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Adsorptive Characteristic Analysis of Graphene Oxide for Hydrogen Sulfide using Quantum Mechanical Simulation

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Abstract: As extreme events increase due to climate change, a variety of problems with sewer systems are rapidly increasing in addition. In this study, we investigated the potential of adsorption materials for hydrogen sulfide, one of the major cases of problems in sewer system. For candidates for filter material, we selected the graphene and graphene oxide, which has a high electrical and thermal conductivity with chemical stability to perform simulation by using quantum mechanical simulation. As results for analysis for hydrogen sulfide with three structures (pristine graphene, graphene oxide with epoxy group and graphene with hydroxyl group), graphene oxide with hydroxyl group showed the most stable structure with lowest binding energy and shortest binding distance. While, graphene oxide with epoxy group showed the adsorptive characteristics with hydrogen sulfide, however the effects by introducing oxide group was negligible. In further study, investigation for the conditions under a large number of hydrogen sulfides or the other hazardous substances should be accompanied.
Keywords: Hydrogen sulfide, graphene, graphene oxide, DFT, simulation

I. INTRODUCTION

Hydrogen sulfide (H2S) is a primary toxic gas emitted from various industrial processes, making its effective control and removal essential for preventing environmental pollution and ensuring operational safety. Hydrogen sulfide is predominantly generated in petroleum and natural gas processing, steel production, and wastewater treatment facilities, posing significant health risks due to its characteristic odor and high toxicity. In South Korea, combined sewer systems that transport both domestic wastewater and stormwater through a single pipeline have recently been associated with asphyxiation incidents, which are attributed to increased organic matter concentrations and insufficient ventilation [1]. Furthermore, as extreme events increase by climate change, problems with sewer systems are making it difficult to respond the hydrogen sulfide emissions. Therefore, a thorough understanding of hydrogen sulfide's adsorption characteristics and the development of efficient removal technologies are critical [2].

While there are multiple methods for hydrogen sulfide removal—such as biological treatment, chemical oxidation, and physical/chemical scrubbing—adsorption technology using filters has attracted substantial interest. This approach is valued for its high removal efficiency and excellent performance under low-temperature and low-pressure conditions, making it suitable for both large- and small-scale applications [3]. Carbon-based material filters, including Activated Carbon, Graphene, Carbon Nanotubes, Carbon Nanofibers, Biochar, and Carbon Aerogels, have shown rapid research advances over the past decade. This trend is largely due to the inherent stability, extensive surface area, and structural versatility of carbon-based materials, which foster new applications across various fields in chemistry, physics, and engineering. These materials demonstrate high adsorption capabilities for a range of pollutants, including toxic metal ions, pharmaceuticals, pesticides, metalloids, and other inorganic and organic compounds [4].

In this study, we investigated the chemisorption behavior of hydrogen sulfide on carbon allotropes, specifically graphene and graphene oxide, through quantum mechanical simulations based on Density Functional Theory (DFT) [5].

II. COMPUTATIONAL METHOD

2.1 Computational details

To model the adsorptive characteristics between H_2S and carbon allotropes, we performed the quantum mechanical DFT calculation using Dmol3 module in Materials studio software for condensed matter system for modelling the surfaces of the electronic structures. [6,7,8] We utilized the gradient approximation (GGA) method with the non-empirical local functional and the Perdew-Burke-Ernzerhof correlation (PBE) and double numerical basis plus polarization (DNP) basis set, which has been used actively in the fields of materials science. [9,10] We performed the calculation at 0 K without pressure, and with zero-point motion. Furthermore, the convergence tolerance for energy and SCF density are 2 × 10−5 Ha and 1 × 10−5 Ha, respectively. Conventional DFT calculation limits to correctly describe the R−6 asymptotic potential for dispersive intermolecular interactions.

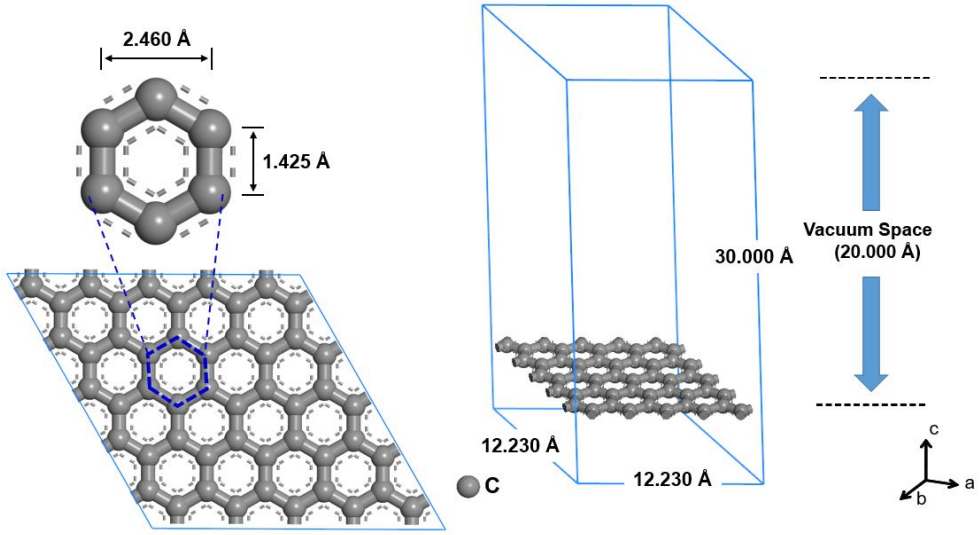

Figure 1Geometry optimization of graphene

2.2 Gemotry optimization

Among various substrates, we performed the geometry optimization for the graphene and graphene oxide, which are widely used as adsorbents for pollutants such as H2S and ammonia, which has excellent thermal and electrical and mechanical properties and a wide range of applications.

As seen in Figure 1, the graphene and graphene oxide are fixed with 12.230 Å× 12.230 Å× 30.000 Å and the vacuum was set to 20.000 Å. For analyzing the electronical effects of k-point sampling for structure and energy, we modelled various k-point sampling for Brillouin zone using Mornkhorst-Pack k-point scheme.

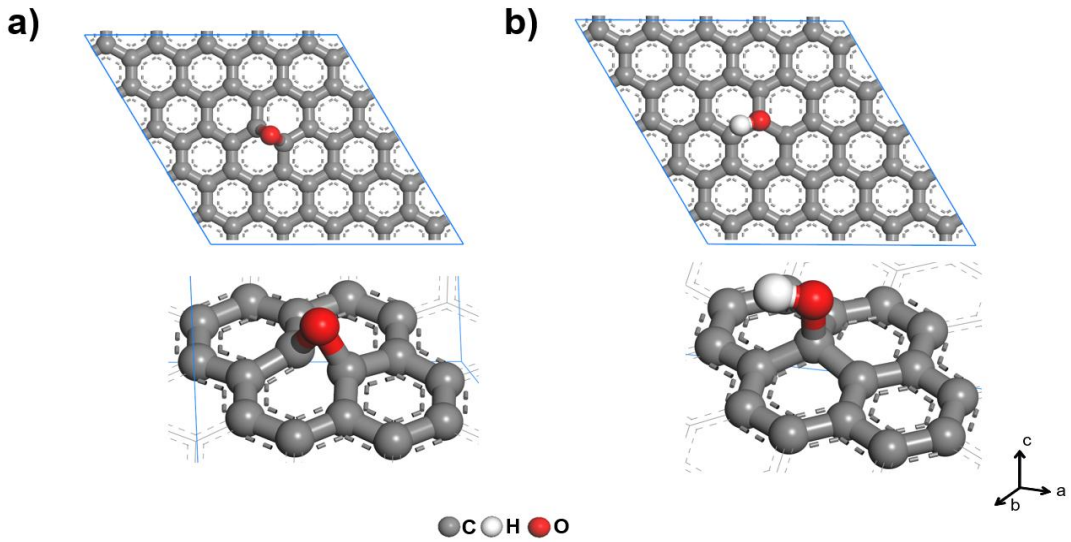

Figure 2 Geometry optimization of graphene oxides with (a) epoxy group and (b) hydroxyl group

Geometry for graphene oxides were analyzed by varying two features (one with epoxy group and one with hydroxyl group) as shown in figure 2. As the graphene has a structure of hexagons in a honeycomb shape, it has three adsorption sites : 1) Hollow site between hexagon, 2) Top site on the carbon atom, and 3) Bridge site on the bridge between carbon atoms. To determine the optimal adsorption position between adsorbent and adsorbate, we calculated each adsorption energy at each condition.

Adsorption energy by total energy calculation is performed with the equation below:

$$\Delta E_a = \frac{E_{adsorbent\ +adsorbate\ } - (E_{adsorbent\ } + nE_{adsorbate\ })}{n}$$

Herein, ΔE_a a means adsorption energy, $E_{adsorbent\ +adsorbate}$ is the total energy of geometry optimized adsorbent with adsorbate, and n is the number of adsorbates. Binding energy is expressed in eV after conversion from the existing Hartree value, and a lower binding energy (a larger negative value) indicates greater stability.

III. RESULTS

To figure out the optimal positions of structures for adsorbing hydrogen sulfide, we calculated and compared the binding energies by locating differently to each position (Hollow site, top site and bridge site). The calculated binding energies for the comparison are listed in table 1.

Table 1 Binding energy dependents on the adsorption location of hydrogen sulfides

	Hollow site	Bridge site	Top site
Graphene	**-0.683860578**	-0.665081991	-0.653522588
Graphene oxide (-O-)	-0.566870606	-0.569393103	**-0.578225923**
Graphene oxide (-OH)	**-0.937209597**	-0.814875306	-0.892283575

As described above, Despites of the graphene oxide with epoxy group (-O-), other two structures a lower binding energy (a larger negative value) indicates greater stability. For the ease visibility for the readers, the lowest (most stable) position was indicated with bold. Despite the graphene oxide with epoxy group (-O-), the other two group (pristine graphene and graphene oxide with hydroxyl group) with hydrogen sulfide located in hollow site showed the lowest binding energy, while the structure with epoxy group showed the lowest binding energy when the hydrogen sulfide is located in top site.

Furthermore, all the calculation was initially set to 3.000 Å based on S atom, thus we also observed the changes in binding distances. The phases of structures for each lowest (most stable) binding energy are shown in figure 3. In addition to the results of binding energy, the binding distance analysis also showed the different phase of the structure with epoxy group (-O-).

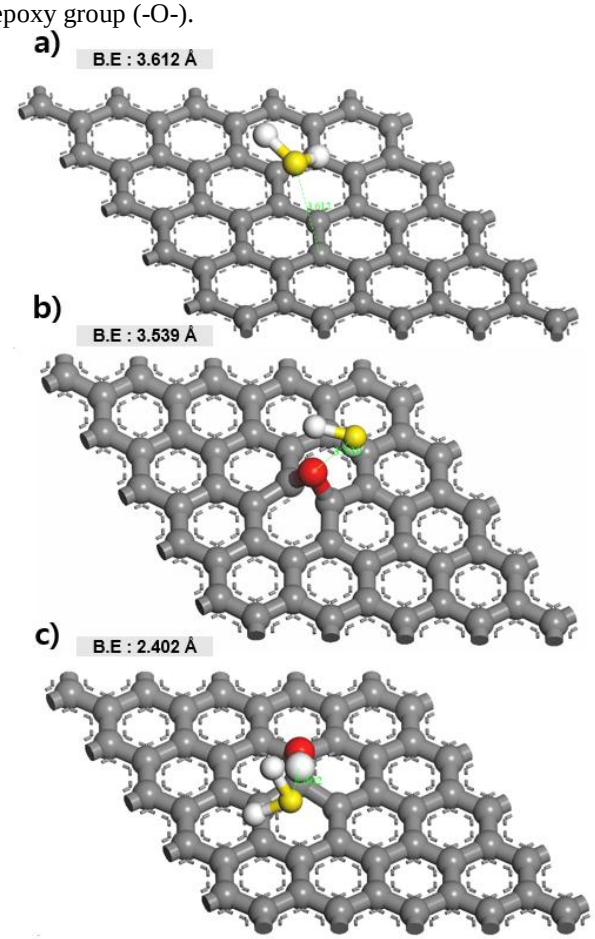

Figure 3 Adsorption phases between hydrogen sulfide and (a) graphene and graphene oxide with (b) epoxy group and (c) hydroxyl group

The binding distance between pristine graphene before introducing oxide group and hydrogen sulfide (figure 3a) was 3.612 Å. After introducing the oxide group, distance between S atom of hydrogen sulfide and C atom of graphene oxide with epoxy group (figure 3b) was slightly shortened to 3.539 Å. While the distance between hydrogen sulfide and graphene oxide with hydroxyl group (figure 3c) was significantly shortened to 2.402 Å, which showed that the graphene oxide with hydroxyl group has the most advantageous structure for adsorbing hydrogen sulfide among three structures.

IV. CONCLUSION

In this study, we analyzed the feasibility of graphene and graphene oxides (with epoxy group and hydroxyl group) as an adsorbent filter for hydroxyl sulfides by performing calculation using quantum mechanical simulation.

For the optimal adsorption location, hydrogen sulfide showed stable status in hollow site of the pristine graphene and graphene oxide with hydroxyl group (-OH), while it showed stability in top site of the graphene oxide with epoxy group (-O-).

Furthermore, as a result of the binding energy, all of three structures showed the negative binding energy, which means the affinity for the adsorption. Binding energy between hydrogen sulfide with graphene oxide (hydroxyl group) significantly became stable, while that with graphene oxide (epoxy group) became slightly unstable after introducing oxide group.

The binding distance between graphene oxide with hydroxyl group was significantly shortened to 2.402 Å compared to that with pristine graphene (3.612 Å), while the distance between graphene oxide with epoxy group was slightly shortened to 3.539 Å, which showed the possibility of graphene oxide with hydroxyl group as a filter material for adsorbing hydrogen sulfide.In further study, investigation for the conditions under a large number of hydrogen sulfides or the other hazardous substances should be accompanied.

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REFERENCES

[1] K.I. Gil, G.C. Shin, J.Y.Im, Investigation of odor release from combined sewer, *Journal of the Korean Society of Hazard Mitigation, 10(6),* 2010, 185-191.

[2] T.J. Bandosz, On the Adsorption/Oxidation of Hydrogen Sulfide on Activated Carbons at Ambient Temperatures, *Journal of Colloid and Interface Science, 246(1),*2002, 1-20.

[3] K. Vikrant, S.K. Kailasa, D.C.W. Tsang, S.S Lee, P. Kumar, B.S. Giri, R.S. Singh and K.H. Kim, *Journal of Cleaner Production, 187(20),* 2018, 131-147.

[4] M. Sabzehmeidani, S. Mahnaee, M. Ghaedi, H. Heidari and V. Roy, Carbon based materials: a review of adsorbents for inorganic and organic compounds, *Mater. Adv., 2*, 2021, 598-627.

[5] T. Kim, Y. Kwon, C. Kang, J. Kim, H. Shin, S. Kwon and S. Cha, The investigation of adsorption properties of filter media for removal efficiency of nitrogen, phosphorus using experimental and density functional theory, *Journal of Wetlands Research, 20(3),* 2018, 263-271.

[6] W. Koch and M.C. Holthausen, *A Chemist's Guide to Density Functional Theory (2nd ed.),* (Weinheim, Wiley-VCH,2001).

[7] DessaultSystemes, *Dmol^3 from Materials Studio 2017,* (San Diego, BIOVIA, 2017).

[8] B. Delly, From molecules to solids with Dmol^3 approach, *Journal of Chemical Physics, 113,* 2000, 7756-7764.

[9] J.P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Physics Review Letters, 77(18),* 1996, 3865-3868.

[10] J.P. Perdew, K. Burke and M. Ernzerhof, Local and gradient-corrected density functionals, *Chemical Applications of Density-Functional Theory, 629(30),* 1996, 453-462.