Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A New Insight into SO_2 Adsorption Behavior on Oxidized Carbon Materials through Using Model Adsorbents and DFT Calculation

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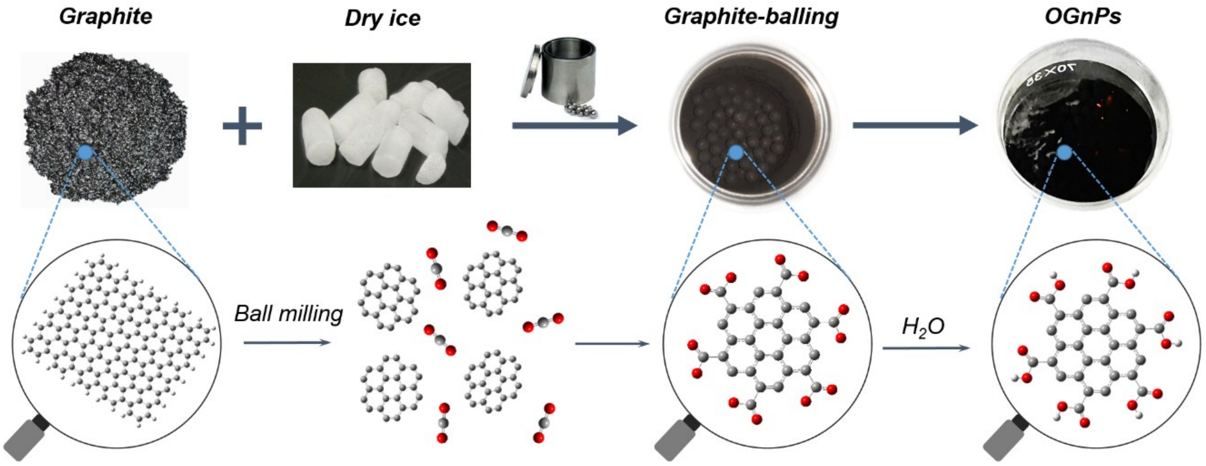

Fig. S1 A schematic representation of edge-carboxylation of graphite by ball milling.

Table S1. O contents, BET surface area and SO_2 adsorption capacity of all the samples.

Sample	O (at-%)	S_{BET} (m^2g^{-1})	SO_2 gravimetric uptake capacity (mg g^{-1})	SO_2 areal uptake capacity (mg m^{-2})
Graphite	1.56	128	2.49	0.02
OGnP-0	1.72	707	17.49	0.03
OGnP-1	4.74	633	36.15	0.06
OGnP-2	7.05	644	46.59	0.07
OGnP-3	14.06	656	52.25	0.08

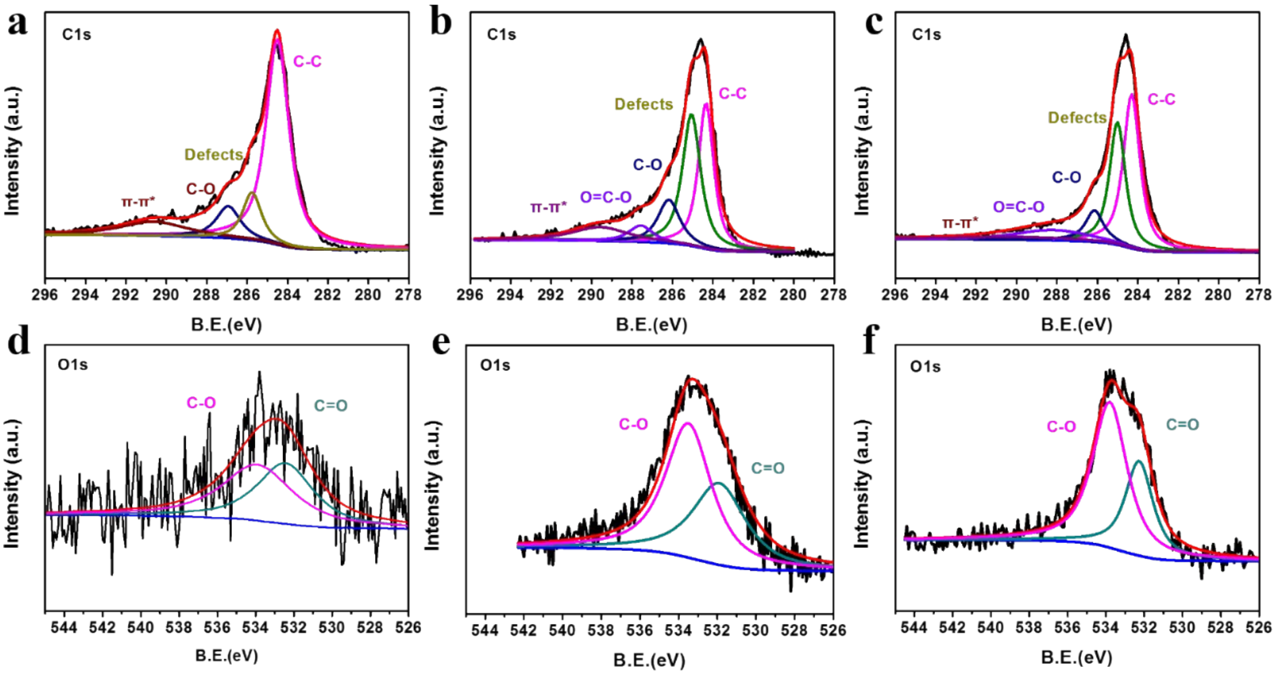

Fig. S2 The high-resolution XPS spectra of C1s for (a) OGnP-0, (b) OGnP-1 and (c) OGnP-2; The high-resolution XPS spectra of O1s for (d) OGnP-0, (e) OGnP-1 and (f) OGnP-2.

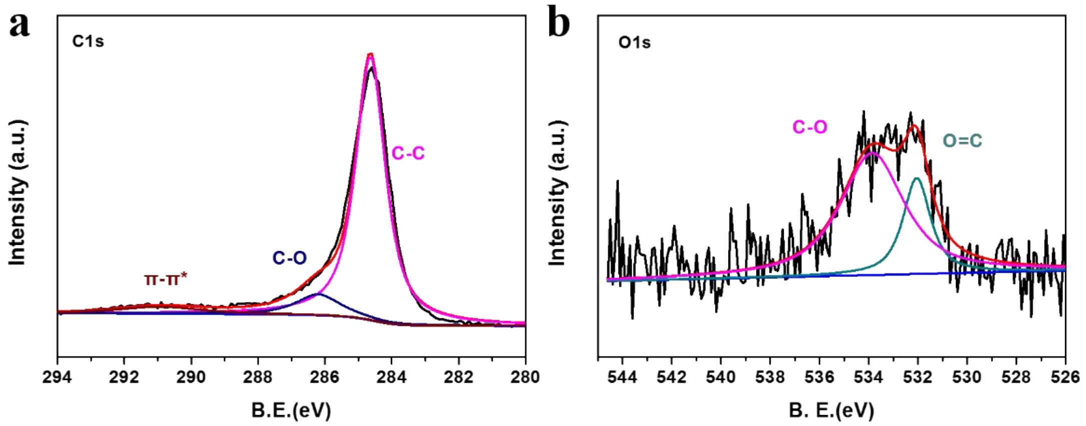

Fig. S3 The high-resolution XPS spectra of (a) C1s and (b) O1s for pristine graphite.

As seen in **Fig. S3a**, the pristine graphite shows a typical C 1s peak at 284.5 eV associated with the graphitic C-C, along with two very weak sub-bands assignable to C-O at 285.5. The pristine graphite also shows a minor O 1s peak at 532.1 eV (**Fig. S3b**), which is mostly related to physically adsorbed oxygen/moisture for C-O.[1]

According to the lowest point of SO_2 desorption concentration as the demarcation point of physical adsorption and chemisorption (250 °C), and integrating the SO_2 desorption curve demarcation point before and after, respectively, the physical and chemical adsorption capacity of SO_2 are obtained, as shown in **Table S2**.

Table S2. Physisorption and chemisorption of SO_2 with different oxygen content samples

Sample	**Physisorption (mg/g)**	**Chemisorption (mg/g)**	**Total desorption (mg/g)**
OGnP-0	7.2	10.1	17.3
OGnP-1	7.6	28.5	36.1
OGnP-2	27.1	19.2	46.3
OGnP-3	37.8	14.2	52.0

Fig. S5 The picture of self-made fixed bed adsorption system.

The TPD results in **Fig. 2f** imply that the oxygenated graphene nanoplatelets could enhance the SO_2 physical adsorption, while carbon framework with unsaturated carbon atoms may enhance SO_2 chemical adsorption. According to abovementioned characterizations, carboxylic groups are the main oxygen-containing functional groups. Thus, carbon cluster models with or without edge-decorated carboxyl groups were constructed. In addition, carbon surface with unsaturated carbon on the edge was also constructed as a comparison. All the calculations were completed by using B3LYP functional and 6-31G (d, p) basis (Gaussian 09 software).[2]

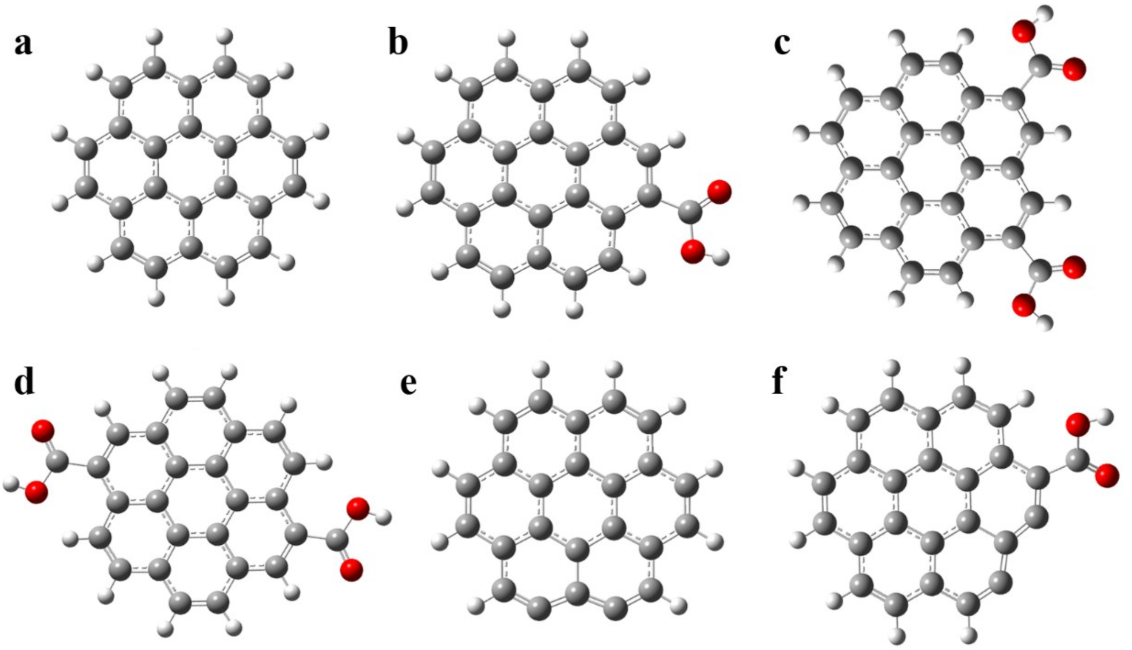

Fig. S6 Cluster models of (a) pristine carbon surfaces, (b) containing one carboxyl, (c) containing two near carboxyls, (d) containing two opposite carboxyls, (e) containing unsaturated carbon atoms and (f) containing both carboxyl and un-saturated carbon atoms. (gray ball: carbon atom; red ball: oxygen atom; yellow ball: sulfur atom; small white ball: hydrogen atom).

The identification of SO_2 adsorption patterns (i.e. physisorption and chemisorption) and adsorption positions (i.e. plane and edge) for this adsorption process is important for mechanistic understanding and for the rational design of future adsorbents. Herein, we employ theoretical calculation by using M06-2X functional and 6-31G (d, p) basis (Gaussian 09 software) to investigate study SO_2 adsorption on various carbon surface models (a total of six configurations) with or without carboxyl group doping. The optimized molecular structures (**Fig. S6**) and electrostatic surface potential (**Fig. S7**) of the carbon surface models with or without carboxyl group doping were obtained.

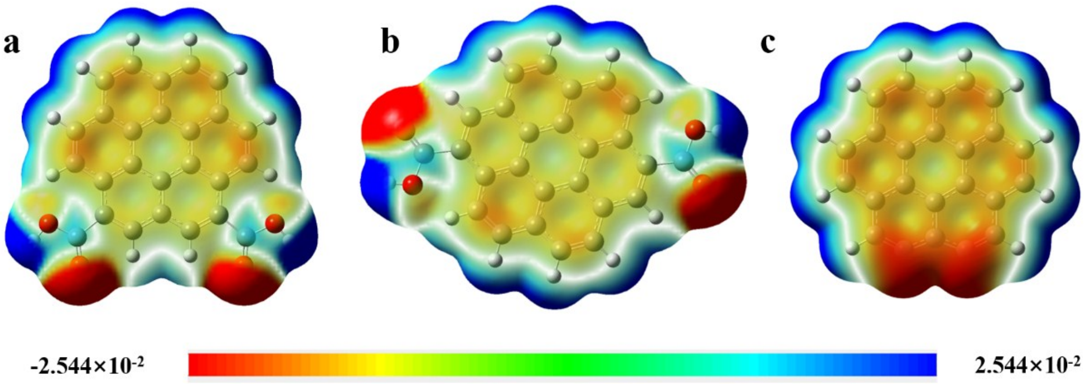

Fig. S7 Electrostatic potential maps of carbon surfaces containing two carboxyls (a and b) and containing un-saturated carbon atoms (c).

To confirm the reliability of the model with unsaturated carbon atom, we compared our calculated results with TPD experiments and calculated the formation energy of unsaturated carbon atom. The radical structure of unsaturated carbon atoms at the edges is more stable due to the stabilization of free radicals by π electron resonance.[3] Then we calculated the formation energy of the model with unsaturated carbon atom to further confirm the reliability of the model used in our calculations. It can be seen from **Fig. S8**, the formation energy E_f of the unsaturated carbon atom at the edge is 2.51 eV, much less positive than that of the defects at the basal plane reported in the literatures (single vacancy: $E_f \approx 7.5$ eV[4, 5], Stone-Wales: $E_f \approx 5$ eV[6, 7]). The lower formation energy suggests that the model with unsaturated carbon atom at the edge is more likely to be generated compared with the defects at the basal plane. Therefore, the model used for SO_2 chemisorption is reliable and expedient.

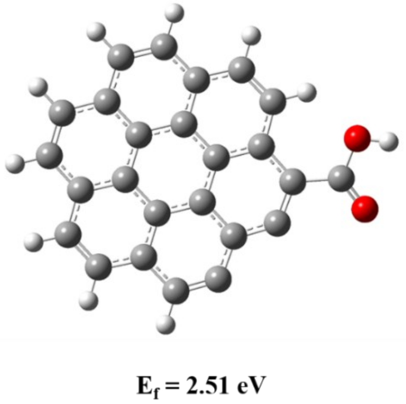

Fig. S8 The edge defect formation energy in carbon surface model with an edge defect containing unsaturated carbon atom.

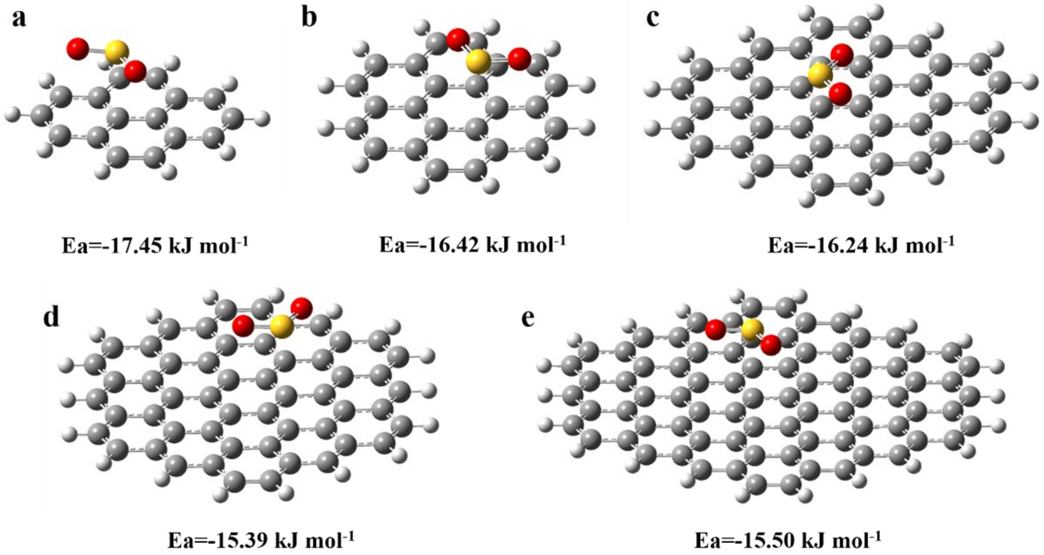

Fig. S9 Physisorption complexes of SO_2 on the basal plane of pristine carbon surface. SO_2 physisorption on the model containing 7a, 9 b, 14c, 19d, or 30e fused aromatic rings.

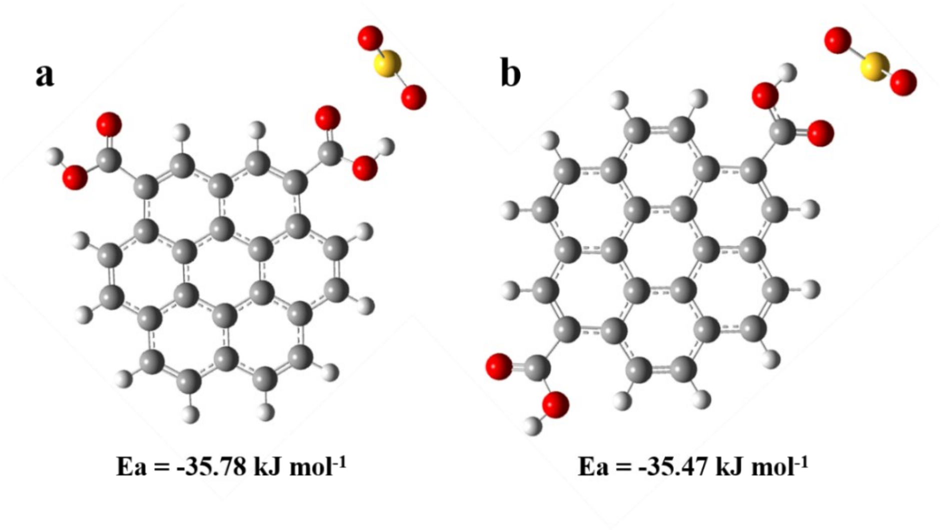

Fig. S10 Adsorption complexes of SO_2 at the edge position of carbon surfaces containing two carboxyl groups.

The adsorption energy results in a pure carbon surface case clearly claim that SO_2 molecule tends to adsorb on the basal edge with an adsorption energy of -5.69 kJ mol^{-1}. When carboxyl groups were embedded into the carbon surface, with two carboxylic groups carbon surfaces (**Fig. S10a** and **S10b**) demonstrate stronger affinity for SO_2 with larger adsorption energies of -35.78 kJ mol^{-1} and -35.47 kJ mol^{-1} (The value is within -100 kJ mol^{-1}, representative as physisorption). That is to say, carboxyl groups doping greatly facilitates SO_2 physisorption on edge locations of carbon surface. The results are in agreement with the above experimental finding that selectively decorating carboxyl groups on the edge of the carbon surface greatly enhanced SO_2 physisorption on the edge position.

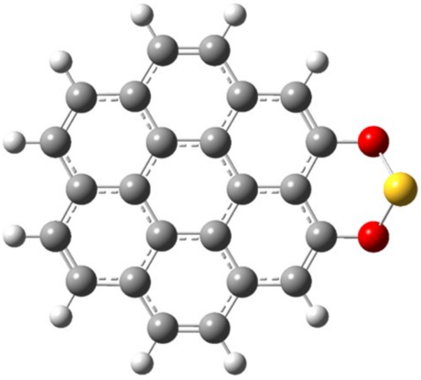

Fig. S11 Adsorption complex of SO_2 at the edge of the carbon surface with unsaturated carbon atoms.

The SO_2 adsorption energy on the edge position of the optimized SO_2 adsorption configurations for two unsaturated carbon surfaces is shown in the **Fig. S11**. (The value is beyond -100 kJ mol^{-1}, representative as chemisorption), which indicate that SO_2 chemisorption of the unsaturated carbon surfaces. The adsorption energies of unsaturated carbon surfaces are close to that of the unsaturated carbon surfaces with carboxyl groups, which indicate that the carboxyl groups doping almost have no influence for SO_2 chemisorption on the edge position.

Notes and references

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