



Robust, self-cleaning, amphiphobic coating with flower-like nanostructure on micro-patterned polymer substrate



Wenhui Yao^{a,1}, Lei Li^{a,1}, Oi Lun Li^a, Young-Wook Cho^a, Myung-Yung Jeong^b, Young-Rae Cho^{a,*}

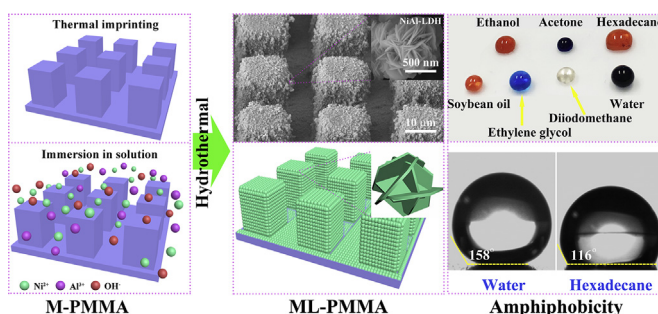
^a Division of Materials Science and Engineering, Pusan National University, 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

^b Department of Cogno-Mechatronics Engineering, Pusan National University, 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

HIGHLIGHTS

- Flower-like nanostructure of NiAl-LDH was synthesized on micro-patterned polymer.
- The hierarchical structure showed good amphiphobicity after fluorination.
- The amphiphobic surface possessed excellent self-cleaning performance.
- The amphiphobic surface exhibited good mechanical and chemical robustness.
- The coating can be used in anti-contaminant, self-cleaning, and biomedical device.

GRAPHICAL ABSTRACT



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ABSTRACT

Many superhydrophobic surfaces lose their repellency to water owing to the contamination of organic liquids or mechanical damage. Though amphiphobic coatings can repel both water and organic liquids, the poor mechanical and chemical stabilities significantly restrict their practical applications. Herein, we demonstrated a hydrothermal method to synthesize micro-patterned substrates bearing NiAl layered double hydroxide with flower-like nanostructures, which resemble the surface morphology of a lotus leaf. The surface was further modified by a low-surface-energy material of perfluorooctanoic acid through a solution immersion method. The binder-free coating formed in-situ on the substrate showed a good adhesion quality of 5B (ASTM D-3359). The coating possessed high repellency to different liquid droplets, including water, diiodomethane, ethylene glycol, soybean oil, etc., with surface tensions ranging from 72.7 to 22.4 mN m⁻¹. Due to the excellent self-cleaning property, the contaminant on the surface was easily cleaned as the water droplet rolled off. Moreover, the coating exhibited good mechanical and chemical robustness in some extreme conditions, such as gas blowing, sea sand abrasion, and chemical immersion tests. These good performances made the coating possible to be applied widely in various practical applications.

1. Introduction

Wettability is one of the most important physicochemical properties of a solid surface [1,2]. Due to the wide applications ranging in the

waterproof surfaces, biomedical devices [3], anti-icing [4], antifouling [5], water/oil separation [6], and self-cleaning property [7], the study on the superhydrophobic surfaces has attracted tremendous attention in both fundamental research and industrial applications [8,9]. Inspired

* Corresponding author.

E-mail address: yescho@pusan.ac.kr (Y.-R. Cho).

¹ The first two authors should be considered as co-first authors.

by natural biological surfaces, the hierarchical surface microstructure and surface chemistry are the two main contributors governing the surface wettability [10–14].

In the real world, most superhydrophobic surfaces are readily contaminated by organic liquids (oil), because of their much lower surface tensions than water. The more extensive applications in the microfluidic and oil transportation promote the research on the amphiphobic surfaces, which are repellent to both water and organic liquids [15]. Because it is easy for organic liquids to wet a surface, the fabrication of amphiphobic surfaces is more difficult than that of hydrophobic surfaces [16]. A flat substrate that is modified by a material with the lowest surface energy can achieve hydrophobicity, but it cannot be amphiphobic [17,18]. However, it is possible to achieve amphiphobicity on a well-defined surface topography with or without fluorination [19–22]. Therefore, a special surface structure is the most significant factor for repelling liquids with a wide range of surface tensions [7,19,22].

Liu *et al.* formed a specific doubly reentrant micro/nanostructure on a completely wettable material (silica), achieving superamphiphobicity without fluorinated materials [19]. Pan *et al.* developed a smart superamphiphobic cotton fabric surface through a controlled fluorosilanization treatment, by means of the inherent texture of fabrics [23]. Yuan *et al.* created T-shaped overhang microstructures based on the soft replication using poly(dimethylsiloxane) as the intermediate mold [24]. Wong *et al.* formed flexible and transparent superamphiphobic surfaces by the large-scale omnidirectional self-assembly of nanoparticle aerosols [25]. Song *et al.* fabricated a reentrant micro/nanometer-scale rough structure on Al substrates by electrochemical etching and immersion in $[\text{Ag}(\text{NH}_3)_2]^+$ solution [26]. As mentioned above, reentrant, hierarchically textured, overhanging, and micro/nanometer-scale rough structures are widely developed to entrap air in the nanoscale concave cavities. On the other hand, there have been few reports of amphiphobic coatings bearing flower-like nanostructures with large specific surface areas and pore volumes [27–30].

For the practical applications of amphiphobic coatings, durability and robustness are important issues [31]. Owing to its poor robustness and durability, a textured surface structure can be readily damaged by different types of actions, leading to the loss of repellency to liquids [32]. Furthermore, even if the robustness is improved, most researches were based upon the usage of commercial adhesives or binders [31,33,34]. On the other hand, Kulinich *et al.* propose alkyl-group coated surfaces would gradually lose their hydrophobicity when they contact with aqueous media [35]. Thus, it is necessary to evaluate the chemical stability of the amphiphobic surfaces. Moreover, the formation of desired structures for amphiphobic surfaces generally requires expensive equipment, complicated chemical synthesis procedures, and strictly controlled conditions, which significantly restrict the mass production and practical application [15]. Therefore, the fabrication of robust amphiphobic surfaces on a large scale is still a great challenging task.

Layered double hydroxides (LDHs) with a distinctive hydroxyl-like structure have attracted great attention recently, owing to their tunable composition, relatively low cost, and environmentally friendly characteristics [36–38]. LDHs are generally denoted by the formula $[\text{M}_1^{II-x}\text{M}_2^{III}(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n}\cdot m\text{H}_2\text{O}$, where M^{II} , M^{III} , and A^{n-} represent divalent, trivalent metallic ions and interlayer anion, respectively [39]. LDHs with the desired structures and properties can be simply achieved by changing the synthesis method and chemical composition [40]. In particular, the hydrothermal method of synthesizing NiAl-LDH can develop a hierarchical flower-like nanostructure, which can effectively entrap air [41,42]. Moreover, without the commercial binders or adhesives, NiAl-LDH can grow in-situ on the substrate, with an excellent adhesion quality of 5B (ASTM D-3359) [43]. Therefore, as a binder-free coating, NiAl-LDH with a unique hierarchical structure is very promising in the liquid-repellent field. To the best of our knowledge, the wettability of NiAl-LDH has received little attention despite the

extensive development of liquid-repellent surfaces by various methods, e.g. etching, lithography, template-assisted synthesis, etc. [44–59].

In this work, we tried to develop a robust amphiphobic coating on a poly(methyl methacrylate) (PMMA) substrate without the use of commercial adhesives or binders, because controlling the wettability of a polymer has been considered to be an important issue in many fields [60]. Hierarchical structures containing textures at multiple length scales can much more effectively entrap air than a single scale texture [22]. In order to form a micro/nano dual-scale structure, well-distributed microscale pillars were firstly developed on the PMMA substrate by a thermal imprinting method. NiAl-LDH, with a hierarchical flower-like nanostructure, was then synthesized on the micro-patterned PMMA surface by a hydrothermal method. Finally, the micro-patterned surface with a hierarchical flower-like nanostructure was modified by a low-surface-energy material of perfluorooctanoic acid (PFOA) through a solution immersion method, due to its simple operation and sufficient contact of the whole surface with fluorinated solution [61]. The lotus-like surface structure with fluorinated functional groups was examined in respects of wettability, self-cleaning property, adhesion quality, mechanical, and chemical robustness.

2. Material and methods

2.1. Materials

Poly(methyl methacrylate) (PMMA, C.Y. Ltd., Korea) was selected as a substrate. Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$), perfluorooctanoic acid (PFOA), Methylene Blue hydrate, and Sudan III were purchased from Sigma-Aldrich (USA). Urea ($(\text{NH}_2)_2\text{CO}$) was supplied by Junsei (Japan). Anhydrous ethanol was purchased from SK Chemical (Korea). Drysurf was supplied by Harves (Japan). All reagents were used as received without further treatment. Deionized (DI) water was used in all experiments.

2.2. Development of the amphiphobic surface

Fig. 1 shows the procedure for the fabrication of the micro/nano structured material and its modification with the low surface energy PFOA. The micro-patterned PMMA (M-PMMA) was formed by a thermal imprinting process (Nano imprinter Jenoptik Jenoptik Hex03) using a nickel stamp (Fig. S1) on the bare PMMA (B-PMMA) substrate, with the force of 4.5 kN and temperature of 120 °C. The M-PMMA sample was then ultrasonically cleaned in DI water for 5 min. In order to synthesize in-situ NiAl-LDH on M-PMMA surface, a mixture of 0.003 mol Ni ($\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 0.001 mol $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ were dissolved in 35 mL DI water with vigorous stirring for 15 min. Then, 0.015 mol $(\text{NH}_2)_2\text{CO}$ was slowly added into the aforementioned solution and stirred for 15 min. The M-PMMA sample was immersed into the solution and transferred to a 50 mL teflon-lined autoclave, which was then sealed and placed in an oven at 95 °C for 24 h. Afterwards, the M-PMMA sample with NiAl-LDH coating (ML-PMMA) was cooled and cleaned using DI water for 3 times. Finally, the ML-PMMA sample was dried in an oven at 60 °C for 12 h.

The ML-PMMA sample was placed into a beaker containing 50 mL of 0.02 mol/L PFOA in the anhydrous ethanol solution. Then, the beaker was transferred to a vacuum container, removing air to force the PFOA solution to penetrate into the hierarchical flower-like nanostructure of NiAl-LDH coating, and kept for 1 h. Later, the fluorinated ML-PMMA (FML-PMMA) sample was placed in a Petri dish and dried in an oven at 60 °C for 6 h. To investigate the effect of surface microstructure and surface chemistry on the wettability, an M-PMMA sample was treated with the same chemical modification of PFOA, which was defined as FM-PMMA. Alternatively, the surfaces of the ML-PMMA and M-PMMA samples were sprayed with 5 mL drysurf solution using an airbrush (HP-CH, IWATA, Japan) connected to a compressed air tank with a pressure of 20 psi.

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