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Fabrication of robust gold superhydrophobic surface on iron substrate with properties of corrosion resistance, self-cleaning and mechanical durability

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A B S T R A C T

Well-defined gold nanoflower superhydrophobic surface (SHS) was constructed on iron foil by chemical deposition and anneal. The as-fabricated sample exerts excellent superhydrophobicity with water contact angle (WCA) up to 169°, a sliding angle of about 3°. The samples were characterized via scanning electron microscopy (SEM), X-ray diffraction pattern (XRD) and energy dispersive analysis of X-ray (EDX) to determine the morphology, structure and composition. The electrochemical measurements showed that the resultant surface displayed good corrosion resistance in 3.5 wt% sodium chloride aqueous solution. The effect of pH on the SHS and corrosion resistance ability of the samples at pH = 2, 7 and 9 were explored. The self-cleaning property of the SHS was analyzed. Also, the surface withstood abrasion by 400 grid SiC sandpaper for 2.0 m under 30 kPa, or water impacting for 120 min without losing its superhydrophobicity, indicating prominent mechanical durability. This successful manufacture of the gold SHS with anti-corrosion, self-cleaning, and mechanical durability can pave a prospective way for a variety of practical situations.

1. Introduction

Superhydrophobic surface (SHS) is an emerging hot topic on material fabrication and application. The SHS has been considered as an important property toward waterproof application, with an extremely high water contact angle (WCA) more than 150° and low contact angle hysteresis (CAH) or roll off angle, which was firstly reported by Ollivier a century ago [1]. Some physical and chemical methods have been developed to prepare SHS. Physical methods cover, such as following: plasma treatment [2], phase separation [3], lithography [4] and spin-coating [5]. Several such chemical methods generally include chemical vapor deposition [6], sol-gel processes [7], electrochemical methods [8], layer-by-layer assembly [9], self-assembly [10] and so forth. In work of Li et al. [11], the antireflective (maximum transmittance: 94% at 550 nm) superhydrophobic coatings were successfully assembled by layer-by-layer assembly method. An interesting proposal was presented by Hu et al. [12] who obtained micro-nano hierarchical structured superhydrophobic nickel films with a WCA of 154° by a simple and low cost electrodepositing method. The extreme water-repellency of biomimetic SHS, as inspired by lotus leaves and butterfly wings, is appealing not only because of its scientific background but also wide range of technological applications including self-cleaning [13,14], special wettability [15], anti-fogging [16], anti-corrosion [17–20], oil–water separation [21,22], and drag reduction [23].

The tendency of metals to absorb water dramatically influences their service life and results in deleterious waste of resources. Heretofore, iron (Fe) and its alloys have been extensively utilized in industry owing to its thermal conductivities and high electrical, relatively noble and mechanical workability properties. Iron that serves as engineering materials is widely applied in many application areas, including mechanical equipment, building construction, and automobile manufacturing. However, it is susceptible to be corroded in a humid environment, causing significant performance degradation and even economic loss [24]. One of the major challenges in iron applications is to impede corrosion which leads to failure and inferior device performance. In recent years, considerable research efforts have been devoted to construct

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superhydrophobic coating on iron substrate to improve its corrosion resistance [25,26]. Wang and coworkers [25] prepared the SHS significantly improved the corrosion resistance of iron in seawater. Shao et al. [26] also obtained a superhydrophobic film on iron substrate, and iron was effectively prevented from corrosion in 3.5 wt% NaCl solution. However, the effect of pH on the SHS and its corrosion resistance ability were not reported in these literature.

The engineering and scientific value of the SHS is dramatically hindered owing to weak mechanical abrasion resistance. As mentioned above, although a slew of superhydrophobic materials have been fabricated by various techniques, in fact, few coatings were reported to be utilized in industrial applications as they had weak surface chemical stability and mechanical abrasion resistance. Even some superhydrophobic coatings were fragile to finger contact. Obviously, it is of vital importance to overcome the vulnerabilities of poor mechanical wear and chemical stability for SHSs, which is an imperative demand for their industrial applications. Recently, Liu et al. [27] fabricated a superhydrophobic Cu surface via a selective etching of high-energy facets, the CA decreased largely (170° vs 153°) after abrasion under an applied pressure of 5 kPa by cotton fabric for only 25 cm. An interesting proposal was presented by She et al. [28] who obtained a robust and stable SHS on magnesium alloy. The superhydrophobic coating plates were abraded using 800 grit SiC sandpaper as an abrasion surface under a pressure of 1.2 kPa, the as-prepared surface still remained the contact angle more than 150° after mechanical wear for 0.7 m. Zhu et al. [29] evaluated the mechanical durability by a simple finger pressing for the obtained superhydrophobic metal/polymer composite.

This paper is focused on the constructing of superhydrophobic gold nanoparticles using etching and simple replacement deposition process without using any seed and organic solvent, and thermal annealing method. The well-defined gold nanoflower superhydrophobic materials provide an excellent barrier and properties for iron corrosion protection. Here a series of electrochemical studies on corrosion protection applications were performed by conducting electrochemical measurements of superhydrophobic coatings, including corrosion current (I_{corr}), polarization resistance (R_p), and corrosion potential (E_{corr}) by using Nyquist plots and electrochemical impedance spectroscopy (EIS) in an electrolyte of 3.5 wt% NaCl. The physical property, including mechanical strength, of the as-prepared nanocomposite was investigated using scratch test and water dripping test. Our findings lead us to conclude that SHSs exhibit excellent anti-corrosion, self-cleaning, and mechanical durability performance.

2. Experimental

2.1. Reagents and methods

Chloroauric acid tetrahydrate ($HAuCl_4$ $4H_2O$, 47.8%), hydrochloric acid (HCl, 36–38%), acetone (C_3H_6O, 99.5%), ethanol (C_2H_5OH, 99.7%) were of analytical grade and a kind gift from China Beijing Fine Chemical Co. Ltd in this study. Aqueous solutions were formulated with copious amount of distilled water and stored in the volumetric flask. Iron specimens were provided by Beijing Cuibolin Non-Ferrous Technology Developing. All chemical solvents were employed directly without further treatment. Distilled water was applied throughout the preparation process.

Herein, we introduced a very simple and economic method to construct a superhydrophobic gold surface on iron substrate. A typical experiment procedure was as follows: Initially, iron substrates with an average size of 1.0 × 1.0 × 0.1 cm^3 (length × width × depth) were ultrasonically cleaned in sequence with ethanol and acetone for approximately 10 min in an ultrasonic machine to remove possible impurities. Afterward, the iron foils were placed in a sealed beaker containing ethanol, ready for using. Subsequently, the as-obtained iron foil was took out and ethanol on it was removed with filter paper, and then was directly etched in diluted hydrochloric acid (2 mol L^{-1}) as the etchant to form a rough surface, rinsing with excess deionized water extensively to dispose of the unreacted acid. After 6 min, the etched iron foil was put perpendicularly into a transparent centrifuge tube containing 10 mmol L^{-1} $HAuCl_4$ aqueous solution at an ambient temperature for 40 min, and then the sample was placed in a petridish, covered with filter paper on both sides of the sample, and annealed at 180 °C in an oven for 30 min under air atmosphere to achieve the superhydrophobic hierarchically structured surface. It can be established by adopting WCA tests.

2.2. Sample characterization

The morphological characterization of the surfaces was scrutinized by the field emission scanning electron microscopy (FESEM) (S-4800, Hitachi, Japan) under an electron beam. The static WCA and sliding angle (SA) were checked by remote computer-controlled goniometer system (FTÅ 200, Data physics Inc, USA) equipped with a video camera (Canon) and a tilting stage. SAs were obtained by slowly tilting the sample stage until the water droplet started moving. In order to ascertain the accuracy of the apparent WCA, a water drop volume of 8 μL was carefully dropped onto the surface, and averaging the values obtained at 5–6 different spots on each sample surface was used as the reported CA. The accuracy of the measurements was±1°, as depicted by the error bar in the graph. The chemical composition of samples was observed using energy-dispersive X-ray spectra (EDX) (INCA Energy, Oxford CO, Japan) attached to SEM. The structure and phase of the samples were confirmed using X-ray powder diffractometer (XRD) (D8 ADVANCE, Bruker, Germany) analysis equipped with Cu Kα radiation at X'Celerator's scanning rate of 5° min^{-1}. The electrochemical measurements were conducted in 3.5 wt% NaCl aqueous solutions under room temperature conditions using electrochemical workstation (CHI 760E, CH Instruments Inc., China). All electrochemical corrosion tests were investigated using the classical three electrode cell with saturated calomel as reference electrode, platinum as the counter electrode and superhydrophobic gold film with an exposed area of 1 cm^2 as the working electrode. The polarization curves were obtained at a scanning velocity of 2 mV s^{-1}.

3. Results and discussions

3.1. Surface morphology, composition and structure

To gain a better understanding on the relationship between the fine micro/nanostructures and surface wettability, SEM is applied to characterize the surface morphology (Fig. 1). Fig. 1 is corresponded to SEM images of the as-obtained SHS with different magnifications. It is obviously shown in Fig. 1a that the protruding clusters evenly distribute on the surface of iron at a 5 K magnification scale. The static WCA can hold up to 169° compared with the pristine hydrophobic iron substrate, reaching the superhydrophobic range (inset of Fig. 1a). Middle-magnification SEM image (Fig. 1b) reveals that protruding clusters are composed of many Au hierarchical nanoflowers with several thin tips as building units. Fig. 1c shows the nanoflower structure in Fig. 1b at 50 K magnification. A network-like structure composed of nanometer-scale sheets align at fairly inclined angles with respect to the surface, resulting in nano-scale pores composed of valleys and hills. These characteristics are similar to the microstructures of lotus leaves, proving that the Au produced is suitable for the preparation