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Nanostructured photocatalytic coatings for corrosion protection and surface repair[☆]

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ABSTRACT

Corrosion is one of the most destructive processes in materials induced by environment. Protection and repair of metallic surfaces are major challenges in many engineering applications. We report a novel polyelectrolyte nanostructured coating incorporating the corrosion inhibitor, 8-hydroxyquinoline (8-HQ), into titanium dioxide (TiO₂) nanoparticles (NPs). The potentiodynamic polarization measurements and real-time electrochemical impedance spectroscopy (EIS) monitoring demonstrated that the nanostructured coating protected aluminum (Al) from corrosion. Photocatalytic TiO₂ was able to release incorporated 8-HQ only with the exposure to UV light resulting in a self-healing effect. Real-time EIS results showed that a new passivated layer was formed after 8-HQ molecules were released. The research in interfaces brings insights in understanding new aspects of corrosion and surface repair.

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1. Introduction

The national annual cost due to corrosion, estimated by the US Department of Transportation, was about \$300 billion [1]. The highly regulated use of chromates as conversion coatings demands the development of eco-friendly methods for metal protection [2,3]. It was reported that harmless polymeric materials could be used as self-repairing coatings [4–6]. When mechanically deformed, these coatings could release certain type of monomers and catalysts resulting in sealing of existing defects. Another approach is to use hybrid sol–gels that release corrosion inhibitors forming a dense passivated barrier against corrosive ion uptake and oxygen diffusion [6,7]. Deactivation of the corrosion inhibitors in these coatings occurred once they came into direct contact with the sol–gel [8]. To overcome this, attempts have been made in entrapping inhibitors in order to prevent their direct interactions with the coating matrix. One method is the utilization of oxide NPs as nanocontainers for adsorption of corrosion inhibitors [9,10]. These coatings must be sensitive to localized stimulation such as mechanical deformation or pH changes. It was reported that changing pH values affected the functional groups of polyelectrolytes, resulting in self-healing coatings on Al [11,12]. This was due to the alteration of electron density and charging states of functional groups enabling release of inhibitors.

Photosensitive materials, such as TiO₂ [13] are able to change their electron density through UV light exposure. This provides the opportunity to develop a photocatalytic approach for metal surface protection. As a photocatalyst, TiO₂ has a bandgap of ~3.2 eV [13], without doping, TiO₂ can play its photocatalytic role only when it is exposed to UV light with photonic energy larger than its bandgap (the UV light's wavelength should be less than 387 nm). This is because electrons in the uppermost valence band will jump to the conduction band under UV irradiation. Consequently, conduction band electrons and valence band holes are generated. Skorb et al. [14,15] demonstrated the optically healable coating for corrosion protection, with the help of a laser for the first time. The lasers used in these reports were either near-infrared (820 nm) or visible (532 nm), which is not in the UV region. Oxide nanoparticles including TiO₂ were used as nanocontainers only for polyelectrolytes and corrosion inhibitors. In the present research, we developed a method to make photocatalytic repairable coatings for corrosion protection. It was noted that a corroded Al surface was healed effectively through TiO₂ photocatalysts under UV irradiation. A coating being developed is thus active, hybrid, controllable, and photosensitive. It is widely accepted that 8-HQ can easily chelate with most metallic ions and prevent the metal surfaces from corroding efficiently [16,17]. We chose 8-HQ as corrosion inhibitor. Supported by TiO₂ NPs, the coating is constructed via a layer-by-layer (LBL) structure containing inhibitor-encapsulated polyelectrolytes. The inhibitors are expected to be released under UV irradiation. This coating can protect and heal Al surfaces. Once made, the coatings will be characterized using an EIS approach. This method is proven to be effective in assessing corrosion inhibitive and self-repairing behaviors as well as in investigating their mechanisms by interfacial evaluations.

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2. Materials and methods

2.1. Materials

The following chemicals were purchased from Sigma-Aldrich, US: Titanium butoxide, absolute ethanol, citric acid, sodium chloride (NaCl), ammonium hydroxide solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28.0–30.0% NH_3 basis), perchloric acid (HClO_4 , ACS reagent, 70%), poly(ethyleneimine), (PEI, ~50% in H_2O with $M_w \sim 600,000\text{--}1,000,000 \text{ g} \cdot \text{mol}^{-1}$), poly(sodium styrene sulfonate) (PSS, $M_w \sim 70,000 \text{ g} \cdot \text{mol}^{-1}$), and 8-HQ. As Al is a metal that can be easily corroded, we chose aluminum alloy AA 6061-T6 to demonstrate improved corrosion resistance and self-healing effect. It had the following chemical composition (wt.%): Si, 0.4–0.8; Fe, 0.7; Cu, 0.15–0.40; Mn, 0.15; Mg, 0.8–0.12; Cr, 0.04–0.35; Zn, 0.25; Ti, 0.1; and balance Al. These Al alloy sheets have dimensions of 10 mm \times 10 mm \times 1.2 mm. Before coatings and corrosion experiments, the Al surfaces were electrochemically polished in a solution of 10 vol.% HClO_4 and 90 vol.% ethanol at 0 °C with graphite as the counter electrode under an applied voltage of 23 V for 3 min, followed by rinsing with ethanol and deionized (DI) water, and finally air dried at room temperature.

2.2. Synthesis of TiO_2 NPs

A wet-chemistry reduction route under ultrasonication was used to prepare TiO_2 NPs [18]. In a typical surfactant-free preparation process, 288.2 mg of citric acid was first dissolved in the solution of 40 mL ethanol and 2 mL DI water. Subsequently, 10 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added to the resulting solution, in which process ammonium citrate crystals were led to form and grow. Next, 6 mL of titanium butoxide and 10 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ were dipped in the above solution simultaneously. The dipping rate for $\text{NH}_3 \cdot \text{H}_2\text{O}$ was about 2 times faster than that for titanium butoxide. After sufficiently stirring for 4 h under ultrasonic vibrations, the mixed solution was left to stand overnight. Then, the white precipitate was filtered, washed with DI water and ethanol thoroughly. Further separation of TiO_2 NPs from these white precipitate was performed by centrifugation at 7000 rpm for 30 min. After that we selected the top white translucent TiO_2 solution for the nanostructured coating.

2.3. Assembly of the nanostructured coating

Initially, 0.1 ml of white translucent TiO_2 solution was slowly dropped on the Al surface. The Al sheet was electrochemically polished and mounted on a spin coater (Laurell, WS-400-6NPP). After dropping, the rotary speed was set at 360 rpm for 40 min until the solvent was dried. In order to obtain thicker TiO_2 coatings, this procedure was repeated three times. The thickness of the TiO_2 coating was measured to be $1.14 \pm 0.38 \mu\text{m}$ using the Zygo NewView™ 700 s optical profilometer. After spin coating with an increase in temperature of 1 °C/s the samples were heat-treated at 300 °C for 4 h. The same heat treatment was conducted on control bare Al alloy sheets to eliminate unwanted difference resulting from annealing in the following corrosion measurements. The PEI and PSS layers were deposited on TiO_2 NPs coated Al alloy sheets by spin-LBL coating from 0.1 ml of 2 $\text{mg} \cdot \text{mol}^{-1}$ solutions of polyelectrolytes in DI water. The rotary speeds for polyelectrolyte coatings were both kept at 700 rpm for 40 min until the solvents were dried. After each deposition step the samples were rinsed with DI water and dried at room temperature. The same method was used to coat 8-HQ: it was placed between two PSS layers from 10 wt.% of 8-HQ in ethanol solution, and kept at 300 rpm for 10 min. After 8-HQ was coated, the excess crystals on the sheets were gently rinsed with a small amount of ethanol solution (50 vol.%). We obtained layer structures on the surface of TiO_2 NPs in sequences of PEI/PSS/8-HQ/PSS/PEI, and each adjacent layer was oppositely charged.

2.4. Structures and composition characterizations

The Transmission Electron Microscope (TEM) images were taken at an accelerating voltage of 100 kV on JEOL 1200 EX. The samples for TEM study were prepared by slow evaporation of a drop of white translucent TiO_2 solution on carbon/copper grids at room temperature. The Field Emission Scanning Electron Microscope (FESEM) image was taken using a FEI QUANTA 600. The X-ray Diffraction (XRD) analysis was performed with a scanning rate of 0.02 s^{-1} in the 2θ range of $20^\circ\text{--}80^\circ$ using a Bruker-AXS D8 advance X-ray diffractometer with Cu K radiation operating at 40 kV. The sample for XRD characterization was deposited on quartz substrates and heat treated at the same condition that was described before. Under attenuated total reflectance (ATR) mode, Fourier Transform Infrared (FTIR) spectra, ranging from 400 to 4000 cm^{-1} , were recorded on the spectrometer (Bruker Optics Alpha-p) by averaging 250 scans at resolution of 1.4 cm^{-1} .

2.5. Corrosion protection and repair measurements

A three-electrode electrochemical cell was employed for potentiodynamic and EIS measurements. The exposed surface areas ($\varnothing 5 \text{ mm}$) were kept the same in all these tests. A platinum filament and a standard saturated calomel electrode (SCE, $\text{Hg}/\text{Hg}_2\text{Cl}_2$) served as counter electrode and reference electrode, respectively. Potentiodynamic tests were performed with a voltage range from -1.1 V to -0.4 V with a scanning rate of $1 \text{ mV} \cdot \text{s}^{-1}$. For corrosion tests, EIS spectra were used as a monitoring technique after samples were immersed into salty solutions ($0.1 \text{ mol} \cdot \text{L}^{-1}$ NaCl). The EIS was recorded and surface was monitored every 2 h for up to 6 h. In order to record EIS spectra, a sinusoidal signal with amplitude of 10 mV and frequency ranging from 100 kHz to 0.1 Hz was applied to the working electrode at open circuit voltage (E_{oc}). The step width was selected to be 10 s per decade. Before performing EIS tests, the electrochemical cell was discharged to E_{oc} , and then was kept at open-circuit condition for 20 min to ensure the equilibrium of cell. All electrochemical measurements were conducted using a Gamry Reference 600™ Potentiostat in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaCl solutions. After measurements, GamryEchem Analyst™ software was used to analyze and model potentiodynamic (Tafel) and EIS data.

3. Results and discussion

3.1. Fabrication and characterization of the nanostructured coating

We used photocatalytic TiO_2 NPs as optical agents and supporting structures for polyelectrolytes and inhibitors. Fig. 1a shows the TEM image. These particles, less than 5 nm in size, are loosely connected promoting channels and surface areas for abundant adsorption of polyelectrolytes and corrosion inhibitors. The calcinations of the TiO_2 coating would remove unnecessary remnant molecules and form good adhesion between TiO_2 NPs and Al substrates. The FESEM image shown in Fig. 1b confirmed this goal of compact adhesion on a nano-scale. In the following corrosion resistance and optically repairing experiments, the calcined TiO_2 coating was not peeled off of Al substrate. Otherwise, TiO_2 coating without calcinations would have been detached shortly after immersing the samples into the solutions. During heat treatments, TiO_2 NPs underwent transformation from amorphous to crystalline. All peaks in XRD pattern in Fig. 2a agree well with that in anatase TiO_2 (JCPDS File No. 21-1272).

Using a spin-coater the LBL structure was obtained with oppositely charged polyelectrolytes, PEI and PSS. The bonding between alternating layers in the LBL structure is mainly electrostatic interaction. In order to encapsulate the positively charged inhibitor, 8-HQ [11], we chose the negatively charged polyelectrolyte, PSS. The surface of TiO_2 is normally surrounded by negative hydroxyl groups [19] which would repel the PSS layer. For this reason a positive charged PEI layer had to be introduced. FTIR spectra are shown in Fig. 2b where visible differences

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