Stearic acid modified zinc nano-coatings with superhydrophobicity and enhanced antifouling performance

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ABSTRACT

In this work, zinc nano-coatings were fabricated on a carbon steel by electrodeposition and stearic acid modification, featuring superhydrophobicity and enhanced antifouling performance. The morphology, composition and structure of the prepared nano-coatings were characterized by various surface analysis techniques. The water and oil contact angles were measured. The superhydrophobicity of the prepared Zn coatings is attributed to the surface micro/nanostructure and the formed stearic acid layer with a low surface energy. The water contact angle is up to $158.4 \pm 1.5°$, with an estimated air-occupied fraction up to 90.8% of the total area of the coating under water droplets. The nano-coatings are also superhydrophobic to tea, milk and a soil solution. Moreover, the coated specimen has an oil contact angle of 48.1°, as compared to 8.6° on bare steel, indicating that the prepared nano-coatings improve the surface oleophobicity.

1. Introduction

Various surface techniques have been developed to improve the performance stability and durability of engineering materials in service [1–4]. In particular, tremendous attention has been paid to the fabrication of superhydrophobic surfaces with a water contact angle greater than 150° due to the versatile functions of these surfaces, including anticorrosion [5], anti-biofouling [6] and self-cleaning [7]. In recent years, materials with superhydrophobic properties have found their use in highly harsh environments such as those encountered in oil/gas and pipeline systems for either corrosion protection [8] or reduction of fluid drag force [9].

It has been acknowledged [10] that the non-wettability of a superhydrophobic material results from the formation of an "air cushion" on its surface due to the combination of low surface energy and hierarchical roughness. This serves as an effective blocking barrier for the diffusion of corrosive species in the environment towards the substrate material. At the same time, a superhydrophobic surface works like a vertical cylindrical tube placed in liquid. Due to the Laplace pressure, the electrolyte can be pushed out of the pores contained in the superhydrophobic surface film [11–13]. For example, Sethi et al. [12] prepared a superhydrophobic coating on steels to create a carbon nanotube mesh structure. The coating is able to withstand environmental attack to the substrate steel. Li et al. [8] used a hydrothermal treatment method to fabricate superhydrophobic ZnO films on a pipeline steel to

achieve a water contact angle of 157.59°, which effectively prevents the steel from contact with the aqueous environment.

Electrochemical techniques possess multiple advantages such as low cost, convenience and high effectiveness to achieve desirable structures [14,15]. Particularly, the electrodeposition technique is able to fabricate micro-/nano-patterned surface structures under controllable conditions, achieving the hydrophobic or superhydrophobic property [16]. Relevant work has been extensively conducted on metals such as Al, Cu, Zn and their alloys [17–21]. While galvanization and other Zn-coating processes have been commonly used to protect carbon steels in aqueous environments, this work attempts to develop, by a facile method, novel Zn nano-coatings on carbon steel, enabling superhydrophobicity and, at the same time, enhanced antifouling performance. The potential applications of the developed coating technology would also include anticorrosion, anti-biofouling, and self-cleaning performance for carbon steel structures.

In this work, Zn nano-coatings were prepared on an X65 pipeline carbon steel by electrodepostion and stearic acid modification. The morphology, composition and structure of the prepared nano-coatings were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectrum (EDS), X-ray diffraction (XRD), and Fourier transform infrared (FTIR). The water and oil contact angles of the coated steels were measured, and the hydrophobicity of the nano-coatings to milk, tea and a simulated soil solution was also determined. Qualitative tests of the preapred nano-coating in mud and soil were

conducted to investigate the potential antifouling performance. Mechanistic aspects of the superhydrophobicity of the prepared Zn nano-coating and its antifouling performance were discussed. The optimal electrodepositing conditions to achieve the superhydrophobity and desired properties of the prepared Zn coatings were determined.

2. Experimental procedure

2.1. Material and specimens

Specimens used in this work were cut from an X65 steel pipe, with a chemical composition (wt%): C 0.04%, Si 0.2%, Mn 1.5%, P 0.011%, S 0.003%, Mo 0.02% and Fe balance. The specimens were machined into $1\,cm \times 1\,cm \times 1\,cm$ square shapes and sealed in epoxy, leaving an exposed area of $1\,cm^2$. The working face of the specimen was subsequently ground with SiC emery papers up to 1200 grit, washed with deionized water, degreased with ethanol and acetone, and dried in air.

2.2. Preparation of Zn nano-coatings on steel specimens

Prior to electrodeposition, the steel specimens were ultrasonically degreased in an alkaline solution containing $20\,g/L$ NaOH, $10\,g/L$ NaCO$_3$ and $10\,g/L$ Na$_3$PO$_4$ at $50\,°C$ for 10 min. The specimens were then immersed in $50\,g/L$ H$_2$SO$_4$ for 1 min at room temperature to remove oxide from the surface, and then rinsed thoroughly with deionized water and dried in high-purity nitrogen (99.999%). Fig. 1 shows schematically the experimental setup for electrodeposition and the post-modification by stearic acid to prepare superhydrophobic Zn nano-coatings on the steel. The steel specimen was installed in a cell containing $250\,g/L$ ZnSO$_4$ solution with a pH of 2.0 adjusted by $50\,g/L$ H$_2$SO$_4$. The specimen, which served as the cathode, was connected to the negative pole of a direct current (DC) power supply. A carbon rod, used as the anode, was connected to the positive pole of the DC power source. The distance between the anode and the cathode was 2 cm. The bath solution, which was under magnetic stirring, was maintained at $50\,°C$ with a heating plate.

After electrodeposition at various current densities (i.e. 50, 100 and $200\,mA/cm^2$) for varied times (i.e. 5, 10, 20 and 30 min), the specimen was removed from the solution, rinsed with deionized water, and dried in air. The Zn-coated specimen was immersed in $0.05\,mol/L$ stearic acid ethanol solution for 5 h at room temperature, where a stearic acid layer was formed on the coating surface. The specimen was then washed with ethanol and dried with cold air to obtain the stearic acid modified Zn nano-coating on the steel substrate. It is noted that, generally, the stearic acid concentration, immersion time, and solution temperature influence the adhesion of the stearic acid layer on the Zn surface. As this work focused on characterization of the electrodepositing current density and time on the prepared Zn coating, the dependence of the stearic acid layer on its concentration and immersion time was not

investigated. However, future studies of the structure and stability of the stearic acid layer would be worthwhile.

To control the reproducibility of the prepared Zn nano-coatings, three parallel steel specimens were used for the coating preparation under identical conditions.

2.3. Characterization of the prepared zinc nano-coatings

The water contact angle of the coated steel was measured with a $3\,\mu L$ water droplet using an environmental goniometer (100-26-TH, Ramé-hart Instrument Co.) at room temperature. A scaler installed at the water container injector was used to control the volume of the water droplet. The water contact angle tester contained a needle that could hold droplets of less than $3\,\mu L$. When the droplet reached $3\,\mu L$, it dropped to the specimen surface under gravity. Five snapshots were taken in $0.01\,s$ when the water droplet dropped on the surface. One of the five snapshots, which was representative of all other snapshots, was shown in this work. Each data point of the water contact angle was the average of five measurements conducted at different locations on the coated specimen. The oil contact angle of the coated steel was measured by the same procedure using a mineral oil droplet. The hydrophobic properties of the coated specimen were also measured by dropping a droplet of tea, milk and a simulated soil solution on the coated specimen following the same procedure described above for water. The mineral oil used in this work had a density of about $0.83\,g/mL$ and Saybolt viscosity of $162\,s$. This was the commonly used mineral oil in the laboratory to simulate the oil in pipelines. The simulated soil solution was prepared by dissolving analytical-grade chemicals in distilled water based on the previously determined chemical composition of an extracted soil solution [22].

The morphology and composition of the prepared Zn nano-coatings were characterized using an SEM equipped with an EDS. The surface roughness of the coated specimens was derived by imaging the topographic profiles of the specimens by an atomic force microscope (Keysight 5500 scanning probe microscope system), where the supplied software enabled calculation of the surface roughness. The surface roughness (root mean square, rms) was defined as the height difference between peaks and valleys in the imaging region.

An FTIR (Model Nicolet iS50) was used to characterize the functional groups and structure of the prepared coatings. For all spectra recorded, the specimens experienced a 64-scan data accumulation in the range of 600–$4000\,cm^{-1}$ at a spectral resolution of $4.0\,cm^{-1}$. An XRD (Rigaku Multiflex θ-θ diffractometer) was used to measure the crystalline structure of the Zn nano-coatings with a Cu Kα radiation ($40\,kV$, $40\,mA$, $\lambda = 1.5418\,Å$). A scan range of $2θ = 20°$–$90°$ and a scan speed of $0.2°/min$ was used.

The potential antifouling performance of the prepared nano-coatings was tested by immersing the coated steel specimen in a mud liquid and under soil on the coating surface. For the former test, the coated
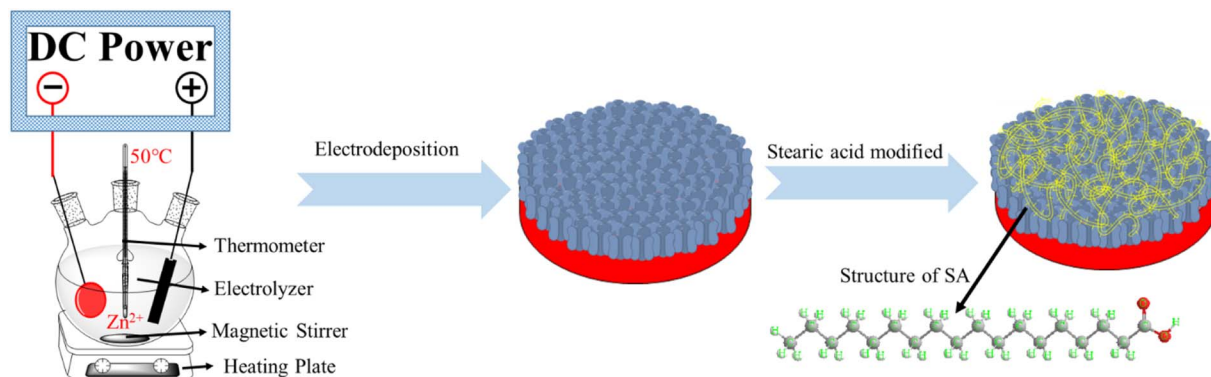

Fig. 1. Schematic diagram of the experimental setup for electrodeposition and the stearic acid modification to prepare superhydrophobic Zn nano-coating on the steel specimen, where SA refers to stearic acid.