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Density functional theory study of CH_4 and CO_2 adsorption by fluorinated graphene

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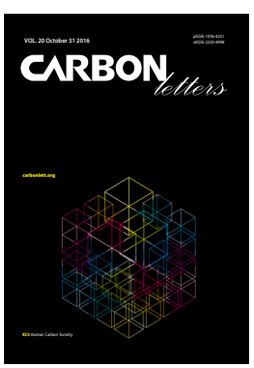

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Phenomena related to global warming have been of particular interest among researchers, strongly encouraging them to identify various methods of adsorbing contributing gases, such as CH_4 and CO_2 [1,2]. Many adsorbents have been widely proposed and studied to remove greenhouse gases from the atmosphere and protect the environment [3,4]. Carbon-based materials for adsorption are an intriguing subject owing to their very high specific surface area, low weight, and elasticity [5,6]. Among various carbonaceous materials, graphene has attracted much attention from researchers for these reasons; consequently, this material has been empirically and theoretically investigated for possible applications, such as gas sensors [7-10].

Yoon et al. [7] reported the fabrication of a graphene-based CO_2 sensing device that exhibited a fast response to CO_2 and high recyclability due to the weak interaction between CO_2 and graphene. Schrier [8] studied the adsorption of several gas molecules, including CO_2 and CH_4, on pristine graphene and fully fluorinated graphene at finite temperature. He reported that complete fluorination of graphene is not an effective method for nonpolar gas molecules, such as CH_4 and CO_2, because the fluorine atom has the lowest polarizability of all atoms, and its dispersion interaction is weak. In addition, for nonpolar molecules, dispersion interactions play the largest role in adsorption. Lee et al. [9] reported the effect of fluorination of a carbon-based substrate on CH_4/CO_2 separation. They reported that the CO_2 adsorption capacity increased up to 22.5% owing to fluorination with an F/C ratio (%) of 32%–43%.

Although experimental studies on the adsorption of gas molecules onto carbon-based substrates have provided much useful information, computational studies at the molecular level can provide detailed information to investigate the interaction between adsorbed gas molecules and substrates. In this study, density functional theory (DFT) calculations were performed to investigate CH_4 and CO_2 adsorption on pristine and fluorinated graphene. This research extends existing knowledge of fluorinated carbon-based materials and their adsorption efficiency from a theoretical viewpoint. The results of this investigation also shed light on further possibilities for computational research on fluorinated carbon-based materials.

The DFT calculations were conducted using the Biovia DFT package DMol3 [11], considering the generalized-gradient-approximation (GGA) as well as the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functionals with the double numerical polarized basis set. The GGA-PBE functional has been successfully used to describe the interaction between organic molecules and a carbon-based substrate [12-18] or an inorganic substrate [19-23]. We used a 5 × 5 × 1 Monkhorst–Pack *k*-point mesh [24] with a 12.30 Å × 12.30 Å × 15.00 Å periodic boundary condition for the graphene substrate.

The adsorption energy (E_{ads}) was defined as

$$E_{ads} = E_{substrate+gas} - E_{substrate} - E_{gas},$$

where $E_{substrate+gas}$ represents the energy of the entire system, $E_{substrate}$ is the energy of the substrate system alone, and E_{gas} is the energy of the isolated gas molecule. Lower adsorption energy values indicate greater stability according to the definition of the equation. Because

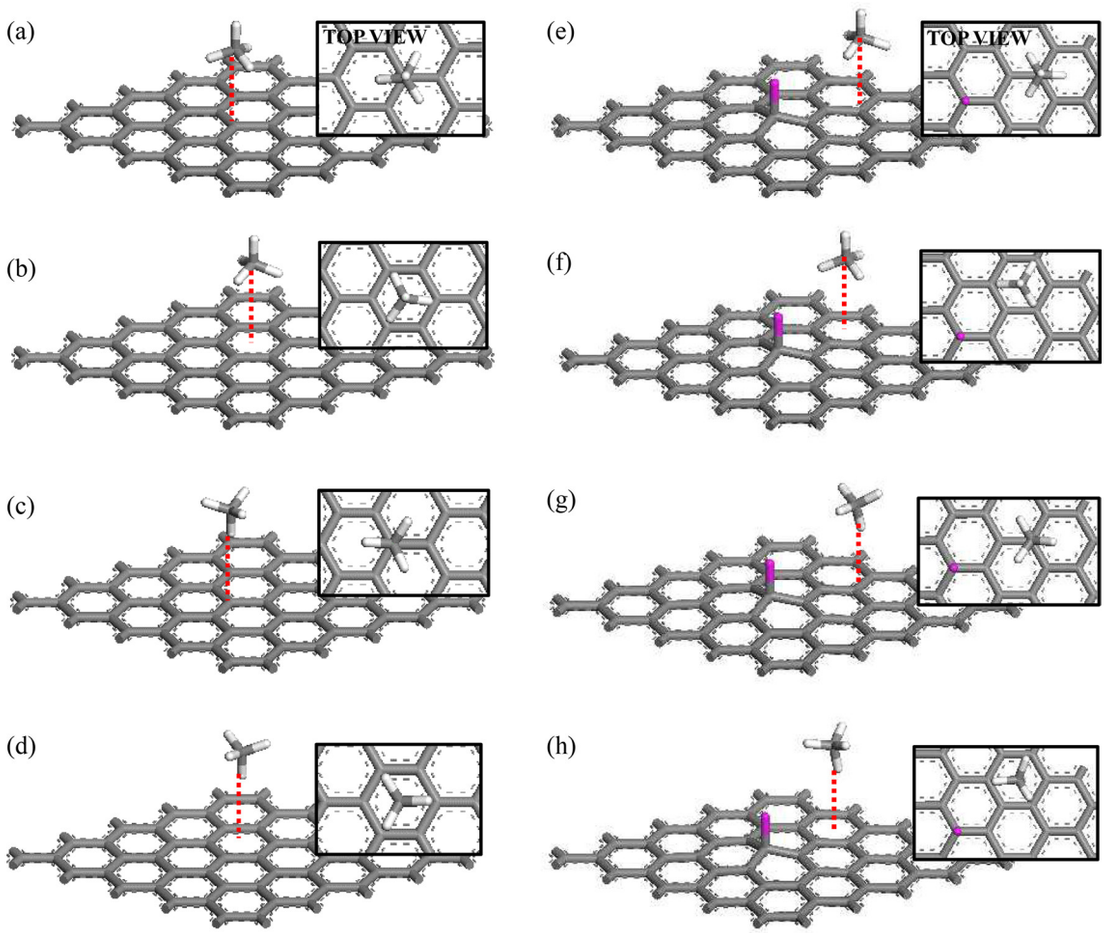

Fig. 1. Optimized geometry of CH_4 molecule on pristine and fluorinated graphene substrates: (a, b) hydrogen tripod of CH_4 directed to the substrate adsorbed onto top and hollow sites of pristine graphene, respectively; (c, d) hydrogen tripod of CH_4 directed away from the substrate adsorbed onto top and hollow sites of pristine graphene, respectively; (e, f) hydrogen tripod of CH_4 directed to the substrate adsorbed onto top and hollow sites of fluorinated graphene, respectively; (g, h) hydrogen tripod of CH_4 directed away from the substrate adsorbed onto top and hollow sites of fluorinated graphene, respectively. Gray, white, and purple denote carbon, hydrogen, and fluorine, respectively.

dispersion interactions play an important role in the interaction between gas molecules and substrates, it is crucial to incorporate accurate calculations of the dispersion forces. Therefore, we applied the dispersion-corrected DFT (DFT-D3) method for a better description [25].

Figs. 1 and 2 show the geometrically optimized structures with adsorption sites at the top, hollow, and bridge sites of pristine and fluorinated graphene to determine the most energetically stable configuration with CH_4 and CO_2 molecules, respectively. The top, hollow, and bridge sites are adsorption sites on the top of the carbon atom, in the hollow of the six-membered carbon ring, and on the bridge of the carbon–carbon bond, respectively. Table 1 summarizes the adsorption energies of all of the configurations with each gas molecule on the substrate.

The DFT calculation showed that the configuration (Fig. 1a) in which the carbon of methane with a hydrogen tripod was placed atop the carbon atom of the graphene substrate was the most stable site for CH_4 adsorption. The adsorp-

Table 1. Adsorption energy (E_{ads}) of CH_4 and CO_2 molecules on pristine and fluorinated graphene substrates

	Site	Pristine graphene	Fluorinated graphene
		E_{ads} (meV)	E_{ads} (meV)
cH4	C-Top (Fig. 1a and e)	–151	–185
	C-Hollow (Fig. 1b and f)	–140	–163
	H-Top (Fig. 1c and g)	–84	–114
	H-Hollow (Fig. 1d and h)	–84	–112
CO_2	2O-Bridge (Fig. 2a and e)	–136	–176
	C-Bridge (Fig. 2b and f)	–188	–224
	2O-CTop (Fig. 2c and g)	–144	–192
	Perpendicular (Fig. 2d and h)	–101	–163

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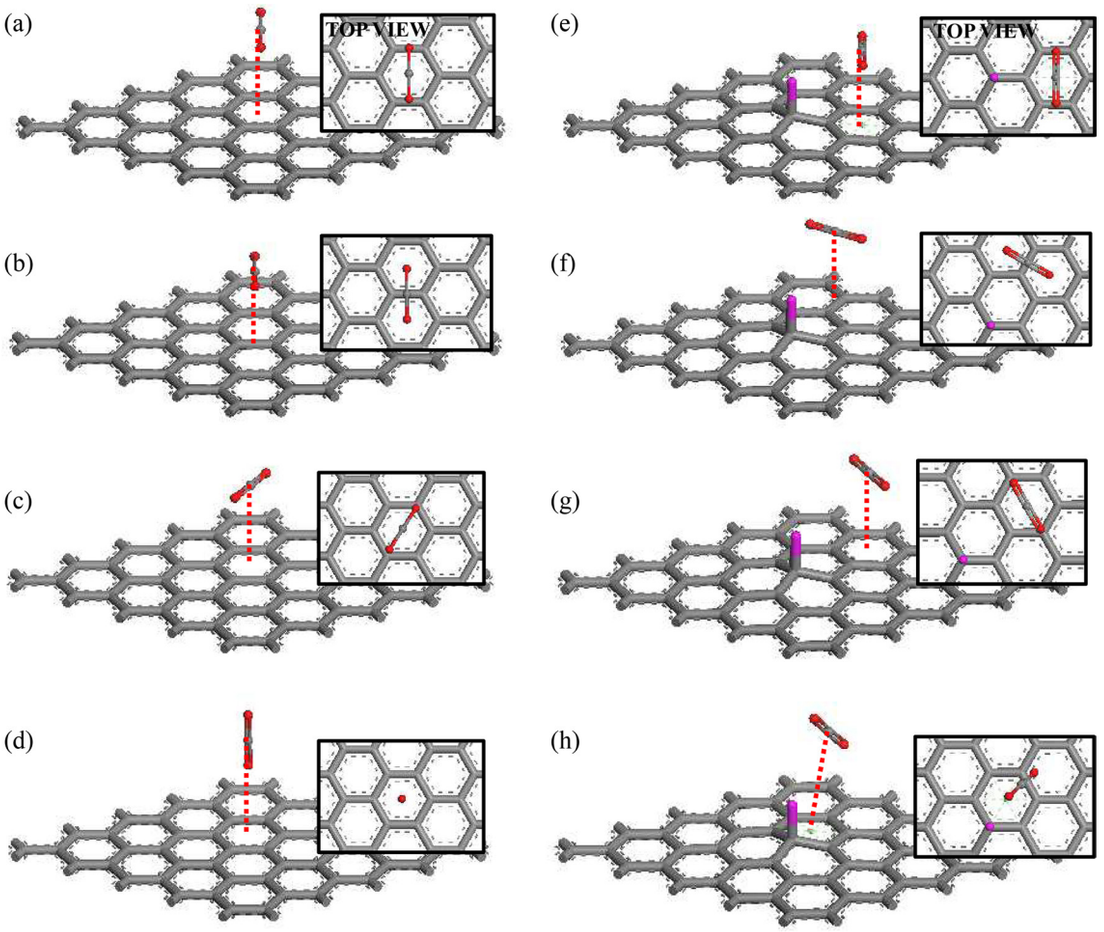

Fig. 2. Optimized geometry of CO_2 molecule on pristine and fluorinated graphene substrates: carbon of CO_2 lying in parallel adsorbed onto (a) a hollow site of pristine graphene with two oxygen atoms on C–C bonds, (b) a bridge site of pristine graphene with two oxygen atoms on adjacent hollow sites, and (c) a hollow site of pristine graphene with two oxygen atoms on two carbon atoms; (d) CO_2 lying perpendicular to pristine graphene adsorbed onto its hollow site; carbon of CO_2 lying in parallel adsorbed onto (e) a hollow site of fluorinated graphene with two oxygen atoms on C–C bonds, (f) a bridge site of fluorinated graphene with two oxygen atoms on adjacent hollow sites, and (g) a hollow site of fluorinated graphene with two oxygen atoms on two carbon atoms; (h) CO_2 lying perpendicular to fluorinated graphene adsorbed onto its hollow site. Gray, red, and purple denote carbon, oxygen, and fluorine, respectively.

tion energy was measured to be −151 meV. The adsorption energy was −140 meV when the carbon of methane was placed at the hollow site of the graphene substrate (Fig. 1b). The configurations (Fig. 1c and d) in which the methane molecule with the hydrogen tripod was directed away from the substrate showed weaker adsorption energies (−84 meV) than those with the hydrogen tripod directed to the substrate. To investigate the effect of fluorination with a single gas molecule, we added a fluorine atom on a carbon of the graphene substrate to partially fluorinate the substrate. The same configurations of the gas molecule were used to calculate the adsorption energy on the fluorinated graphene, as shown in Fig. 1e-h. The results indicate that the adsorption energies of the CH_4 molecule were increased by 17%–35% (−112 to −185 meV) compared to those on the pristine graphene substrate.

For CO_2 adsorption, the most stable configuration (Fig. 2b) has the carbon placed in the middle of a covalent bond between two carbon atoms of the substrate, with the two oxygen atoms placed atop the adjacent hollow hexagonal sites. The adsorption energy was measured to be −188 meV. Other configurations (Fig. 2a, c, and d) for the interaction between CO_2 and pristine graphene showed weaker adsorption energies of −136, −144, and −101 meV, respectively, in comparison to the configuration mentioned above (Fig. 2b). The adsorption energy in the perpendicular orientation (Fig. 2d) was almost half that of the most stable orientation. As seen in Table 1, CO_2 is more strongly adsorbed on graphene than CH_4. Because CO_2 has a higher quadrupole moment [$(-14.27 \pm 0.61) \times 10^{-40}$ Cm^2] [26] than CH_4, whose quadrupole moment is zero, it is reasonable to conclude that graphene shows a preference for CO_2 over CH_4 in terms of adsorption. This trend agrees with the result reported by Wood et al. [27].

The same gas molecule configurations were used to calculate the adsorption energy of a CO_2 molecule on the fluorinated graphene substrate, as shown in Fig. 2e-h. The results show that adsorption of CO_2 on the fluorinated graphene improved by 19%–62% (−163 to −224 meV) compared with that on the pris-

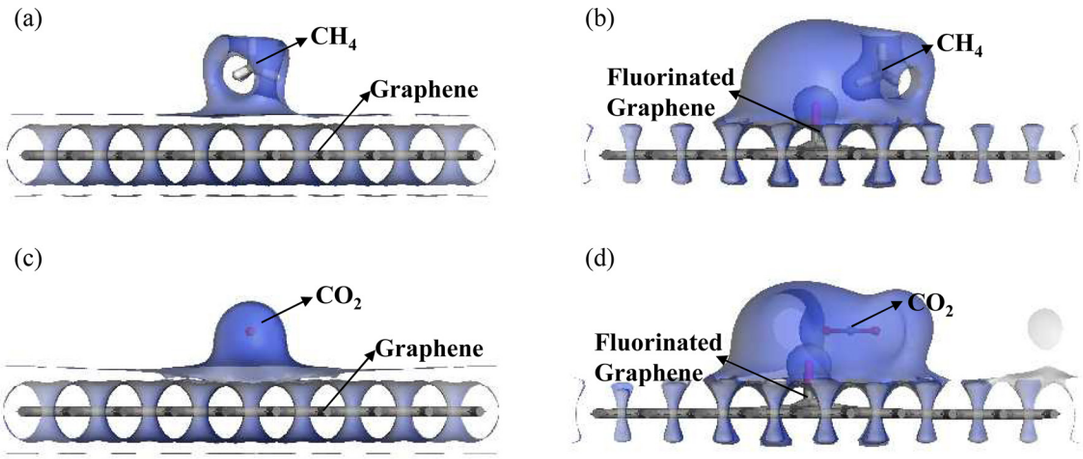

Fig. 3. Electrostatic potential maps of (a) pristine graphene with CH_4 molecule, (b) fluorinated graphene with CH_4 molecule, (c) pristine graphene with CO_2 molecule, and (d) fluorinated graphene with CO_2 molecule.

tine graphene substrate. When we look at the effect of fluorination of graphene, because of the quadrupole moment in CO_2, the negatively charged fluorine atom on graphene [28] interacted more strongly with CO_2, which led to the better adsorption compared to the CH_4 molecule. We also calculated the electrostatic potential maps of the most stable configurations of the adsorbed CH_4 and CO_2 molecules on the pristine and fluorinated graphene substrates (Figs. 1b and f, 2b and f), as shown in Fig. 3. The bluish region of the map indicates a possible reactive region with respect to nucleophilic attack. The electrostatic potential maps suggest that fluorinated graphene has a larger reactive region with the gas molecule than pristine graphene. Therefore, this result demonstrates that partially fluorinated graphene helps enhance CH_4 and CO_2 adsorption.

In summary, we performed DFT calculations on the interaction between CH_4 and CO_2 gas molecules and graphene substrates. We found that CH_4 was most strongly adsorbed on pristine graphene when the methane hydrogen tripod was directed to the carbon atom on the substrate, and CO_2 was most strongly adsorbed on pristine graphene when the carbon dioxide oxygens were placed on adjacent hollow hexagonal sites on the substrate. The CO_2 molecule was more strongly adsorbed on the graphene substrate than the CH_4 molecule. Finally, fluorination of graphene helps enhance CH_4 and CO_2 adsorption.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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References

[1] Herzog H, Eliasson B, Kaarstad O. Capturing greenhouse gases. Sci Am, **282**, 72 (2000). http://dx.doi.org/10.1038/scientificamerican0200-72.

[2] Lashof DA, Ahuja DR. Relative contributions of greenhouse gas emissions to global warming. Nature, **344**, 529 (1990). http://dx.doi.org/10.1038/344529a0.

[3] Liu Y, Wilcox J. CO_2 adsorption on carbon models of organic constituents of gas shale and coal. Environ Sci Technol, **45**, 809 (2011). http://dx.doi.org/10.1021/es102700c.

[4] Saha D, Bao Z, Jia F, Deng S. Adsorption of CO_2, CH_4, N_2O, and N_2 on MOF-5, MOF-177, and zeolite 5A. Environ Sci Technol, **44**, 1820 (2010). http://dx.doi.org/10.1021/es9032309.

[5] Han S, Kim S, Lim H, Choi W, Park H, Yoon J, Hyeon T. New nanoporous carbon materials with high adsorption capacity and rapid adsorption kinetics for removing humic acids. Microporous Mesoporous Mater, **58**, 131 (2003). http://dx.doi.org/10.1016/S1387-1811(02)00611-X.

[6] Wahby A, Ramos-Fernández JM, Martínez-Escandell M, Sepúlveda-Escribano A, Silvestre-Albero J, Rodríguez-Reinoso F. High-surface-area carbon molecular sieves for selective CO_2 adsorption. Chemsuschem, **3**, 974 (2010). http://dx.doi.org/10.1002/cssc.201000083.

[7] Yoon HJ, Jun DH, Yang JH, Zhou Z, Yang SS, Cheng MMC. Carbon dioxide gas sensor using a graphene sheet. Sens Actuators B Chem, **157**, 310 (2011). http://dx.doi.org/10.1016/j.snb.2011.03.035.

[8] Schrier J. Fluorinated and nanoporous graphene materials as sorbents for gas separations. ACS Appl Mater Interfaces, **3**, 4451 (2011). http://dx.doi.org/10.1021/am2011349.

[9] Yu HR, Cho S, Bai BC, Yi KB, Lee YS. Effects of fluorination on carbon molecular sieves for CH_4/CO_2 gas separation behavior. Int J Greenhouse Gas Control, **10**, 278 (2012). http://dx.doi.org/10.1016/j.ijggc.2012.06.013.

[10] Im JS, Kang SC, Bai BC, Bae TS, In SJ, Jeong E, Lee SH, Lee YS. Thermal fluorination effects on carbon nanotubes for preparation of a high-performance gas sensor. Carbon, **49**, 2235 (2011). http://

dx.doi.org/10.1016/j.carbon.2011.01.054.
[11] Dassault Systemes, Biovia Corp. Materials Studio 8.0 Software, Biovia, San Diego (2015).
[12] Moon HS, Lee JH, Kwon S, Kim IT, Lee SG. Mechanisms of Na adsorption on graphene and graphene oxide: density functional theory approach. Carbon Lett, **16**, 116 (2015). http://dx.doi.org/10.5714/CL.2015.16.2.116.
[13] Moon HS, Yun JM, Kim KH, Jang SS, Lee SG. Investigations of the band structures of edge-defect zigzag graphene nanoribbons using density functional theory. RSC Adv, **6**, 39587 (2016). http://dx.doi.org/10.1039/C6RA03458F.
[14] Koh W, Choi JI, Jeong E, Lee SG, Jang SS. Li adsorption on a fullerene–single wall carbon nanotube hybrid system: density functional theory approach. Curr Appl Phys, **14**, 1748 (2014). http://dx.doi.org/10.1016/j.cap.2014.09.031.
[15] Koh W, Lee JH, Lee SG, Choi JI, Jang SS. Li adsorption on a graphene–fullerene nanobud system: density functional theory approach. RSC Adv, **5**, 32819 (2015). http://dx.doi.org/10.1039/C4RA15619F.
[16] Koh W, Moon HS, Lee SG, Choi JI, Jang SS. A first-principles study of lithium adsorption on a graphene–fullerene nanohybrid system. Chemphyschem, **16**, 789 (2015). http://dx.doi.org/10.1002/cphc.201402675.
[17] Lee JH, Kang SG, Kim IT, Kwon S, Lee I, Lee SG. Adsorption mechanisms of lithium oxides (Li_xO_2) on N-doped graphene: a density functional theory study with implications for lithium–air batteries. Theor Chem Acc, **135**, 50 (2016). http://dx.doi.org/10.1007/s00214-016-1805-0.
[18] Lee JH, Kang SG, Moon HS, Park H, Kim IT, Lee SG. Adsorption mechanisms of lithium oxides (Li_xO_2) on a graphene-based electrode: a density functional theory approach. Appl Surf Sci, **351**, 193 (2015). http://dx.doi.org/10.1016/j.apsusc.2015.05.119.
[19] Kwon S, Choi JI, Lee SG, Jang SS. A density functional theory (DFT) study of CO_2 adsorption on Mg-rich minerals by enhanced charge distribution. Comput Mater Sci, **95**, 181 (2014). http://dx.doi.org/10.1016/j.commatsci.2014.07.042.
[20] Kwon S, Ham DJ, Lee SG. Enhanced H_2 dissociative phenomena of Pt–Ir electrocatalysts for PEMFCs: an integrated experimental and theoretical study. RSC Adv, **5**, 54941 (2015). http://dx.doi.org/10.1039/C5RA07228J.
[21] Kwon S, Lee SG. Influence of defective sites in Pt/C catalysts on the anode of direct methanol fuel cell and their role in CO poisoning: a first-principles study. Carbon Lett, **16**, 198 (2015). http://dx.doi.org/10.5714/CL.2015.16.3.198.
[22] Lee JH, Kang SG, Choe Y, Lee SG. Mechanism of adhesion of the diglycidyl ether of bisphenol A (DGEBA) to the Fe(100) surface. Compos Sci Technol, **126**, 9 (2016). http://dx.doi.org/10.1016/j.compscitech.2016.02.002.
[23] Brunello GF, Lee JH, Lee SG, Choi JI, Harvey D, Jang SS. Interactions of Pt nanoparticles with molecular components in polymer electrolyte membrane fuel cells: multi-scale modeling approach. RSC Adv, **6**, 69670 (2016). http://dx.doi.org/10.1039/C6RA09274H.
[24] Monkhorst HJ, Pack JD. Special points for brillouin-zone integrations. Phys Rev B, **13**, 5188 (1976). https://doi.org/10.1103/PhysRevB.13.5188.
[25] Grimme S, Antony J, Ehrlich S, Krieg H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J Chem Phys, **132**, 154104 (2010). http://dx.doi.org/10.1063/1.3382344.
[26] Graham C, Pierrus J, Raab RE. Measurement of the electric quadrupole moments of CO_2, Co and N_2. Mol Phys, **67**, 939 (1989). http://dx.doi.org/10.1080/00268978900101551.
[27] Wood BC, Bhide SY, Dutta D, Kandagal VS, Pathak AD, Punnathanam SN, Ayappa KG, Narasimhan S. Methane and carbon dioxide adsorption on edge-functionalized graphene: a comparative DFT study. J Chem Phys, **137**, 054702 (2012). http://dx.doi.org/10.1063/1.4736568.
[28] Jeong E, Jung MJ, Lee SG, Kim HG, Lee YS. Role of surface fluorine in improving the electrochemical properties of Fe/MWCNT electrodes. J Ind Eng Chem, **43**, 78 (2016). http://dx.doi.org/10.1016/j.jiec.2016.07.050.