Progress in Organic Coatings 125 (2018) 109–118

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Preparation of mussel-inspired perfluorinated polydopamine film on brass substrates: Superhydrophobic and anti-corrosion application

Ning Cao[a,b,*], Yuanyuan Miao[a], Dalei Zhang[a], Rabah Boukherroub[b], Xueqiang Lin[a], Hong Ju[a], Huiping Li[c]

[a] College of Mechanical and Electronic Engineering, China University of Petroleum (East China), Qingdao, Shandong Province, 266580, PR China
[b] Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 - IEMN, F-59000 Lille, France
[c] School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao, Shandong Province, 266590, PR China

ARTICLE INFO

Keywords:
Brass
Copper
Perfluorinated polydopamine
Film
Superhydrophobicity
Anti-corrosion

ABSTRACT

Inspired by the adhesive properties of protein of mussels, perfluorinated polydopamine (*f*PDA) film on brass surface was obtained through spontaneous polymerization of dopamine monomer, followed by functionalization with *1H,1H,2H,2H*-perfluorodecanethiol (PFDT). Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and water contact angle (WCA) measurements revealed the formation of uniform, compact and superhydrophobic film. Electrochemical tests indicated that brass-coated with *f*PDA possessed a low corrosion current density and high film resistance. The modified sample dipped in 3 wt.% NaCl aqueous solution was well preserved. The results clearly indicate that the remarkable anti-corrosion capability was the result of the synergistic/cooperative effects of the superhydrophobicity and enhanced adhesion of the *f*PDA film.

1. Introduction

Metal corrosion causes heavy loss in many industries each year. Brass is widely used in heat exchangers, plumbing, and other utilities for its excellent thermal conductivity [1–4]. In addition, brass exhibits a reasonable corrosion resistance in aqueous media. However, the corrosion rate of brass varies depending on the temperature, pH, and solutes of the water [2,4–7]. It is thus very important to explore appropriate and effective approaches to decrease these water-related corrosion processes [8,9]. Among all these techniques, the most promising one is the modification of the surface with water repellent films, which restricts the contact of the metal surface with the aqueous media in full measure [10–12].

The discovery of the surface microstructure of natural lotus leaves inspired the preparation of plenty of artificial superhydrophobic surfaces; these non-wetting surfaces are characterized by a water contact angle greater than 150°. This observation serves as an underlying mechanism for the preparation of water repellent films. As we all know that the wettability behavior of a solid surface is dependent on its roughness and chemical composition. In the past, a huge variety of superhydrophobic films have been used to modify metal surfaces with the aim to improve their anti-corrosion resistance properties [13,14]. Superhydrophobic brass surfaces have been described in some reports using for instance laser beam machining and low thermal annealing at 100 °C [15], sol-gel spray film method [16] or chemical oxidation/etching in antifoaming solution followed by chemical functionalization with heptadecafluorodecyltrimethoxysilane or stearic acid [17]. Meng et al. developed a relatively easy and straightforward method to produce superamphiphobic surfaces on various metals, including brass *via* a simple immersion technique in ethanolic solution of nonadecafluorodecanoic acid, $CF_3(CF_2)_8COOH$, for about 10 days at room temperature [18]. By combining alternate current etching and chemical functionalization with stearic acid, Wang et al. prepared superhydrophobic brass surfaces with a WCA of 155 ± 3° [19,20]. A similar approach *i.e.* chemical etching and chemical functionalization with stearic acid was adopted to achieve superhydrophobicity on brass surfaces [21,22]. However, the lack of strong adhesion between the metal surface and the film always led to poor anti-corrosion properties of many superhydrophobic films overtime. Thus, there is an urgent need to find a suitable superhydrophobic film for long-term corrosion resistance application.

In recent decades, mussel-inspired polydopamine (PDA) has generated great interest as a new functionalization scheme, due to its simplicity (dopamine polymerization takes place under slightly alkaline

* Corresponding author at: College of Mechanical and Electronic Engineering, China University of Petroleum (East China), Qingdao, Shandong Province, 266580, PR China.
E-mail address: caoning1982@gmail.com (N. Cao).

https://doi.org/10.1016/j.porgcoat.2018.09.007
Received 1 June 2018; Received in revised form 13 August 2018; Accepted 1 September 2018

Table 1
Brass chemical composition.

Element	Cu	Fe	Pb	Sb	Bi	P	Zn
wt.%	60.5	0.15	0.08	0.005	0.002	0.01	39.627

Table 2
Roughness of brass samples after polishing with different types of SiC paper.

Sample	S1	S2	S3	S4	S5
Roughness (μm)	4.76	2.76	1.12	0.65	0.42

conditions at room temperature), strong adhesion, and the capability to form consistent film on any substrate. Thus, PDA film has been investigated in many fields such as corrosion protection, oil/water separation and drug delivery [23–27]. More importantly, the PDA film offers plenty of catechol, amido and other groups on the substrate surface, which provide active sites for subsequent immobilization of various molecules/ligands *via* Michael addition or Schiff base reaction [28–30]. PDA film was also applied for the preparation of hydrophobic and corrosion resistant films [27,29,30].

Herein, a facile and straightforward method was employed to obtain superhydrophobic brass surfaces. The samples were first polished by water abrasive paper, followed by spontaneous polymerization of dopamine to generate PDA film. The PDA was subsequently functionalized with *1H,1H,2H,2H*-perfluorodecanethiol (PFDT) to yield a perfluorinated film (*f*PDA) on the brass substrate. The morphology, chemical composition and thermal properties of the film were assessed using various analytical tools. The anti-corrosion performance of the *f*PDA film was examined through immersion in salt solution and exposure to salt spray condition.

2. Experiment

2.1. Materials and chemicals

1H,1H,2H,2H-perfluorodecanethiol (PFDT), dopamine hydrochloride (DA), tris (hydroxymethyl) aminomethane hydrochloride (Tris−HCl), sodium chloride (NaCl), ethanol, and acetone were obtained from Sigma-Aldrich and used as-received.

The brass sample was obtained from Xiangwei Machinery Co., LTD., China. Its chemical composition is depicted in Table 1.

2.2. Sample preparation

The brass samples, with dimensions of 10 × 10 × 6 mm. The samples were abraded by silicon carbide sandpaper with different grits: 320#, 600#, 1000#, 2000#, and 3000#. The as-prepared samples with different surface roughness were respectively named as S1, S2, S3, S4 and S5. For degreasing, all the samples were ultrasonically washed in acetone and anhydrous ethanol for 2 min. After being completely dried

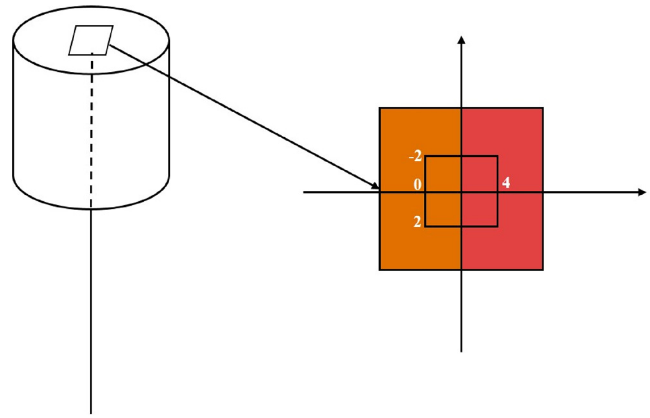

Fig. 2. Schematic representation of the brass sample used in SVET test, scanning area on the surface of brass sample was 4 × 4 mm (the left: bare brass, the right: Cu-*f*PDA).

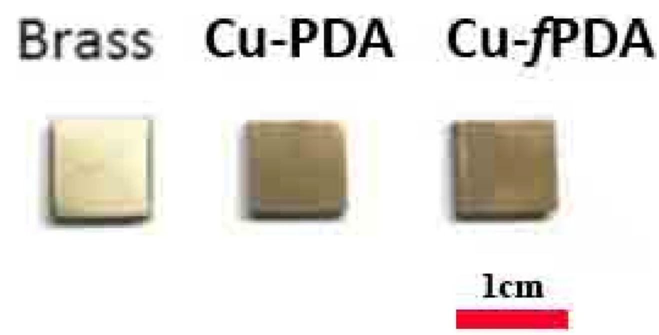

Fig. 3. Photos of the brass samples before and after functionalization with PDT and *f*PDA thin films.

at 95 °C in hot air, a Zeta-20-type three-dimensional surface profilometer (American Zeta Company, USA) was employed to test the roughness of the samples, as shown in Table 2.

2.3. Construction of superhydrophobic fPDA film on brass substrates

The as-polished sample was placed in a Tris−HCl (0.1 mol/L, pH = 8.5) solution containing dopamine monomer (DA, 10 mmol/L). The reaction lasted for 4 h at 40 °C under a constant rotation speed of 20 r/min. The resultant sample was removed, washed with absolute ethanol, deionized water, and finally dried at room temperature. The rinsing process was repeated twice.

The PDA-coated brass sample was reacted with a methanolic solution of *1H,1H,2H,2H*-perfluorodecanethiol (PFDT, 0.025 wt%) for 48 h at room temperature, then washed copiously with anhydrous ethanol and dried. The whole reaction process is depicted in Fig. 1.

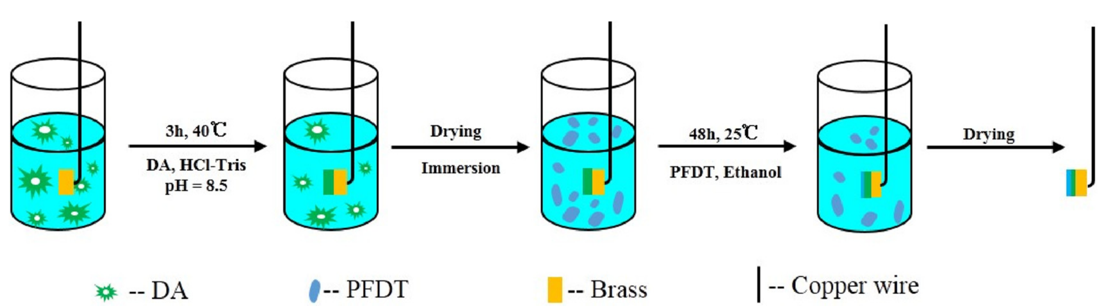

Fig. 1. The flow chart of the modification of the brass sample.