prepare a colloid solution (20 mg/mL). The pH of the mixture solution was adjusted to 10 by dropping the $NH_3 \cdot H_2O$ aqueous solution, and then continually stirred for 10 min. The homogeneous negative SiO_2 colloid was obtained and kept stable without aggregation for more than 2 weeks.

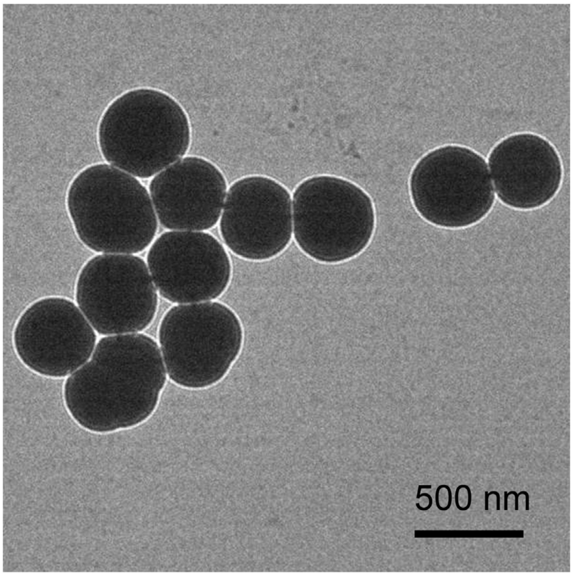


Fig. 1. TEM images of SiO_2 NPs prepared from the system of 9 mL of H_2O, 84.6 mL of ethanol, 3.2 mL of TMOS and 6.4 mL of $NH_3 \cdot H_2O$.

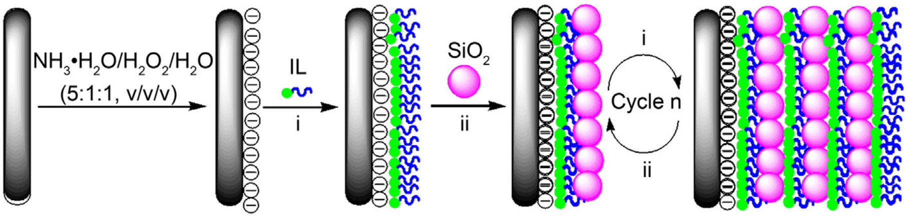
2.4. Assembly of multilayer films

The treated glasses were firstly immersed in the [C_{12}mim]Br aqueous solution for 20 min, rinsed by abundant deionized water, and dried by N_2 flow. Subsequently, the substrates coated with [C_{12}mim]Br were immersed into negatively charged SiO_2 colloid for 20 min, rinsed by deionized water and dried by N_2. Recycling above steps, that is, positively charged [C_{12}mim]Br and negatively charged SiO_2 NPs were successively adsorbed, offering multilayer films which was described as (SiO_2/[C_{12}mim]Br)$_n$, where n is the number of bilayers. Finally, they were sealed with [C_{12}mim]Br, and dried in oven at 80 °C for 1 h. The assembly procedure of multilayer films is shown in Scheme 2.

2.5. Characterization

Transmission electron microscopy (TEM) images were obtained by a JEOL JEM 1400 TEM that was operated at 120 kV. The surface morphologies of the resulting materials were characterized by using a JEOL JSM6701F scanning electron microscope (SEM, Japan). The zeta-potential (ζ) and Z-average of the negative SiO_2 NPs were measured using a Malvern Zetasizer Nano-ZS (England). UV–vis absorption spectra were recorded using a UV2450 spectrophotometer to monitor the growth process of multilayer films. In order to confirm the atomic composition of the films, the X-ray photoelectron spectroscopy (XPS) analyses were performed on a PHI-5702 multifunctional X-ray photoelectron spectroscope, using Al Kα radiation (photon energy 1476.6 eV) as the excitation source.

The static contact angles (SCAs) were measured by the sessile drop method with a deionized water droplet (3.0 μL) being placed on the surfaces using Dataphysics, OCA 15EC (Germany) at room temperature. Using the same instrument, the dynamic contact angles (DCAs) were measured by the method which increases and decreases the volume



Scheme 2. Schematic illustration of the assembly procedure of (SiO_2/IL)$_n$ multilayer film.