Supplementary Information

A novel nitrogen doped carbon dot enhancing the anticorrosive performance of waterborne epoxy coatings

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Table S1. Product traits and specifications.

Project	Specification
Exterior	Yellow transparent liquid
Active hydrogen equivalent	280-320
Viscosity	7000-14000 mPa. S *25℃
Density	1.01
Available time	40-60 min *25℃

The waterborne curing agent (BSA-60) is an amine modified self-emulsifying epoxy curing agent, which has a strong hydrophilic group and excellent lipophilicity. It can emulsify bisphenol-A epoxy resin with molecular weight of 370-1000. Further, it can be added with 1-3 times of water to dilute without breaking the emulsion. And after fully curing, the composite serves as a physical barrier for corrosion protection with excellent mechanical strength and a certain gas permeability.

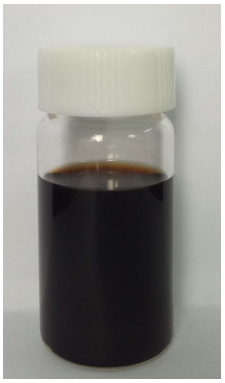

Fig. S1. The photograph of NCDs dispersed in ethanol.

We demonstrated that the resulted N-CDs could be homogeneously dispersed into ethanol, producing a dark brown solution as revealed in Fig. S1. No particles appear in the vial, so it can be concluded that the N-CDs can be dissolved in the ethanol solution.

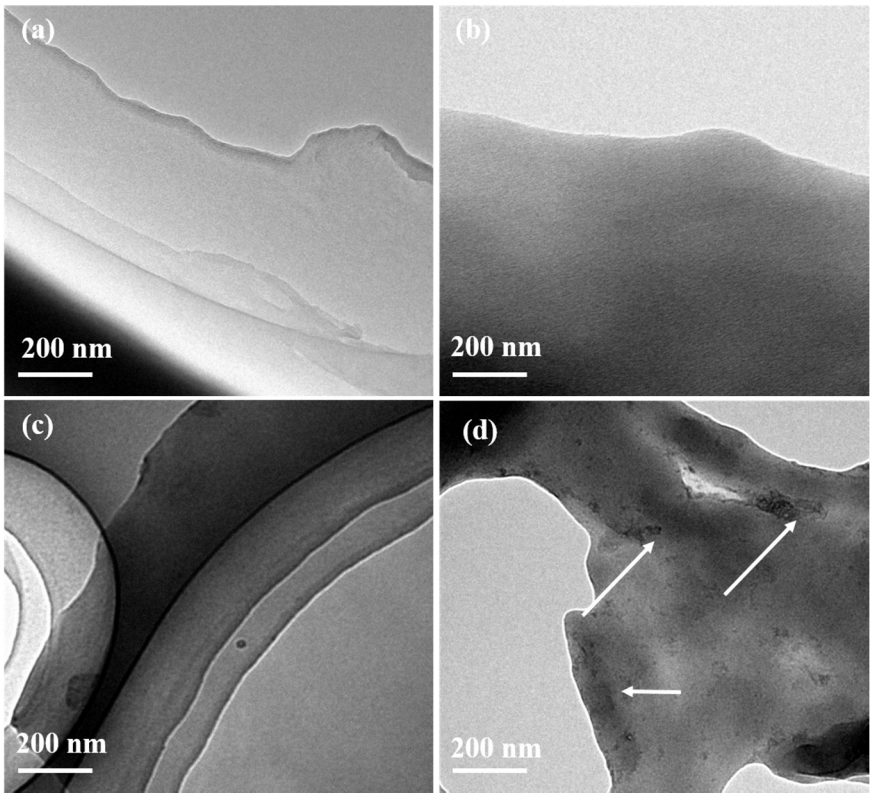

Fig. S2. TEM images of (a) pure EP, (b) 0.5% N-CDs-EP, (c) 1.0% N-CDs-EP, and (d) 2.0% N-CDs-EP.

To investigate the effect of the NCDs on the disperbility of waterborne epoxy coatings, the dispersion of NCDs in the EP matrix was studied by TEM. As can be seen in Fig. S2, the grey areas were related to the domain of the epoxy resin, while the profile of NCDs was displayed as dark points. Compared with the pure EP coating, serious aggregation was observed due to van der Waals forces in the 2.0% N-CDs-EP. Therefore, excessive N-CDs will cause an increase in coating defects which resulted in partial unevenness. Conversely, it was clearly observed that the appropriate content nanodots evenly dispersed or dissolved in in the epoxy matrix. These results confirmed that the compatibility between N-CDs and epoxy matrix was perfect (after adding into 0.5% and 1.0% N-CDs).

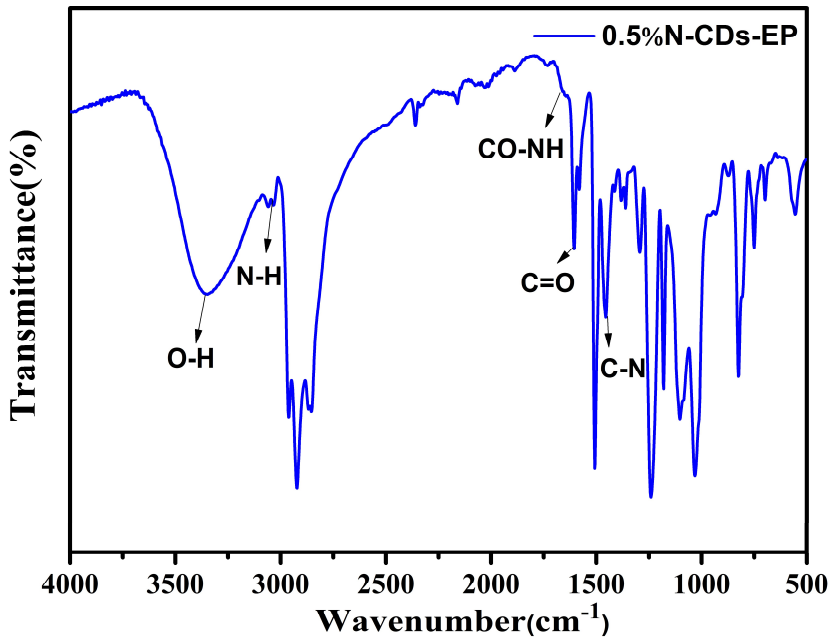

Fig. S3. FTIR spectra of 1.0% N-CDs-EP (marked with the main interactions).

The FTIR spectrum of the composite coating shows a 1732 cm−1 peak attributed to CO-NH, which is associated with the formation of covalent bond of CO-NH between N-CDs. Hydrogen bonding may be formed between two N-CDs or between N-CDs and the polymer chain. So the intensity of the absorption peaks increase and widen due to the dipole moment have a significant change compared with the pristine N-CDs (Fig. 3). The hydrogen bonding may involve the different functional surface groups of CDs forming O-H-N, O-H-O, N-H-N and N-H-O.

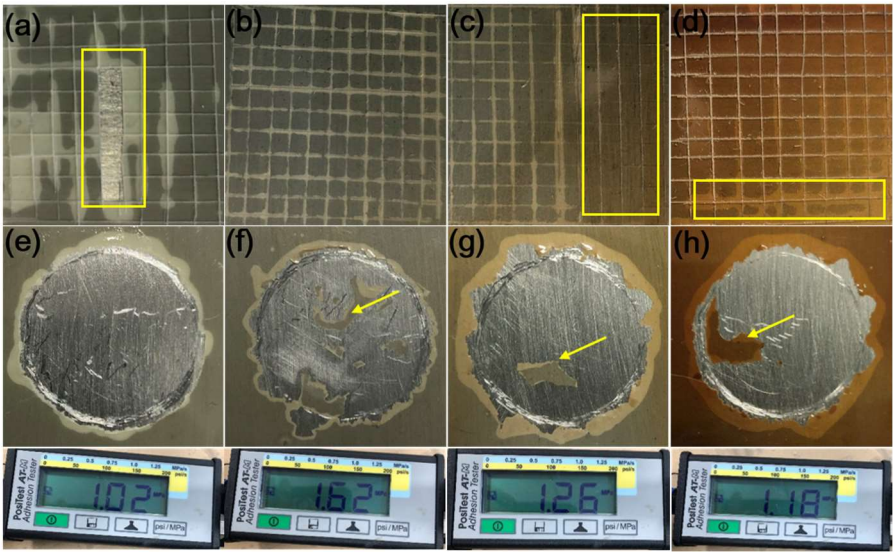

Fig. S4. Results of all as-prepared specimens after Machu and pull-off tests (a) (e) EP; (b) (f) 0.5% N-CDs-EP; (c) (g) 1.0% N-CDs-EP; (d) (h) 1.0% N-CDs-EP.

Adhesion strength was a key role to affect the stability and integrity of coatings on substrate, which was widely detected by Machu and pull-off tests. By test, the results were listed in Fig. S4. After Machu test, desquamation proportion of sample is a critical index to reflect the adhesion. By tearing three times, 6 grids of EP coating fell off from substrate, implying the relatively weak adhesion strength (Fig. S4a). After the addition of 0.5 wt% N-CDs, the adhesion strength was improved to some extent. There was no obvious desquamation for the samples with 0.5 wt% N-CDs, demonstrating good adhesion strength among all prepared coatings. Furthermore, compared with 0.5 wt% N-CDs-EP specimen, some delamination phenomena were detected on 2.0 wt% N-CDs-EP sample, revealing the declined trend of adhesion strength (Fig. S4d). The smallest adhesion strength (1.02 MPa), indicating the enhancement of adhesion strength after adulteration (Fig. S4e). Meanwhile, the largest value of adhesion strength was observed for 0.5 wt% N-CDs-EP specimen (1.62 MPa), implying the best strengthen effect (Fig. S4f).

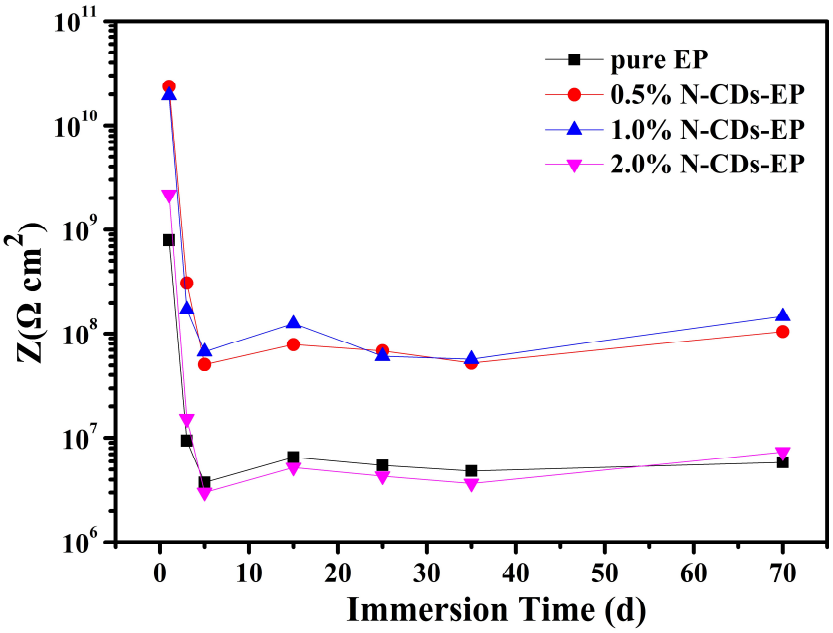

Fig. S5. The trends chart of impedance value at the frequency of 0.01 Hz.

The dependence of the impedance moduli at 10 mHz content is shown in Fig. S5. All the impedance moduli were higher than $10^{8.5}$ Ω·cm² at the time of beginning, indicating that all the surface coatings provided sufficient protection on the substrate. After 90 days of soaking, the impedance modulus of the coating film containing 1.0% N-CDs-EP was 1.48×10^{8} Ω·cm². The approximate impedance modulus (1.05×10^{8} Ω·cm²) is observed on the sample of 0.5% N-CDs-EP. The further increase on N-CDs content has no positive contribution in the impedance modulus. The modulus decrease in addition of 2.0% N-CDs suggests that the superfluous nanofiller might count against the film structure rather than improve the coating compactness.

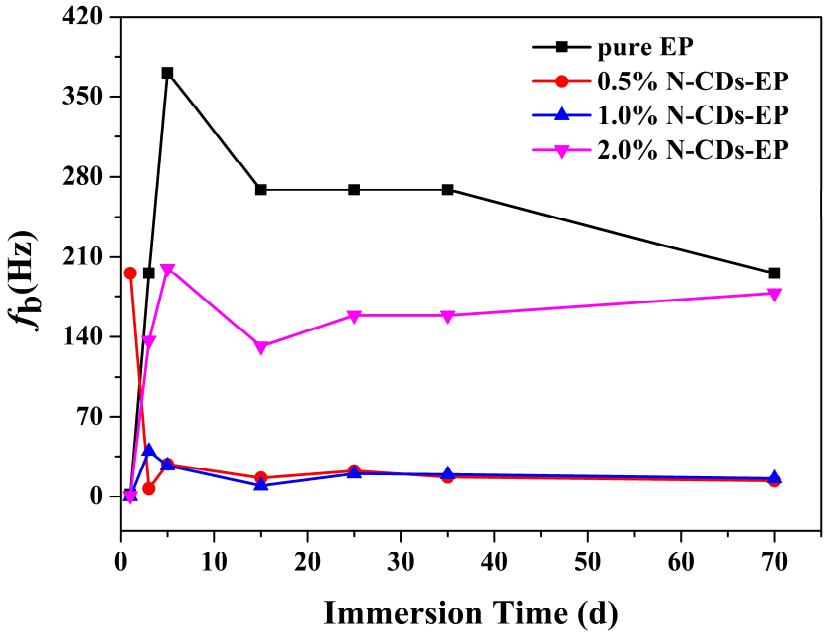

Fig. S6. The breakpoint frequency value (fb) as a function of immersion time for different coatings.

The coating can be evaluated by the breakpoint frequency value (f_b) on the Bode-impedance modulus curve. The f_b value generally refers to the corresponding frequency value when the phase angle is 45°. The f_b value is corresponding to the electrochemically active surface area (peeling area) of the electrode surface. In general, the larger the peeling area, the larger the f_b value. As shown in Fig. S6, the f_b value of a pure EP coating increases with soaking time. It indicated that the pure EP coating peeled off from the carbon steel substrate during the soaking process, and the peeling area increased continuously. However, the f_b value of 0.5% and 1.0% N-CDs-EP coatings did not change significantly during the immersion process, indicating that the corrosive medium has not yet reached the steel/coating interface, no peeling between the coating and the carbon steel substrate. The result proved that the N-CDs-EP coating had better adhesion to the carbon steel substrate.