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Super-hydrophobic Polyaniline-TiO_2 Hierarchical Nanocomposite as Anticorrosion Coating

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ABSTRACT

Conducting polymer based composite coatings with the functions of both chemical and physical barriers are developed as eco-friendly alternatives for traditional polluting chromium based anticorrosion coatings. A novel super-hydrophobic polyaniline-titanium oxide (PANI-TiO_2) based hierarchical nanocomposite coating was designed and fabricated by a surfactant free nano-precipitation method. The developed nanocomposite coating was confirmed to possess superior water repellency (water contact angle >150°) and better anticorrosion performance than traditional epoxy coating in our analysis. A positive relationship between the TiO_2 content and thermal conductivity of the coating was observed. All the results have confirmed the developed coating to be a superior anticorrosion coating with superior water repellency and anticorrosion performance.

Keywords: Super-hydrophobic, Anti-corrosion, Polymer nanocomposites, Hierarchical structure

1. INTRODUCTION

Corrosion is primarily attributed to electrochemical reactions that are caused by the inhomogeneity in metals or its environment[1]. One or both of these two strategies are usually adopted for corrosion resistant applications: (i) incorporation of inhibitors to provide chemical barriers and (ii) introduction of impermeable physical barriers from moisture[2]. The usage of chromium and various chromate anticorrosion coatings have caused server enviromental problems. As electrochemical barriers by restricting the electrons transfer from metal to oxidizing substances[3-5], conducting polymers are considered as potential eco-friendly materials for anticorrosion applications. Recently, The applications of super-hydrophobic coatings with superior water repellency as physical barriers against metal corrosion have attracted much interest. Multifunctional coatings containing both the conducting polymer as an inhibitor and the super-hydrophobic coating as an impermeable barrier for enhanced anticorrosion performance are proposed most recently[6-9]. Many factors concerning the durability of the coating, such as thermal conductivity, are rarely considered in the design of existing super-hydrophobic PANI based coatings. In the development of novel super-hydrophobic PANI based coating, more facile fabrication techniques need to be developed.

To integrate the synergistic effects of super-hydrophobicity, high thermal conductivity, simplified preparation process and superior anticorrosion performance, novel PANI-TiO_2 nanocomposite particles with micro/nano structures were designed and a facile surfactant free fabrication method was developed in this research. TiO_2 nanoparticles were introduced to improve coating conductivity and generate the hierarchical structure. The incorporated TiO_2 nanoparticles were modified with perfluorosilane to reduce surface energy. With the development of surfactant free nano-precipitation method, fabrication was simplified by avoiding the extra process steps for the addition and removal of the surfactant. Wettability, structure, thermal conductivity and anticorrosion performance of the prepared PANI-TiO_2 hierarchical composite and the corresponding super-hydrophobic coating were investigated.

2. EXPERIMENTAL

2.1 Materials

TiO_2 nanoparticles (mean diameter: ~25nm and ~100nm) were obtained from the Beijing DK Nano technology Co., Ltd. Modifier 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFTES) and polyaniline (PANI, emeraldine base, Mw:~50000), epoxy resin (Araldite®506) were purchased from the Sigma-Aldrich. N-Methyl-2-pyrrolidinone (99%, NMP), sulfuric acid (~98%, H_2SO_4), ammonium hydroxide (NH_4OH), and ethanol were supplied by the Merk & Co. Pure water was used in all experiments.

2.2 Preparation of PANI-TiO_2 hierarchical composite particles

PANI solution of 20mg/ml was prepared by dissolving measured PANI powder in a certain amount of NMP under sonication. Calculated parts of the TiO_2 and the modifier

(PFTES) were ultrasonically dispersed in 2 ml of the as-prepared PANI solution. This PANI suspension was added dropwise into 20 ml H_2SO_4 solution of pH=1.5 under mild agitation. After 2-hour agitation, the entire suspension was filtrated using vacuum filtration with a membrane of 25 nm pore size. The PANI-TiO_2 hierarchical composite particles were obtained after being dried in a vacuum oven for 1 day at 50°C.

2.3 Preparation of surface coating

Steel (1 cm^2) substrates were polished before usage. PANI-TiO_2 super-hydrophobic coating solution with 1% solid content was prepared by dispersing the as-prepared PANI-TiO_2 hierarchical particles into ethanol under sonication. 0.5 ml of the prepared coating solution was added dropwise onto the surface of the as-prepared steel substrate and dried at room temperature until a flat coating film was formed. In preparation of the epoxy coating, calculated amounts of epoxy and corresponding hardener were added in ethanol to give 1% of epoxy coating solution. The subsequent coating process underwent the same preparation process with the nanocomposite coating.

2.4 Characterization

The morphology and structure of the PANI-TiO_2 hierarchical composite particles and the coatings were observed by scanning electron microscopy equipped (SEM) (JEOL JSM-6490). The surface topography of the sample was observed by 3D Optical Measuring System (Alicona IFM G4). Water contact angles of the coating were measured via a contact angle goniometer (Sindatek Model 100SB). Thermal conductivity was measured by a thermal conductivity analyzer (Anter Flashline 2000).

The anticorrosion performances of the coatings were evaluated through electrochemical impedance spectroscopy (EIS). The system was powered by Model 600E Series Electrochemical Workstation (supplied by Model 600E Series, China). The samples of 1 cm^2 were employed as working electrodes. A carbon rod and a saturated calomel electrode (SCE) were adopted as the counter and reference electrodes respectively. A sine wave potential of 10 mV amplitude and a frequency range of 0.01Hz to 10kHz was employed.

3. RESULTS AND DISCUSSION

3.1 Microstructure PANI-TiO_2 nanoparticles

The nano-roughness of the PANI-TiO_2 nanocomposite particle is observed in Fig.1(a), which was ascribed to the presence of TiO_2 nanoparticles in the composition. The hierarchical structures of the PANI-TiO_2 super-hydrophobic coatings are confirmed in Figs.1(b)&(c). Surface roughness of the samples in Fig.1(c) is quantified in terms of average roughness (Sa, 1.956μm), root mean square roughness (Sq, 2.595 μm) and peak to valley roughness (Sz, 30.219 μm).

3.2 Thermal conductivity analysis

Thermal conductivity is one of the important properties for the durability of the nano-composite coating. Enhanced thermal conductivity is beneficial for heat dissipation and thus prevents the delamination of a coating resulting from heat expansion. Referring to Fig.2, the thermal conductivity is positively and linearly related to the TiO_2 content in the nanocomposite coating. Incorporation of the TiO_2 into the coating not only contributed to the improvement of hydrophobicity, but also the thermal conductivity and thus durability of the coating. No significant difference was discovered on the thermal conductivity of nanocomposite coatings fabricated with two different sizes (100nm and 25 nm) of the TiO_2 nanoparticles, which may result from the small size gap between the two different sizes of nanoparticles used in current study.

3.3 Wettability of the nanocomposite coating

3.3.1 Effect of TiO_2 Size

According to Wenzel's model10, a high surface roughness and a low surface energy are required to achieve a high water contact angle. To achieve the low surface energy, fluorine based surface modifier was introduced. To create a high surface roughness, binary hierarchical structures (micro-nano structure formulated with only one size of the nanoparticles) and ternary hierarchical structures (micro-nano structure formulated with two different sizes of the nanoparticles) of the nanocomposite particles were designed by incorporating TiO_2 nanoparticles of single size and two different sizes (1:1 weight ratio mixture of 100 nm and 25 nm) correspondingly. According to Fig.3(a), water contact angles of the samples with a ternary structure are higher than those with a binary structure, for the TiO_2 - modifier weight ratios up to 3, because a higher surface roughness of the ternary hierarchical structure led to a higher hydrophobicity at its surface. The difference in the water contact angles for two different samples as in

Fig.3(a) becomes more apparent especially when the TiO_2 - modifier weight ratio is equal to 2 or 3, because the contribution of surface roughness to the hydrophobicity was mitigated for a low TiO_2 - modifier ratio which means a higher modifier content.

3.3.2 Effect of TiO_2-PANI ratio and TiO_2-modifier weight ratio

According to Figs.3(a)&(b), higher modifier content (or lower TiO_2-Modifier ratio) and higher TiO_2 content (or higher TiO_2-PANI ratio) lead to increasing water contact angles. With the increase of modifier content, the surface energy of the coating was reduced. With the increase of the TiO_2 content, more TiO_2 particles were exposed on the surfaces of the nanocomposite particles and thus there were more spaces to graft the modifier. In high TiO_2 content, the positively proportional impact of modifier content on the water contact angle was mitigated, which indicated a saturated TiO_2 content. No significant difference is observed for different TiO_2-modifier weight ratios for the samples of 7.5 TiO_2-PANI weight ratio in Fig.3(b). The difference of the water contact angles between the samples with TiO_2-PANI weight ratios of 5 and 7.5 was lower than those with weight ratios of 2.5 and 5.

3.4 Anticorrosion Performance

EIS of the samples are expressed in Fig.4(a) in the form of Nyquist plots. The EIS data was analyzed by the ZSimpWin program with an appropriate equivalent electrical circuit (ECC) in Fig.4(b). Generally, the corrosion process of the substrate primarily depends on penetration and diffusion of the corrosive ions through the coating. This corrosion process was reflected in Nyquist curve and quantified in terms of corrosion transfer resistance, R_{corr}[9]. The larger of the diameter of the Nyquist curve and the value of corrosion transfer resistance, the better of the anticorrosion performance of the coating. According to Figs.4(a)&(c) the anticorrosion performance of nanocomposite coating exhibited the best anticorrosion performance. As the increase of modifier content in nanocomposite coating, better anticorrosion performance was obtained, which was consistent with the trends observed in Fig.3.

4. CONCLUSIONS

The PANI-TiO_2 nanocomposite super-hydrophobic coating was successfully fabricated by a novel surfactant free nano-precipitation method. The water contact angle of the developed nanocomposite coating was greater than 150°, confirming its super-hydrophobicity. The PANI-TiO_2 nanocomposite coatings with incorporation of the TiO_2 of two different sizes possessed better hydrophobicity. The developed coating exhibited superior anticorrosion performance among the samples with epoxy coating and unfilled PANI coating in the corrosion tests. The introduction of TiO_2 was beneficial for the improvement of thermal conductivity of the coating, which can mitigate the delamination of the coating caused by heat expansion. All these findings have confirmed the PANI-TiO_2 nanocomposite super-hydrophobic coating to be advantageous in anticorrosion application. These results can also provide useful guidelines for the design of nanocomposite coatings.

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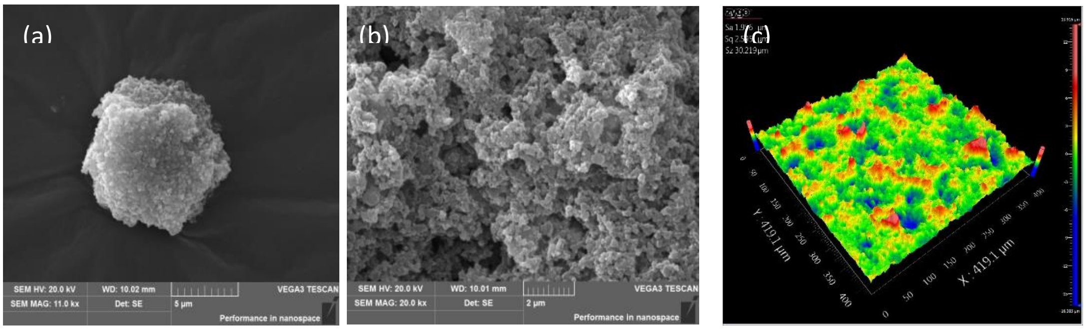

Figure 1 SEM image of (a) PANI-TiO_2 nanocomposite particle and (b) nanocompoiste coating; (c) 3D surface topography of nanocomposite coating

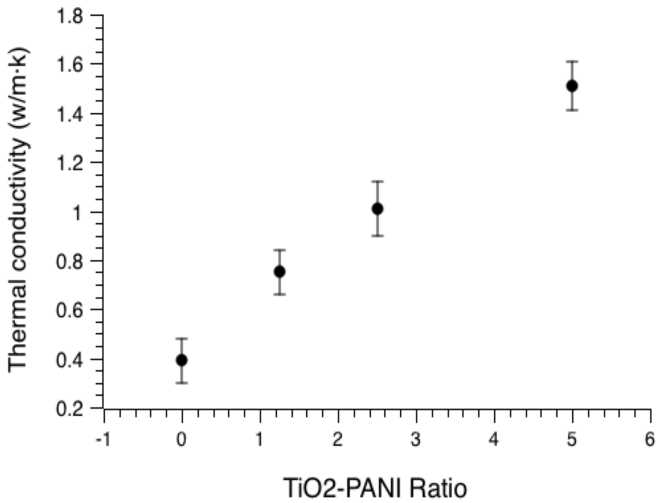

Figure 2 Thermal conductivities of the TiO_2-PANI nanocomposite coatings with different TiO_2 contents

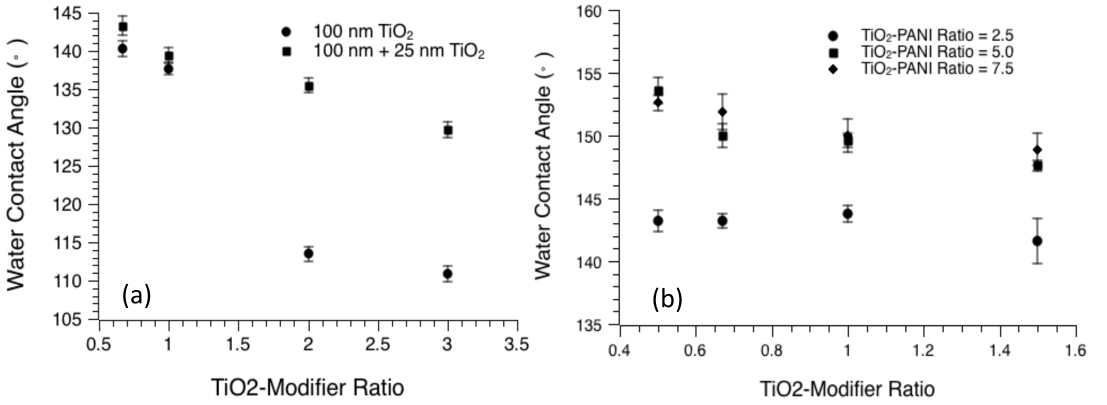

Figure 3 (a) Water contact angles of nanocomposite coatings with different sizes of TiO_2 versus TiO_2 - modifier weight ratios (TiO_2-PANI weight ratio=1.25)**;** (b) water contact angles of the nanocomposite coatings with different TiO_2 - modifier weight ratios and TiO_2-PANI weight ratios (TiO_2 type: 1:1 mixture of 100nm and 25 nm)

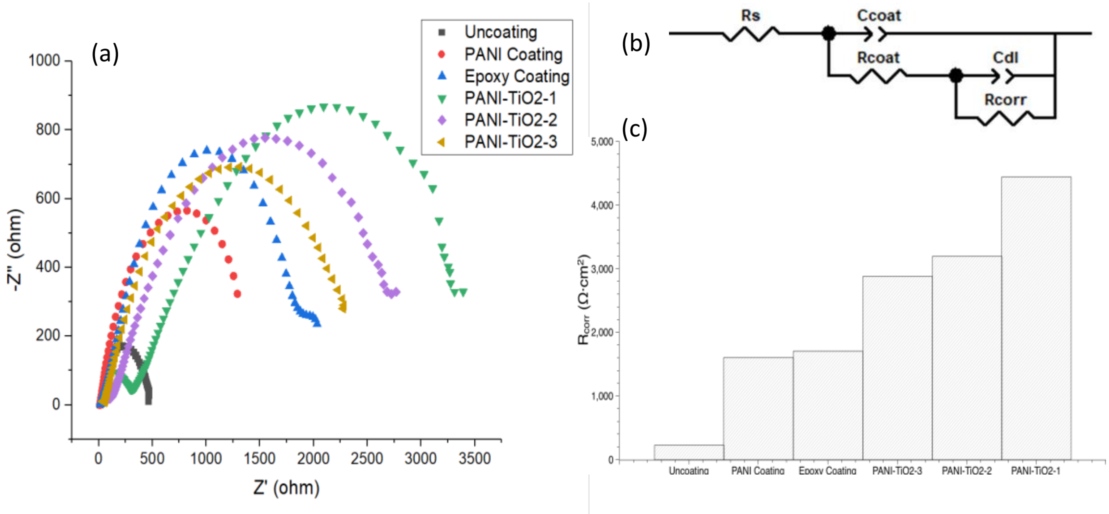

Figure 4 (a) Nyquist plot for uncoated steel, PANI-coated steel, epoxy-coated steel, PANI-TiO_2-1 (TiO_2 - modifier weight ratio = 0.5) coated steel, PANI-TiO_2-2 (TiO_2 - modifier weight ratio = 1) coated steel, PANI-TiO_2-5 (TiO_2 - Modifier weight ratio = 1.5) coated steel in 3.5% NaCl solution. (b) The equivalent electric circuit for modeling the EIS spectra; (c) Corrosion transfer resistance of samples