Applied Surface Science 443 (2018) 145–156

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Novel nitrogen doped carbon dots for corrosion inhibition of carbon steel in 1 M HCl solution

Mingjun Cui [a,b,1], Siming Ren [a,b,1], Haichao Zhao [a,*], Liping Wang [a,*], Qunji Xue [a]

[a] Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 3 December 2017
Revised 5 February 2018
Accepted 26 February 2018

Keywords:
Q235 carbon steel
NCDs
Electrochemical measurements
SVET method
Corrosion inhibition

ABSTRACT

Nitrogen doped carbon dots (NCDs) were synthesized and used for inhibiting the corrosion of Q235 carbon steel in hydrochloric acid (HCl) solution. Inhibition effectiveness in short- and long-term immersion was examined using electrochemical measurements, weight loss and surface analysis. Results revealed the inhibition efficiency was improved significantly after adding NCDs and strongly dependent on the concentration of NCDs. SVET results showed that the sample immersed in HCl solution with NCDs showed lower anodic current density mapping than that in blank HCl solution. According to the data extracted from the Langmuir adsorption, the absorption of NCDs involved both chemisorption and physisorption.

1. Introduction

Organic inhibitors have been employed to inhibit the corrosion of industrial metals and alloys for acid pickling, cleaning, descaling and oil-well acidizing. Generally, the organic inhibitors containing heteroatoms (such as nitrogen, sulfur, oxygen and phosphorus), aromatic rings and π bonds can adsorb on the metal surface via formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the metal and inhibitor (physical adsorption), thus inhibiting the corrosion of the metals [1–4]. A number of organic compounds have been investigated and employed as corrosion inhibitors to prevent the corrosion of the metals. However, many conventional corrosion inhibitors are being prevented owing to the increasing awareness of human health and ecological pollution associated with traditional inhibitors. Thus, attempts have been made with the hope of developing highly efficient, safe and non-toxic corrosion inhibitors.

Carbon dots (CDs) with high water solubility, good biocompatibility, low toxicity and unique photoluminescence (PL) properties, have attracted ever-increasing attention [5–8]. The major investigations on the CDs focus on the multicolor cellular imaging capability with a single excitation wavelength. However, in recent report, Zhu and coworkers [9] first reported that CDs incorporated polymers not only possessed self-healing properties but also had superior anticorrosion properties, as a comparison with those of the pure polymer coatings, which were attributed to the bonding between CDs, CDs-polymer chain bonding and the four-electron path ORR capability that could reduce oxygen to water. Subsequently, Cui et al. also prepared N doped carbon dots (NCDs) with aminosalicylic acid (ASA) as precursor and found that these NCDs could effectively inhibit the corrosion of carbon steel in 1 M HCl solution owing to its special structure [10]. However, there was still rare investigation on this novel and eco-friendly corrosion inhibitor. Therefore, in the present work, the corrosion inhibition ability of NCDs obtained from p-phenylenediamine (p-PD) and o-phenylenediamine (o-PD) on Q235 carbon steel in 1 M HCl solution were studied using potentiodynamic polarization curves, scanning vibrating electrode technique (SVET), electrochemical impedance spectroscopy (EIS), weight loss measurement and scanning electron microscope (SEM).

2. Experiment sections

2.1. Materials

p-phenylenediamine (p-PD) and o-phenylenediamine (o-PD) were purchased from Aladdin. Ethanol and hydrochloric acid (HCl, 39%) were purchased from Sinopharm Chemical Reagent

---

* Corresponding authors.
E-mail addresses: zhaohaichao@nimte.ac.cn (H. Zhao), wangliping@nimte.ac.cn (L. Wang).

[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.apsusc.2018.02.255
0169-4332/© 2018 Elsevier B.V. All rights reserved.

Co., Ltd (Shanghai, China). Q235 carbon steel substrates (3.0 cm × 2.0 cm × 1.5 mm) were purchased from local suppliers. Deionized water (DI) was used during whole experiments.

2.2. Synthesis of NCDs (p-CDs and o-CDs)

The synthesis of the p-CDs and o-CDs followed a similar procedure reported by Lin et al. [7]. p-PD or o-PD (0.60 g) was first ultrasonically dissolved in ethanol (60 mL), and then the mixtures were transferred into poly(tetrafluoroethylene) autoclaves. After heating at 180 °C in oven for 12 h and cooling down to room temperature naturally, dark-red and orange suspensions were obtained from p-PD and o-PD. The crude product was purified with a dialysis bag (molecular weight cut-off ~3.0 kDa) for 1 day to remove the non-reactive molecules. After removal of solvents and further drying under vacuum, p-CDs and o-CDs were obtained.

2.3. Preparation of electrode and solutions

The Q235 carbon steel substrates (2.0 cm × 3.0 cm × 1.5 mm) were abraded with SiC abrasive papers of 300, 800 and 1000 grit, respectively. Then they were cleaned successively with acetone and alcohol, and finally dried with nitrogen gas. The 1 M HCl solution in the absence and presence of various concentrations (10, 50, 100 and 200 mg L^{-1}) of p-CDs or o-CDs was prepared from concentrated hydrochloric acid.

2.4. Characterization of NCDs

Scanning probe microscope (SPM, Veeco Dimension 3100 V) and transmission electron microscopy (TEM, Tecnai F20) were performed to examine the morphology and size of the prepared p-CDs and o-CDs. X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD) was employed to examine the chemical composition and bonding status. The Raman spectrum was recorded with a Renishaw inVia Reflex excited by 532 nm laser. UV–vis absorption spectra were recorded by a Lambda 950 UV–Vis spectrophotometer.

2.5. Electrochemical measurements

Polarization and electrochemical impedance spectroscopy (EIS) were conducted in a CHI660E electrochemical station with a conventional three-electrode system. A platinum foil and saturated calomel electrode (SCE) was used as counter and reference electrode, respectively. The Q235 carbon steel with the exposure area of 1 cm^2 was the working electrode. All tests were conducted at room temperature. Before the test, open circuit potential test (OCP) was carried out for 30 min to reach a steady state. Then EIS was performed in a frequency range of 100 kHz–10 mHz at the OCP with 10 mV of disturbance signal. The EIS data were fitted and analyzed with Zsimpwin 3.21 software. Eventually, potentiodynamic polarization tests were conducted in the potential range of ±500 mV versus the OCP with a scan rate of 5 mV s^{-1}. The same test was performed for 3 times to ensure reliability.

The current density mapping at the Q235 carbon steel surface during the immersion in corrosive medium was measured by the VersaScan SVET module from Princenton Applied Research (USA) using a Pt/Ir probe with a 10 μm of diameter. The amplitude of vibration was about 30 μm, the vibration frequency was 80 Hz along the Z direction and the scanned area was 1.0 mm × 1.0 mm. Before the test, the Q235 carbon steel was immersed in the corrosive medium for 2 h.

2.6. Weight loss tests

Weight loss tests were carried out in a 20 mL vessel placed in a constant temperature thermostat. Samples with a dimension of 1.0 cm × 1.0 cm × 1.5 mm were immersed in 1 M HCl solution in the absence and presence of various concentrations of p-CDs and o-CDs. The samples were removed, washed with DI, dried and weighed at various time intervals. The average value of weight loss was used for calculations.

2.7. Surface analysis

In order to measure the surface roughness of Q235 carbon steel sample after 72 h of immersion in 1 M HCl solution in the absence and presence of 200 mg/L of p-CDs and o-CDs, laser scanning confocal microscope (LSCM, LSM700) was employed. The morphology and surface composition of Q235 carbon steel after 72 h immersion in 1 M HCl solution in the absence and presence of 200 mg L^{-1} of p-CDs and o-CDs were examined with scanning electron microscopy (SEM, Zeiss) and energy dispersive spectroscopy (EDS).

3. Results and discussions

3.1. The characterization of p-CDs and o-CDs

The synthesis of p-CDs and o-CDs are achieved by heating the p-PD and o-PD in ethanol at 180 °C for 12 h. During the heating process, CDs were synthesized by the polymerization of precursor (condensation and intra-molecular cyclization), leading to the formation of CDs containing amino/hydroxyl functional groups on their surfaces. The corresponding structures are proposed according to previous reports [11–14]. The resulting products can be homogeneously dispersed into various solvents. As shown in Fig. 1, crimson and yellow solutions (from p-CDs and o-CDs, respectively) are observed when they are dispersed in ethanol. Red and orange solutions (from p-CDs and o-CDs, respectively) are observed when they are dispersed in 1 M HCl solution.

Subsequently, SPM and TEM are performed to examine the morphologies of p-CDs and o-CDs. As shown in Fig. 2a and 2b, the average sizes are about 15–20 nm for p-CDs and 4–6 nm for o-CDs, respectively, which are consistent with the TEM insets in Fig. 2. Most of the CDs are monodispersed while there are also some aggregated CDs. The variations of chemical compositions and bonds of the samples are checked with XPS spectra. The full XPS spectra of p-PD, p-CDs, o-PD and o-CDs as well as the corresponding contents of the elements are shown in Fig. 3 and Table 1. It can be found that they have same elemental compositions (i.e. C, N and O). However, the content of O and N shows a distinct variation after solvothermal reaction, owing to the occurrence of the decomposition, intermolecular cyclization, and condensation reactions during the formation of CDs.

Further, a detailed analysis on the XPS spectra of p-CDs and o-CDs is performed. It can be found from Fig. 4 that p-CDs and o-CDs exhibit similar C 1s, N 1s and O 1s spectra. The C1s spectra of p-CDs and o-CDs (Fig. 4a and d) display two peaks at 284.2 and 285.2 eV, which are attributed to C═C and C—N, respectively [7]. The N1s spectra are shown in Fig. 4b and e where the two component peaks are assigned to pyridinic N (398.8 eV) and pyrrolic N (400.4 eV) [6,7,15]. For O 1s spectra (Fig. 4c and 4f), the peak at binding energy of 531.8 eV is assigned to C—OH/C—O—C.

The Raman spectra of p-PD, p-CDs, o-PD and o-CDs are shown Fig. 5. For the p-PD, the peaks at 1612 cm^{-1}, 1264 cm^{-1}, 1174 cm^{-1}, 843 cm^{-1} and 647 cm^{-1} are assigned to benzene ring stretching deformation, C—N stretching, C—H in plane bending, the benzene ring breathing and bending deformation, respectively