PH-Sensitive Self-Healing Waterborne Epoxy Coating: Poly-dopamine grafted Graphene Oxide with 2-Mercaptobenzimidazole Inhibitors and Cerium Cation towards Anti-Corrosion Performance

Shengle Hao [1,2], Shiyu Hou [1] *, Ding Nan [3], Deping Xu [1] *, Wanci Shen [2], Feiyu Kang [4] and Zheng-Hong Huang [2]

[1] School of Chemical & Environmental Engineering, China University of Mining & Technology (Beijing), Beijing 100083, China
[2] Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[3] College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China
[4] Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen, 518055, China
* Correspondence: housy@cumtb.edu.cn (S. Hou), xdp1073@163.com (D. Xu)

1. Characterization of MCPG

As shown in **Figure S1**, PDGO and MCPG were synthesized using a straightforward and facile method. After dry freezing, 136.4 mg of MCPG composites were obtained.

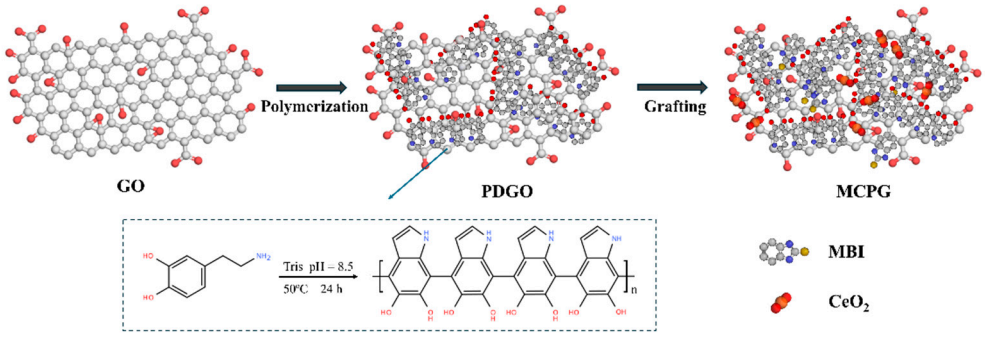


Figure S1. The preparation schematic of PDGO and MCPG composite materials.

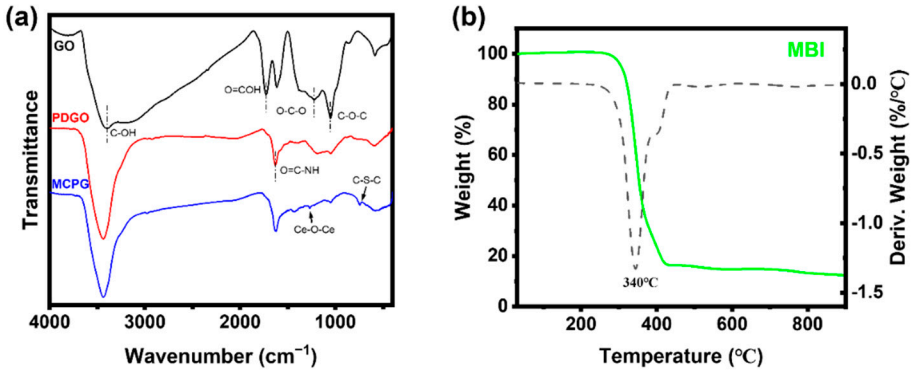


Figure S2. (a) FT-IR spectra of GO, PDGO and MCPG; (b) TGA curves of MBI

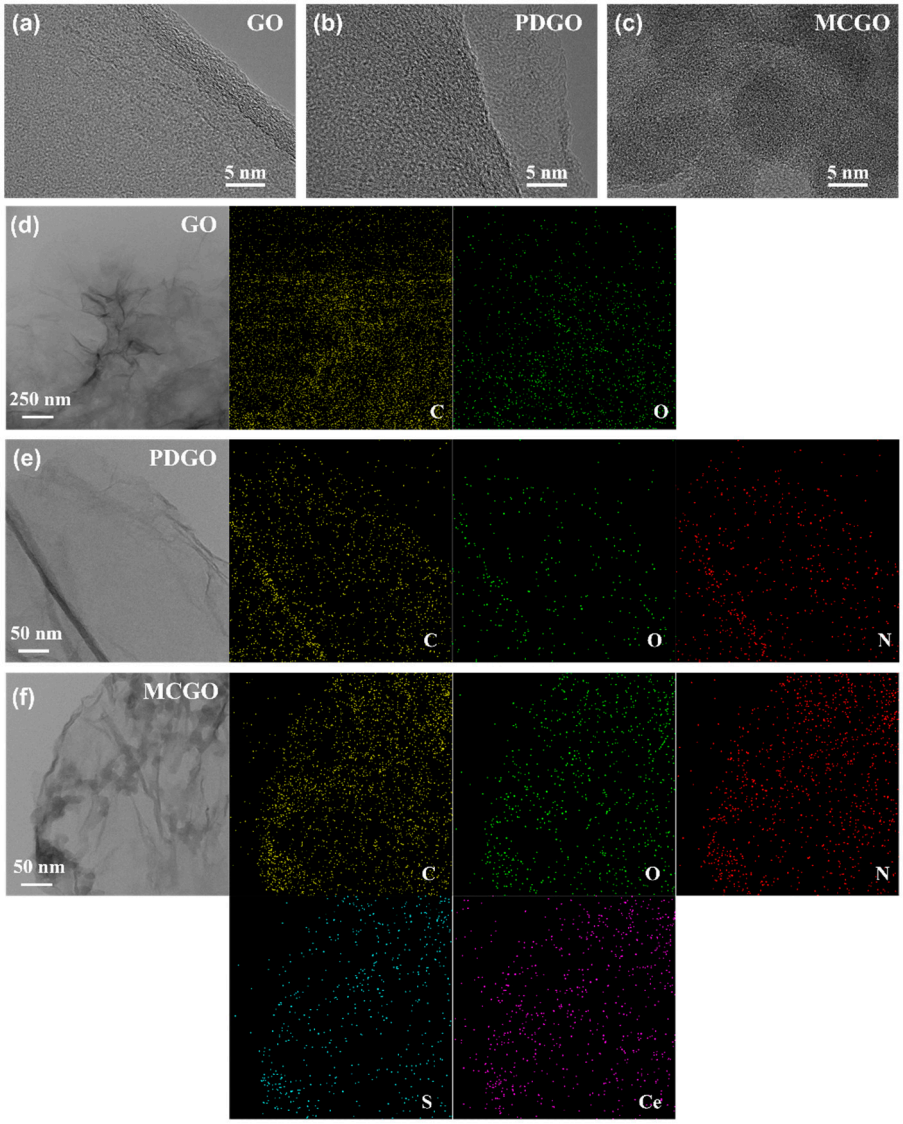


Figure S3. (a-c) TEM image in high magnification and (d-f) EDS mapping of GO, PDGO and MCPG.

2. Anti-corrosion performance of composite coatings

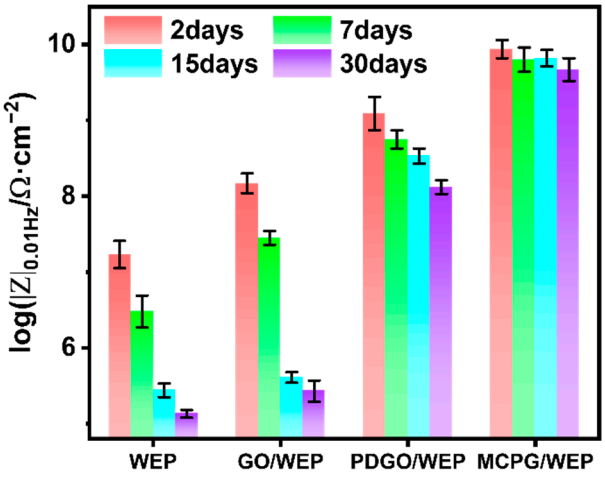


Figure S4. $|Z|_{0.01}$ Hz of different coatings during immersion

Table S1. The fitted electrochemical parameters of corresponding equivalent electrical circuit models

Samples	Times	CPE_{coat}		R_c	CPE_{dl}		R_{ct}
		$\times 10^{-9}$ $F \cdot s^{(n-1)}/cm^2$	n_1	$\times 10^7$ Ω/cm^2	$\times 10^{-8}$ $F \cdot s^{(n-1)}/cm^2$	n_2	$\times 10^7$ Ω/cm^2
WEP	2 d	35.2	0.96	1.19	74.9	0.52	3.86
	7 d	53.2	0.95	0.10	86.6	0.43	2.14
	15 d	354.8	0.70	0.02	5601	0.83	0.04
	30 d	617.6	0.68	0.01	5807	0.68	0.01
GO/WEP	2 d	6.3	0.93	15.8	3.92	0.65	80.6
	7 d	12.3	0.84	1.98	28.3	0.78	18.6
	15 d	44.7	0.81	0.03	1957	0.38	0.07
	30 d	132.5	0.73	0.02	3340	0.73	0.03
PDGO/WEP	2 d	1.20	0.82	64.7	7.23	0.74	92.3
	7 d	2.04	0.80	35.8	11.3	0.28	44.7
	15 d	2.88	0.86	24.0	16.9	0.74	9.95
	30 d	3.63	0.91	15.8	86.1	0.73	1.65
MCPG/WEP	2 d	0.21	0.99	1318	\	\	\
	7 d	0.28	0.89	794.3	\	\	\
	15 d	0.25	0.93	645.7	0.18	0.53	674.5
	30 d	0.36	0.94	213.8	2.88	0.88	215.4

3. Anti-Corrosion Effect on Q235 Steel of Different Inhibitors

SEM/EDS tests after EIS tests of scratched coatings.

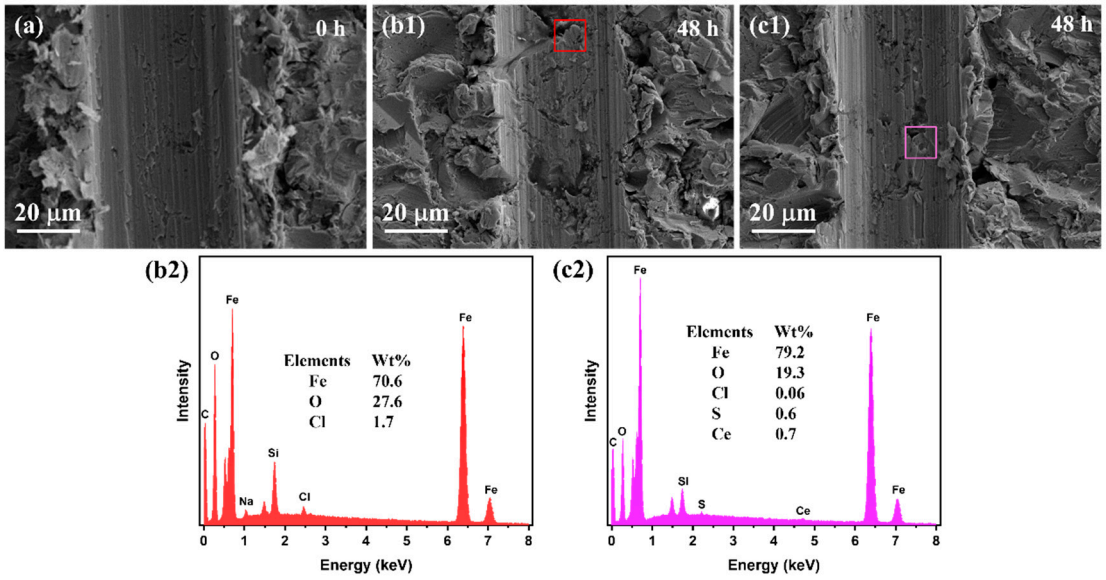


Figure S5. (a) SEM image of scratched WEP-coated sample; SEM/EDS exploration of rust layer beneath (b1, b2) WEP and (c1, c2) MCPG/WEP scratched coatings after EIS tests.

Weight Loss Method

As shown in **Figure S6**a, the corrosion inhibition efficiencies (η) of inhibitors composed by the 3.5 wt.% NaCl solution containing 150 mg/L of PDA, MBI or $Ce(NO_3)_3 \cdot 6H_2O$ at various pH of 3, 5, 7, 9 and 11 were calculated by weight loss method after immersing the blank Q235 steel specimens for 8 h at 25ºC.

$$\eta = \frac{\Delta m_0 - \Delta m}{\Delta m_0}$$

where Δm and Δm_0 is the weight loss (mg) of samples in the NaCl solutions with and without inhibitors. The Q235 steel specimens were sonicated successively with DI water, acetone and ethanol for 10 min, and then dried before weighing.

Tafel Test

Figure S6b presents the dynamic potential polarization curves for blank Q235 steel in 3.5 wt.% NaCl solutions containing 150 mg/L of PDA, MBI and $Ce(NO_3)_3 \cdot 6H_2O$. **Table S1** shows the relevant electrochemical corrosion parameters. The polarization curves demonstrated lower corrosion current densities (I_{corr}) for the PDA, MBI and $Ce(NO_3)_3 \cdot 6H_2O$ inhibited solutions compared to the blank solution. Furthermore, the greater impact on the cathodic than the anodic Tafel slopes suggested that

the inhibitory mechanism of these inhibitors is largely cathodic.

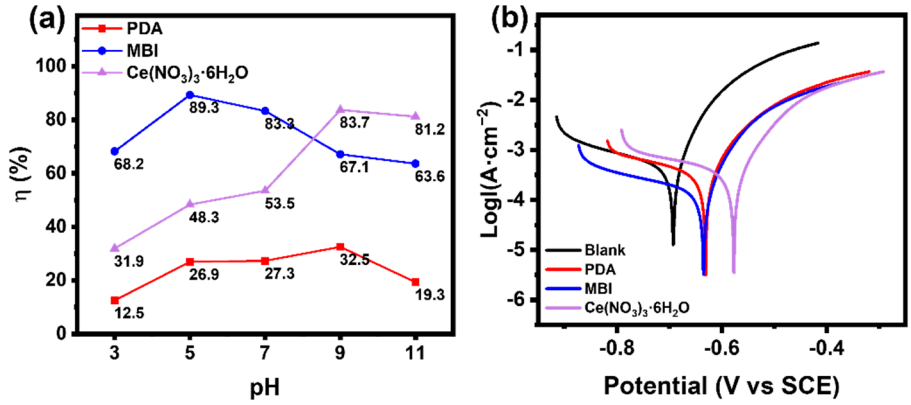


Figure S6. (a) Corrosion inhibition efficiency and (b) Tafel curves of different inhibitors for Q235 steels

Table S2. Electrochemical parameters via Tafel extrapolation fitting

Inhibitor	β_a (mV/dec)	$-\beta_c$ (mV/dec)	E_{corr} (mV)	I_{corr} (μA/cm^2)	η (%)
Blank	143.9	308.5	-693	0.792	/
PDA	159.8	319.4	-632	0.548	30.8%
MBI	165.2	395.0	-637	0.323	59.2%
$Ce(NO_3)_3·6H_2O$	159.0	413.0	-578	0.481	39.3%