Supplementary Information

Dispersion and parallel assembly of sulfonated graphene in waterborne epoxy anticorrosion coatings

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The morphology of SG and fracture surfaces of the SG/WEP coatings was observed by scanning electron microscope (SEM, FEI Quanta FEG) with an accelerating voltage of 20 kV. Atomic force microscopy (AFM, AR-Cypher ES Oxford Instruments) images were obtained in non-contact mode. Raman spectroscopy was excited using a LabRAM spectrometer with a laser of 532 nm.

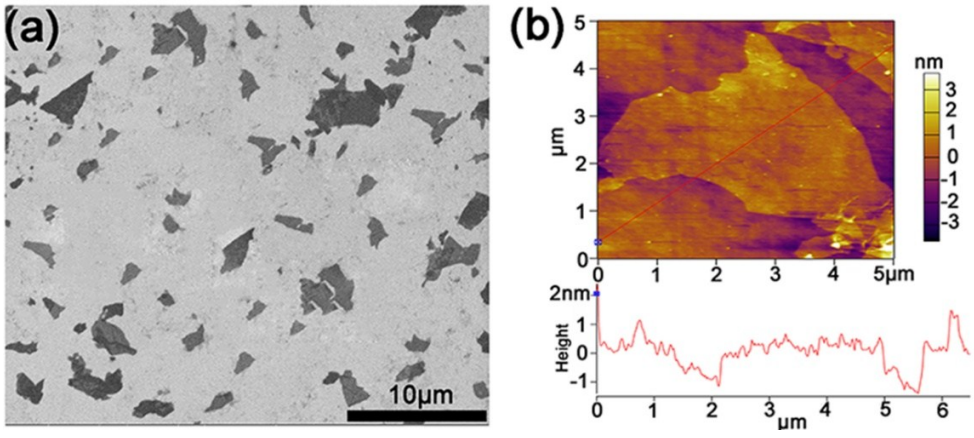

Fig. S1. (a) SEM image of SG nanosheets on Si/SiO_2 substrate. (b) AFM image of SG nanosheets on Si substrate.

The morphologies of SG nanosheets were shown in Fig. S1. The lateral size of SG nanosheets was about 4 μm on average, as shown in the SEM image. The thickness of SG nanosheets was around 1 nm, as measured by AFM, indicating that SG was composed of single atomic layer.

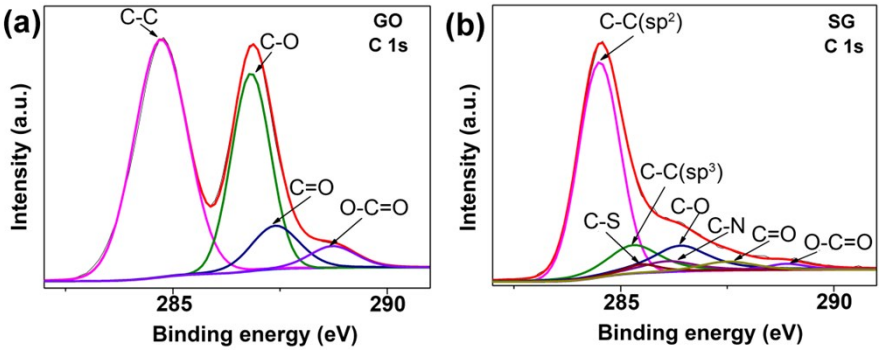

Fig. S2. XPS spectra of GO (a) and SG (b).

The C1s XPS spectrum of GO (Fig. S2a) showed a considerable degree of oxidation with functional groups including C–O (286.2 eV), C=O (287.8 eV) and O–C = O (289.0 eV). The C1s XPS spectrum of the SG, in Fig. S2b, the intensities of the peaks corresponding to C-O (286.2 eV), C=O (287.8 eV) and O–C = O (289.0 eV) were decreased, while the additional components at 285.3 and 285.9 eV were assigned to the C-S and C-N bonds.

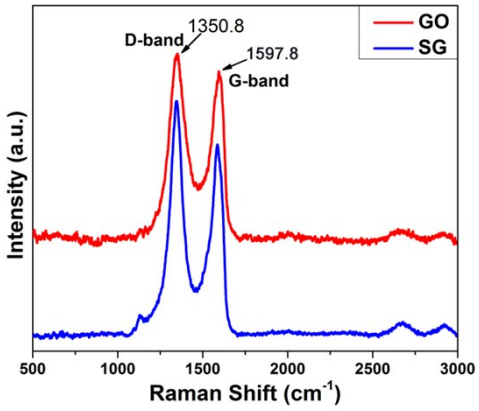

Fig. S3. Raman spectra of GO and SG.

Fig. S3 showed the Raman spectra of GO and SG. The G band at ~ 1597.8 cm^{-1} associated with the vibration of sp^2 carbon atoms in a graphitic 2D hexagonal lattice; The D band at ~ 1350.8 cm^{-1} related to the vibrations of sp^3 carbon atoms of defects and disorder [1]. The intensity ratio of the D band to the G band increased from 1.086 (for GO) to 1.192 (for SG) after the reduction and sulfonation process, suggesting an increased number of smaller graphitic domains formed during the reduction process [2].

Fig. S4 showed the SEM morphologies of the fracture surfaces of the coatings. The thickness of the composite coatings was about 15 μm. All the coatings showed smooth fracture surface, indicating a good dispersion of SG. With low magnification, the uniform distribution of SG was shown Fig. S5.

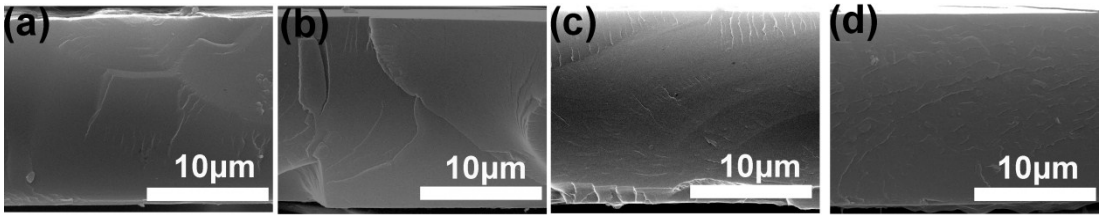

Fig. S4. SEM micrographs of fractured surfaces of (a) SG-0, (b) SG-0.2, (c) SG-0.5 and (d) SG-1.0.

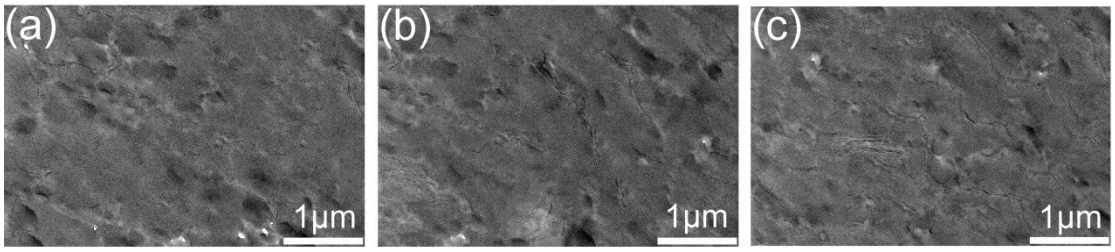

Fig. S5. TEM micrographs of (a) SG-0.2, (b) SG-0.5 and (c) SG-1.0.

The EIS results were fitted by the equivalent circuits in Fig. S6. A constant phase element (CPE) was utilized to represent a shift from the ideal capacitor during the real electrochemical process. The impedance plots with one time constant were simulated by the equivalent circuit of Fig. S6a, where R_s represents the solution resistance, R_c is the resistance of coating and CPE_c is the calibration of the capacitance of coating. The equivalent circuit of Fig. S6b was used to simulate the data for the impedance plots with two time constant, where CPE_{dl} was used to represent the double layer capacitance at the metal/coating interface, R_{ct} is the charge transfer resistance of corrosion electrochemical reaction at the interface. The electrical parameters (R_c, CPE_c, CPE_{dl} and n) obtained from the curve fitting were presented in Table S1.

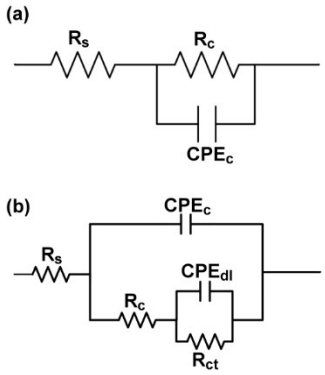

Fig. S6. Equivalent circuits used to fit the EIS data with (a) one time constant, (b) two time constants.

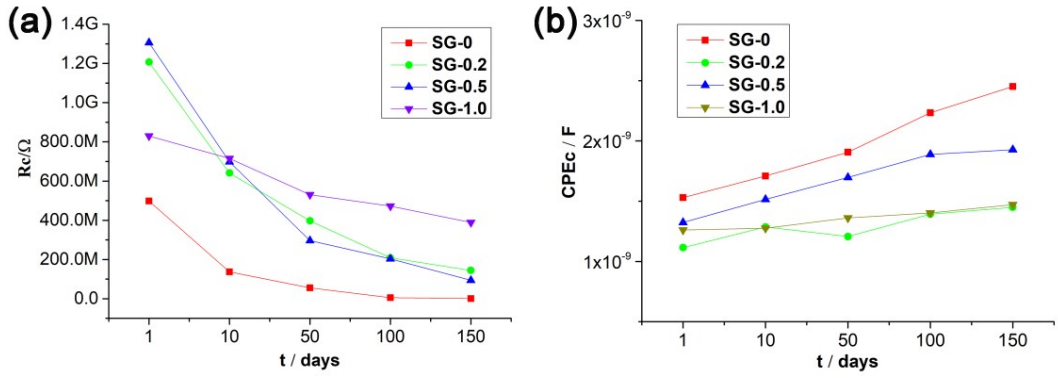

Fig. S7. Evolution of (a) R_c and (b) CPE_c of the coatings with immersion duration.

Table S1. Fitting results of the EIS plots of the different coatings

Samples	Time (day)	R_c (Ω)	CPE_c (F)	n_c	CPE_{dl} (F)	n_{dl}
Pure WEP coatings	1	4.979×10^{8}	1.530×10^{-9}	0.9386	--	--
	10	1.368×10^{8}	1.710×10^{-9}	0.9208	--	--
	50	5.547×10^{7}	1.906×10^{-9}	0.9004	--	--
	100	4.741×10^{6}	2.234×10^{-9}	0.8546	1.086×10^{-6}	0.9146
	150	6.693×10^{5}	8.352×10^{-10}	0.9357	9.125×10^{-7}	0.6962
0.2 wt% SG/WEP coatings	1	1.207×10^{9}	1.915×10^{-9}	0.903	--	--
	10	6.411×10^{8}	1.286×10^{-9}	0.939	--	--
	50	3.972×10^{8}	1.207×10^{-9}	0.944	--	--
	100	2.085×10^{8}	1.393×10^{-9}	0.929	--	--
	150	1.443×10^{8}	1.450×10^{-9}	0.929		
0.5 wt% SG/WEP coatings	1	1.306×10^{9}	$1.323.\times10^{-9}$	0.9395	--	--
	10	6.986×10^{8}	1.515×10^{-9}	0.9274	--	--
	50	2.961×10^{8}	1.997×10^{-9}	0.9087	--	--
	100	2.037×10^{8}	2.089×10^{-9}	0.9089	--	--
	150	9.423×10^{7}	2.828×10^{-9}	0.8952		
1.0 wt% SG/WEP coatings	1	8.303×10^{8}	1.261×10^{-9}	0.9317	--	--
	10	7.156×10^{8}	1.276×10^{-9}	0.9283	--	--
	50	5.307×10^{8}	1.361×10^{-9}	0.9232	--	--
	100	4.724×10^{8}	1.403×10^{-9}	0.9210		
	150	3.891×10^{8}	1.471×10^{-9}	0.9173		

The electrochemical parameters R_c and CPE_c were plotted in Fig. S7a and b as a function of immersion duration. A higher R_c implied that less electrolytes were penetrated into the coatings. R_c values decrease with increasing immersion time for all coating systems. R_c of the SG-1.0 coating was found to be the highest among all the coatings after immersion for 10 days. CPE_c was increased with the absorption of electrolytes [3]. As shown in Fig. S7 (b), the CPE_c increased with the immersion duration. The incorporation of SG nanosheets had two effects on the absorption of electrolytes: 1) they blocked the penetration of electrolytes in the coatings; 2) they absorbed more electrolytes at the SG/WEP interfaces due to the existence of hydrophilic sulfonic acid groups. Therefore, the CPE_c values changed with different SG content, but they were smaller than the

CPE_c values of SG-0.

References

1. E. Goki and C. Manish, *Adv. Mater.*, 2010, **22**, 2392-2415.
2. K. Haubner, J. Murawski, P. Olk, L. M. Eng, C. Ziegler, B. Adolphi and E. Jaehne, *Chemphyschem.*, 2010, **11**, 2131-2139.
3. M. Y. Jiang, L. K. Wu, J. M. Hu and J. Q. Zhang, *Corros. Sci.*, 2015, **92**, 118-126.