

Supporting Materials: Size Effect of Graphite Nanosheets Induced Anti-Corrosion of Hydrophobic Epoxy Coating

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1. Electrochemical measurements

Electrochemical experiments were performed on the electrochemical work station (Zahner-Elektrok IM6e), and 3.5 wt% NaCl solution was used as the electrolyte. The three electrodes system was adopted, in which the working electrode, Ag/AgCl electrode (the saturated KCl solution) and Pt sheet were used as the counter electrode, respectively. The Q235 steel with coatings sample was used as the working electrode, and the effective working area was 1 cm². The electrochemical impedance spectroscopy (EIS) was performed using the frequency range of 10 mHz–100 kHz and 10 mV in amplitude. Before the measurements, the coating samples were immersed in 3.5 wt% NaCl solution with 7 day, 30 day or 60 day. In addition, the tafel polarization test was carried out with a constant scan rate of 1 mV/s, the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were obtained by this method. In order to ensure the scientificity and repeatability of the electrochemical datas, parallel experiments were performed and repeated five times.

2. Recording Water Contact Angle

Sessile drop water contact angle (WCA) were recorded using an Attension theta optical tensiometer (JC2000D2, China KSV instruments, Finland). For WCA measurements, at least five different locations on the samples were probed by autodropping a 10 μ L the deionized water. The static contact angle was recorded after 120 s of droplet stability. The auto video record of static contact angle was recorded by setting the time sequence of 0.05 s for each frame to the end of water stability.

3. Computational Details

The calculations were carried out using density functional theory with the PBE form of generalized gradient approximation functional (GGA)^[1]. The Vienna ab-initio simulation package (VASP)^[2–3] was employed. The plane wave energy cutoff was set as 400 eV. The Fermi scheme was employed for electron occupancy with an energy smearing of 0.1 eV. The first Brillouin zone was sampled in the Monkhorst–Pack grid^[4]. The 3×3×1 k-point mesh for the surface calculation. The energy (converged to 1.0 ×10^{−6} eV/atom) and force (converged to 0.01 eV/Å) were set as the convergence criterion for geometry optimization. The spin polarization was considered in all calculation. To accurately describe the van der Waals (vdW) interaction, a semiempirical DFT-D3 force-field approach^[5] is employed in our calculations.

4. Model

The graphite (001) surface was obtained by cutting graphite along [001] direction. The thickness of surface slab was chosen to be a single- and two-layer slab, respectively. In the geometry optimizations, all the positions of the atoms were allowed to relax. A vacuum layer of 18 Å was employed along the c and a direction to avoid periodic interactions.

The adsorption of ΔE_{ads} is defined as follows:

$$\Delta E_{ads} = E_{spices/slab} - (E_{slab} + E_{spices})$$

where the $E_{spices/slab}$ is the total energy of spices adsorption on slab, E_{slab} is the total energy of the slab and E_{spice} is the energy of spices. The first two terms are calculated with the same parameters. The third term is calculated by setting the isolated spices in a box of $12 \text{ \AA} \times 12 \text{ \AA} \times 12 \text{ \AA}$.

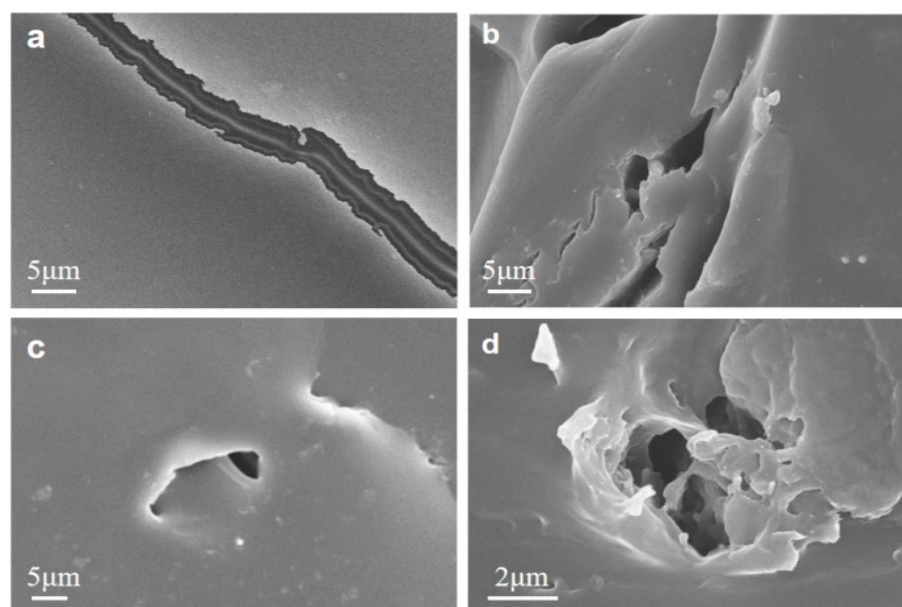


Figure S1. The EP coatings surface SEM of EP for same micro-holes or micro-cracks morphology.

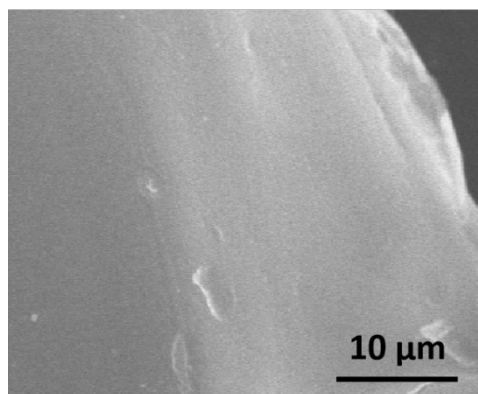


Figure S2. The coatings surface SEM of EG₅₀₀₀/C₁P_{0.2}EP morphology.

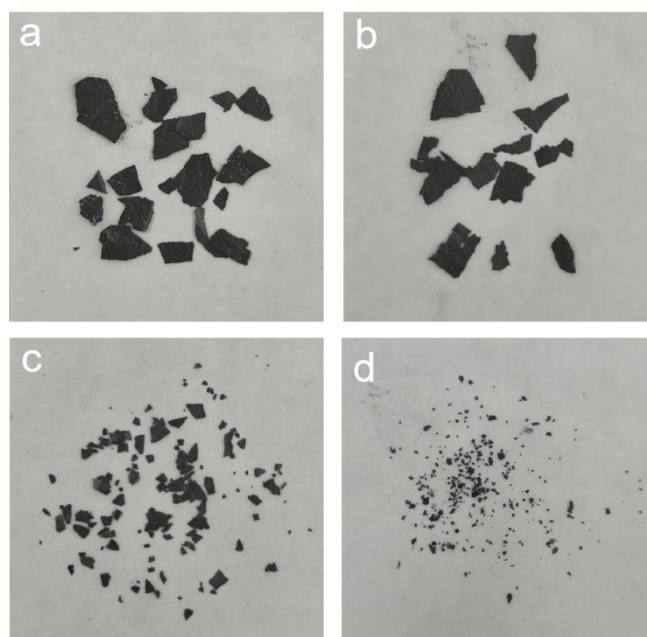


Figure S3. The photos of EG₁₀₀₀ (a), EG₃₀₀₀ (b), EG₅₀₀₀ (c) and EG₈₀₀₀ (d).

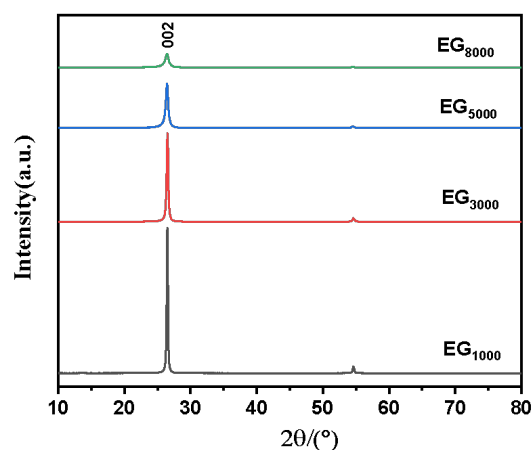


Figure S4. XRD spectra of EG₁₀₀₀, EG₃₀₀₀, EG₅₀₀₀ and EG₈₀₀₀, respectively.

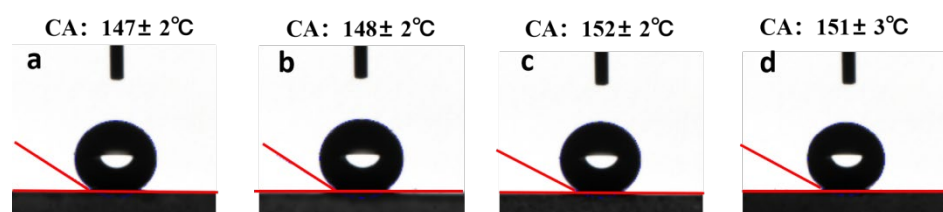


Figure S5. Water contact angle of (a) EG₁₀₀₀/C₁P_{0.2}EP, (b) EG₃₀₀₀/C₁P_{0.2}EP, (c) EG₅₀₀₀/C₁P_{0.2}EP and (d) EG₈₀₀₀/C₁P_{0.2}EP coatings.

Table S1. Water contact angle of EG₁₀₀₀/C₁P_{0.2}EP, EG₃₀₀₀/C₁P_{0.2}EP, EG₅₀₀₀/C₁P_{0.2}EP and EG₈₀₀₀/C₁P_{0.2}EP coatings with different storage time.

Time Sample	1 day	7 day	14 day	30 day	60 day
EG ₁₀₀₀ /C ₁ P _{0.2} EP (°)	147.0±1.0	146.3±0.5	146.0±1.0	145.3±0.5	143.6±1.2
EG ₃₀₀₀ /C ₁ P _{0.2} EP (°)	148.0±1.0	147.0±1.0	146.6±0.57	146.0±1.0	144.3±1.2
EG ₅₀₀₀ /C ₁ P _{0.2} EP (°)	152.0±1.0	150.0±1.0	149.3±0.6	147.6±0.6	146.6±0.6
EG ₈₀₀₀ /C ₁ P _{0.2} EP (°)	150.6±1.5	149.0±1.0	147.0±1.0	145.0±1.0	144.0±1.0

Table S2. Water contact angle of EG₅₀₀₀/C₁P_{0.2}EP with different EG₅₀₀₀ content.

Time Contact Angle (°)	1 day	7 day	20 day	30 day	40 day
EG ₅₀₀₀ /C ₁ P _{0.2} EP(0.025%)	147.0±0.3	146.3±0.2	145.0±0.3	143.7±0.3	143.0±0.3
EG ₅₀₀₀ /C ₁ P _{0.2} EP(0.04%)	148.0±0.3	147.3±0.2	146.0±0.3	145.8±0.3	144.0±0.3
EG ₅₀₀₀ /C ₁ P _{0.2} EP(0.05%)	152.0±0.3	151.5±0.3	150.0±0.3	148.0±0.3	147.0±0.2
EG ₅₀₀₀ /C ₁ P _{0.2} EP(0.075%)	146.0±0.3	145.5±0.3	144.0±0.2	143.1±0.3	143.0±0.3

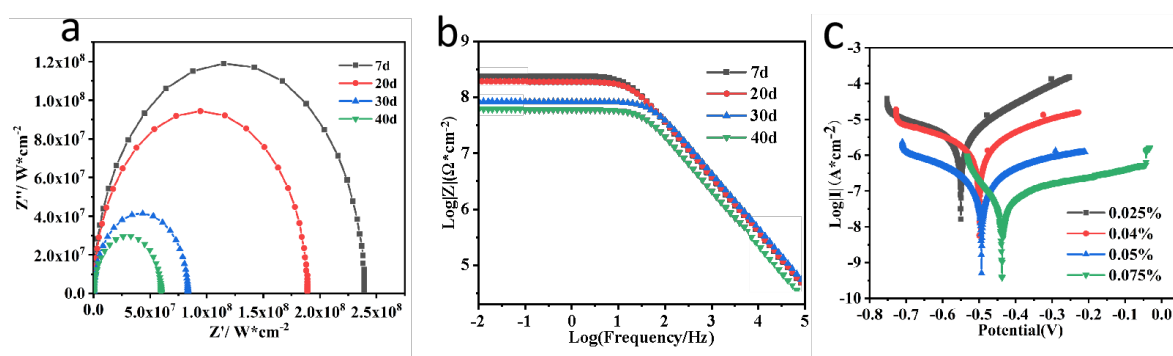
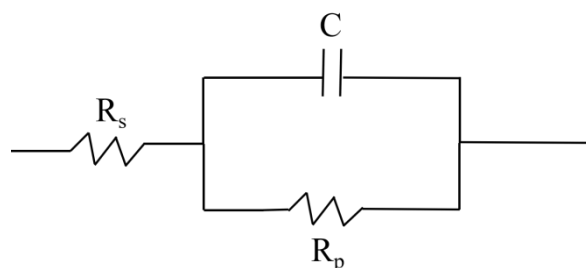
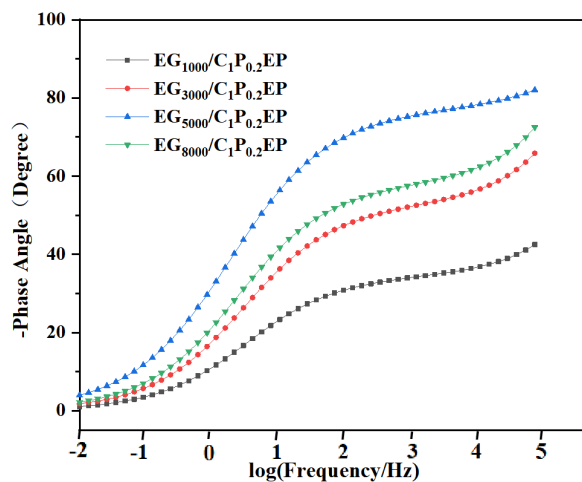
**Figure S6.** (a) After 7 d, 20 d, 30 d and 60 d of immersion, the Nyquist plots (a) and the Bode modulus plots (b) for EG₅₀₀₀/C₁P_{0.2}EP of 0.75 wt% EG₅₀₀₀. (c) The polarization curve of EG₅₀₀₀/C₁P_{0.2}EP with different addition amounts of EG₅₀₀₀ after 40 d of neutral salt spray test.**Figure S7.** Equivalent electric circuits of the collected EIS results.**Figure S8.** Bode plots (phase angle) of different EG_x/C₁P_{0.2}EP coatings at 7d immersion times.

Table S3. Electrochemical parameters extracted from EIS experiment for EG₁₀₀₀/C₁P_{0.2}EP, EG₃₀₀₀/C₁P_{0.2}EP, EG₅₀₀₀/C₁P_{0.2}EP and EG₈₀₀₀/C₁P_{0.2}EP immersed with different immersed time.

Time (day)	Samples	C ($\Omega^{-1}\text{cm}^{-2}\text{s}$)	R _c (Ωcm^2)
7	EG ₁₀₀₀ /C ₁ P _{0.2} EP	4.86×10^{-11}	1.59×10^8
	EG ₃₀₀₀ /C ₁ P _{0.2} EP	4.53×10^{-11}	1.98×10^8
	EG ₅₀₀₀ /C ₁ P _{0.2} EP	3.94×10^{-11}	2.58×10^8
	EG ₈₀₀₀ /C ₁ P _{0.2} EP	4.46×10^{-11}	2.09×10^8
30	EG ₁₀₀₀ /C ₁ P _{0.2} EP	3.59×10^{-11}	1.57×10^7
	EG ₃₀₀₀ /C ₁ P _{0.2} EP	3.43×10^{-11}	3.50×10^7
	EG ₅₀₀₀ /C ₁ P _{0.2} EP	3.33×10^{-11}	5.75×10^7
	EG ₈₀₀₀ /C ₁ P _{0.2} EP	3.31×10^{-11}	4.00×10^7
60	EG ₁₀₀₀ /C ₁ P _{0.2} EP	3.32×10^{-11}	1.17×10^7
	EG ₃₀₀₀ /C ₁ P _{0.2} EP	9.42×10^{-11}	1.66×10^7
	EG ₅₀₀₀ /C ₁ P _{0.2} EP	2.97×10^{-11}	3.18×10^7
	EG ₈₀₀₀ /C ₁ P _{0.2} EP	8.14×10^{-11}	1.87×10^7

Table S4. The value of corrosion potential, corrosion current and corrosion inhibition efficiency of for Q235, EG₁₀₀₀/C₁P_{0.2}EP, EG₃₀₀₀/C₁P_{0.2}EP, EG₅₀₀₀/C₁P_{0.2}EP and EG₈₀₀₀/C₁P_{0.2}EP in Tafel image.

Samples	E _{corr} /mV	i _{corr} /mA cm ⁻²	η/%
Q235	-631.36	9.40×10^{-3}	—
EG ₁₀₀₀ /C ₁ P _{0.2} EP	-574	5.78×10^{-3}	38.51
EG ₃₀₀₀ /C ₁ P _{0.2} EP	-543	6.88×10^{-4}	92.68
EG ₅₀₀₀ /C ₁ P _{0.2} EP	-308	5.53×10^{-5}	99.41
EG ₈₀₀₀ /C ₁ P _{0.2} EP	-486	1.64×10^{-4}	98.26

Table S5. Electrochemical parameters extracted from EIS experiment for EG₅₀₀₀/C₁P_{0.2}EP with different immersed time.

Time (day)	C ($\Omega^{-1}\text{cm}^{-2}\text{s}$)	R _c (Ωcm^2)
7	3.94×10^{-11}	2.58×10^8
14	6.83×10^{-11}	1.06×10^8
30	3.33×10^{-11}	5.75×10^7
60	2.97×10^{-11}	3.18×10^7

Table S6. Electrochemical parameters extracted from EIS experiment for EG₅₀₀₀/C₁P_{0.2}EP with different EG₅₀₀₀ content.

Time (day)	Samples (wt%)	C ($\Omega^{-1}\text{cm}^{-2}\text{s}$)	R _c (Ωcm^2)
7	0.025	5.06×10^{-11}	1.47×10^8
	0.04	7.41×10^{-11}	1.96×10^8
	0.05	4.59×10^{-11}	2.18×10^8
	0.075	4.39×10^{-11}	2.39×10^8
20	0.025	6.22×10^{-11}	1.22×10^8
	0.04	5.69×10^{-11}	1.35×10^8
	0.05	3.81×10^{-11}	1.50×10^8
	0.075	4.24×10^{-11}	1.89×10^8
40	0.025	9.38×10^{-11}	4.16×10^7
	0.04	8.88×10^{-11}	4.74×10^7
	0.05	7.28×10^{-11}	5.33×10^7
	0.075	7.63×10^{-11}	5.95×10^7

Table S7. The value of corrosion potential, corrosion current and corrosion inhibition rate of for Q235 and EG₅₀₀₀/C₁P_{0.2}EP with different EG₅₀₀₀ content.

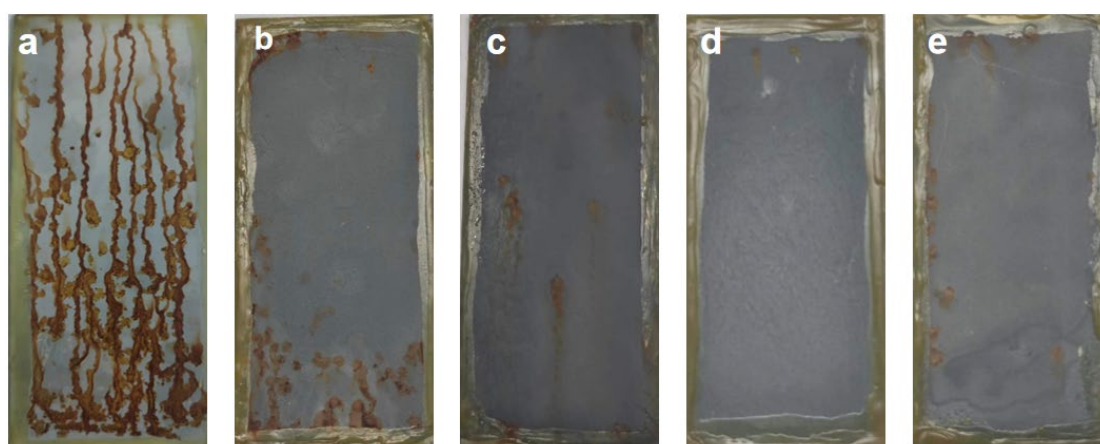
Samples (EG ₅₀₀₀ wt%)	E _{corr} /mV	i _{corr} /mAcm ⁻²	η/%
Q235	-631.36	9.40×10 ⁻³	—
0.025	-549.51	1.78×10 ⁻³	81.06
0.04	-498.62	7.39×10 ⁻⁴	92.14
0.05	-475.34	7.21×10 ⁻⁵	99.23
0.075	-442.76	2.51×10 ⁻⁵	99.73

Table S8. Electrochemical parameters extracted from EIS experiment for EG₅₀₀₀/C₁P_{0.2}EP of 0.075 wt% EG₅₀₀₀ with different immersed time.

Time (day)	C (Ω ⁻¹ cm ⁻² sn)	Rc (Ωcm ²)
7	7.63×10 ⁻¹¹	2.39×10 ⁸
20	7.28×10 ⁻¹¹	1.89×10 ⁸
30	8.88×10 ⁻¹¹	8.33×10 ⁷
40	9.38×10 ⁻¹¹	5.95×10 ⁷

Table S9. Anticorrosion properties of graphene derivatives reinforced WEP.

Samples	Graphene content (wt%)	Immersion duration in 3.5% NaCl (days)	Coating thickness (μm)	Rc (Ω cm ²)	CPEc (F)	Reference
EG ₅₀₀₀ /C ₁ P _{0.2} EP	0.05	7	25 ± 2	2.58 × 10 ⁸	3.94 × 10 ⁻¹¹	This Work
PGHEP-G	0.5	5	25 ± 0.5	2.5 × 10 ⁴	unknown	17
G-CAT ⁻	0.5	4	20 ± 2	2.72 × 10 ⁴	5.71 × 10 ⁻⁷	18
Sodium poly-acrylate graphene	0.5	2	50 ± 2	1.14 × 10 ⁵	1.5 × 10 ⁻⁸	28
lignin-OH/graphene	0.5	2	50 ± 5	2.8 × 10 ⁴	7.6 × 10 ⁻¹⁰	29
graphene/epoxy (GEP06)	0.6	3	20 ± 2	29.07	unknown	30

**Figure S9.** Digital photographs of C₁P_{0.2}EP (a), EG₁₀₀₀/C₁P_{0.2}EP (b), EG₃₀₀₀/C₁P_{0.2}EP (c), EG₅₀₀₀/C₁P_{0.2}EP (d) and EG₈₀₀₀/C₁P_{0.2}EP (e) coatings after immersion for 300 h by neutral salt spray test.

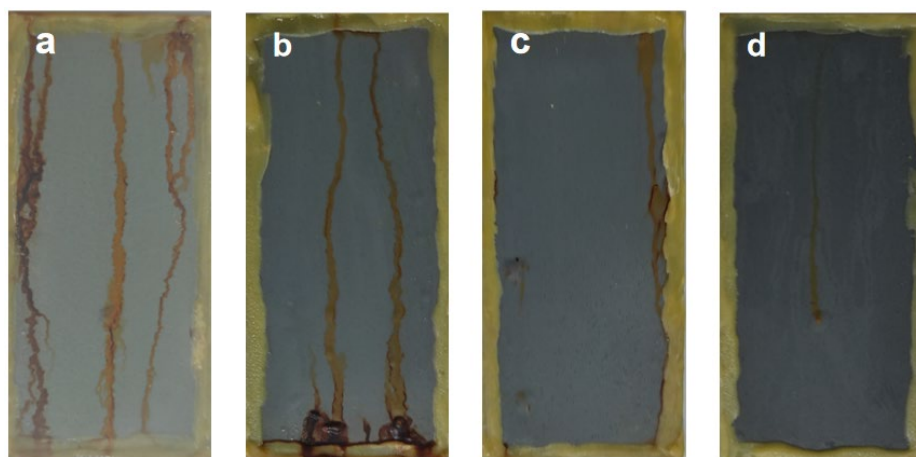


Figure S10. Digital photographs of EG₅₀₀₀/C1P_{0.2}EP with 0.025 wt% of EG₅₀₀₀ (a), 0.04 wt% of EG₅₀₀₀ (b), 0.05 wt% of EG₅₀₀₀ (c) and 0.075 wt% of EG₅₀₀₀ for 400 h by neutral salt spray test.

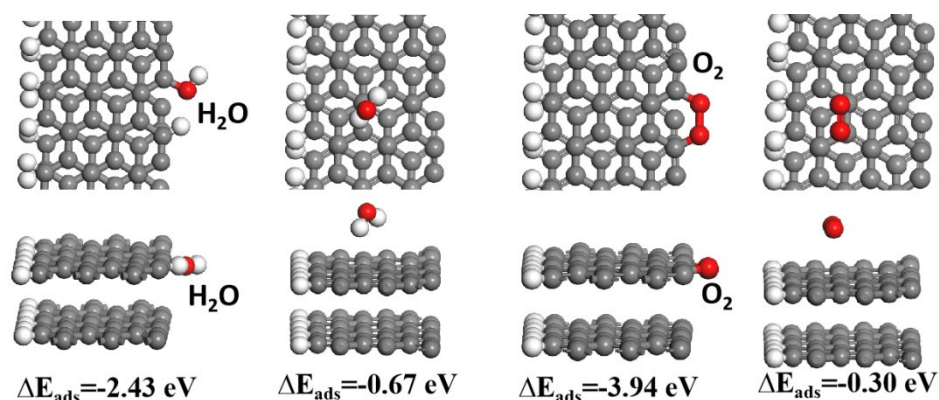


Figure S11. The adsorption structures and energies of O₂ and H₂O at the varying sites of double layers of graphite sheet.

Reference

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