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Eco-friendly functionalization of hexagonal boron nitride nanosheets with carbon dots towards the reinforcement in protective performance of water-borne epoxy coatings

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1. Experimental Section

1.1 Synthesis of CDs

Citric acid monohydrate (2 g) was abraded with agate mortar, then covered on the watch glass and heated at 200 °C for 30 min. During the heating process, the white citric acid powders first became into orange-red liquid and finally turned into brown solid that adhered on the watch glass. After natural cooling to room temperature, deionized water was added to dissolve the products with ultrasonication, and then the mixed solution was dialyzed for 2 d and centrifuged at 9000 r for 5 min. The obtained sediments were dried to a constant weight in drying oven at 60 °C.

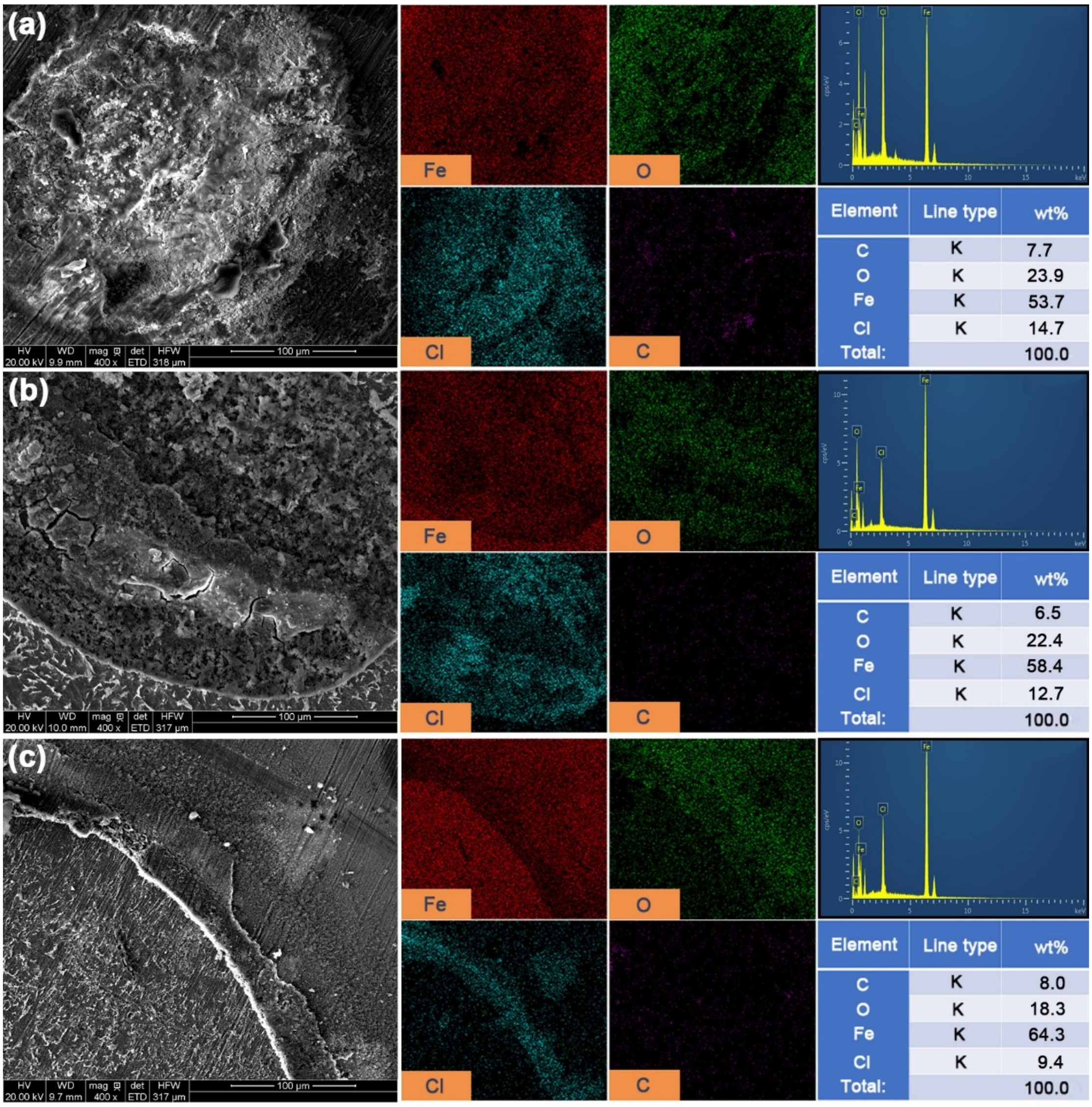
1.2 Characterization of Protective Performance of Coatings

Long-term EIS tests of the samples were carried out on the electrochemical workstation (CHI-660E, Chenhua, Shanghai) after different immersion time in 3.5 wt% NaCl solution, in which Q235 carbon steel electrode coated with different coatings, saturated calomel electrode, and platinum sheet was used as working electrode, reference electrode, and auxiliary electrode, respectively. Each EIS test was conducted at a stable OCP value with the frequency varying from 100 kHz to 10 mHz, and the amplitude sinusoidal voltage was 20 mV. The EIS results were fitted with Zview software.

LEIS was conducted on a VersaSCAN electrochemical scanning system, and more details could be seen in our previous investigation[1]. During the measurement, an artificial scratch with 4 mm of length was introduced into the coating surface using scalpel, and the tested area was 5 mm × 5 mm. In order to improve the visualization of the data, the final results were plotted as an admittance mapping.

In addition to the electrochemical techniques, salt spray tests based on ASTM B117 were used to evaluate the corrosion protection performance of samples. During the test, the samples with artificial scratches (3 cm of length) by scalpel were placed in a salt spray cabin containing 5 wt% NaCl solution at 45 °C.

2. Results



Element	Line type	wt%
C	K	7.7
O	K	23.9
Fe	K	53.7
Cl	K	14.7
Total:		100.0

Element	Line type	wt%
C	K	6.5
O	K	22.4
Fe	K	58.4
Cl	K	12.7
Total:		100.0

Element	Line type	wt%
C	K	8.0
O	K	18.3
Fe	K	64.3
Cl	K	9.4
Total:		100.0

Fig. S1. SEM images, EDS maps and elemental composition for the corrosion regions on the substrate surface beneath (a) pure WEP, (b) h-BN/WEP and (c) h-BN@CDs/WEP.

To monitor the corrosion status of the underlying metal substrate, the coating was first removed mechanically from the substrate surface after 34 d of immersion in 3.5 wt% NaCl solution, followed by cleaning the exposed metal surface with ethanol. As presented in Fig. S1a and b, the corrosion regions for the substrate surface coated with pure WEP and h-BN/WEP are very rough because of the severe corrosion, and a large number of corrosion products composed of C, O, Fe and Cl covers on the substrate surface. In contrast, the corrosion region underlying h-BN@CDs/WEP coating is relatively smooth, with less corrosion products, and corresponding contents of O and Cl elements are also lower than the contrast groups (Fig. S1c).

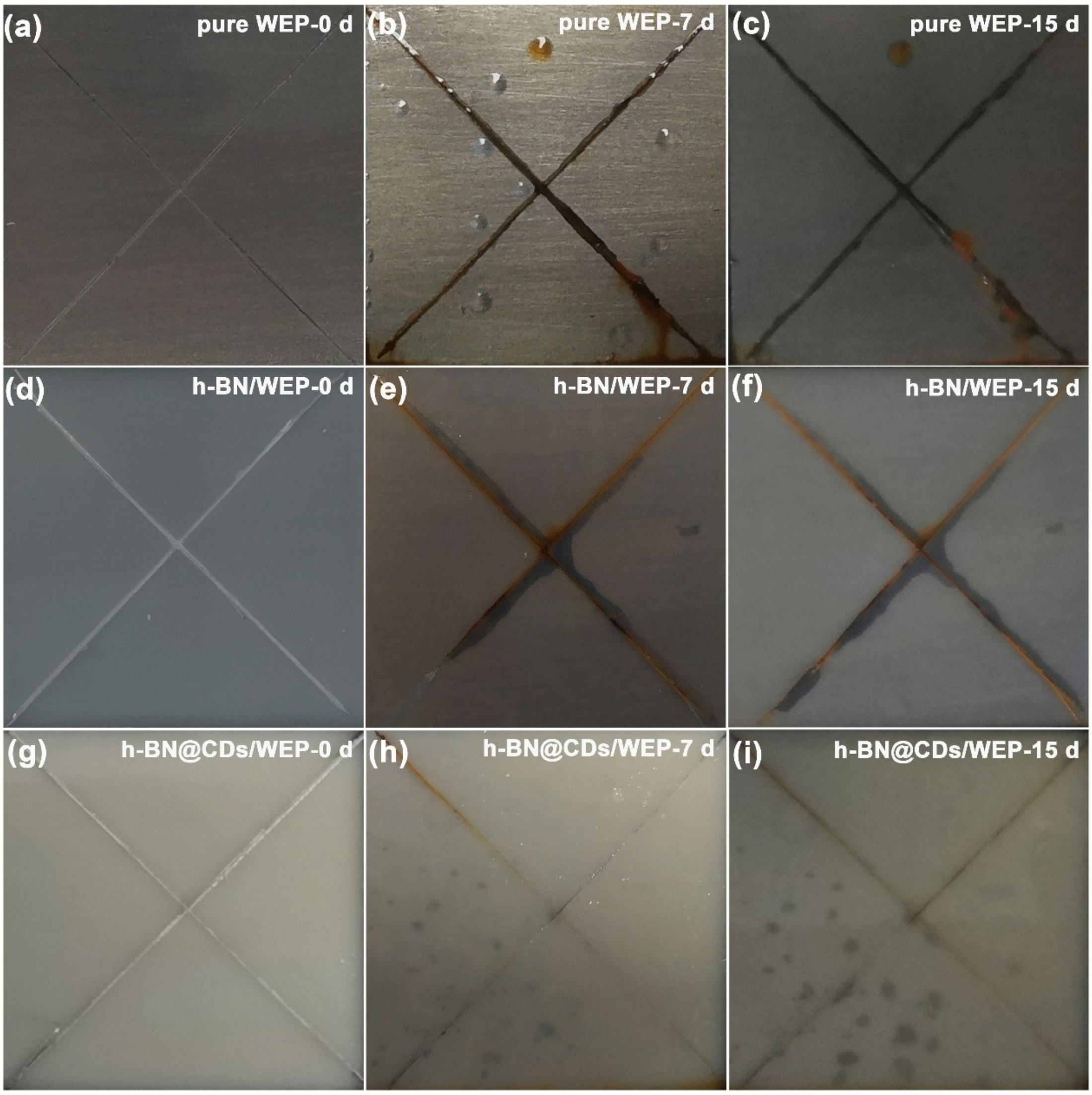


Fig. S2. Digital photos for the samples during the salt spray tests at various exposure time, (a, b, c) pure WEP, (d, e, f) h-BN/WEP and (g, h, i) h-BN@CDs/WEP coatings.

In case of pure WEP, obvious blister and rust appear at the edge of scratches after 7 d of salt spray test, and more corrosion rusts are formed and accumulated at the scratches with the exposure time up to 15 d (Fig. S2a-c). Similar with pure WEP, the scratches of h-BN/WEP have also been corroded seriously, and the black rust beneath the scratches of coating increases with the increasing exposure time (Fig. S2d-f). However, the substrates coated with h-BN@CDs/WEP show a different corrosion behavior from Fig. S2g-i. Owing to the penetration of corrosive medium, some small corrosion spots can be seen after 7 d of salt spray test, and the size of these corrosion spots increases with the exposure time up to 15 d.

1. M. Cui, S. Ren, J. Pu, Y. Wang, H. Zhao and L. Wang, *Corros. Sci.*, 2019, **159**, 108131.