Ionic Modification of Graphene Nanosheets to Improve Anti-corrosive Property of Organosilicon Composites Coatings

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1. Experimental details

1.1 Materials

Octamethyl cyclotetrasiloxane (D4) and (3-chloropropyl) diethoxymethylsilane (YDH-701) was purchased from Shanghai Sigma Aldrich Trade Co., Ltd. It has been purified by vacuum distillation; Sulphuric acid (H_2SO_4, 98 wt%), acetone (AR) and diethyl ether (AR) were purchased from Yantai Yuandong Fine Chemical Co., Ltd.

1.2 Methods

Nuclear magnetic resonance (^1H NMR) spectrometer (Bruker Advance II 400 Hz) using deuterated chloroform ($CDCl_3$) as solvent for the characterization of silicon.

Fourier Transform Infrared Spectroscopy (Shimadzu Affinity-1S FTIR spectrometer) was used to analyze the functional group composition of GO and M-GO. Potassium bromide (KBr) was used as the calibration substance over the wavenumber range 4000-400 cm^{-1} at a resolution of 1 cm^{-1}.

Ultraviolet-visible Spectrophotometer (Shimadzu UV-2600) was used to measure the light absorption properties of M-GO in organic solvents with a scanning range of 200-800 nm.

Raman analysis of GO and M-GO was performed by In-Via Raman spectrometer with laser excitation source of 532 nm and laser exposure time of 10 s.

Thermogravimetric analysis (Yusno TGAQ50) was used to analyze the thermal stability of GO and S-GOs. The temperature range was 30-800 °C and the heating rate was 10 °C/min. The test was carried out in a nitrogen atmosphere with the flow rate of 100 ml/min.

SAXS test adopts small angle X-ray scatterometer (Anton Paar, Austria), the tube pressure is 50 kV and the current is 40 mA. The distance between sample and detector is 264.5mm and the X-ray wavelength is 0.1542 nm. The test time of each sample was 900 s.

Morphology of silicone composite coatings were obtained by scanning electron microscopy (SEM, Phenom pure plus), the dispersion of M-GO in organic solvents was observed by Transmission electron microscopy (TEM, JEOL JEM-1400 Flash).

Water contact angle of silicone composite coatings was tested by contact angle measuring instrument (KRUSS DSA25) and the contact angle measurement range was from 0 to 180 °. The tensile properties of PDMS composite coatings were measured by a universal testing machine (WSM-20 KB type).

The protective properties were characterized using an electrochemical workstation (AMETEK VersaSTAT4, Princeton Applied Research). A classical three-electrode cell system was used, wherein the coated copper surface as the working electrode with an exposed area of 0.25π cm^2, an Ag/AgCl (0.205 V/SHE) as the reference electrode and a platinum net as

the counter electrode. The coating samples were immersed in 3.5 wt% NaCl aqueous solution for 30 min before the test. The testing time of open circuit potential is 600 s, then we test the PDP and EIS. EIS tests were recorded in frequency range of 10^{-2} to 10^4 Hz utilizing AC amplitude of 10 mV. The obtained electrochemical data were analyzed with the help of Versa Studio software. The surface of the copper sample was cleaned with ethanol, then rinsed with distilled water to remove contaminants, and then coated with silicone composite coatings.

2. Additional Data

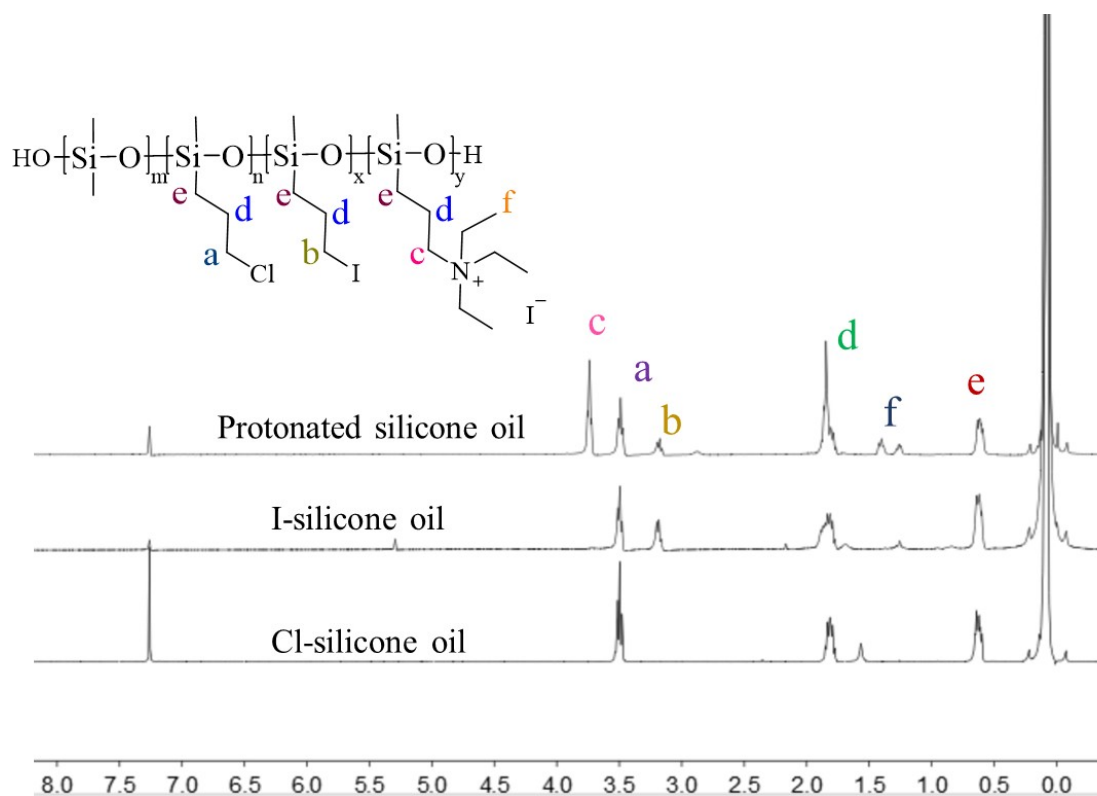2.1 Characterization of different silicone oil

Figure S1 ^{1}H NMR of protonated silicone oil, I- silicone oil, Cl-silicone oil.
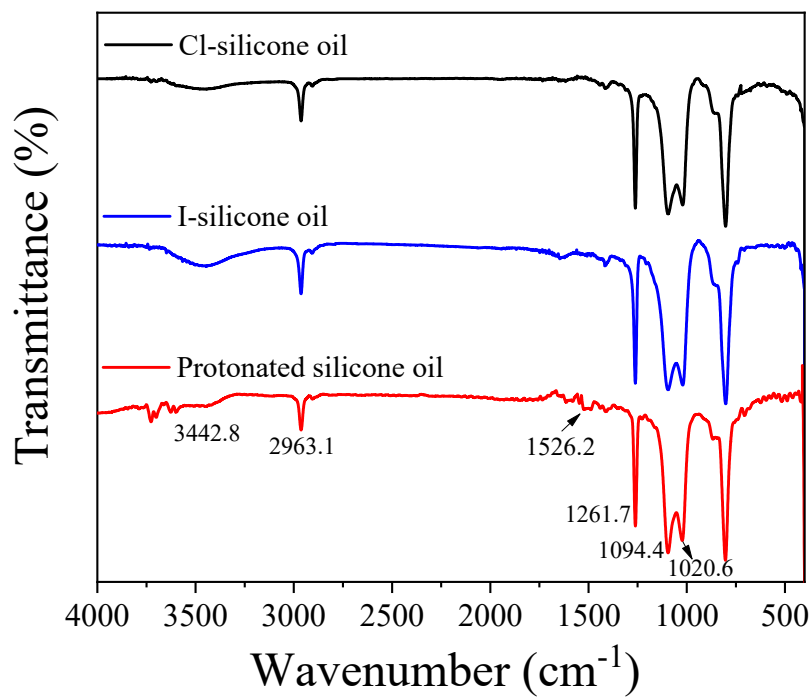
Figure S2 FT-IR diagram of protonated silicone oil, I-silicone oil, Cl-silicone oil.
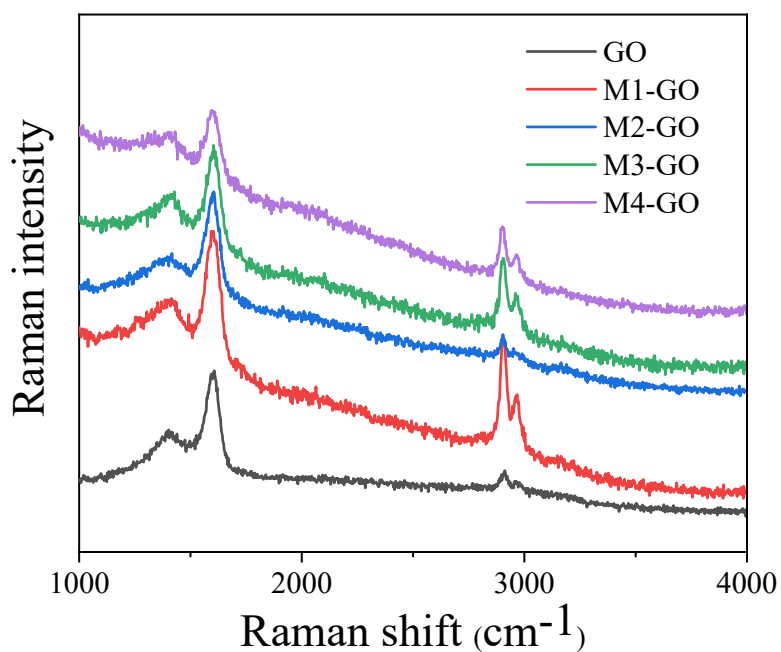
2.2 Characterization of M-GO

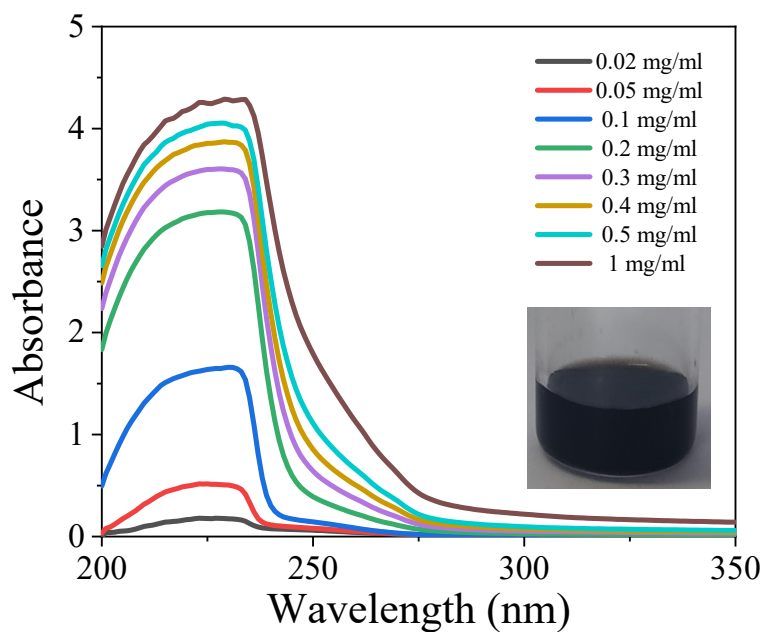
Figure S3 Raman spectra of GO and M-GO.

Figure S4 UV spectra of M-GO dissolved in chloroform solvent, photo of the sample (c=2 mg/ml) is also included inset.

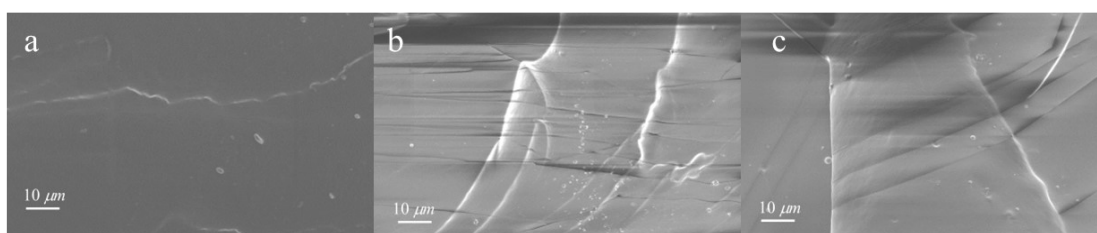## 2.3 Characterization of composite coatings

Figure S5 SEM cross-sectional images of pure silicone coating a), silicone coating with GO b), silicone coating with M-GO c).
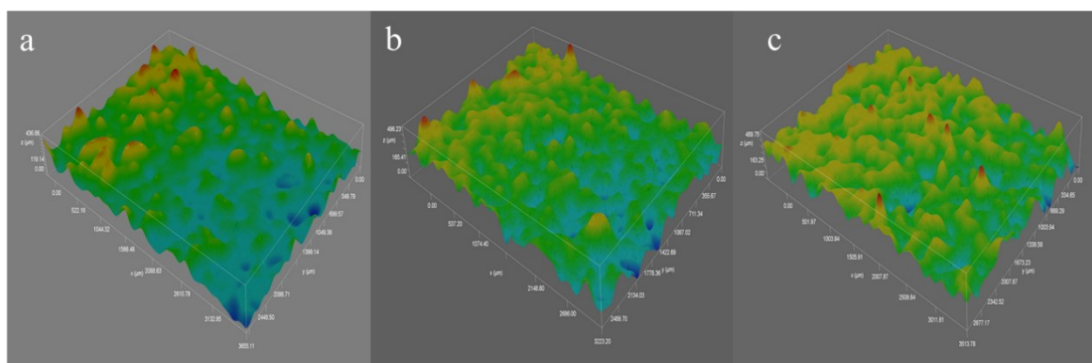

Figure S6 Surface morphologies of silicone coating with GO a), M-GO (5%, 10%) as additives b) and c).
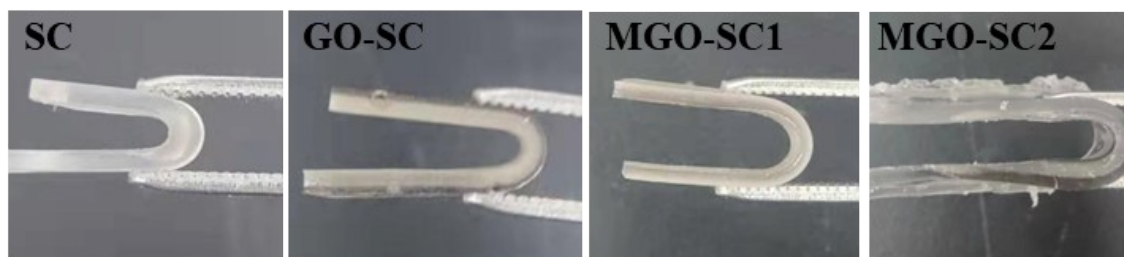
Figure S7 Folding resistance of different silicone composite coatings.

Table S1. Electrochemical parameters from the Tafel curves of bare copper and composite coatings.

Compound	E_{corr} (mV)	I_{corr} (A/cm^2)	B_c (mV/dec)	b_a (mV/dec)	P_{EF} (%)
Pure Cu	-287	$1.807e^{-5}$	-2.55	1.93	-
SC	-211	$3.793e^{-6}$	-4.74	0.16	79.01
GO-SC	-198	$1.799e^{-6}$	-4.76	5.32	90.04
MGO-SC1	-137	$1.979e^{-7}$	-4.61	13.06	98.93
MGO-SC2	-158	$1.394e^{-8}$	-7.37	19.29	99.92
MGO-SC3	-121	$6.058e^{-9}$	-4.92	4.56	99.97

Table S2. The fitting parameters of composite coatings equivalent circuits.

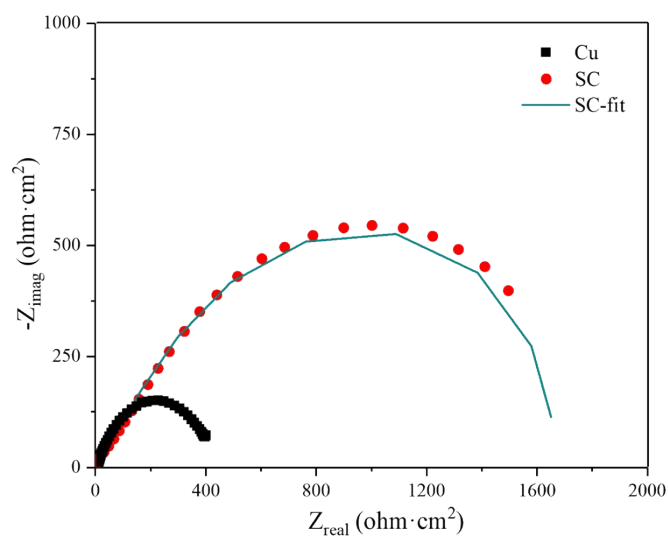| Sample	CPE_{coat}		R_{coat}	CPE_{dl}		Rit (Ω*cm2)	Chi squared (χ2)
	Y_0 (Ω^{-1}cm^{-2}s^n)	n	(Ω*cm^2)	Y_0 (Ω^{-1}cm^{-2}s^n)	n		
SC	$6.30e^{-6}$	0.64	$2.20e^3$	-	-	-	$4.59e^{-4}$
GO-SC	$5.75e^{-6}$	0.51	$3.68e^4$	-	-	-	$6.58e^{-5}$
MGO-SC1	$9.28e^{-7}$	0.93	$3.22e^4$	$1.75e^{-5}$	0.80	$1.28e^4$	$7.80e^{-4}$
MGO-SC2	$5.53e^{-7}$	0.70	$1.58e^5$	$5.019e^{-7}$	0.70	$1.66e^5$	$4.84e^{-4}$
MGO-SC3	$2.49e^{-7}$	0.68	$5.78e^5$	$2.06e^{-5}$	0.87	$1.45e^5$	$8.44e^{-4}$

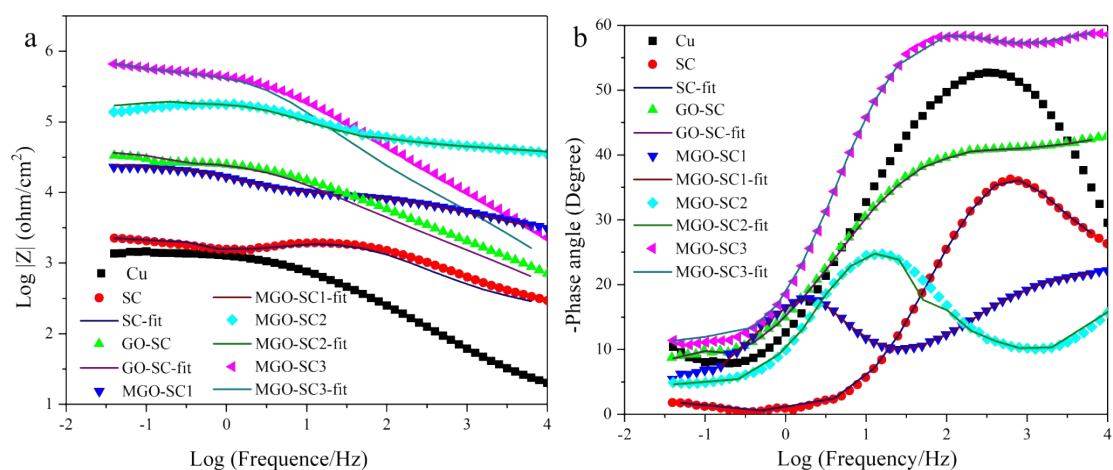Figure S8 Nyquist plots of Cu, SC and SC-fit.

Figure S9 Bode plots of Cu and PDMS, PDMS/ GO and PDMS/ M-GO composite coatings (a) Impedance-frequency, b) Phase angle-frequency).

3. Syntheses

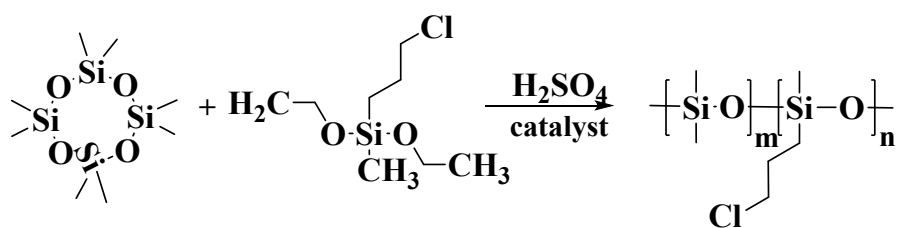3.1 Synthesis of chloropropyl silicone oil

Figure S10 Schematic diagram of chloropropyl silicone oil formation process.

D$_4$ (14.83 g, 0.05 mol) and chloropropylsilane monomers (7.42 g, 0.035 mol) were added to a 250 ml four-port flask equipped with a thermometer, spherical condensing tube and strong mechanical agitation. The H$_2$SO$_4$ (3.43 g, 0.035 mol) was slowly dropped into the reaction flask with strong agitation. Then temperature was raised to 60 °C for 6 hours. After the reaction, the product was extracted with distilled water and dichloromethane for 3 times, and then the organic solvents was removed by rotary evaporation at 40 °C to obtain the crude product.

^{1}H NMR of Cl-silicone (400 MHz, CDCl$_3$, 298 K): a: 3.62 (t, 2H, Cl-CH$_2$-); d: 1.76 (d, 2H, -CH$_2$-); e: 0.61 (m, 2H, Si-CH$_2$-).

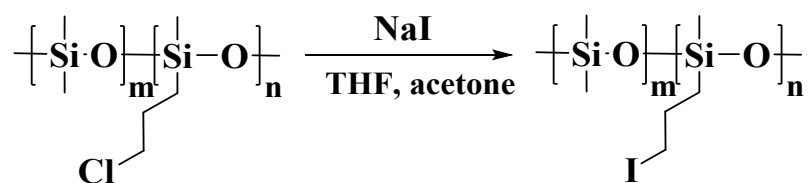3.2 Preparation of iodopropyl silicone

Figure S11 Schematic diagram of iodopropyl silicone oil formation process.

Sodium iodide was dissolved in acetone solvent. Chlorpropyl silicone was dropped into above solution with stirring at room temperature. After refluxed at 70 °C for 48 hours, white solids were filtered out and the solvents was removed by decompression at 60 °C. The residue was extracted with ether in a separation funnel for 3 times, then ether was removed under 35 °C decompression. The yellowish iodopropyl silicone was obtained.

^{1}H NMR of I-silicone oil (400 MHz, CDCl$_3$, 298 K): b: 3.27 (t, 2H, I-CH$_2$-); d: 1.76 (d, 2H, -CH$_2$-); e: 0.61 (m, 2H, Si-CH$_2$-).