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Corrosion Inhibition of Polydopamine Nanoparticles on Mild Steel in Hydrochloric Acid Solution

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The spherical polydopamine (PDA) nanoparticles with a uniform particle size around 230nm were synthesized successfully by self-polymerization of dopamine hydrochloride in Tris-buffer solution. The inhibitor effects of PDA nanopartilces on mild steel in 1 M HCl were investigated by weight loss, potentiodynamic polarization, electrochemical impedance (EIS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results confirmed that PDA nanopartilces adsorbed onto the mild steel surface and efficiently inhibited the corrosion process. The inhibition efficiency of polydopamine inhibitor was up to 86% at a concentration of 40 mol/L, and the adsorption obeyed Langmuir adsorption isotherm. Meanwhile, potentiodynamic polarization studies showed that the corrosion inhibitor was a mixed inhibitor. SEM and AFM further confirmed the formation of a protective film on the mild steel surface.

Keywords: Polydopamine, hydrochloric acid solution, mild steel, adsorption, corrosive inhibitor.

1. INTRODUCTION

In industry, the acid treatment is usually used to remove of scale rust in a variety of industrial processes such as oil well acidification [1], acid pickling [2], acid cleaning [3] and acid descaling [4, 5]. Mild steel has become the most commonly used equipment materials for acid-related industrial processes due to its good mechanical properties and low price [6]. However, the corrosion problem of mild steel is very serious [7], resulting in the failure of engineering components and premature

deterioration, increased repair and maintenance costs and waste of mineral resources. The use of organic inhibitors represents one of the most efficient ways to mitigate the corrosion rate by blocking the anodic and/or cathodic reactions between the metal and the corrosive medium, protecting metal against corrosion and preserve industrial facilities [8]. Such organic inhibitors usually bear heteroatoms with electronegative functional groups such as oxygen [9], nitrogen [10], sulfur [4], phosphorus [11], unsaturated bonds or conjugated aromatic rings [12]. Despite the effectiveness of the above mentioned organic inhibitors, many of these compounds are toxic and don't meet requirements of environmental protection standards [2, 3]. At present, the focus of the research is to develop environmentally friendly inhibitors instead of toxic compound [10].

Polydopamine (PDA), a mimetic of mussel adhesive proteins, has attracted much attention due to strong adhesion to different substrates, such as Au, Ag, stainless steel, graphene, CNTs, aramid fibers, clay and other materials [15]. PDA has two advantages: one is dopamine monomer can be self-polymerized easily into poly(dopamine) in basic solutions on a variety of materials, such as metals, inorganic materials, and polymer materials [16, 17]. Another is the chemical structures of PDA contain several functional groups, such as catechol and amine groups which were easily modified by functionalization crosslinking [18, 19]. In recent years, PDA is mainly used for materials surface modification while the study of inhibition is limit. In this work, we aim to synthesize PDA nanoparticles by self-polymerization dopamine hydrochloride in presence of Tri buffer and investigate the corrosion inhibitive effect of resulting PDA nanoparticles on mild steel in HCl solution by using weight loss experiments, potentiodynamic polarization, EIS, SEM images and AFM analysis.

2. EXPERIMENTAL

2.1. Materials

Tris, methanol, dopamine hydrochloride used in this study were purchased by Aladdin Industrial Corporation. Acetone and HCl were obtained from Sinopharm Chemical Reagent Co. Ltd. All chemicals and solvents were used without further purification. Corrosion tests were performed on a mild steel (1 cm X 1 cm X 0.1 cm) of the following composition (wt.%): C (1.39%), Mn (0.29%), Al (0.18%) and balance Fe. They were polished using 150, 400 and 800-grit sand papers and degreased with acetone before immersion in the acid solution. The acidic medium was prepared by dilution of 35% AR grade HCl.

2.2. Synthesis of PDA nanoparticles

The synthetic route for the PDA nanoparticles was shown in scheme 1. Tris-buffer solution (1.2 L, 100 mmol/L) that was adjusted to PH=8.5, was added to 300 mL of methanol to form a homogeneous solution under magnetic stirring for 3 h. Then, 2.048 g (10 mmol) dopamine hydrochloride was dissolved in 200 mL Tris-buffer solution and poured into the above mixed solution reaction for 20 h at room temperature. After the reaction, the products were centrifuged under 10,000

rpm for 5 min, washed with deionized water three times and dried in vacuum at 40 °C to obtain polydopamine nanoparticles.



Scheme 1. The synthesis of the PDA nanoparticle by self-polymerization of dopamine.

2.3. Characterization

The structure of the synthesized PDA nanoparticles was characterized by Fourier transform infrared (FT-IR) spectrum over a wavelength range of 400–4000 cm⁻¹, which was recorded on NICOLET 6700 spectrometer. The morphology and size distribution of PDA nanoparticles were observed by scanning electron microscopy from HITACHI S4800 and laser particle size analyzer. Meanwhile, the uninhibited and inhibited Q235 steel surface morphologies were used to observe by scanning electron microscopy and atomic force microscopy (AFM Dimension3100V).

2.4. Weight loss measurements

Each steel specimen was dried and weighed before immersing in 1 M HCl solution in the absence and presence of 10, 20, 30, 40, 50 mg/L of PDA nanoparticles for 24 h. After immersion for 24 h, the mild steel specimens were carefully removed, rinsed with distilled water, dried, and weighed again. The inhibition efficiency (*IE%*) was calculated from the weight loss data according to the equation:

$$IE\% = \frac{W_0 - W}{W_0} \times 100\%$$

where W_0 and W are the weight loss values in the absence and presence of the inhibitor.

2.5. Electrochemical methods

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were conducted in a conventional three-electrode cell consisting of mild steel sample as working electrode, a platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode, using working station of CHI-660E, Chenhua, Shanghai. The working electrode was immersed in the 1 M HCl until the steady state open circuit potential (OCP) was obtained before

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potential of -250 mV to +250 mV vs OCP at a scan of 0.2 mV/s. The EIS measurements were performed at steady open circuit potential over a frequency range of 100 kHz to 10 mHz with amplitude of 10 mV. The inhibition efficiency (IE%) was calculated by polarization curves as following equation:

$$IE\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100\%$$

 i_{corr}^{0} and i_{corr} signify the corrosion current density in the absence and presence of inhibitors. The *IE*% was calculated by impedance values as following equation:

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100\%$$

 R_{ct} and R_{ct}^{0} are charge transfer resistance in the presence and absence of the inhibitors.

2.6. Adsorption isotherm

Quantitatively study the formation of the adsorption layer of organic inhibitors hinders the aggressive species from corrosion environment to the metal surface by adsorption isotherms is the best way [20, 21]. Langmuir adsorption isotherm was most suitable in various adsorption isotherm, including Frumkin [22], Freunlich [23] and Temkin [24], which given by the following equation:

$$\frac{c_{inh}}{\theta} = \frac{1}{K_{ads}} + c_{inh}$$

 C_{inh} is the inhibitor concentration and K_{ads} is the equilibrium constant for the adsorption–desorption process.

$$K_{\rm ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\rm ads}}{RT}\right)$$

where R is the gas constant and T is the absolute temperature (K), ΔG_{ads} is the standard free energy of adsorption. The value of 55.5 is the concentration of water in solution in mol L⁻¹.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of PDA nanoparticles

The FTIR spectrum of PDA nanoparticles was shown in Fig. 1. The sharp absorption peak at 3378.87 cm⁻¹ was assigned to stretching vibration of N-H. The absorbance bands located at 1507.52 cm⁻¹ and 1603.20 cm⁻¹, which were attributed to the stretching vibration of benzene ring. The absorption peak at 1286.30 cm⁻¹ was associated with the stretch of C–O band. In addition, the peaks at 2937.12 cm⁻¹ could be attributed to the stretch of the C–H bond and the absorption of amide located at 1558.62 cm⁻¹ [25]. These results indicated that the PDA nanoparticles had been successfully synthesized.



Figure 1. The FTIR spectrum of PDA nanoparticles.

Fig. 2 showed the morphology and size distribution of PDA nanoparticles. It was clearly seen that the PDA nanoparticles had been successfully synthesized with uniform spherical particles from Fig. 2a. The size distribution was further measured by laser particle size analyzer, exhibiting size distribution in the range of 190~250 nm, mainly focused on 230 nm (Fig. 2b). PDA nanoparticles were smaller and uniform in aqueous solution compared with the previously reported literature [25, 26].



Figure 2. The morphology (a) and size distribution (b) of PDA nanoparticles.

3.2. Weight loss measurements in the absence and presence of different concentrations of PDA nanoparticles

The corrosion inhibition of mild steel in 1 M HCl in the absence and presence of different concentrations of PDA nanoparticles was studied using weight loss technique, which data was given in Table 1. It was obvious that the inhibition efficiency (*IE*%) increased with the increase of the corrosion

inhibitor concentration, that best corrosion inhibition effect was to 75.88% at a concentration of 40 mg/L, which implied that the adsorption of PDA nanoparticles on the steel surface form an insulating interfacial layer [27, 28].

Conc.	ΔW	IE	θ
(mg/L)	(mg)	(%)	
0	87.9		
10	38.7	55.97	0.5597
20	27.1	69.17	0.6917
30	23.1	73.72	0.7372
40	21.2	75.88	0.7588
50	24.6	72.01	0.7201

 Table 1. Corrosion parameters obtained from weight loss measurements for mild steel in 1M HCl containing various concentrations of PDA nanoparticles.

3.3. Potentiodynamic polarization measurements



Figure 3. Polarization curves for mild steel in 1 M HCl containing different concentrations of PDA nanoparticles.

Fig. 3 showed the polarization curves of mild steel in 1 M HCl solution with and without different concentrations of PDA nanoparticles after 2 h immersion. The corresponding values of electrochemical parameters [29, 30], including corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes (b_a , b_c), linear polarization resistance (R_p) were listed in Table 2. The b_a and b_c increased with the concentration of PDA nanoparticles increased, which led to a negative shift of corrosion potential and a decrease in corrosion current density, implying that the

corrosion inhibitor was a mixed inhibitor [31, 32]. Meanwhile, the value of R_p showed an upward tendency until the content of PDA nanoparticles at 40mg/L. These results demonstrated the corrosion inhibition effect (86.42%) was the best when the concentration up to 40mg/L, which were attributed to the adsorption film by PDA nanoparticles on the surface of mild steel [33, 34].

Conc.	$-E_{corr}$	<i>i</i> _{corr}	b_a	b_c	R_p	IE
(mg/L)	(mV)	$(\mu A \text{ cm}^{-2})$	$(mV dec^{-1})$	$(mV dec^{-1})$	$(\hat{\Omega})$	(%)
0	410	1204	98.36	78.36	20.4	
10	430	543.9	103.70	83.37	47.2	54.83
20	430	424	128.93	94.34	45.9	64.78
30	446	336.7	121.43	85.50	62.4	72.03
40	445	163.5	122.79	90.31	124.8	86.42
50	447	242.6	104.15	112.16	82.9	79.85

Table 2. Electrochemical parameters and inhibition efficiencie of mild steel in 1 M HCl in the absence and presence of different concentrations of PDA nanoparticles.

3.4. Electrochemical Impedance Spectroscopy

Fig. 4 presented the Nyquist diagrams of the mild steel with and without various concentrations of PDA nanoparticles after immersion 2 h in 1M HCl solution. The Nyquist plots revealed a single semicircle, which data was fitted by equivalent electric circuit using the ZSimpwin software as shown in Fig. 5. The solution resistance (R_s), double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), inhibition efficiency (*IE* %) values without and with different concentrations of PDA nanoparticles were given in Table 3. From the table, the incorporation of PDA nanoparticles increased the charge transfer resistance R_{ct} while reducing the capacitance C_{dl} . This suggested that the addition of PDA nanoparticles formed a protective film for enhancement of corrosion protection of mild steel [35, 36], the IE% reached 86.37% at 40 mg/L.



Figure 4. Nyquist plots in the absence and presence of different concentrations of PDA nanoparticles.



Figure 5. Electrochemical equivalent circuit used to fit the impedance.

Table 3. Nyquist data for mild steel in 1M HCl for different concentrations of PDA nanoparticles.

Conc.	R _s	C _{dl}	R _{ct}	IE%
(mg/L)	$(\Omega \text{ cm}^2)$	$(\Box F \text{ cm}^{-2})$	$(\Omega \text{ cm}^2)$	
0	1.103	603.6	19.09	
10	0.9627	525.5	33.49	42.99
20	0.4013	282.2	45.95	58.45
30	0.9856	230.7	64.77	70.53
40	1.238	165.8	140.1	86.37
50	0.8753	191.7	134.1	85.76

The Bode plots were shown in Fig. 6, which included two plots of bode impedance plot and bode phase plot. The phase angle presented a good corrosion inhibition of PDA nanoparticles effect at high frequencies. With the concentration of PDA increased, there is an increase in values of absolute impedance at low frequencies, indicating the incorporation of PDA nanoparticles into 1 M HCl solution had good corrosion inhibition effects [37].



Figure 6. Bode plots for mild steel in the 1 M HCl solution containing different concentrations of PDA nanoparticles.

3.5. Absorption isotherm

Absorption isotherm could confirm the adsorption of interaction of PDA nanoparticles / metal on steel surface. The plot of C_{inh}/θ vs C_{inh} were obtained by linear-fit as shown in Fig. 7, suggesting that the inhibitor obeyed Langmuir adsorption. The equilibrium constant (K_{ads}) was calculated by the adsorption isotherm plot and its adsorption type and standard free energy (ΔG_{ads}) related. It was an established fact that ΔG_{ads} values around $-20 \text{ kJ} \cdot \text{mol}^{-1}$ or less were identified to physisorption and ΔG_{ads} values were more negative than $-40 \text{ kJ} \cdot \text{mol}^{-1}$ deemed to chemisorption. The ΔG_{ads} were calculated as $-23.33 \text{ kJ} \cdot \text{mol}^{-1}$, implied the spontaneity of the adsorption process and formation of the adsorbed film, which probably combined of physisorption as well as chemisorption [38, 39].



Figure 7. Langmuir adsorption plots for mild steel in 1 M HCl at different concentrations of PDA nanoparticles.

3.6. Surface morphology



Figure 8. SEM images for polished steel (a); uninhibited specimen in 1 M HCl (b); inhibited specimen in 1 M HCl with 10 mg/L PDA nanoparticles (c); inhibited specimen in 1 M HCl with 40 mg/L PDA nanoparticles (d).



Figure 9. AFM analysis of (a₁, a₂) polished steel , (b₁, b₂) uninhibited specimen in 1 M HCl, (c₁, c₂) inhibited specimen in 1 M HCl with 10 mg/L PDA nanoparticles, (d₁, d₂) inhibited specimen in 1 M HCl with 40 mg/L PDA nanoparticles.

The surface morphology of mild steel specimens in the absence and presence of different concentrations of PDA nanoparticles inhibitors immersed in 1 M HCl solution for 2 h at 20 °C by SEM were shown in Fig. 8. SEM images (Fig. 8a) of mild surface showed scratches due to polishing without obvious defections such as pits and cracks before immersion in 1 M solution. Fig. 8b showed the steel specimen immersed in 1 M HCl solution without inhibitors, resulting in severely corroded and a strongly damaged surface, while the corrosive effect of HCl in the presence of PDA nanoparticles (Fig. 8c and 8d) was greatly reduced and existed scattered pits and the pits of Fig. 8d were smaller than

those shown in Fig. 8c. This was due to the formation of the absorption film with some defects [40, 41] and the inhibition effect at the concentration of 40mg/L was relatively better.

AFM images of mild steel specimens in the absence and presence of different concentrations of PDA nanoparticles inhibitors were shown in Fig. 9. It showed very rough surface for mild steel immersed in 1 M HCl, while the surface roughness in presence of PDA nanoparticles significantly reduced. To quantify the surface roughness, mean roughness factor (R_a) reflected more intuitive. The R_a value of the polished steel surface was 46.4 nm, while the specimen immersed in 1 M HCl reached 317 nm due to dissolution of metal. However, the addition of 10 mg/L PDA nanoparticles decreased the R_a to 71.1 nm. With addition of 40 mg/L PDA nanoparticles, R_a further decreased to 50.6 nm, indicating that the formation of the adsorbed layer of inhibitor restrained effectively the corrosion of metal [6].

4. CONCLUSIONS

The spherical PDA nanoparticles with a uniform particle size around 230nm were synthesized successfully, and the inhibitor effects on mild steel in 1 M HCl with different concentrations of PDA nanoparticles were investigated by weight loss, potentiodynamic polarization, electrochemical impedance (EIS), scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The EIS and polarization measurement results showed that PDA nanoparticles enhanced the inhibition efficiency due to the adsorption on the steel surface and the corrosion inhibitor was a mixed type inhibitor. Meanwhile, the inhibition efficiencies increased with increasing PDA nanoparticles concentration reached 86% at 40mg/L. The adsorption of PDA nanoparticles was spontaneous, obeying Langmuir adsorption isotherm through physical as well as chemical adsorption. The SEM and AFM images further proved that PDA nanoparticles had adsorptive interaction between inhibitor molecules and steel surface.

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