Supplementary material

1 Experimental procedure

1.1 Sample preparation

The chemical reagents (analytically pure) used in the test including TEOS, polyvinylpyrrolidone (PVP, K30), cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH, 98%), ammonia ($NH_3 \cdot H_2O$, ≥28%) and MBT were from Shanghai Maclean’s Biochemical Technology Co., Ltd. And sodium chloride(NaCl), hydrochloric acid (HCl, 37%), ethanol, CS, span 80, acetic acid, formaldehyde, liquid paraffin were from Sinopharm Group Chemical Reagent Co., Ltd. The organic coating was SYLGARD 184. Polydimethylsiloxane (PDMS, part A) and 2,4,6,8-tetraethyl-2,4,6,8-tetramethylcyclotetrasiloxane (Curing agent, TEETMCT, part B) were from Dow Chemical Company (analytically pure). Cu electrode (99.99%, 10 mm×10 mm×10 mm) was from Shengxin Corrosion Detection Equipment Specimen Processing Centre, Yangxin County, Binzhou. The water used in all experiments was distilled water.

1.2 Preparation of HMSN

HMSNs prepared by sol-gel method were referenced TENG et al [1]. A 100 mL beaker was taken, and 15 mL of ethanol, 25.5 mL of water were added to make a mixture. Then 0.5 mL of TEOS, 0.08 g of CTAB and 0.5 mL of $NH_3 \cdot H_2O$ were added. The product was stirred continuously for 3 h at 100 r/min using a magnetic stirrer. The product was washed with distilled water and ethanol alternately for centrifugation at least five times after stirring. It was dried under vacuum, and roasted in a muffle furnace at a ramping rate of 5 °C/h. The product was kept at 200 °C for 2 h and then ramped up to 600 °C for 6 h. The preparation of HMSNs was showed as Step 1 in Figure S1(a).

1.3 Loading MBT into HMSN

1 g of ground HMSNs was placed in a reaction beaker, and 40 mL of ethanol solution with MBT content of 40 mg/mL was added to the beaker. The mixture was magnetically stirred for 48 h. The mixture was absorbed under absolute vacuum in a vacuum drying oven for 1 h, and then left at atmospheric pressure for 30 min. Then vacuum operation was repeated three times to ensure that the HMSN was fully loaded with MBT. Finally, the solid was separated by centrifuge, washed with anhydrous ethanol three times, and put into a blast drying oven for drying at 80 °C for 24 h. After drying, the HMSN loaded with MBT was obtained (HMSN-MBT). This was described as Step 2 in Figure S1(b).

1.4 CS coated HMSN-MBT

The CS-acetic acid solution was prepared. 3 g of CS was dissolved in 100 mL of 3 % acetic acid solution at room temperature. It was magnetic stirred in a water bath at 50 °C for 1 h. The solution was cooled and left to stand until the bubbles were eliminated. A certain amount of HMSN-MBT was placed in a beaker containing 80 mL liquid paraffin. 2 mL Span80 was added under magnetic stirring. The temperature was raised to 40 °C after stirring. 10 mL of CS-acetic acid solution was added slowly drop by drop at 40 °C under constant stirring. Then it was emulsified at constant temperature for 2 h. Gradually, 6 mL of formaldehyde was added drop by drop. The product was crosslinked and cured for 4 h, and then allowed to cool. After centrifugation and separation, the sample was washed with anhydrous ethanol 4 times. Then sample was put into a vacuum drying oven at 60 °C for 24 h to prepare CS-HMSN-MBT. The complete preparation process of the CS-HMSN-MBT is shown as Step 3 in Figure S1(c).

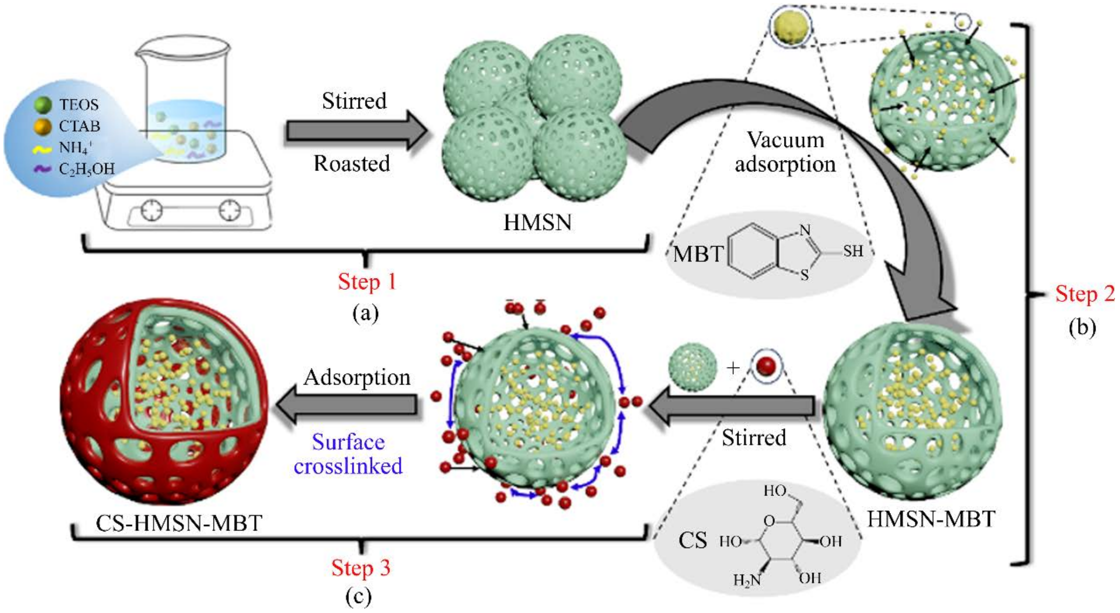


Figure S1 Synthetic process of CS-HMSN-MBT

1.5 Preparation of active protection coating

The PDMS (part A) and TEETMCT (part B) components were mixed at 10:1 and divided into three groups. The first group without adding any microspheres named blank coating. The other two groups were added with 18 wt.% of HMSN-MBT and 18 wt.% of CS-HMSN-MBT respectively. And two groups were named HMSN-MBT coating and CS-HMSN-MBT coating, respectively. The prepared coatings were coated on the surface of copper electrodes with a thickness of about 100 μm. And then the coated electrodes were cured at 40 °C for 48 h. Before the following experiments, scratches with a width of about 50 μm were created on the prepared three sets of coatings.

1.6 Test procedures

pH-responsive kinetic test was based on conditions of UV-Vis test and EIS test. pH=3 and 9 were chosen in the work. CS and MBT were dissolved in two sets of 3.5 wt.% NaCl solutions with pH=3 and 9 respectively. The pH of the solution was adjusted by HCl and NaOH. The absorbance of the mixed CS and MBT solutions was measured in the range of 200−400 nm. The absorbance values of CS and MBT were determined by fixing the maximum absorption wavelength. The standard absorbance curves of CS and MBT were obtained. CS-HMSN-MBT was dissolved in NaCl solution at pH=3 and pH 9, respectively. Absorbances of mixed solutions at different times were measured (20 min, 1 h, 3 h, 12 h, 24 h, 36 h, 48 h, 72 h, 100 h). Finally, the results were substituted into the standard absorbance curve for quantitative analysis. The HMSN-MBT coating and CS-HMSN-MBT coating were subjected to immersion tests at pH=3, 7 and 9 for 72 h, respectively. Based on the release kinetic equation, the MBT release rate at different pH was calculated. Corrosion protection of pH response was analyzed. Test frequency was 10^{-2}−10^{5} Hz, and AC voltage amplitude was 10 mV. The change of the scratch voltage of CS-HMSN-MBT coating before and after healing was analyzed by SKP. The test area covered the scratch’s 2 mm×2 mm with a scanning step of 100 μm.

2 Additional results and discussion

2.1 TG testing

TGA and DTG were carried out on the CS-HMSN-MBT, HMSN-MBT and other components to detect the loading capacity of HMSN. The results of tests are shown in Figure S2. According to the TGA results, CS was completely burned up in the selected temperature range of 30−800 °C (Figure S2(a_1)). The mass of MBT began to decrease rapidly at 230 °C until it became zero at 650 °C. MBT was also completely pyrolyzed in the selected temperature range (Figure S2(a_2)). The mass of HMSN did not change significantly in the temperature range of 30–800 °C, and eventually there was only about 1 wt.% (Figure S2(a_3)). Therefore, it is reasonable to choose the temperature range of 30–800 °C for the TGA testing.

The TGA results can prove the loading capacity of HMSN for two functional reagents and reflect the loading to a certain extent. Three rapid mass loss phases started at about 88, 280 and 510 °C (Figure S2(b)). This was consistent with the mass loss characteristics of CS and MBT. After TGA testing, the final mass loss of HMSN-MBT was about 6 wt.% (Figure S2(a_4)). The onset of mass loss was consistent with the weight loss curve of MBT. Therefore, according to the calculation, it can be obtained that HMSN-MBT was formed. And HMSNs were loaded MBT with 6 wt.%. The final mass loss of CS-HMSN-MBT was about 50 wt.% (Figure S2(a_5)). Therefore, the test phenomenon proved that HMSN loaded with MBT was coated by CS.

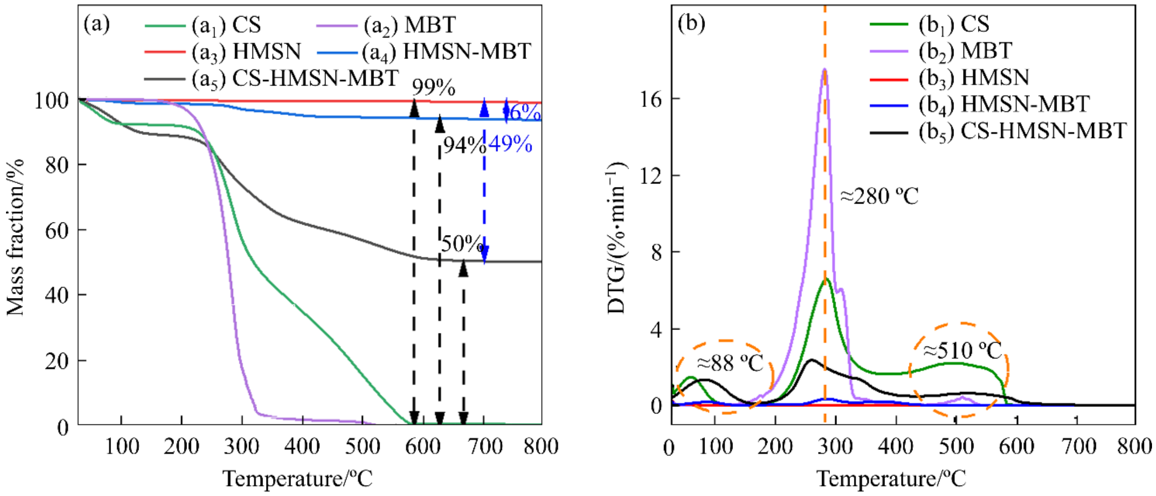


Figure S2 TG test (a) of CS (a_1), MBT (a_2), HMSNs (a_3), HMSN-MBT (a_4), and CS-HMSN-MBT (a_5); DTG test (b) of CS (b_1), MBT (b_2), HMSN (b_3), HMSN-MBT (b4), and CS-HMSN-MBT (b_5)

2.2 Dispersion testing

1 wt.% HMSN (Figure S3(a)), 1 wt.% HMSN-MBT (Figure S3(b)) and 1 wt.% CS-HMSN-MBT (Figure S3(c)) added to the PDMS suspensions and sustained from 0 to 48 h are shown in Figure S3. HMSN, HMSN-MBT and CS-HMSN-MBT were dispersed and suspended in the PDMS at the initial stage (Figures (a_1, b_1, c_1)). As time went by, CS showed a tendency of good compatibility, while the first two had already agglomerated. After standing for 24 h, it was observed that a small amount of HMSN and HMSN-MBT particles had already settled at the bottom of glass bottles (Figures (a_2, b_2)). After 48 h standing, the PDMS suspensions with HMSN and HMSN-MBT underwent large settlement (Figures (a_3, b_3)). There was almost no settlement in the PDMS suspensions of CS-HNTs-MBT (Figure (c_3)). That indicated CS improved the compatibility of inorganic HMSN (Figure (c)). And the dispersion property of composite microspheres in the coatings also was improved.

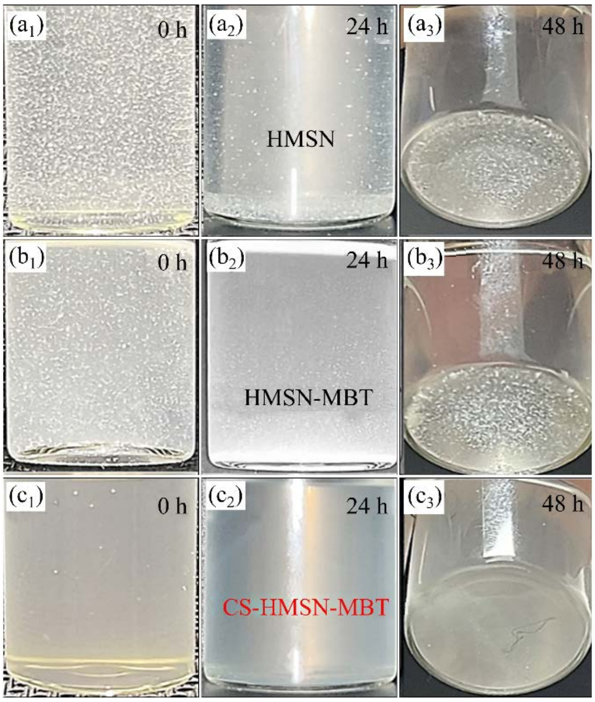


Figure S3 Sedimentation phenomena of HMSNs (a_1, a_2, a_3), HMSN-MBT (b_1, b_2, b_3), and CS-HMSN-MBT (c_1, c_2, c_3) in PDMS from 0 to 48 h

2.3 EIS testing

From the circuit element parameters, the C_{dl} showed a significant decreasing trend from 6.52×10^{-6} F·cm^{-2} to 6.54×10^{-7} F·cm^{-2}. That represented that the exposed scratch surface area was reduced due to the rapid repair of the coating damage. The water penetration in the scratches was significantly reduced. Q_c also decreased significantly from 2.49×10^{-5} F·cm^{-2}·s^{n} to 5.08×10^{-7} F·cm^{-2}·s^{n}. R_c increased from 1.27×10^{4} Ω·cm^{2} to 1.85×10^{5} Ω·cm^{2}. The resistance of the CS-HMSN-MBT coating, R_c, at the scratch of electrolyte increased. The increase in R_{ct} indicated that metal dissolution reaction was weakened. There was a repair effect that hinders the reaction between metal and electrolyte solution.

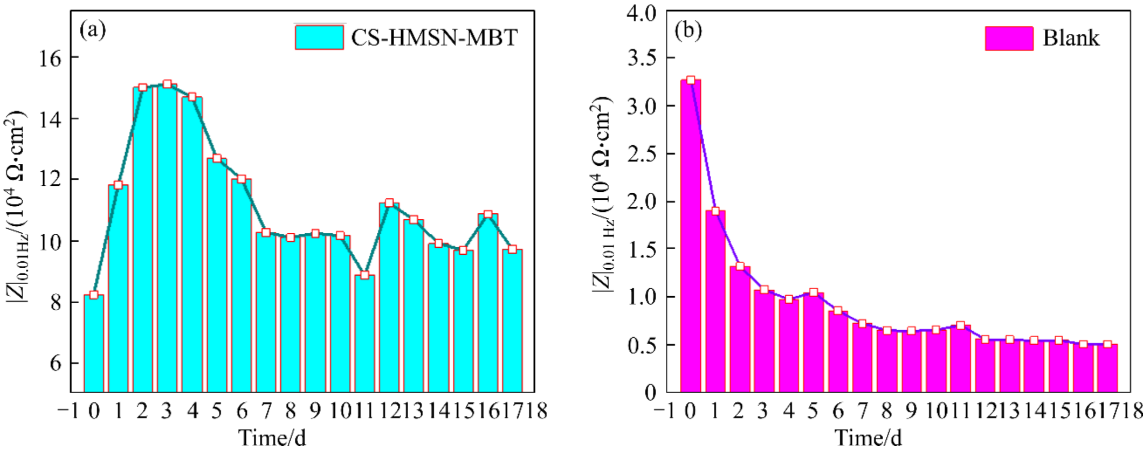


Figure S4 $|Z|_{0.01Hz}$ of CS-HMNSN-MBT coating (a) and blank coating (b) from 0 d to 18 d

The Q_c and C_{dl} of blank coating gradually increased. The Q_c increased from 1.97×10^{-5} F·cm^{-2}·s^{n} to 9.17×10^{-4} F·cm^{-2}·s^{n} and C_{dl} increased from 3.71×10^{-5} F·cm^{-2} to 4.52×10^{-3} F·cm^{-2} proved that the corrosion of copper at the scratch was not inhibited. The water penetration in the scratches was significantly increased. The values of R_c decreased from 8.00×10^{2} Ω·cm^{2} to 29.5 Ω·cm^{2} and R_{ct} decreased from 5.12×10^{2} Ω·cm^{2} to

28.7 Ω·cm^2 indicated that corrosion reaction was increased. The resistance of the blank coating reaction resistance at the scratch of electrolyte decreased. In this test, the damaged blank coating did not have function of repairing the scratch. R_c from fitting results showed a decreasing trend. At the end of test, anticorrosive property of CS-HMNSN-MBT coating was much larger than that of the blank coating.

Table S1 Fitting impedance data of CS-HMSN-MBT coating

Time/d	R_s/(Ω·cm^2)	Q_c/(F·cm^{-2}·s^n)	n	R_c/(Ω·cm^2)	C_{dl}/(F·cm^{-2})	R_{ct}/(Ω·cm^2)	Z_w/(Ω·cm^2)
0	63	2.49×10^{-5}	0.67	1.27×10^{4}	6.52×10^{-6}	8.56×10^{4}	1.78×10^{-4}
3	62	5.08×10^{-7}	0.74	1.85×10^{5}	6.54×10^{-7}	4.28×10^{5}	3.80×10^{-5}
6	67	9.54×10^{-7}	0.84	8.54×10^{4}	8.53×10^{-6}	2.42×10^{5}	2.15×10^{-5}
10	64	1.05×10^{-6}	0.54	3.90×10^{4}	2.14×10^{-6}	1.54×10^{5}	5.07×10^{-5}
18	61	2.07×10^{-6}	0.61	2.87×10^{4}	4.82×10^{-6}	7.71×10^{4}	4.25×10^{-5}

Table S2 Fitting impedance data of blank coating

Time/d	R_s/(Ω·cm^2)	Q_c/(F·cm^{-2}·s^n)	n	R_c/(Ω·cm^2)	C_{dl}/(F·cm^{-2})	R_{ct}/(Ω·cm^2)
0	64	1.97×10^{-5}	0.72	8.00×10^{2}	3.71×10^{-5}	5.12×10^{2}
3	62	8.84×10^{-5}	0.77	3.55×10^{2}	1.10×10^{-4}	4.78×10^{2}
6	67	3.05×10^{-4}	0.65	1.12×10^{2}	1.32×10^{-2}	2.67×10^{2}
10	62	4.28×10^{-4}	0.90	69.8	3.37×10^{-4}	77.1
18	61	9.17×10^{-4}	0.84	29.5	4.52×10^{-3}	28.7

2.4 pH-responsive testing

Under alkaline conditions, CS can be stably coated on HMSN. CS plays a certain role in the encapsulation of MBT. It was possible to achieve 0.81 of relative release rate at pH=9. The release rate of CS-HMSN-MBT coating was slower than that of HMSN-MBT coating. CS avoided excessive release of MBT under alkaline environment. In pH=3, metals were susceptible to corrosion. CS dissolved in acidic solutions and the rate of CS-HMNSN-MBT coating repair increased. This was due to the dissolved CS synergizing with the MBT to repair the coating scratches. The repair rate of CS-HMNSN-MBT coating was twice that of HMSN-MBT coating, which is partly due to chitosan dissolution and partly due to the uniform dispersion of CS-HMNSN-MBT. The CS-HMNSN-MBT coating achieves fast repair and avoids excessive corrosion of metal scratches in acidic environments. Unlike alkaline conditions, the metal itself is not prone to corrosion, a similar interpretation for CS-HMNSN-MBT coating in pH=7 solution with that in pH=3 solution.

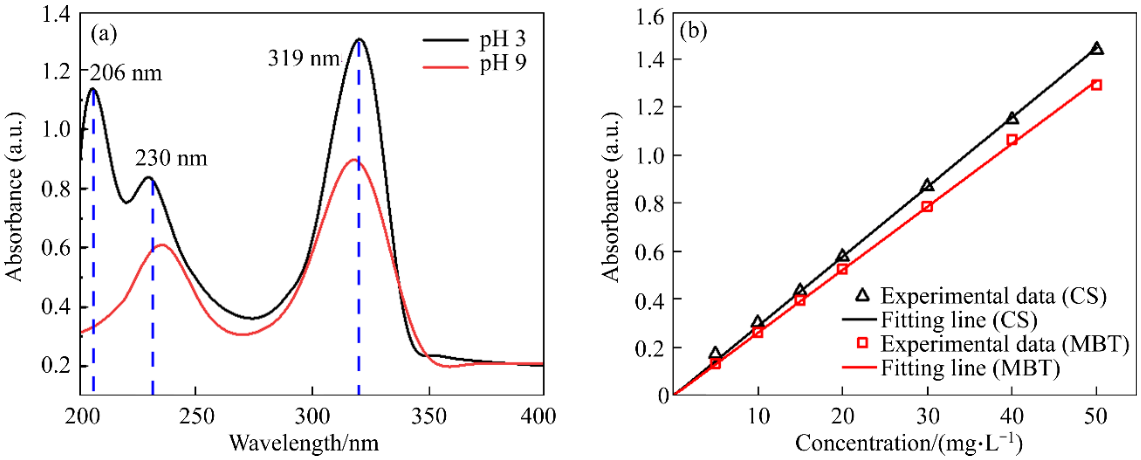
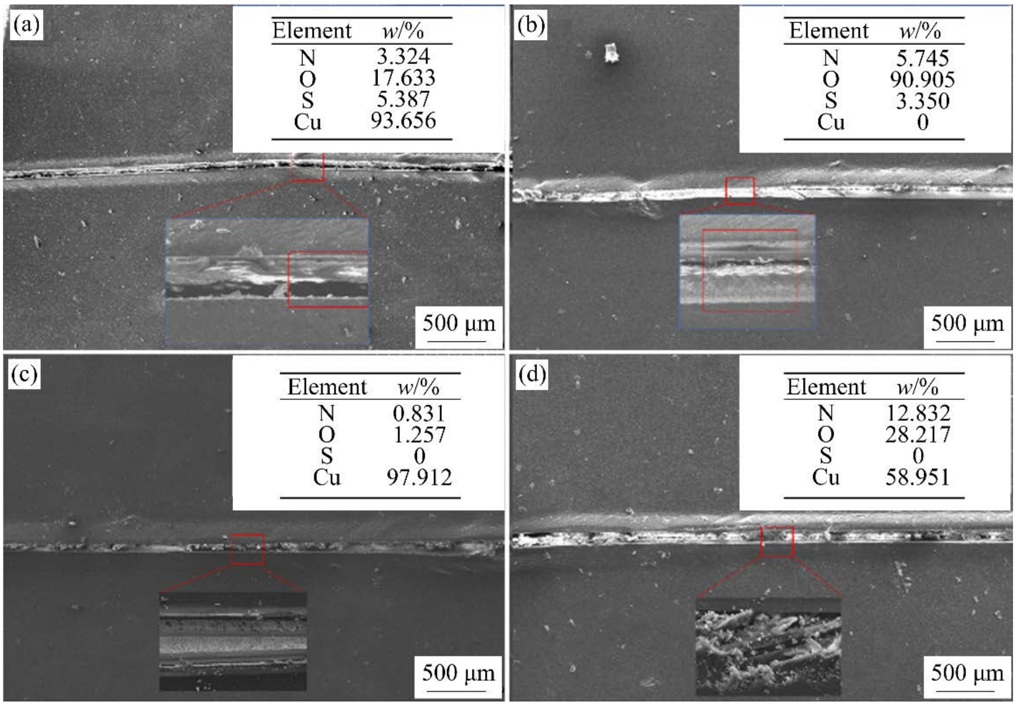


Figure S5 UV-Vis absorption spectra of CS and MBT in 3.5 wt.% NaCl solution with pH=3 and pH=9 (a), UV-Vis absorption standard curves of CS and MBT obtained by linear fitting (b)

3.7 Active protection performance testing

SEM and EDS were carried out on the scratched area of CS-HMSN-MBT coating and blank coating immersed in 3.5 wt.% NaCl solution after 0 d and 3 d are shown in Figure S6. The copper substrate was exposed to the external environment in the initial immersion. The copper content of CS-HMSN-MBT coating in the scratched area reached 93.656 wt.% (Figure S6(a)). The copper content of blank coating in the scratched area reached 97.912 wt.% (Figure S6(c)). Subsequently, when coating was immersion in 3.5 wt.% NaCl solution, CS-HMSN-MBT coating responded to the alterative miro-environment. MBT was released from HMSN and gradually repaired the coating. However, blank coatings continue to corrode due to without active protective fillers. After 3 d immersion, the oxygen content of blank coating scratches increased and the copper content decreased. Corrosion products appeared on the scratched surface (Figure S6(d)). The copper content of blank coating scratches remained at 58.951 wt.%. MBT produced a dense protective film with the copper substrate in CS-HMSN-MBT coating. The bare scratches were covered by a protective film (Figure S6(b)). The substrate was isolated from the external environment. The copper content at the scratches was significantly reduced to 0.000 wt.%. Therefore, it can be proved that the scratches were repaired by MBT.



(a)

Element	*w*/%
N	3.324
O	17.633
S	5.387
Cu	93.656

(b)

Element	*w*/%
N	5.745
O	90.905
S	3.350
Cu	0

(c)

Element	*w*/%
N	0.831
O	1.257
S	0
Cu	97.912

(d)

Element	*w*/%
N	12.832
O	28.217
S	0
Cu	58.951

Figure S6 SEM and EDS images of CS-HMSN-MBT coating (a, b) and blank coating (c, d) after immersion in 3.5 wt.% NaCl solution for 0 d (a, c), 3 d (b, d)

References

[1] TENG Zhao-gang, HAN Yan-dong, LI Jun, et al. Preparation of hollow mesoporous silica spheres by a sol-gel/emu/sion approach [J]. Microporous and Mesoporous Materials, 2010, 127(1): 67−72. DOI: 10.1016/j.micromeso.2009.06.028.