DEVELOPMENT OF TiO_2-PTFE NANOCOMPOSITE COATINGS WITH ANTIBACTERIAL AND ANTI-CORROSION PROPERTIES ON STAINLESS STEEL SURFACE

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ABSTRACT

In this work, a range of TiO_2-PTFE coatings with different TiO_2 and PTFE contents were prepared on stainless steel substrates by a sol-gel technique. The antibacterial and anti-adhesion efficiencies of the coatings were evaluated with both Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) strains. The experimental results showed that the TiO_2-PTFE coated surface with surface energy 26 mJ/m^2 performed best and reduced the adhesion of *E. coli* and *S. aureus* by 70.9% and 65.0%, respectively as compared with uncoated stainless steel surface. The anti-corrosion properties of the coatings were also evaluated using an electrochemical method in NaCl solution. The TiO_2-PTFE coatings protect the stainless steel substrate from corrosion by decreasing corrosion current by over one order of magnitude.

INTRODUCTION

Biofouling has been recognized as a widespread problem in design and operation of processing equipment such as heat exchangers and cooling water systems [1,2]. Biofouling does not only present a considerable hygiene risk in the food industry, but also causes economic losses. Any method of preventing biofouling or lengthening processing time will give substantial cost benefits. Titanium dioxide (TiO_2) represents a type of broad-spectrum bactericide and corrosion resistance [3]. Activation of TiO_2 particles with adequate UV light generates electrons and holes that react with adsorbed water and dioxygen molecules to form reactive oxygen species (ROS), killing or inhibiting the growth of bacteria by penetrating their cell walls [4,5]. Zhao et al. [6] incorporated TiO_2 nanoparticles into Ni-P coatings and found that the electron donor surface energy (γ^-) of the Ni-P-TiO_2coatings increased significantly with increasing TiO_2 content after UV irradiation. They also found that the number of adhering bacteria decreased with increasing electron donor surface energy of the coatings. Recently, Liu and Zhao [7] demonstrated that the ratio of the Lifshitz-van der Waals (LW) apolar component to electron donor surface-energy components of substrates (γ^{LW}/γ^-, also called the CQ ratio) controls bacterial adhesion. They found that surfaces with the lowest CQ ratio had the lowest bacterial adhesion.

Polytetrafluorethylene (PTFE) is a well-recognised non-stick material with low surface energy, and numerous studies have shown that the incorporation of PTFE nanoparticles into the metallic matrix significantly reduced the γ^{LW} component of the coatings, which is one of the main reasons for the coatings to have non-stick or antibacterial properties [8].

However, no research has been reported on the antibacterial properties of TiO_2-PTFE nanocomposite coatings. In this work, we aimed for the first time to develop a TiO_2-PTFE nanocomposite coating to protect 316L stainless steel substrate from bacterial infection and corrosion.

MATERIALS AND METHODS

Preparation of TiO_2-PTFE nanocomposite coatings

Commercially available 316L stainless steel plates (25mm × 25mm × 1mm) were cleaned by ultrasonication in ethanol and deionised water, respectively. The mussel-inspired strategy [9, 10] to prepare polydopamine (PDA) sublayer onto the surface of 316L stainless steel, and the sol-gel process to prepare TiO_2-PTFE nanocomposite coatings are illustrated in Fig. 1a. In brief, prior to TiO_2-PTFE sol-gel coating, the plates were treated with 2mg/mL dopamine in 10 mM Tris-HCl buffer for 24h under constant stirring at 100 rpm at 25°C. A TiO_2 precursor sol was prepared via the acid catalysed controlled hydrolysis of titanium (IV) butoxide (TBOT) in ethanol (EtOH). In this study, 0.1M nitric acid (HNO_3) was used as a catalyst. Then 1.0 - 2.0g/L TiO_2 nanoparticles (anatase, <25 nm) and 2.0 g/L of PTFE particles with a mean particle size of 200 - 300 nm were introduced into the sol and thoroughly mixed by ultrasonication.

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The plates were then vertically immersed into the mixture for 30s and withdrawn at a constant speed of 5mm/s. Finally, the coated plates were heat-treated at 100°C for 2h.

Surface characterisation

The surface morphology of the coatings was characterised using scanning electron microscopy (SEM). For surface composition analysis, energy-dispersive X-ray spectrometry (EDX) was used. Before contact angle measurement, all the coatings were exposed to UV light for 2h: the contact angle on the coatings was obtained using a sessile drop method with a Dataphysics OCA-20 contact angle analyser. The surface energy and its components of the coatings were calculated using the van Oss approach [7]. X-ray diffraction (XRD) was used to identify crystalline materials. Mineral phases were identified with reference to patterns in the International Centre for Diffraction Data Powder Diffraction File (PDF)

Antibacterial activity

The anti-adhesion efficacy of the TiO2-PTFE coatings was determined with Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* as model bacteria. The detailed cell culture was described in details previously [11]. In this research 10^6 CFU/mL *E. coli* and *S. aureus* were prepared in PBS and six replicates of each sample were incubated with 30 mL of the bacterial suspension at 20 rpm at 37°C. Bacterial adhesion was examined by counting the number of adhered cells at 2, 6, 12 and 24h, respectively using fluorescence microscopy. A LIVE/DEAD Baclight bacterial viability kit L13152, a fluorescence microscope and Image Pro Plus software were used to quantify the adhered bacteria.

The anticorrosion properties of the samples were evaluated electrochemically using a CorrTest Electrochemistry Workstation in NaCl solution.

Statistical analysis

Statistical analysis was performed using SPSS software (version 19.0) and data were represented as the means ± standard deviation. Group comparison was conducted using a one-way ANOVA combined with a Student-Newman-Keuls (SNK) post hoc test to determine the level of significance. $p < 0.05$ was considered significant and $p < 0.01$ was considered highly significant.

RESULTS AND DISCUSSION

Characterisation of TiO_2-PTFE nanocomposite coatings

As shown in Fig. 1b, the XRD diffraction pattern of the pure TiO_2 sol did not exhibit clear peaks indicating that the coating without anatase TiO_2 incorporation is amorphous in nature. In comparison, the diffraction patterns of TiO_2 and TiO_2-PTFE coatings (see Fig. 1b) showed clear peaks corresponding to the plane of anatase TiO_2, which confirms the presence of anatase phase of TiO_2 in the coatings. Moreover, the morphology of TiO_2-PTFE coated surfaces was also investigated using SEM. The coatings on bare steel substrates showed obvious cracks which could be a result of shrinkage during the thermal process (Fig. 1d-1 and Fig. 1d-2); while after coating with the PDA sublayer, the coating uniformity was significantly improved (Fig.1d-3). This could be attributed to the improvement of hydrophilicity of the substrate surface that enhances the tendency of the film to resist rupture and lowers the crack propagation velocity [12]. In this study, the hydrophilicity of the substrate surfaces was characterised by measuring the water contact angle (WCA) (Fig. 1c). After polishing and PDA coating, WCA values decreased from 68.8 ± 0.4° (untreated 316L SS) to 44.5 ± 1.6° and 18.6 ± 1.2°, respectively (Fig. 1c).

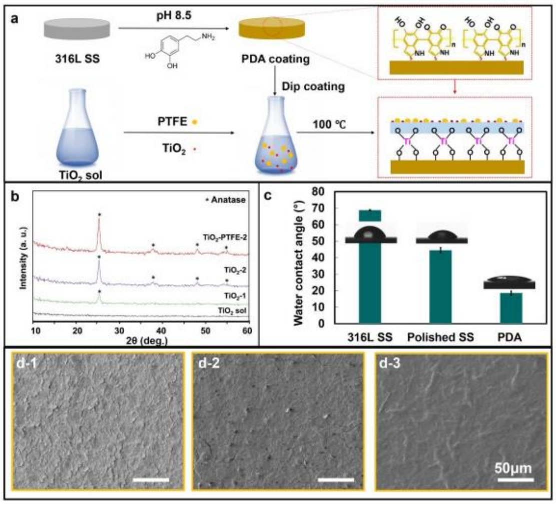

Figure 1. (a) Illustrative diagrams of the TiO_2-PTFE coating process; (b) XRD patterns of different coatings; (c) Water contact angles for different substrate surfaces The inserts are images of the water droplets after deposition on the surface for 60s; (d) SEM images of typical TiO_2-PTFE nanocomposite coatings on untreated 316L SS, polished SS and PDA coated surfaces, respectively (all scale bars correspond to 50 μm). Typical data are shown from one of several examinations.

At higher magnification, the TiO_2 nanoparticles and PTFE particles (with an average diameter of 200 - 300 nm) were uniformly distributed in the coatings (Fig. 2a, b). Fig. 2c shows the typical surface composition of the TiO_2-PTFE coating. The major surface constituents included C, O, F, Ti, Cr and Fe. The Fe and Cr were from the 316L SS substrate. Fig. 2d shows the

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distributions of C, O, F and Ti in the coatings obtained by EDX elemental mapping, which further verifies the uniform distribution of TiO_2 and PTFE particles throughout the coating.

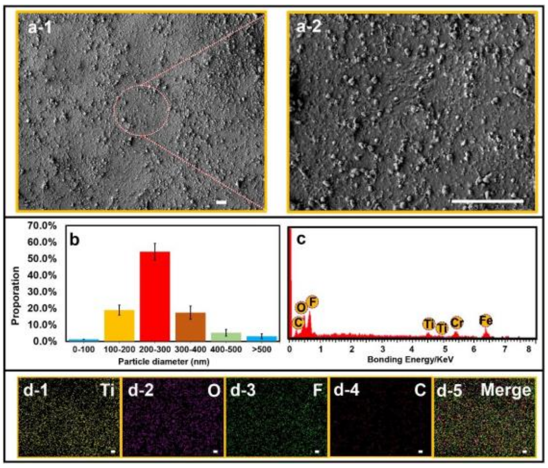

Figure 2. (a) SEM images of TiO_2-PTFE nanocomposite coatings at two different magnifications (scale bars correspond to 5 μm);(b) Size distribution of the PTFE particles; (c) Semi-quantitative results of EDX; (d) EDX mappings of the a-1 SEM image (scale bar corresponds to 5 μm). Typical images are shown from one of several examinations.

Effect of surface energy on bacterial adhesion

The influence of surface energy on bacterial adhesion has been investigated extensively with the frequent conclusion that low-energy surfaces are less prone to bacterial adhesion due to weaker binding at the interface [7]. In this study, a range of coatings with total surface energy from 18.21 mJ/m^2 to 42.60 mJ/m^2 were prepared and the effects of surface energy on adhesion of *E. coli* and *S. aureus* were studied after different contact times. As shown in Fig. 3, the TiO_2-PTFE coated surface with the surface energy 26 mJ/m^2 performed best against bacterial adhesion at all contact times. The results also showed that there existed an optimal value for the surface energy (between 20 - 30 mJ/m^2) at which bacterial adhesion is minimal. These results were consistent with the Baier curve [13].

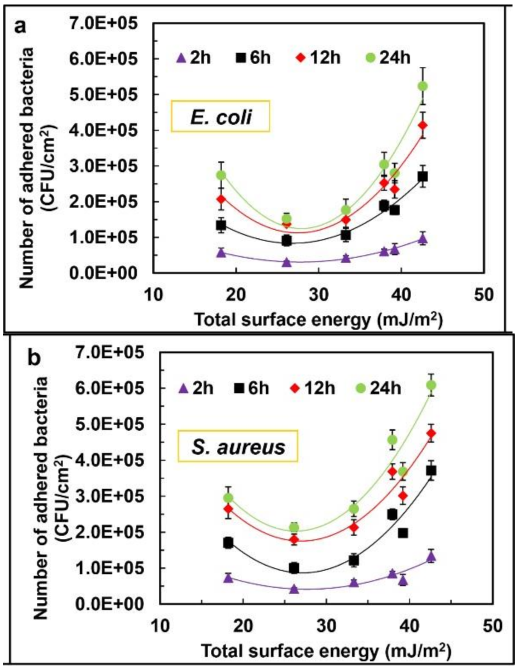

Figure. 3. Effect of surface energy on (a) *E. coli* and (b) *S. aureus* adhesion at various contact times (N = 10, bars are standard error of the mean).

Corrosion resistance

In this study, the corrosion resistance of the coatings was determined via an electrochemical method. The test samples included 316L stainless steel (316L SS), PTFE coating (PTFE), TiO_2 coatings (TiO_2-1, TiO_2-02), and TiO_2-PTFE coatings with different TiO_2 contents (TiO_2-PTFE-1, TiO_2-PTFE-2).

As shown in Fig. 4a, after coatings, all the open circuit potentials (OCP) values of the samples shifted positively. The OCP shift in the noble direction suggested the formation of a passive film that acted as a barrier for metal dissolution and reduced the corrosion rate. The TiO_2-PTFE-2 coating had the highest OCP value indicating the best thermodynamic stability. From the Tafel plots (Fig. 4b), all the coated samples demonstrated a more positive corrosion potential (E_{corr}) and a lower corrosion current density(I_{corr}). In particular, the TiO_2-PTFE-2 coating exhibited the best substrate protection by decreasing the I_{corr} of 316L SS by more than one order of magnitude. These results also demonstrated that the combination of TiO_2 and PTFE in coatings resulted in a synergistic effect in improving corrosion resistance, compared to the pure TiO_2 or PTFE coatings.

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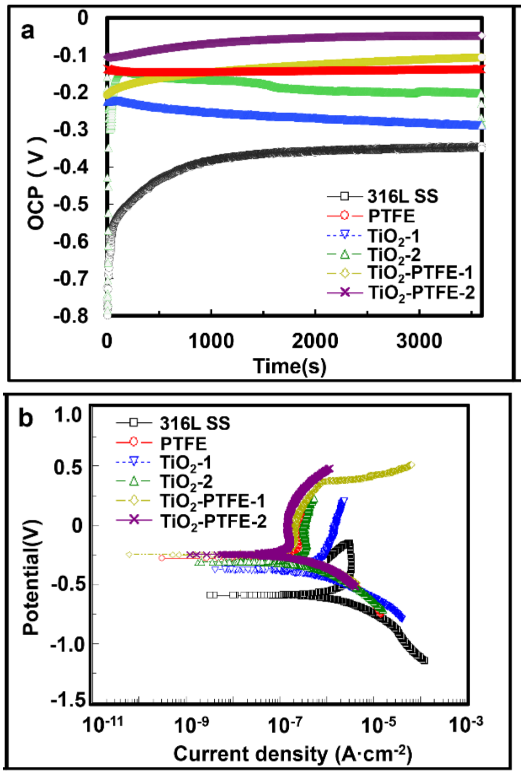

Figure 4. (a) Open-circuit potential characteristics and (b) potentiodynamic polarization curves of different samples in NaCl solution.

CONCLUSION

In this research, we have demonstrated a facile and cost-effective approach to produce TiO_2- PTFE coatings on stainless steel substrate by combining a sol-gel coating technique and mussel-inspired surface functionalisation. The resultant coatings showed effective antibacterial efficacies against both Gram-negative *E. coli* and Gram-positive *S. aureus.* The coatings also exhibited improved corrosion resistance. The positive results obtained in this study make the TiO_2-PTFE coating a promising candidate for the development of novel antibacterial and anti-corrosion coatings for heat exchangers and for metallic biomedical implants.

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