Influence of water adhesion of superhydrophobic surfaces on their anti-corrosive behavior

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ABSTRACT

The water adhesion is important for superhydrophobic materials. Compared with considerable research on metal corrosion protection using superhydrophobic coatings, research involving the different water adhesion of superhydrophobic coating on its anti-corrosive behavior is neglected. Herein, superhydrophobic coatings with controllable water adhesion were successfully fabricated by spraying different percentages of hydrophobic SiO$_2$ nanoparticles (NPs) on the Al substrate, and then the influence of water adhesion of superhydrophobic surfaces on their anti-corrosive behaviour was studied. The electrochemical test was carried out on the superhydrophobic surface with different water adhesion to reveal the influence of water adhesion on anti-corrosion capability. The results showed that the anti-corrosion was markedly influenced by the water adhesion of the superhydrophobic coating, and their corrosion resistance was varied in the order of low-adhesion > medium-adhesion > high-adhesion. Moreover, the superhydrophobic coating with the percentage of OTS-SiO$_2$ = 100 possesses unexpected corrosion protection property with lower corrosion rate (CR) and higher polarization resistance (R$_p$). The corrosive current reduced and impedance modulus (R$_{ct}$) increased with the decrease of adhesion. In addition, the anti-corrosion mechanism of superhydrophobic coatings with different adhesion was elaborated.

1. Introduction

Over the past few years, superhydrophobic surfaces, which exhibit apparent contact angles as high as 150°, have been applied in many fields, such as anti-corrosion [1–3], antifogging [4,5], self-cleaning [6,7] and oil/water separation [8–10]. In these applications, the water adhesion on the target surface is particular important. According to different adhesion of water droplets on the surface, superhydrophobic surfaces are generally classified into two kinds: low-adhesion surface and high-adhesion surface. The superhydrophobic surfaces with low-adhesion property are generally inspired by self-cleaning lotus leaves [11–14]. Water on these surfaces almost forms spherical droplets that readily roll away carrying dust and dirt from the surfaces. On the other hand, superhydrophobic surfaces with high adhesion are usually inspired by the rose petals and gecko's attachment system in nature [15]. For example, Karapanagiotis et al. fabricated superhydrophobic polymer-nanoparticle surfaces with the high droplet adhesion by simulating rose petal and further studied their potential applications [16,17]. These surfaces have a high adhesive force and the water droplets can be tightly fixed at any titled angles. The water adhesion

ultimately determined dynamic behaviors of droplets on the superhydrophobic surface, so it was of great importance for superhydrophobic surfaces with tunable water adhesion in practical applications [18,19]. In fact, the water adhesion of superhydrophobic surfaces is mainly governed by the geometrical structure and the chemical composition of the surfaces [20]. Therefore, we can dynamically adjust the two factors to control the adhesion force.

Corrosion poses significant threats and considerable economic loss to the engineering materials and structures, thus anti-corrosion issues are clearly of great importance in modern societies and industry manufacture [21–23]. The corrosion is caused by the contact of metal substrates and corrosive solution, so the reduction of the contact area between corrosive solution and metal surfaces is considered to be the prominent method of corrosion protection [24]. Due to the unique water-repelling feature, superhydrophobic surfaces can effectively reduce deterioration of metallic materials caused by corrosion [25]. Recently, through controlling surface superhydrophobization to improve the anti-corrosion property of metal surfaces has become the most popular and effective research method in the field of corrosion protection [26,27]. For example, Qing et al. fabricated superhydrophobic

TiO$_2$/polyvinylidene fluoride composite surface with reversible wettability switching and anti-corrosion performances [28]. Xiao et al. developed a simple method to fabricate superhydrophobic CuO nanoneedle-covered copper surfaces and revealed the anti-corrosive mechanism of superhydrophobic coating [29]. Zang et al. reported anticorrosive superhydrophobic coatings on Mg alloy surfaces inspired by lotus seedpod [30]. According to the results of electrochemical test, they concluded that the superhydrophobic surface greatly improved the corrosion resistance of metal materials [31]. Even more remarkable, water adhesion was of great importance for superhydrophobic surfaces, because the adhesive property ultimately determined dynamic behaviors of droplets on the superhydrophobic surface. Although there has been a great deal of works on the use of superhydrophobic coatings for corrosion protection of metals, however, thus far, we are not aware of some previously study reports about the influence of the adhesive property of superhydrophobic surfaces on anti-corrosion capability. In fact, these reports are greatly important for it not only guide us to understand the corrosive mechanism more deeply, but also provide the theoretical basis for the preparation of superhydrophobic coatings with excellent anti-corrosive property.

Compared with the abundant research on metal corrosion protection using superhydrophobic coatings, research relating to the influence of the water adhesion of superhydrophobic coating on their anti-corrosive behavior is extremely neglected. In our work, superhydrophobic SiO$_2$ coatings with different water adhesion were fabricated via a one-step spray-coating process through simply tuning the percentage of hydrophobic SiO$_2$ (which were obtained by modifying hydrophilic SiO$_2$ with octadecyltrichlorosilane, termed as OTS-SiO$_2$) in the hydrophobic/hydrophilic SiO$_2$ NPs mixture. Increasing the percentage of OTS-SiO$_2$ of superhydrophobic SiO$_2$ coatings to 100, the analysis of electrochemical measurements indicated that the superhydrophobic SiO$_2$ coatings maintained the more excellent anti-corrosion property. It was found that the water adhesion of superhydrophobic coatings has a huge effect on their anti-corrosion capability. Besides, the corrosive mechanism for superhydrophobic surfaces with different adhesive property was elaborated by explaining differences of wettability of droplets on the surface. With the percentage of OTS-SiO$_2$ increasing to 100, the adhesive force between the droplets and the coating was ultra-weak and droplets contact the top of asperities (the Cassie state), leading to an increase of trapped air and a decrease of contact area between the corrosive solution and the substrate. That means, the significant improvement of anti-corrosion property mainly derived from the fact that the superhydrophobic coatings can drastically slow down the penetration of NaCl solution. We believe that this research will provide an important reference value for corrosion protection of metals.

2. Experiments

2.1. Materials

Pure Aluminum (Al) substrate was obtained from the Tianjin Chemical Reagent Factory. Hydrophilic SiO$_2$ NPs (~50 nm) were obtained from Aladdin Chemical Co., Ltd., China. Octadecyltrichlorosilane (OTS) was purchased from Shanghai Boer Chemical Reagent Co., Ltd.

2.2. Fabrication of superhydrophobic coating with tunable water adhesion

Depending on our literature reported [32], hydrophobic SiO$_2$, which are used widely in fields of scientific research, were obtained by modifying hydrophilic SiO$_2$ with OTS (Fig. S1). Firstly, 1 g SiO$_2$ nanoparticles and 40 mL toluene were placed into a round-bottom flask. Subsequently, 1 mL of OTS was added into the solution and refluxed for 3 h. After filtration, the obtained SiO$_2$ nanoparticles were dried at 353 K and ground to a fine powder using a mortar; then, superhydrophobic SiO$_2$ nanoparticles were successfully prepared. The XRD pattern

indicates the amorphous structure of SiO$_2$ (Fig. S2). SiO$_2$ NPs (0.2 g) were dispersed in 20 mL ethanol to obtain a homogeneous suspension under magnetically stirring for 60 min. Subsequently, the homogeneous suspension was sprayed onto bare Al substrates with a 0.2 MPa compressed air gas using a spray gun connected to an air compressor. The distance between the spray gun and the substrate was about 15 cm. By simply altering the quality percentage of hydrophobic SiO$_2$ NPs in SiO$_2$ NPs mixture, low-adhesion surfaces (pure hydrophobic SiO$_2$ NPs), medium-adhesion surfaces (70 wt% hydrophobic SiO$_2$ NPs) and high-adhesion surfaces (40 wt% hydrophobic SiO$_2$ NPs) were successfully prepared. It should be noted that the medium-adhesion surfaces included 70 wt% hydrophobic SiO$_2$ NPs and 30 wt% hydrophilic SiO$_2$ NPs. Similarly, the high-adhesion surfaces included 40 wt% hydrophobic SiO$_2$ NPs and 60 wt% hydrophilic SiO$_2$ NPs.

2.3. Characterization

Fourier transform infrared (FT-IR) spectroscopy was performed with a Bio-Rad FTS-165 instrument using KBr as the background. The XRD pattern was carried out on an X-ray diffractometer (Rigaku Corp., D/max-2400) equipped with the graphite monochromatized Cu Kα radiation. The morphological structures were examined using field emission scanning electron microscopy (FE-SEM, Zeiss). The surface chemical composition of the samples was analyzed on a PHI-5702 electron spectrometer using Mg Kα radiation as the excitation source and the binding energies were referenced to the C 1s at 284.80 eV. Water (5 μL) apparent contact angles (CAs), sliding angles (SAs), advancing angles (θ_{adv}) and receding angles (θ_{rec}) on the superhydrophobic surfaces were measured by SL200KB apparatus. Besides, the adhesion between surface and water droplet was determined using high sensitivity micro-electromechanical balance system (Dataphysics DCAT 11, Germany). The 3D image of superhydrophobic SiO$_2$ surface was performed by non-contact 3D surface contour graph (MicroXAM-800, USA). Electrochemical properties such as AC impedance and Tafel plot were measured in a 3.5 wt% NaCl corrosive solution at room temperature using a computer-controlled CHI660E electrochemical workstation, which was equipped with a three-electrode system with a saturated Ag/AgCl reference electrode, a platinum electrode as the counter electrode and the samples (bare Al substrate or superhydrophobic coatings with different water adhesion formed on the Al substrate) as the working electrode. The superhydrophobic coatings formed on the Al substrate were immersed in a 3.5 wt% NaCl corrosive solution to establish the open-circuit potential (E_{ocp}). The Tafel plot was obtained at a sweep rate of 5 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was conducted at E_{ocp} in the frequency ranged from 10 mHz to 100 kHz using an ac perturbation of 5 mV.

3. Results and discussion

Superhydrophobic SiO$_2$ surfaces with tunable water adhesion were fabricated by spraying hydrophobic and hydrophilic SiO$_2$ NPs mixture onto the Al substrate. The surface morphology acted a pivotal part in the development of the superhydrophobic surface. As shown in Fig. 1a, the as-prepared SiO$_2$ coating with the percentage of OTS-SiO$_2$ = 100 possessed rough and rugged morphology characteristics (the magnification of 10,000 times), and the Al substrate has been randomly and entirely covered by a great deal of SiO$_2$ NPs. The further magnified FE-SEM image of 30,000 times in Fig. 1b shows that a large number of SiO$_2$ NPs agglomerate form larger nanoclusters, resulting in hierarchical micro- and nano-scale roughness. As exhibited in Fig. 1c and d, the SiO$_2$ coating with the percentage of OTS-SiO$_2$ = 70 (the magnification of 10,000 and 30,000 times, respectively) possessed rough and rugged morphology characteristics. It can also be observed that the SiO$_2$ coating with the percentage of OTS-SiO$_2$ = 40 (the magnification of 10,000 and 30,000 times, respectively) displays almost identical rough surfaces and morphology characteristics in Fig. 1e and f as compared to