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Fabrication of superhydrophobic iron with anti-corrosion property by ultrasound

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ABSTRACT

The creation of superhydrophobic (SH) surfaces requires a combination of surface roughness and surface free energy reduction. For this purpose, wire-like ZnO particle (with micro scale in length and nano-scale in width) deposition was performed on iron surface by means of an ultrasound approach. After that, stearic acid (STA) ethanol solution was utilized for surface energy reduction. The optimization of various parameters was conducted based on Minitab software and Taguchi design method. After reaching a SH iron with ultrasound at optimized conditions, the corrosion resistance was compared between SH iron resulted by classical method (SH iron (C)) under the same conditions as ultrasound method (SH iron (U)). The potentiodynamic estimates indicated that when ultrasound was employed for particle deposition, the corrosion current (I_c) was 1000 times lower than that for bare iron one. However, using classical method for particle deposition had no dramatic effect on corrosion resistance. Moreover, when ultrasound was used for particle deposition, the stability of the resulted SH iron versus immersion in NaCl solution (3.5%) was higher compared to SH iron acquired by classical technique. Finally, different characterization methods were used for further study. For example, scanning electron micrograph (SEM) was carried out for topographical investigation of the surfaces obtained. Other techniques such as attenuated total reflection in combination with Fourier transform infrared (ATR-FTIR) and energy-dispersive X-ray spectroscopy (EDX) verified ZnO particle deposition. Moreover, for verification of STA grafting on SH iron, EDX analysis was helpful.

1. Introduction

One of the significant properties related to the solid surfaces is wettability that is controlled using both surface morphology and chemical composition of surfaces. SH surfaces with water contact angle (WCA) larger than 150°, have appealed greatly interest in central research and prospective industrial applications [1–3]. These surfaces are classified into two categories based on sliding angle (SA) value. These classes are named as low-adhesive and high-adhesive SH surfaces. Low–adhesive SH surfaces possess SA value lower than 10°. In this case, water droplet can roll easily as SH surface tilted partially. In contrast, high-adhesive SH surfaces have high SA value. In this instance, water droplets stick to the surface even with turning upside down the surface.

The lotus leaves, the rice leaves and the legs of water strider are examples of low-adhesive SH surfaces in natural world. Moreover, the usual high-adhesive SH surfaces in natural surroundings are rose petals, peanut leaves, and feet of bees. Because of numerous applications of low-adhesive SH surfaces, great studies has been focused on these surfaces [4,5]. The new researches exhibit that the superhydrophobicity of the lotus leaves mainly results from the existence of dualistic structures at micro and nano-meter measures and waxy materials with low surface energy on the surfaces [6]. To date, several techniques such as lithography, laser etching, plasma treatment and template duplication have been established to manufacture SH surfaces based on lotus leaf structure [7–12]. The metal surfaces are simply wetted and covered with a coating of water film, causing in severe troubles counting icing and corrosion. Consequently, the design of metal products with superhydrophobicity property is sensible [13,14]. There are several works related to this issue. For example, Wei et al. [15] employed a trouble-free way to produce SH magnesium alloy. Their method consisted of etching of magnesium in copper chloride and modification of resulted surface with STA as surface free energy reducer agent. Polarization and impedance examinations demonstrated corrosion resistance enhancing of SH magnesium in comparison with bare alloy. Moreover, the SH surface exhibited long-term stability in NaCl aqueous solution (3.5%) [15].

In another work, Zhang et al. synthesized anti-corrosion magnesium alloy with SH characteristic. The superhydrophobicity was obtained using simple immersion process and modification in STA during a

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hydrothermal production method [16]. With the exception of magnesium alloy, there are similar efforts for iron surfaces. For example, micro/nano structures were fabricated on iron surfaces via chemical etching with a solution of hydrochloric acid or galvanic substitution using silver nitrate. The modification of obtained hierarchical iron with STA led to SH iron surface. The anti-icing property examination revealed that SH iron exhibited outstanding anti-icing characteristic in comparison with bare ones [17]. In another study, Hao-Jie Song et al. used a straightforward and economic hydrothermal method based on K_2CO_3 mediated process to manufacture structures with micro/nano scales on iron plates. The vinyl triethoxysilane was employed as surface energy reducer to yield superhydrophobic property [18]. In spite of simplicity and cost-effectively of mentioned works, anti-corrosion property was not explored. However, in a study performed by Wang et al. anti-icing, UV-durability and corrosion resistance characteristics of resulted SH steel was investigated [19]. But, the surface energy reduction was carried out using 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS-17), that is not environmentally suitable. In current study, STA as biocompatible modifier is utilized for surface energy reduction. Besides, ultrasonic waves have been employed as novel technique for ZnO particle deposition on iron substrates. Ultrasound is a competent and powerful method for the production of many materials with variable characteristics. There are several published papers related to ultrasound-assisted synthesis of different nanoparticles. For example, ZnO nanoparticles with dissimilar morphologies, Fe_3O_4 nanoparticles, gold and silver nanostructures were synthesized using ultrasound [20–23]. In spite of numerous attempts for the nanoparticle synthesis, there are a few work about utilizing ultrasound as a practical technique for particle deposition in SH creation field. Therefore, the major novelty of our work is achievement to SH iron with enhanced anti-corrosion property using ultrasound. Ultrasound generates exceptional conditions that result in special changes. These changes are due to cavitation phenomenon that is consisted of creation, expansion and collapse of bubbles in aqueous environment. The bubble collapse in heterogeneous surrounding is non-symmetric. As a result, the topography of surface can be influenced by shock waves and micro-jets creation. It is predictable that distinctive morphology has remarkable influence on the wettability of surface and durability of the acquired SH surface. In this work, ultrasound demonstrated a vital function in particle deposition to conclude SH iron surface with outstanding anti-corrosion property in corrosive environment. Moreover, in this work the ultrasound parameters have been optimized simultaneously to have higher WCA and lower SA on SH surfaces. At the end, a comparison has been conducted between anti-corrosion property of SH iron surfaces fabricated using simple immersion (classic), and ultrasound methods.

2. Experimental section

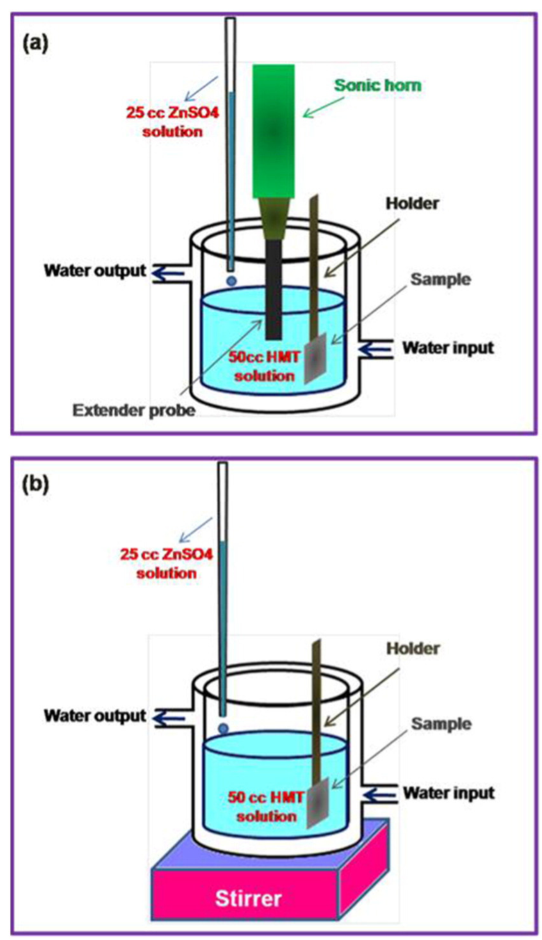
2.1. Materials

Pure Iron plate in dimensions of 20 mm × 15 mm × 1 mm was used in current work. Hexamethylenetetramine (HMT, 99%) was supplied by Samchun Company. Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, 99%) was made available by Merck Company. Stearic acid (STA, 99%) and ethanol (96%) were purchased from BDH and Riedel companies, respectively. All chemicals were utilized as received.

2.2. Superhydrophobic iron formation with ultrasound

Firstly, the iron surfaces were polished mechanically using sand paper (400 and 800#). Afterward, the plates were washed thoroughly with distilled water, ethanol and acetone and dried at 80 °C. Then, the cleaned iron plates were vertically immersed into 50 cm^3 aqueous solution of HMT (with changeable concentration) and after 1 min sonication, 25 cm^3 aqueous solution of $ZnSO_4$ (with variable concentration) was added. Sonication was continued for various interval times at different temperatures. Schematic 1a demonstrates the experiment conducted under ultrasound. The output frequency and power of ultrasound equipment (XL 2020(were 20 Hz and 550 W, respectively. The horn tip was immersed 1 cm into the solution and located in the middle of the cell. It should be noted that calorimetry method was used for acoustic power determination for three levels of acoustic amplitude (25%, 35% and 45%). Based on this method, the acoustic power for acoustic amplitude of 25%, 35% and 45% were 0.50 W, 2.07 W and 11.33 W, respectively. The acoustic power measurements were carried out for 75 mL of solution, since the final solution volume reached to this value.

Three levels of concentrations (0.01 M, 0.05 M and 0.10 M) were selected for starting materials of HMT and $ZnSO_4$ in final solution. It is worthy to note that, for all experiment runs, the starting material molar ratio is 1:1. After withdrawing the plate from HMT-$ZnSO_4$ solution, the iron plates were rinsed completely with distilled water and dried for 1 h at 100 °C. In this stage ZnO-deposited iron surface was concluded. The surface energy reduction as a final step was performed using immersion of ZnO-deposited iron surface in STA ethanol solution with changeable concentrations and various immersion times. After moving back from STA solution, iron plates were completely rinsed with ethanol and dried for 10 min at 80 °C. It should be pointed out that the WCA and SA measurements have been accomplished on the samples after attainment to room temperature. The optimization of variables in these experiments (concentration of starting materials, reaction time, reaction temperature, acoustic amplitude, STA concentration, immersion time in STA) was carried out simultaneously with Minitab 14 software with Taguchi design method. Taguchi technique employs standard Orthogonal Arrays (OA) for creating an experiment matrix. Utilizing an OA to experiment design facilitates the study of



Schematic 1. a) ultrasound and b) classical deposition methods.