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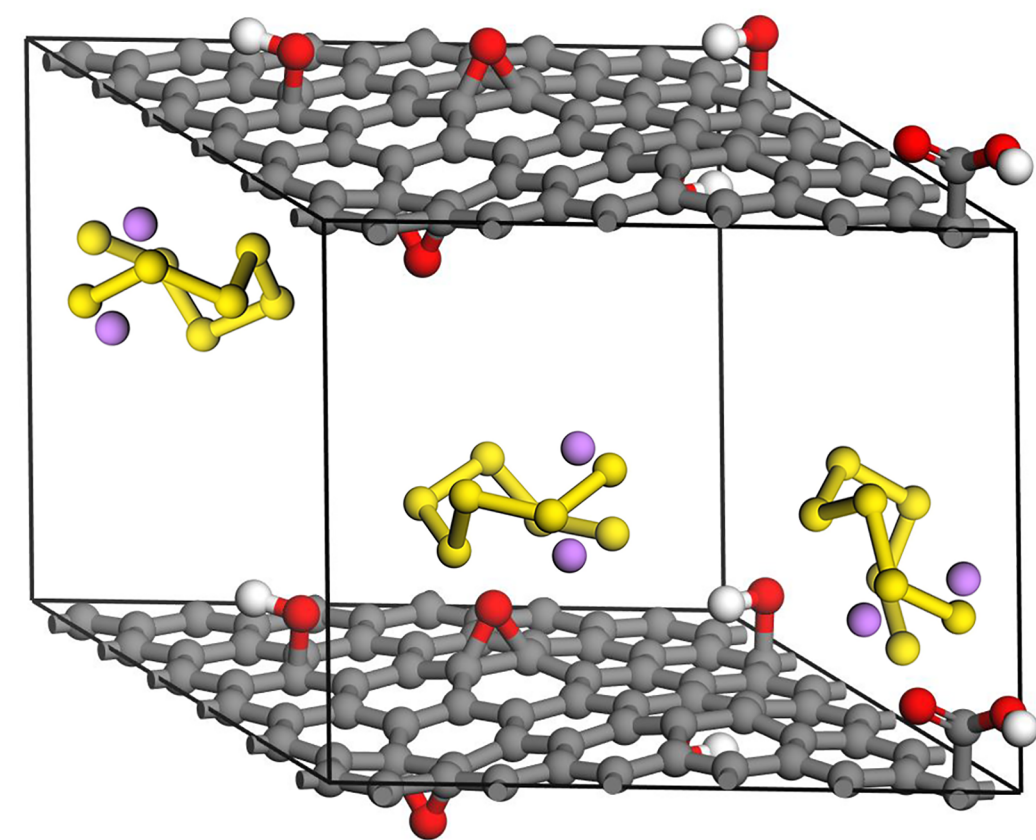
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First-Principles Study of Sulfur Species Adsorption on Microporous Reduced Graphene Oxide (rGO)

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INTRODUCTION



Lithium-sulfur (Li-S) battery has revolutionized the energy storage arena due to its high theoretical energy density, which is 5 times greater than Li-ion battery, non-toxic nature and the high abundance of sulfur in nature. However, due to the fact that the entire mechanism is governed by a complex chemistry where the anode, electrolyte and the cathode interact with each other, several issues have prevented the practical applications of Li-S batteries so far. In this study, a systematic first-principles density functional theory calculation is employed to gain insight into how microporous reduced graphene oxide (rGO) influences the adsorption of unlithiated S_8 and long chain lithium polysulfides (Li_2S_x , $x \geq 4$) in terms of van der Waals interaction and chemical bonding. At the early stage of lithiation, the interaction between non-polar S_8 and the substrate is dominated by physical interaction, thus smallest pore size induces the strongest interaction. Graphene domains and polar groups or rGO have the same adsorption strength towards S_8 , however functional groups develop a slight charge barrier at the interface. As discharge proceeds, functional groups enhances the interaction between long chain polysulfides by forming strong Li-O bonds and improve the conductivity of the cathode by facilitating the electron transfer at the interface.

RESULTS AND DISCUSSION

Influence of microporous structure towards anchoring of S species

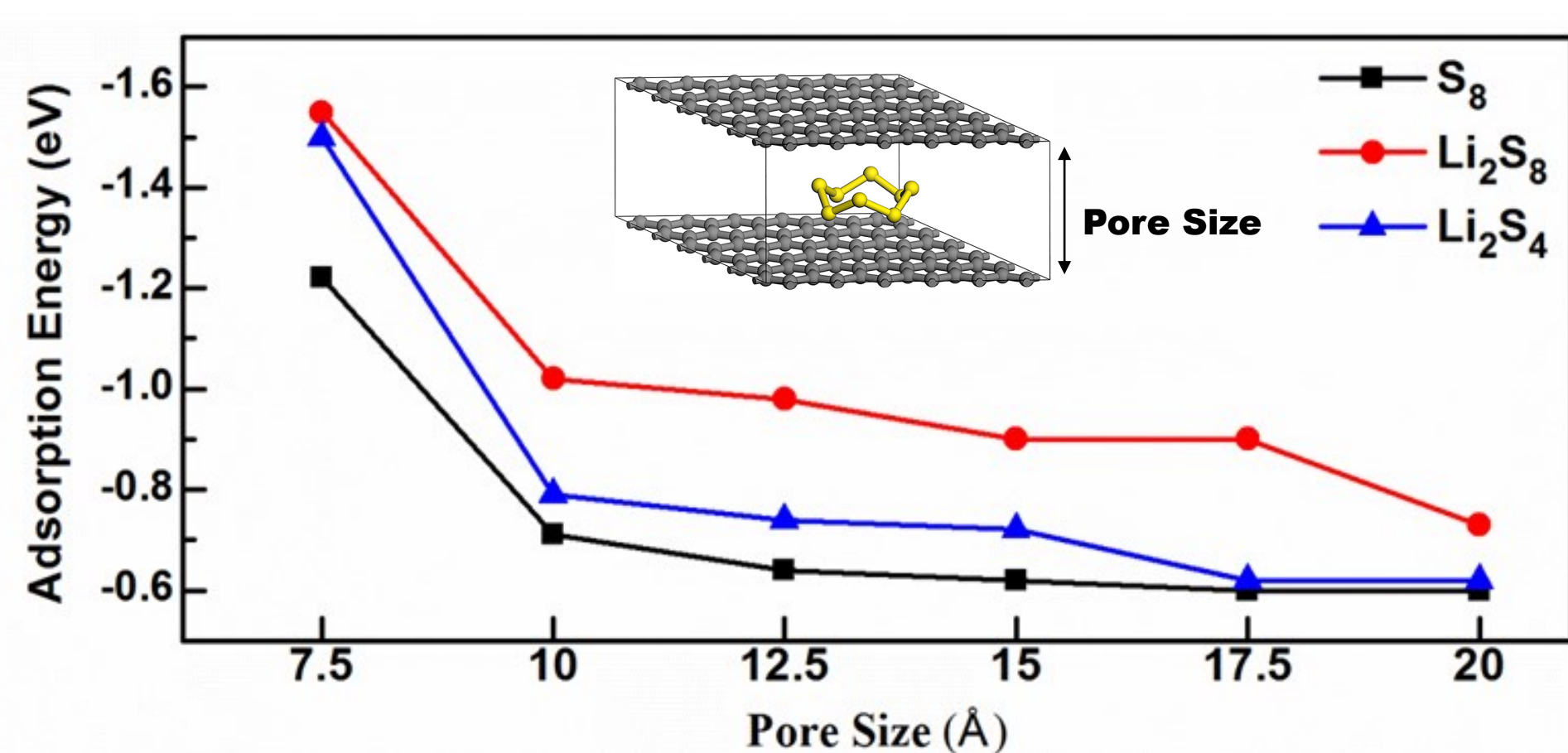
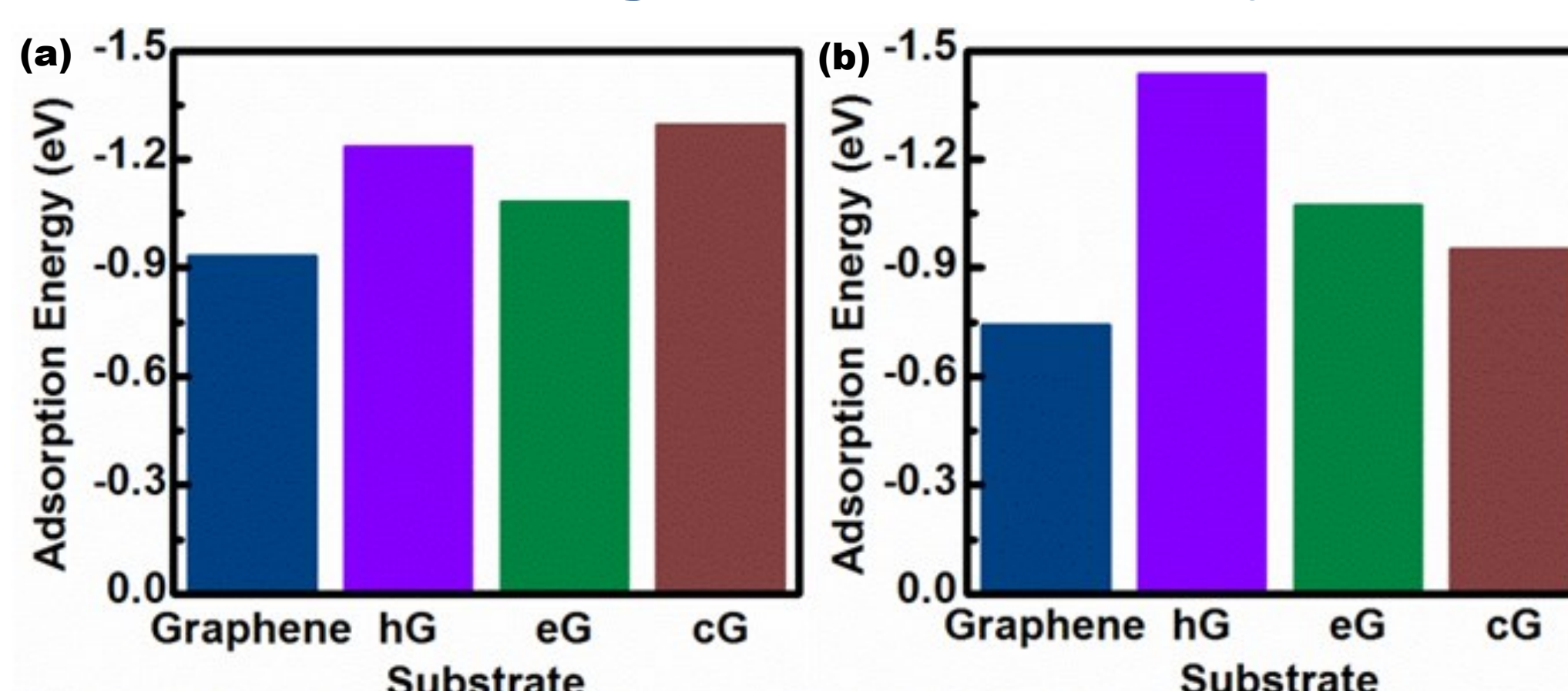


Fig. 1 Adsorption energies (E_{ads}) of S_8 , Li_2S_8 and Li_2S_4 to microporous graphene

- The variation in the energy profiles indicates that E_{ads} increases as the pore size decreases suggesting that the smallest pore has the highest adsorption strength.

Effect of different oxygen functional groups in rGO towards the adsorption of long chain lithium polysulfides



- All the functional groups in rGO show significantly higher adsorption energies for Li_2S_8/Li_2S_4 when compared with pristine graphene.

Fig. 7 Adsorption values of (a) Li_2S_8 and (b) Li_2S_4 interacting with graphene, hG, eG and cG

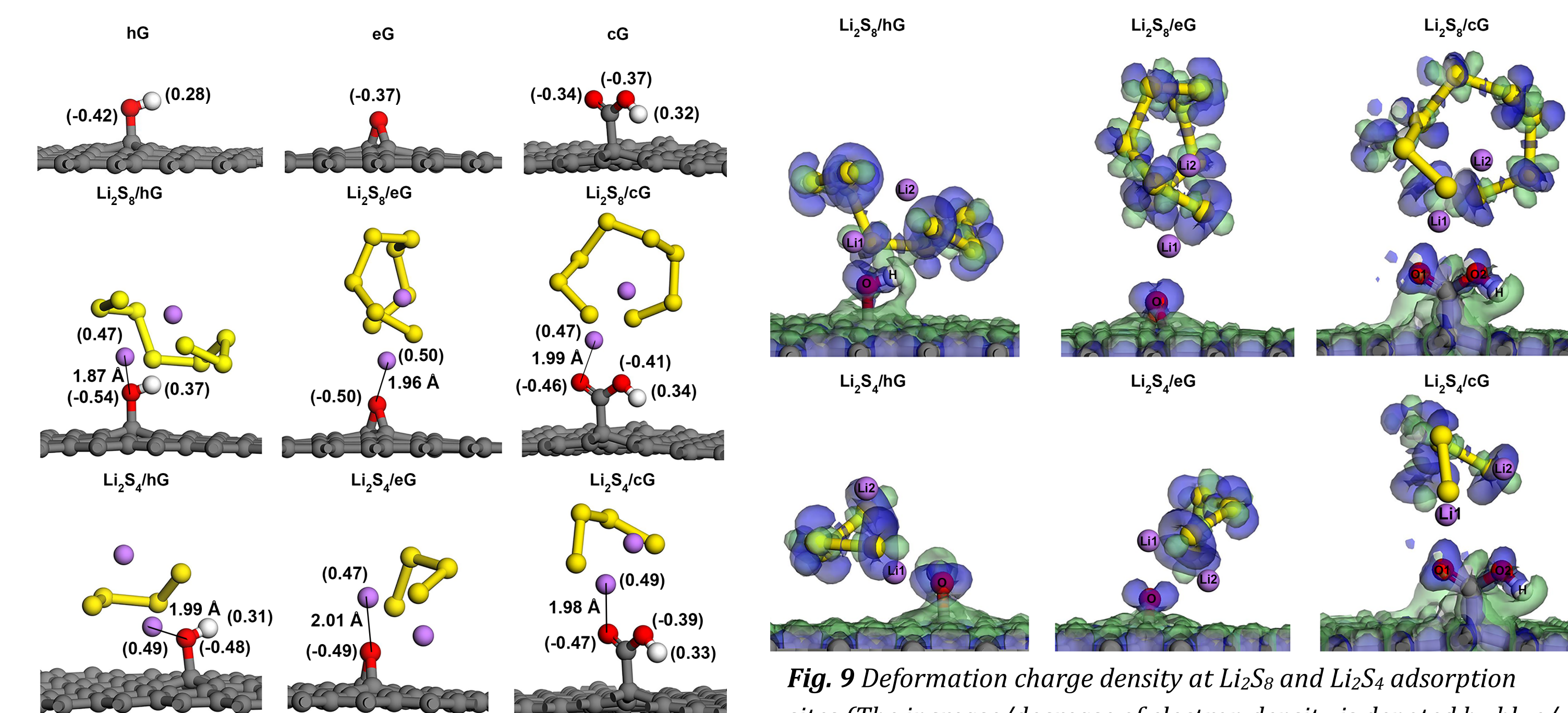


Fig. 8 Before and after adsorption of Li_2S_8 and Li_2S_4 (Charge of each atom is shown in parentheses. The shortest distance between Li (pink) atom and O (red) atom is shown in Å)

Fig. 9 Deformation charge density at Li_2S_8 and Li_2S_4 adsorption sites (The increase/decrease of electron density is denoted by blue/green, respectively)

- According to the deformation charge density analysis, electron charge has been transferred inside the S species and inside the graphene surfaces, yet no apparent charge transfer has occurred between them, suggesting no strong chemical interaction.

Effect of different oxygen functional groups in rGO towards the adsorption of S_8

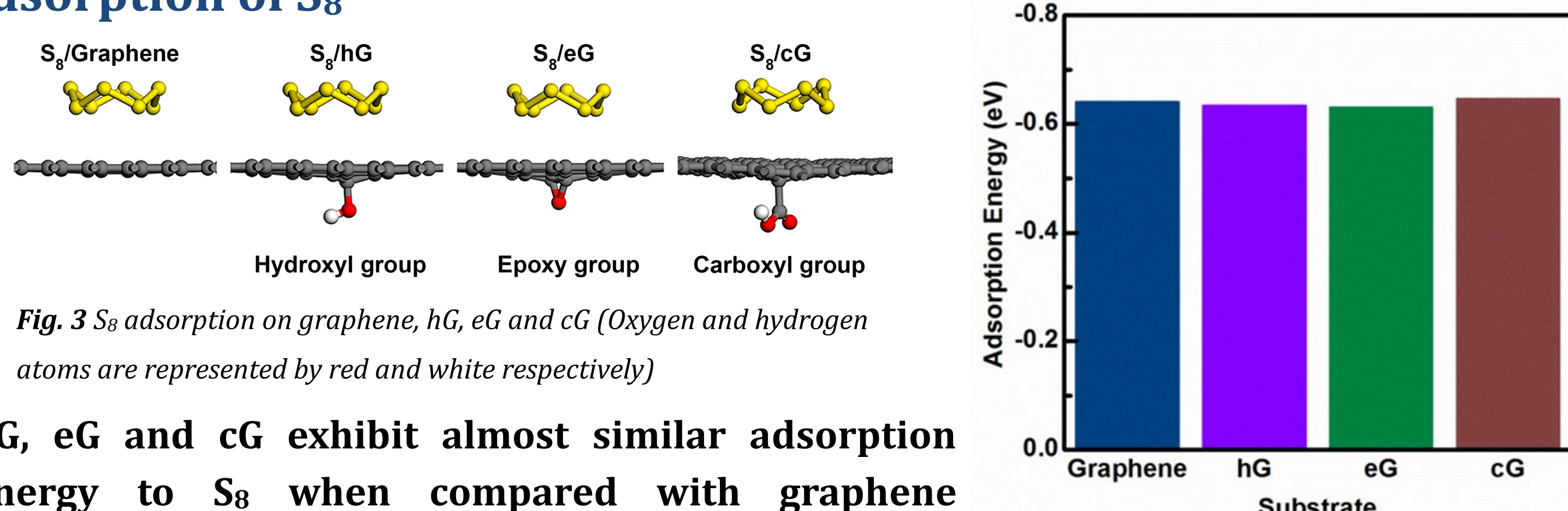


Fig. 3 S_8 adsorption on graphene, hG, eG and cG (Oxygen and hydrogen atoms are represented by red and white respectively)

Fig. 4 Adsorption values of S_8 interacting with graphene, hG, eG and cG

- hG, eG and cG exhibit almost similar adsorption energy to S_8 when compared with graphene illustrating that oxygen functional groups in rGO do not have a major influence on the adsorption of S_8 , as interfacial interaction between non-polar S_8 is dominated by van der Waals attraction.

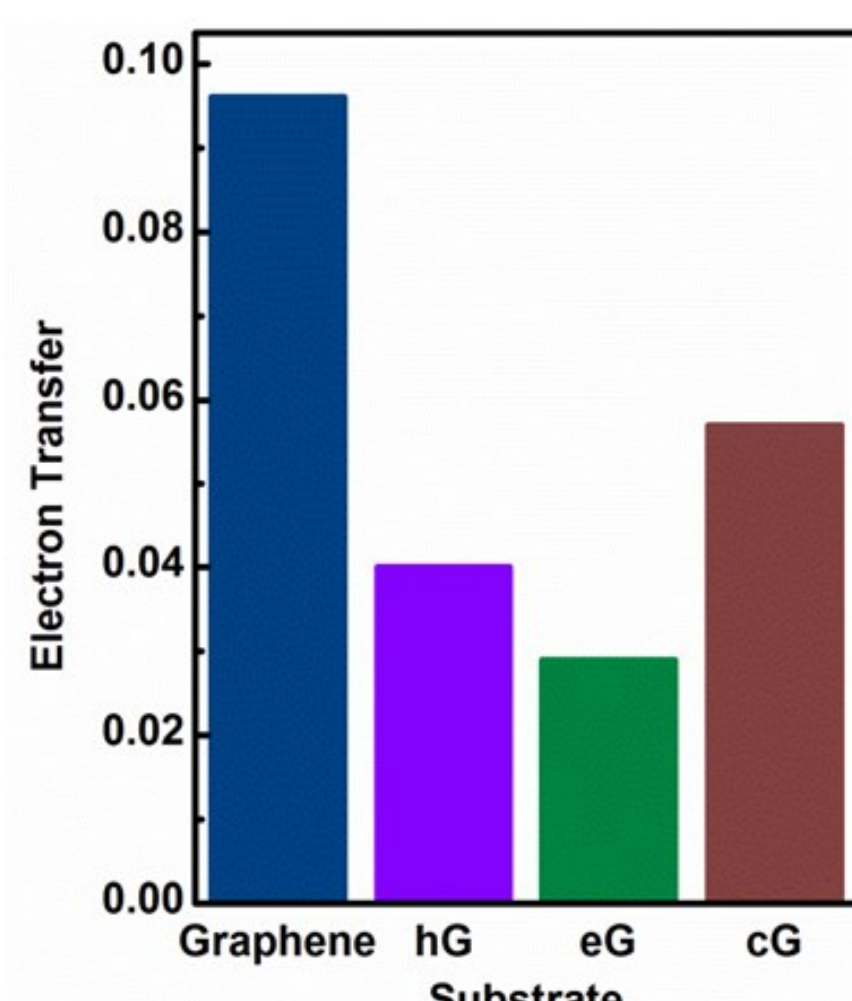


Fig. 5 Electron transfer from S_8 to different substrates

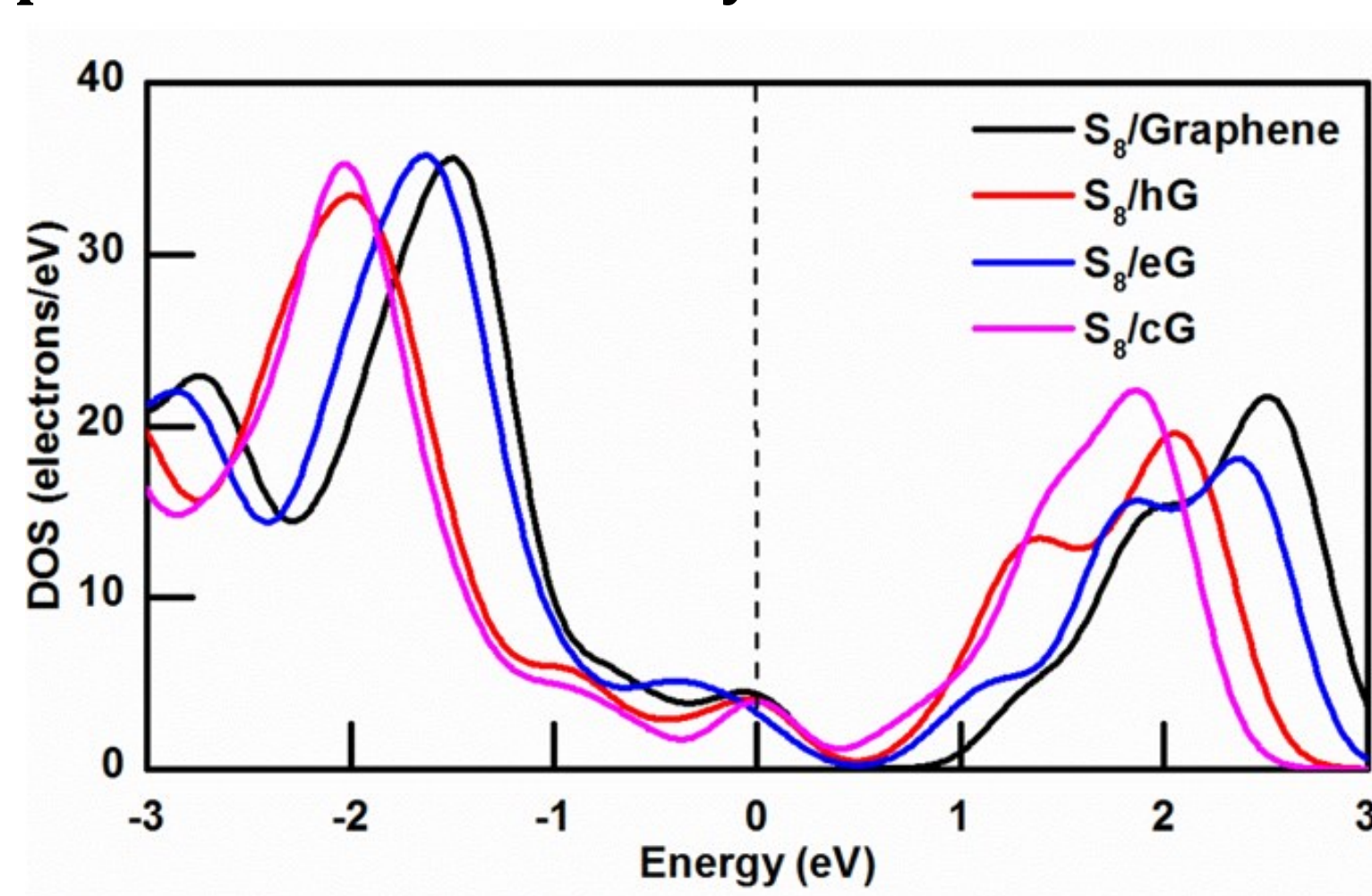


Fig. 6 Density of states (DOS) near Fermi energy region (E_f)

- There is only a minor contribution to charge transfer between S_8 to rGO surface where only 0.04, 0.03 and 0.06 electrons have been withdrawn from hG, eG and cG respectively.

- DOS value at E_f drops to 3.1 electrons per eV when eG adsorbs S_8 , suggesting that electron transfer at the interface is slightly hindered due to the oxygen functional groups on the graphene surface which then leads to building up of ohmic resistance at the S_8 /substrate interface.

- The calculated Li-O distances of adsorption geometries are almost similar with the strong ionic bond length of Li_2O molecule implying the existence of a strong attraction between Li and O.

- A significantly high electron density is visible around the lone pairs of the O atom strengthening the fact that extra pairs of electrons act as electron rich donor to interact with strong Lewis acid of Li ion.

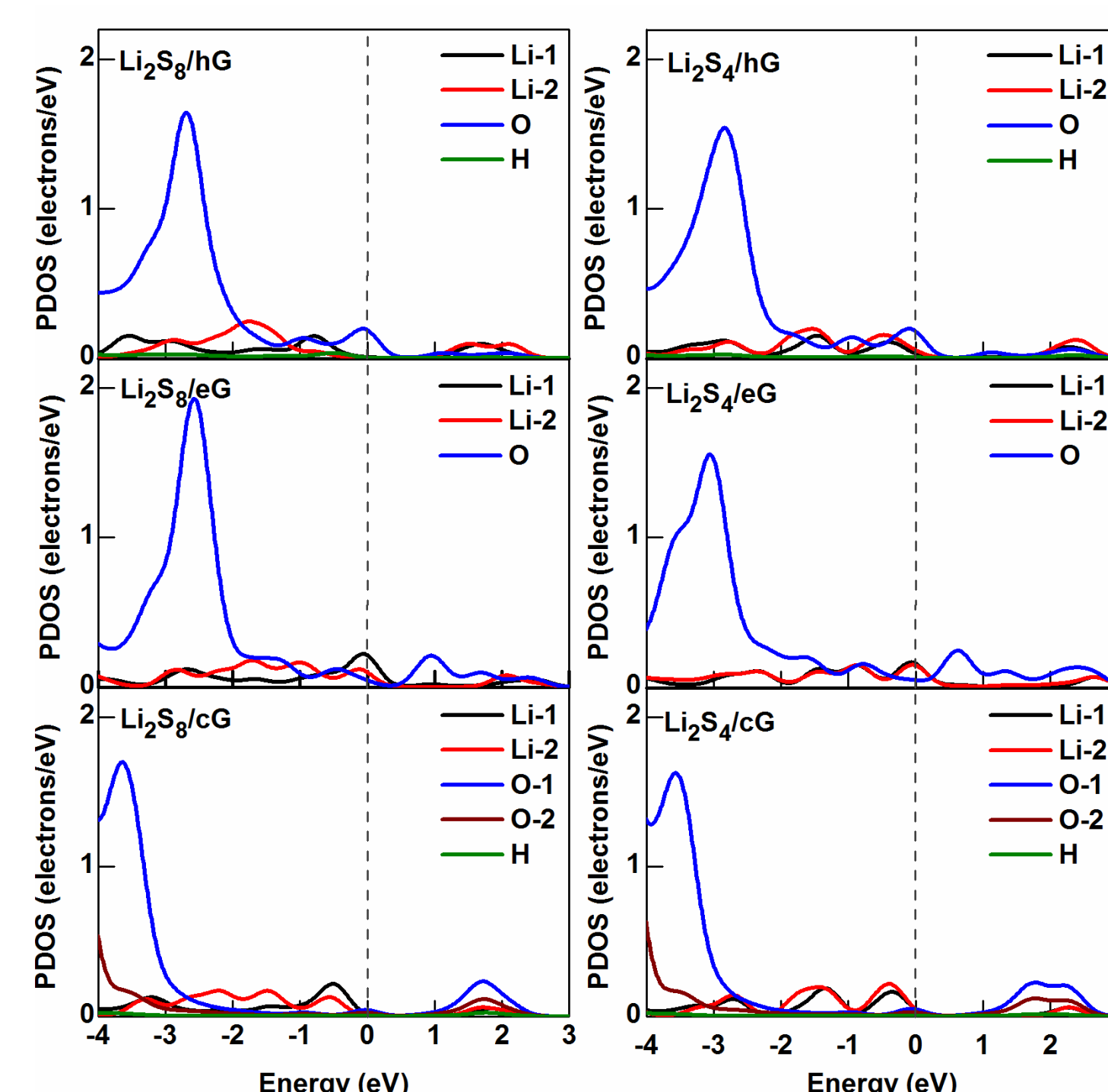


Fig. 10 Atomic partial density of states (PDOS) near the Fermi energy region for (a) Li_2S_8 and (b) Li_2S_4 on hG, eG and cG

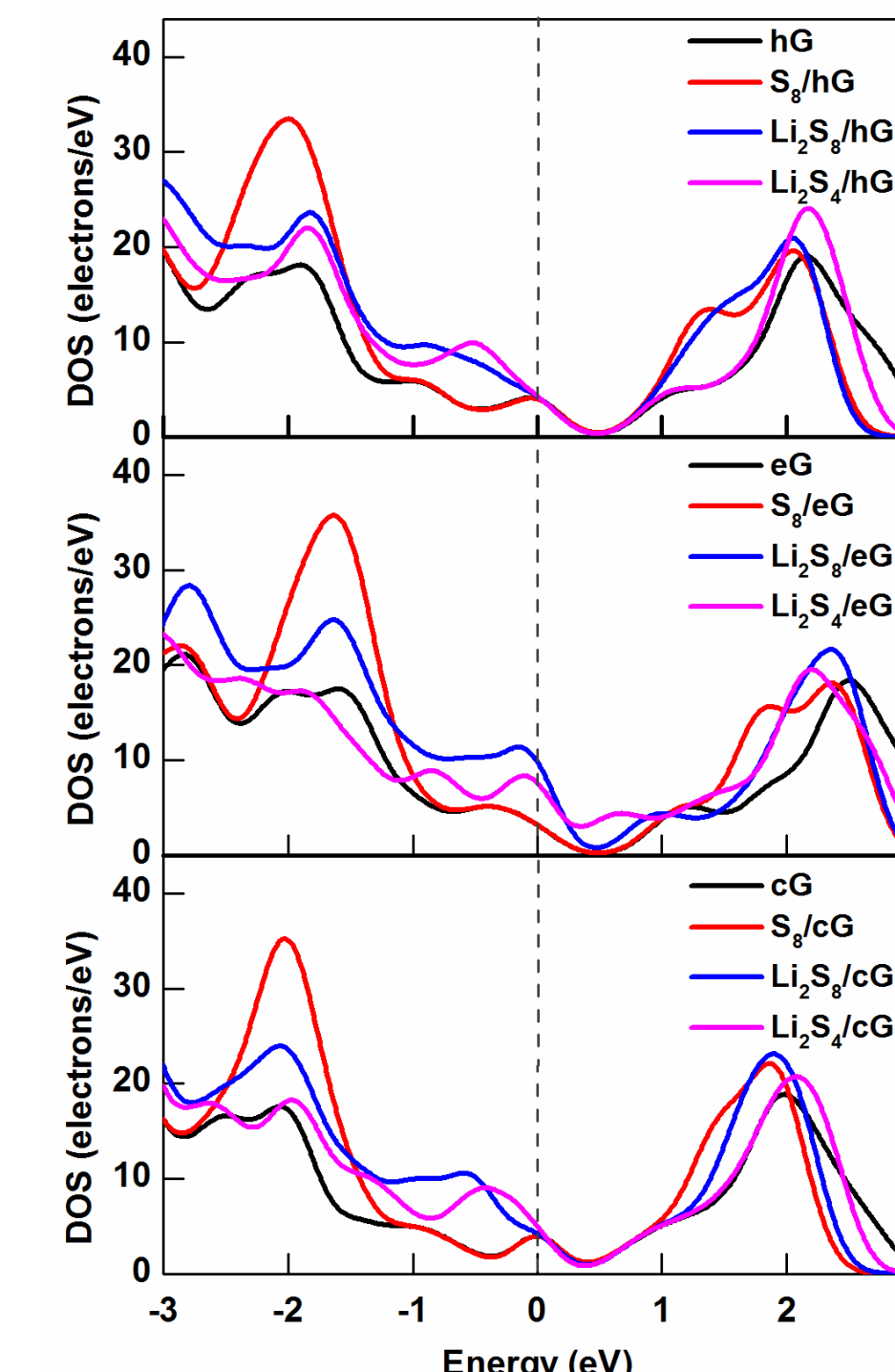


Fig. 11 Total density of states (DOS) near the Fermi energy region for S_8 , Li_2S_8 and Li_2S_4 on (a) hG, (b) eG and (c) cG

- The PDOS for Li-1 and O-1 atoms (indicated by black and blue colour) are seen to overlap at the upper part of the valence band (just below the Fermi level) suggesting that there is a hybridization between Li-2s and O-2p orbitals (Fig. 10).

- When Li_2S_8 and Li_2S_4 are adsorbed, due to the newly formed Li-O covalent bond, electron transfer at the interface has been improved and the DOS curve exhibits a higher value at E_f when compared with the S_8 adsorbed system.