

Self-healing and anti-corrosion performances of 1, 2, 4 - Triazole modified nano-silica hydrogels

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ABSTRACT

Nano-silica hydrogel modified by 1, 2, 4-triazole used as anti-corrosion additive was prepared, and the self-healing property as well as the anti-corrosion performance of the unmodified and modified hydrogels coatings on Q235 steel surfaces were investigated. In comparison to the anti-corrosion properties of the unmodified hydrogel, the migration of the corrosive media to the modified hydrogel coatings was significantly improved due to the addition of the 1, 2, 4-triazole and the increased compactness degree of the film. Electrochemical impedance spectroscopy results indicated that several stages did appear during the self-healing process. Finally, the self-healing as well as the anti-corrosion mechanism of the modified hydrogels was discussed.

1. Introduction

Owing to the convenient manipulation and cost-effective application, anti-corrosion coatings are widely used in preventing the corrosion of metals. Small cracks is likely to appear on anti-corrosion coating during its explosion to the corrosive condition, such underwater service, underground transportation and atmosphere corrosion environment. Extended exposure can accelerate the expansion of cracks [1,2], the protection performance of the coatings decrease with increasing the size of these crack. Based on this, the self-healing materials provided a new direction for the development of smart coatings [3–7]. White et al. [8–10] proposed a concept of self-healing composites called microcapsules. Microcapsules encapsulated with repairing agents were embedded into the coatings to repair cracks. Once the coatings on the metal substrate cracked, the capsules could rupture and release the repairing agents. The repairing agents flowed along the crack and repaired it through capillary action.

Hydrogel is a kind of safety, durable and environmental-friendly self-healing material, which has attracted much attention of researchers, especially in the biomedical field. Hydrophilic groups on polymer chains, such as amides, carboxyl, and hydroxyl, can absorb large amounts of water without distorting their original structures [11–14]. Due to the cross-linking with covalent bonds, notably, chemical hydrogels exhibited remarkable stability. Damaged areas can be

repaired owing to the reversible dynamic covalent bonds of the hydrogel, that is, new covalent bonds formed with or without specific stimuli (heat, light, or pH) [15–18]. Most importantly, in comparison to other methods, large cracks can be repaired continuously and repeatedly due to the nature of the hydrogel.

Self-healing materials are divided into two kinds, one is the extrinsic self-healing material, while the other is the intrinsic self-healing material [19]. The most commonly used anti-corrosion coatings are those based on the extrinsic self-healing system, cracks can be repaired by healing the agent which is stored in microcapsules [20–22], microvasculature [23–26], or other microcarriers [27–30]. However, there is a limitation that the extrinsic self-healing system can capacitate one-time repairing cycle at a certain position. On account of dynamic covalent crosslinking, the intrinsic self-healing materials achieved healing process [31–34], crack can be healed repeatedly at the same position [35]. Nano-silica hydrogel is a kind of innocuous and environment-friendly intrinsic self-healing material, which has potential usage in protecting metals from corrosion. Based on the aforementioned insights, this study will focus on the application of hydrogels in anti-corrosion coatings. The anti-corrosion coatings base on novel hydrogel and modifier will possess self-healing properties and anti-corrosion properties simultaneously, and provide a new route for coating modification.

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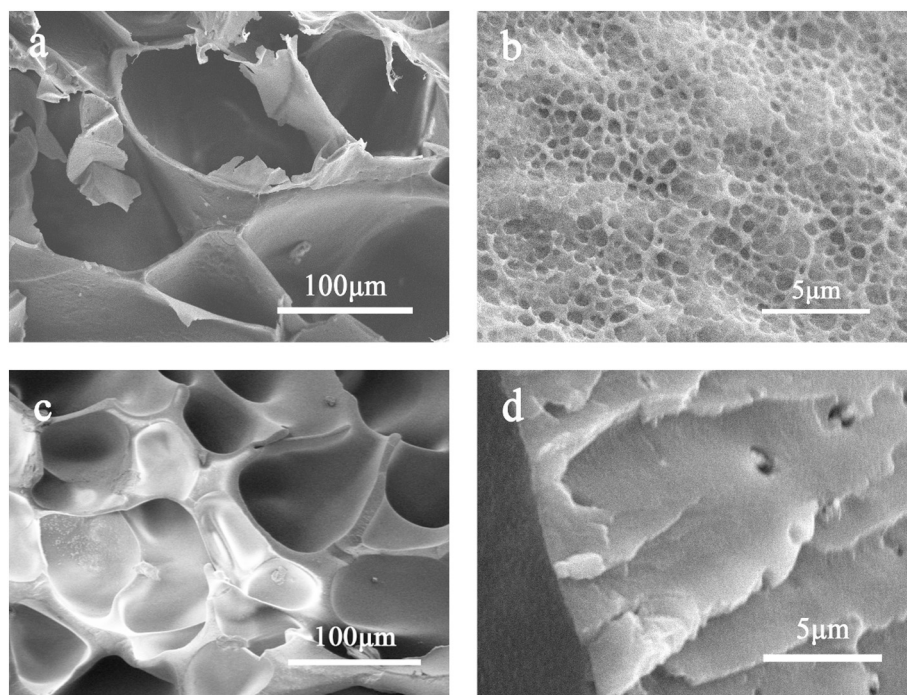


Fig. 1. SEM images of unmodified hydrogel (a-b) and modified hydrogel (c-d).

2. Experimental

2.1. Materials

Nano-silica hydrogel was chosen as self-healing polymer. In the synthesis of nano-silica hydrogels, potassium persulfate (KPS, Sigma-Aldrich) acted as redox initiator and tetramethylethylenediamine (TEMED, Sigma-Aldrich) acted as promoter, which induced free radical polymerization between N, N - dimethylacrylamide (DMA, Sigma-Aldrich) chains and nano-silicon (sol, LudoxTM-50, Sigma-Aldrich). Nano-silica hydrogel was modified by 1, 2, 4 - triazole (99%, Sigma-Aldrich).

2.2. Preparation of the hydrogels

7.80 mL of deionized water and 5.71 g of silicon sol were mixed and were stirred at room temperature. Then, 1.50 g DMA, 0.0410 g KPS, and 23 μ L TEMED were added. After stirring for 45 min, nano-silica hydrogel solute ion was obtained. The hydrogel solution was polymerized at 25 $^{\circ}$ C for 12 h. Then, nano-silica hydrogel was obtained. 1, 2, 4 - triazole was used to modify hydrogel. The modified nano-silica hydrogel solution was obtained by injecting 0.008 g 1, 2, 4 - triazole into the 15 mL nano-silica hydrogel solution and polymerized at the same condition. Finally, the modified hydrogel was obtained.

2.3. Characterization of the hydrogels

2.3.1. Morphological representation

The hydrogel was quickly frozen in liquid nitrogen and dried by freeze-dryer. The microscopic morphologies of the unmodified and modified hydrogels were observed using Hitachi S4800 scanning electron microscope.

2.3.2. Component analysis

The structures of the unmodified and modified hydrogels were analyzed using Ultimate IV X-ray diffractometer. The specific scanning parameters were operating voltage of 40 kV, current of 40 mA, radiation source of CuK α (wavelength of 0.154 nm), scanning range of

5 $^{\circ}$ –80 $^{\circ}$ and sweep speed of 10 $^{\circ}$ /min. Nicolet iS10 Fourier transform infrared spectrometer (FT-IR) was used to analyze the composition of unmodified hydrogel and modified hydrogel, and the spectrum was recorded in range of 600 cm^{-1} –4000 cm^{-1} .

2.3.3. Electrochemical characterization

Q235 steel electrodes were used as the metal substrates with exposed area of 1 cm^2 after ultrasonically degreased in acetone. The electrodes were sequentially polished by sandpaper of 120 $^{\#}$, 400 $^{\#}$ and 800 $^{\#}$, and dried after washing with distilled water and anhydrous ethanol for twice. The unmodified and modified hydrogels were coated on the surface of electrodes. The coated electrodes were stood for 12 h before electrochemical impedance test. The thickness of coatings on the surface of the electrode was about 2 mm. All electrochemical measurements were performed on an Autolab PGSTAT302N system. The classic three-electrode test system was adopted. The working electrode was hydrogel coated metal electrode, the reference electrode was saturated calomel electrode (SCE) and the auxiliary electrode was platinum electrode. The criterion of EIS measurements under steady state condition was estimated that the fluctuation of OCP was \pm 2 mV within 600 s. The frequency range was from 10 5 Hz to 10 $^{-2}$ Hz. 3.5 wt% NaCl was used as the corrosive electrolyte. All the tests were performed at 25 $^{\circ}$ C.

3. Results and discussion

3.1. Microscopic morphology of nano-silica hydrogels

There were significant differences in micromorphologies of the unmodified and modified hydrogel surfaces as shown in Fig. 1. The size of the pores of unmodified hydrogel (Fig. 1a) was in the range of 100 μ m to 200 μ m, which was larger than that of the modified hydrogel. Previously reported literatures suggested that these pores on the surface were caused by a great quantity of carboxylate ions [36–38]. Many micropores on the inner walls of these large pores. This phenomenon facilitated the absorption of water by promoting the diffusion of the water into the hydrogel structure [11–14]. After modification of the hydrogel using 1, 2, 4 - triazole (Fig. 1c and d), the inner wall of these

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