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A novel electrodeposition route for fabrication of the superhydrophobic surface with unique self-cleaning, mechanical abrasion and corrosion resistance properties

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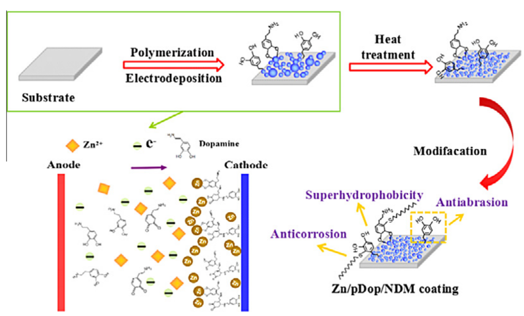
HIGHLIGHTS

- We have prepared superhydrophobic Zn/pDop/NDM coatings on different substrates.
- Dopamine was successfully integrated into the electrodepositing system.
- The electrodeposition and polymerization processes showed a synergistic effect.
- The prepared coatings had excellent anti-abrasion and anti-corrosion properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Inspired by the adhesive proteins in mussels, a novel electrodeposition route has been developed to create multifunctional zinc (Zn)/polydopamine (pDop)/n-dodecyl mercaptan (NDM) composite coatings on different substrates, where oxidative polymerization of dopamine was simultaneously integrated during electrodeposition process. Hierarchical cauliflower-like structure was obtained on the electrodeposited Zn/pDop coatings. After modification with NDM, the prepared Zn/pDop/NDM coatings on different substrates (steel, Al and Cu) possessed excellent superhydrophobicity, exhibiting a maximum water contact angle (WCA) of 167.6° and a sliding angle (SA) less than 1° on the steel substrate. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) were employed to investigate the morphology and the chemical composition of the coatings. The mechanisms of electrodeposition process were discussed. The integrated electrodeposition and polymerization processes promised a synergistic effect on promoting the superhydrophobicity of coating. Results indicated that the dopamine greatly improved the mechanical abrasion resistance of the prepared superhydrophobic coatings. Additionally, these coatings demonstrated superior superhydrophobic stability, corrosion resistance and self-cleaning properties. It is believed that this novel and facile electrodeposition route for fabricating superhydrophobic coatings on various metallic materials will generate great impacts in practical applications.

1. Introduction

Steel, aluminum and copper are widely used as engineering metal materials based on their unique characteristics of low-cost, high mechanical strength and good electrical/thermal conductivity [1–3]. However, corrosion and rusting cause enormous resources wastes and economic loss. Various strategies have been developed to regulate metal corrosion, such as cathodic protection [4], electrochemical etching [5], fabrication of protective coatings [6,7], etc. In recent years, inspired by the natural self-cleaning lotus leaf

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and the wings of butterflies, fabrication of superhydrophobic coatings has been applied in various engineering metal surfaces such as steel, aluminum, copper, magnesium and zinc, to realize the protection purpose because they can suppress the contact of a metal surface with water and corrosive medium from the environment [8,9].

Up to now, various methods have been developed for fabricating superhydrophobic surfaces on metal substrates, such as chemical vapor deposition [10], sol–gel processing [11,12], electrospinning [13,14], chemical etching [15,16] and anodic oxidation [17]. Nevertheless, most of these methods usually require special devices, complicated conditions, small substrate size and simple shape, limiting their widespread industrial applications.

Electrodeposition has been considered as a promising technique to construct large area superhydrophobic surfaces taking advantage of its simplicity, easy control, low-cost and suitability for practical applications [18–20]. Some researchers have prepared superhydrophobic surfaces with stable micro and/or nanoscale structures via electrodeposition. For instance, Haghdoost et al. [21] used a two-step electrodeposition technique to produce a superhydrophobic copper coating with a water contact angle of 160 ± 6° and sliding angle of 5 ± 2°. In 2015, Li et al. [22] developed hierarchical structures with micro-flowers and secondary nanosheets through electrodeposition. After fluorination, an excellent self-cleaning and superamphiphobic surface was obtained. Recent studies demonstrated that electrodeposited superhydrophobic surfaces could achieve outstanding superhydrophobicity, self-cleaning and corrosion resistance properties. Unfortunately, to the best of our knowledge, the abrasion resistance and bonding strength of superhydrophobic surfaces have been rarely investigated in literatures. In fact, the industrial applications of superhydrophobic surface are greatly restricted by its poor mechanical properties and low adhesion strength. Some superhydrophobic coatings are even fragile to the finger-wipe and easily peeled off from substrates with mild abrasion. Hence, excellent mechanical abrasion resistance and strong adhesion to substrate are crucial factors to achieve practically useful superhydrophobic coatings.

In nature, marine mussels as a kind of promiscuous fouling organisms can easily attach to virtually all types of substrates by secreting *Mytilus edulis* foot protein-5 (Mefp-5) [23,24]. Further studies revealed that the adhesive proteins are rich in catecholic analogues (3,4-dihydroxy-phenylalanine, DOPA), which can form strong covalent and noncovalent bondings on substrates [25]. According to Lee et al. [26], dopamine mimics the repetitive catechol-amine structure of DOPA, which can self-polymerize and deposit on numerous material surfaces in mild environment, and therefore its polymeric form (polydopamine) can be used as an efficient mechanical reinforcing agents. Recent investigations have found that divalent cations such as Cu^{2+}, Ni^{2+}, and Zn^{2+} can act as oxidants to polymerize dopamine, promoting the formation of adhesive melanin films [27]. Surprisingly, dopamine can also serve as an effective reducing agent to promote the electrodeposition process of metals. Hence, if the oxidative polymerization of dopamine and electrodeposition of metal can be processed simultaneously, this technique would open a new approach to construct functional superhydrophobic surfaces. Despite the unparalleled capability of dopamine, the application of dopamine in the electrodepositing system remains unexplored.

In this paper, a new route was developed to fabricate superhydrophobic coatings on steel, aluminum (Al) and copper (Cu) substrates. It was achieved by simple electrodeposition process on these substrates with both zinc ions and dopamine in the electrolyte solution. The influence of the electrodeposition parameters including time and voltage on the wettability of the coatings was investigated. Additionally, the prepared superhydrophobic coatings achieved excellent anti-abrasion, anti-corrosion and self-cleaning properties. Therefore, it is expected that this research will pave a new way to design superhydrophobic functional coatings for the industrial application.

2. Experimental

2.1. Materials and reagents

Cu (T2), Al (1100) and steel sheet (Q235B) were obtained from Qingyuan Metal Co., China. The dimensions of these simples were 60 mm × 12 mm × 1 mm. N-dodecyl mercaptan (NDM) was purchased from Shanghai Zhanyun Chemical Co., Ltd. Dopamine was provided by Suzhou Tianke Trade Co., Ltd. Anhydrous ethanol, acetone, zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$), potassium chloride (KCl), hydrochloric acid (HCl), nitric acid (HNO_3) and sodium chloride (NaCl) were all analytical grade and used without further purification. Deionized (DI) water with a resistivity great than 18.0 MΩ m was used.

2.2. Modification of metal substrate

The steel sheets were abraded with successive grades of SiC paper from 400 to 1200 grade. After that, steel substrates were degreased in a mixture of ethanol and acetone (v/v: 1/1) for 15 min under sonication, then thoroughly washed by DI water. In addition, steel sheets were polished in 7 mol/L HCl solution for 1 h, then rinsed thoroughly with distilled water and dried under atmospheric conditions. The surface treatments of Cu substrates were first abraded and rinsed, similar to the steel sheets. Then the Cu substrates were etched in 3 mol/L HNO_3 solution for 5 min to create a rough structure. The Al substrates were polished with SiC paper (from 400 to 1200 grade) and used without further treatment.

2.3. Preparation of Zn/pDop/NDM coatings

As shown in Fig. 1, the superhydrophobic Zn/pDop/NDM coating with hierarchical micro/nano structure was obtained in the following processes. The electrodeposition process was performed in a two-electrode electrochemical cell with a pre-treated substrate as cathode and a Cu plate as anode. The distance between the cathode and the anodic plate was fixed at 2 cm. $ZnSO_4$ (0.02 mol/L), KCl (0.1 mol/L) and dopamine (0.0065 mol/L) dissolved in distilled water was used as electrolyte. The solution pH was about 6.0 due to the addition of $ZnSO_4$ and was not readjusted. The electrodeposition temperature was kept at 40 °C. After electrodepositing process, the cathode specimens were removed from the solution and heat treated at 180 °C for 1 h in air. Finally, the samples were immersed in 0.25 mmol/L NDM anhydrous ethanol for 24 h at room temperature. Then the samples were taken out and adequately cleaned in anhydrous ethanol, followed by drying at room temperature.

2.4. Surface characterization

The surface wettability of the coatings was measured by contact angles (CAs) and sliding angles (SAs) with 5 μL liquid droplets using a contact-angle meter (JGW-360A, Chengdeshi Shipeng Detection Equipment Co., Ltd) at room temperature. In order to evaluate the hydrophobicity and oleophobicity of the coatings, the variations of CAs of water and glycol were investigated. The CAs reported were averages of three measurements per specimen. The surface morphologies of the prepared coatings were characterized by a scanning electron microscope (SEM, ZEISS, Germany). Fourier transform infrared (FT-IR) measurement was conducted