



## Short Communication

## Corrosion protection of mild steel by one-step electrodeposition of superhydrophobic silica film



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## ABSTRACT

Superhydrophobic silica films were deposited onto mild steel substrate for the purpose of corrosion protection. The superhydrophobicity was obtained by one-step electrodeposition of inorganic/organic hybrid sol-gel films from tetraethoxysilane and dodecyltriethoxysilane mixed sol-gel precursors, as a result of simultaneous generation of high roughness and low-energy surface. The corrosion performance was investigated by monitoring the change of water contact angle, by the electrochemical impedance spectroscopy measurements and by iron dissolution test over the whole immersion time. The results show that the superhydrophobic film provides an effective barrier coating for the mild steel interface.

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## 1. Introduction

Traditionally, phosphating and chromating are commonly used strategies for metal protection. However, both the two methods are not environmentally compliant. Phosphorous pollution is the major factor contributing to water eutrophication and chromium (VI) is well-known for its high toxicity and carcinogenic effects on humans [1,2]. Therefore, the use of chromate and phosphate compounds is becoming stricter and is even forbidden in many countries in corrosion protection industry. Various types of alternative materials, based on the use of self-assembled layers [3], sol-gel-derived films [4–8], and the films of rare-earth compounds [9–11] etc. have been shown their potentiality using for corrosion protection.

Recently, superhydrophobic materials, which are defined when the water contact angle is larger than 150°, have emerged as a new method to improve the corrosion performance of metals. Materials with such superhydrophobicity property possess the capacity as physical barrier to prevent corrosion electrolyte from penetrating onto metal substrate. Superhydrophobic films have been successfully prepared on lots of metals and their alloys, such as aluminum [12–14], magnesium [15,16], copper [17,18] and zinc [19,20] for corrosion protection. The preparation procedure of superhydrophobic films described in previous literature, however, is relatively complicated [21,22]. Two-step method was commonly used. A surface with sufficient roughness is constructed by a variety of physical and chemical methods, then further modified with low-

surface-energy materials. Therefore, it is much more attractive to use simple one-step methodologies, by which high roughness and low-energy surfaces are obtained simultaneously. Successful examples of one-step procedures include the use of phase-separated [23] or nanofiller-added polymers [24], strongly corrosive solutions containing hydrophobic agents [25], reactive metal salts and low-surface-energy materials [26]. Conventionally, fluorinated chemicals were often used as the low-surface-energy materials in either one- or two-step techniques [27–29], which is not essentially environmentally friendly.

In our recent work, we have reported one-step fabrication of superhydrophobic surface on ITO glass and stainless steel substrates [30]. The superhydrophobicity was achieved as a result of simultaneous generation of high roughness and low energy surface by electrodeposition of organic/inorganic hybrid sol-gel film. In the hybrid film, inorganic silica component ensures the formation of highly porous and rough framework, and the environmentally compliant organosilanes, e.g. dodecyltriethoxysilane, DTMS, provide low surface energy. Noting that electrodeposition plays a key role for the acceleration growth of sol-gel films and for the eventual achievement of superhydrophobicity. Such acceleration is based on the enhancing sol-gel condensation process due to the increased pH in solution near the substrate when applying cathodic potentials on metallic substrates [1,31–33]. The benign preparation conditions and low-cost and environmentally compliant chemicals used ensure its wide application in constructing superhydrophobic surfaces on conducting substrates.

In the present communication, we have borrowed the same strategy to prepare electrodeposited SiO<sub>2</sub>/DTMS superhydrophobic films (E-SiO<sub>2</sub>/DTMS films) on mild steel (MS) substrate, the major-

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ity of metallic materials used in industry and are highly susceptible to corrosive attack [34,35], for the purpose of corrosion inhibition. Noting that although as described above, superhydrophobic film has been used for corrosion protection of various metallic materials, it has not yet been applied for corrosion protection of steels. It should also be noted that unlike some other traditional surface treatments, such as phosphate or chromate conversion layers, which are often used with the combination of organic coatings for long-term corrosion protection, superhydrophobic thin film is usually applied for temporary (short-term) protection of metals. Experimental results show that the as-prepared superhydrophobic film provides an effective barrier layer against the attacking of corrosion medium for MS interface.

## 2. Experimental

### 2.1. Materials and chemicals

Mild steel (MS) sheets (kindly supplied by Pentatomic Science & Technology, Hangzhou, China, wt.%: C 0.01, Si 0.35, P 0.018, Cr 0.04, Mo 0.03, Ni 0.017, Cu 0.02, Al 0.06; Fe balance) were cut into 3.0 cm × 4.0 cm plates (0.1 cm thickness). The plates were abraded consecutively finer emery papers to 400 grade, degreased with home-made alkaline solution (composition: Na<sub>2</sub>CO<sub>3</sub> 8 g/L, Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O 5 g/L, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> 8 g/L, C<sub>12</sub>H<sub>25</sub>NaO<sub>3</sub>S 1 g/L, Triton X-100 5 mL/L) for 10 min at 60 °C under sonication, then thoroughly rinsed with de-ionized (DI) water and ethanol, and finally blew-dried with warm air. Tetraethoxysilane (TEOS) (≥98.5 %, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and dodecyltrimethoxysilane (DTMS) (>93 %, Tokyo Chemical Industry Co., Ltd.) were used without further purification. The precursor solution (pH = 4.0, adjusted by HCl) for electrodeposition consists of 20 mL 0.2 M KNO<sub>3</sub>, 80 mL ethanol and 2 mL TEOS and 2 mL DTMS. Prior to electrodeposition, the MS plates were seal with insulation paster, only leaving one side of exposure. The solution was pre-hydrolyzed for 12 h at 25 °C under vigorous stirring.

### 2.2. Electrodeposition of superhydrophobic film

The electrodeposition was carried out on a 630d electrochemical working station (CHI instrument, Shanghai, China), using a conventional three-electrode compartment. A Pt plate (2.5 cm × 2.0 cm) was used as the counter electrode and a commercial Ag/AgCl electrode (in saturated KCl solution) as the reference. Hybrid silica sol-gel film was deposited onto MS substrate from the precursor solution by applying a cathodic potential. As a comparison, dip-coating hybrid film was also prepared by directly immersing the substrate into the precursor for 300 s. After deposition, the film was rinsed with ethanol and dried in an oven at 40 °C. And then, the edge area of the whole film was sealed with epoxy resin again to neglect the un-uniformity.

### 2.3. Physical characterization

The thickness and roughness of as-prepared film were measured by a profilometer (Dektak 150, Veeco, USA). A notch was made artificially by using a wood stick. Morphology observation was carried out by scanning electron microscopy (SEM, UTRA-SEM, Zeiss Company, German) with an operating voltage of 5.0 kV. The film wettability during 1-week immersion was qualitatively examined by water contact angle (CA) measurement on a JC200D contact angle instrument (Shanghai Zhongchen Dignal Technic Apparatus Co., Ltd., China). A 5 μL water drop was used. The CA value was obtained by averaging measured data at five randomly selected points.

### 2.4. Corrosion property assessment

Electrochemical impedance spectroscopy (EIS) measurements were performed on a M273 model potentiostat (Princeton Applied Research, USA) combined with a M5210 model lock-in amplifier (Signal Recovery, USA) in a classical three-electrode cell with a working area of 4.5 cm<sup>2</sup>. Ag/AgCl (in saturated KCl) and platinum electrodes were used as the reference and counter electrodes, respectively. The impedance measurements were carried out at open-circuit potential (OCP) in the frequency range from 100 kHz to 10 mHz by applying an AC excitation of 10 mV amplitude (peak-to-zero) of sinusoidal voltage. Before measurements all samples were immersed in 3.5 wt.% NaCl aqueous solution for 30 min to obtain a steady state.

### 2.5. Iron dissolution determination

Iron dissolution rate was determined by ultraviolet and visible spectrophotometer (UV759S, Shanghai, China) according to ISO 6332-1988 (“Water quality-determination of iron”) using 1,10-phenanthroline as the indicator. Mild steel samples (exposing area of 4.5 cm<sup>2</sup>) were immersed in 50 mL 3.5 wt.% NaCl solution for 24 h. After then 2 mL H<sub>2</sub>SO<sub>4</sub> was added into the above solution to make sure the corrosion products attached on the surface and precipitated in the solution were entirely dissolved to formed iron ions. 0.05 wt.% thiourea was introduced as corrosion inhibitors together with H<sub>2</sub>SO<sub>4</sub> in order to protect mild steel against the undesired corrosion.

## 3. Results and discussion

One major advantage of electrochemically assisted deposition technique, comparing with the conventional dip-coating or spin-coating methods, lies in the fact that it offers a feasible way to control the growth kinetics of sol-gel film by varying electrochemical parameters, such as deposition potential and duration time. SEM observation shows that only some discrete silica particles can be found on the substrate after deposition for a short time (Fig. 1a, 20 s). Prolonging the deposition time results in the consecutive deposition of porous hybrid silica film (Fig. 1b, 100 s). When lengthening the deposition time up to 300 s, the derived hybrid silica films with highly porous structure cover the whole surface (Fig. 1c). The films exhibit hierarchical morphology. Altering the applied potential can lead to similar results (Fig. 1d–f). More porous and rougher films are formed when the deposition potential shifts negatively, because of a greater amount of OH<sup>-</sup> catalyst being generated.

The insets in the SEM images are the water droplets on corresponding surface. It is shown that the surface of the hybrid silica films becomes more water-repellent with prolonging the electrodeposition time and negatively shifting the applied potential. Superhydrophobicity is achieved when the potential is below -1.3 V vs. Ag/AgCl and the electrodeposition time is upon 300 s as indicated in the insets of Fig. 1. The success in obtaining superhydrophobicity was believed as a result of high surface roughness combined with low-surface-energy [36].

Fig. 2 quantitatively describes the deposition potential and time-dependent film thickness and roughness (upper part). Either applying more negative potential or prolonging electrodeposition time leads to forming thicker and rougher films. Summarized in the bottom part in Fig. 2 clearly reflects the constantly increased CA with electrodeposition time and negatively shifted potential.

As described above, superhydrophobic films, a kind of short-term protection system, are usually used in moderate atmospheric environment. In order to shorten the assessment period, a much

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