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Supplementary File

Synergistic effect of graphene oxide@phosphate intercalated hydrotalcite for improved anti-corrosion and self-healable protection of waterborne epoxy coating in salt environments

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Experimental section

Materials

Graphite powder was purchased from Sigma-Aldrich (Germany). Hydrogen peroxide (H_2O_2), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98 wt.%), sodium hydroxide (NaOH), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) and sodium phosphate tribasic dodecahydrate ($Na_3PO_4{\cdot}12H_2O$) were supplied by Aladdin Chemical Co., Ltd. Epoxy resin (E-51, epoxide number is 0.5) and waterborne curing agents (epoxide equivalent is 293) were purchased from Sichuan Xing Li coating material Co., Ltd.

Preparation of PIH nanoplates

The preparation method of PIH is as follows: 0.02 mol (6.22 g) of $Na_3PO_4{\cdot}12H_2O$ and 0.06 mol (2.4 g) of NaOH were dissolved in 50 mL deionized water without carbon dioxide. Subsequently, 0.02 mol (5.14 g) of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.01 mol (3.74 g) of $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in another 100 mL deionized water containing no carbon dioxide. The above two solution were simultaneously added dropwise to a three-necked flask and adjusted the pH at 9-10. Afterwards, the mixture was reacted at 90 °C for 24 h under N_2 atmosphere and the obtained suspension was aged 12 h at ambient temperature. Finally, the mixture was filtered and washed three times with deionized water, and dried at 80 °C.

Fabrication of GO@PIH hybrids

The GO nanosheets were synthesized by modified Hummers' method [1]. Then, 0.05 g GO were added in 100 mL deionized water and oscillated for 30 min to obtain a uniformly dispersed solution. The as-prepared PIH nanoplates were added in above solution under ultrasonic vibration for another 30 min. Subsequently, the GO@PIH hybrids were obtained through freeze drying for 24 h.

Materials Characterization

The chemical compositions of GO@PIH hybrids were investigated by FT-IR analysis (WQF520 spectrometer) in the range of 500-4500 cm^{-1}. The phase composition of these samples were examined by X-ray diffraction (XRD, with Cu Kα radiation). The morphology of GO@PIH hybrids were estimated by TEM (JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.). Electrostatic interactions between GO and PIH are tested by Zeta potential (Zeta PALS 190 Plus). The chemical bond of GO@PIH hybrids were characterized by X-ray Photoelectron Spectroscopy (XPS, KRATOS XSAM 800, Monochromatic Al Ka (HV = 1486.6 eV), power 150 W; Combination can be calibrated with C1s 284.8).

Fabrication of GO@PIH/WECs

The GO@PIH/WECs were fabricated as follow steps: The metal substrate

was processed by sand blasting machine (Yuxin Machinery Equipment Limited Company, Sichuan, China) in order to achieve a surface roughness of Sa 2.5 level. Then 20 g of waterborne epoxy resin was added in to the above dispersions, and the excess water were removed by rotary evaporation at 40 °C. Subsequently, 10 g of waterborne curing agent were added into the mixture and stirred for 10 min. The final solution was coated on the pretreated substrate by high pressure spraying equipment and cured at room temperature for 3 days (the thickness of the coating remains about 40 ± 5 μm). The sample filled with 0.3 wt.% of GO@PIH (7:3) and GO@PIH (5:5) hybrids were named as GO@PIH/WECs (7:3) and GO@PIH/WECs (5:5), respectively. For comparison, the epoxy loaded with 0.3 wt.% of PIH and GO nanosheets were also prepared.

Ion exchange performance test of PIH

2 g of PIH nanoplates were dispersed in 50 mL NaCl solution (3.5 wt.%) and then the concentration of PO_4^{3-} in the filtrate after different time of immersion and stirring were tasted by the ion chromatograph.

Electrochemical measurement

The electrochemical measurements were tested by the CorrTest CS350 electrochemical work station. A conventional three-electrode system was used, including the reference electrode (SCE), the counter electrode (Pt sheet) and the working electrode (the coating samples). The EIS measurements were measured with a frequency range of 100 kHz to 10 mHz with applied 10 mV sinusoidal

perturbations. The polarization curve was characterized in a range of -200mV to +250 mV around OCP at a scan rate of 1 mV/s.

Salt spray test of composite coatings

The long-term anticorrosion properties of WECs filled with GO, PIH and GO@PIH hybrids (the samples size are about 5 cm ×10 cm) were further discussed by neutral salt spray test (NSST). Based on the ASTM B117 standard, the scratches (with a width and length of 2 mm and 4 cm, respectively) were made on the neat WECs, PIH/WECs, GO/WECs, GO@PIH/WECs (7:3) and GO@PIH/WECs (5:5) using a knife, and then located these samples in the salt spray cabinet (YWX-750). The atomized 5.0 wt.% NaCl solution was continuously sprayed on the samples under 40 ℃.

Table S1. The electrochemical parameters extracted from EIS data for composites coatings for different times.

Coating	Time	CPE_{coat}		R_{pore} (Ω cm^2)	CPE_{dl}		R_{ct} (Ω cm^2)	R_c ($M\Omega cm^2$)
		Y_0 ($\Omega^{-1}cm^{-2}$ s^n)	n_{coat}		Y_0 ($\Omega^{-1}cm^{-2}$ s^n)	n_{dl}		
WECs	7 d	6.73×10^{-9}	0.899	1.25×10^{4}	7.88×10^{-7}	0.584	1.068×10^{6}	—
	15 d	4.49×10^{-8}	0.961	5092	1.71×10^{-6}	0.436	6.924×10^{5}	—
	30 d	9.811×10^{-7}	0.972	2326	2.18×10^{-6}	0.485	3.092×10^{5}	—
	40 d	9.49×10^{-7}	0.875	1304	1.454×10^{-5}	0.514	7.373×10^{4}	—
PIH/WECs	7 d	1.811×10^{-9}	0.931	1.036×10^{5}	1.467×10^{-7}	0.650	6.968×10^{6}	—
	15 d	9.451×10^{-8}	0.923	8.84×10^{4}	2.102×10^{-6}	0.427	7.232×10^{5}	—
	30 d	1.083×10^{-8}	0.886	2.42×10^{5}	2.416×10^{-7}	0.564	4.771×10^{6}	—
	40 d	4.706×10^{-8}	0.861	1.08×10^{5}	1.54×10^{-6}	0.558	1.071×10^{6}	—
GO/WECs	7 d	6.099×10^{-10}	0.866	—	—	—	—	3.17×10^{7}
	15 d	9.11×10^{-10}	0.908	9.437×10^{5}	1.591×10^{-7}	0.728	8.663×10^{6}	—
	30 d	6.542×10^{-9}	0.575	3.715×10^{4}	2.106×10^{-7}	0.746	4.348×10^{6}	—
	40 d	2.359×10^{-9}	0.977	1.309×10^{4}	5.26×10^{-7}	0.654	2.01×10^{6}	
GO@PIH/WECs (7:3)	7 d	8.005×10^{-11}	0.809	—	—	—	—	1.409×10^{8}
	15 d	5.692×10^{-10}	0.911	2.165×10^{6}	9.102×10^{-8}	0.801	2.85×10^{7}	—
	30 d	3.931×10^{-10}	0.884	9.918×10^{6}	2.113×10^{-8}	0.522	9.252×10^{7}	—
	40 d	5.012×10^{-10}	0.912	2.431×10^{6}	5.771×10^{-8}	0.623	4.812×10^{7}	
GO@PIH/WECs (5:5)	7 d	1.624×10^{-11}	0.955	—	—	—	—	5.65×10^{8}
	15 d	7.762×10^{-11}	0.926	—	—	—	—	2.07×10^{8}
	30 d	5.215×10^{-10}	0.889	9.639×10^{5}	7.328×10^{-8}	0.695	2.918×10^{7}	—
	40 d	3.458×10^{-10}	0.899	3.642×10^{6}	1.575×10^{-8}	0.766	9.494×10^{7}	—

Table S2. Elemental composition of regions for epoxy and nanocomposite coatings

Element (wt.%)	C	O	Fe	Cl	Na	P	Mn	Au
Region 1	10.08	39.53	46.06	1.22	0.6	/	1.23	1.27
Region 2	8.85	19.72	67.62	0.88	0.53	0.25	0.98	1.19
Region 3	8.51	13.82	74.98	0.46	0.38	/	0.72	1.13
Region 4	8.37	8.65	79.6	0.27	0.24	0.43	1.05	1.3
Region 5	9.81	3.84	83.7	0.04	0.02	0.67	1.14	1.06

Table S3. The electrochemical parameters obtained from polarization curves

system		E_{corr}(Volts)	β_a (mv)	β_c (mv)	i_{corr}(Amp/cm^2)/E-7
WECs	40 d	-0.648	68.21	-188.48	3.031
PIH/WECs	40 d	-0.623	97.37	-126.76	0.462
GO/WECs	40 d	-0.608	84.74	-361.92	0.102
GO@PIH/WECs (7:3)	40 d	-0.586	199.5	-209.09	0.034
GO@PIH/WECs (5:5)	40 d	-0.498	207.77	-190.54	0.0074

Notes and references

1. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *Acs Nano*, 2010, **4**, 4806-4814.