Remarkably Enhanced Dynamic Oxygen Migration on Graphene Oxide by Copper-Substrate

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Abstract

The dynamic covalent properties of graphene oxide (GO) are of fundamental interest to a broad range of scientific areas and technological applications. However, to realize feasible reactions by reversibly breaking/reforming the strong covalent bonds on GO remains a great challenge. Using the density functional theory calculations, we elucidate that the presence of copper substrate can remarkably enhance the dynamic oxygen migration on GO, which is achieved by the C–O bond breaking reaction and proton transfer between the neighboring epoxy and hydroxyl groups. The energy barriers are sharply reduced, to less than or comparable to thermal fluctuations, ensuring the dynamic oxygen migrations (also named as "para-oxygen migration") on copper-substrate supported GO (GO@copper). More importantly, an unexpected "meta-oxygen migration" occurring between a pair of hydroxyl and epoxy groups on the meta-positions of an aromatic ring is shown, which has never been reported on GO. Assisted by para- and meta-oxygen migrations, the hydroxyl can migrate between the para- and meta-positions of an aromatic ring of GO@copper. This work provides new insights into the understanding of metal substrate effects on the dynamic properties of GO, and also gives a simple strategy to realize GO-based dynamic materials in desired applications.
Introduction

The emergence of dynamic covalent materials for over decades gained tremendous attention in a broad range of scientific areas, such as chemical separation, biological imaging or sensing and drug delivery, especially advances the technological innovations in the manufacturing of materials with novel mechanical and thermal features including self-healing, shape-memory and thermoset reprocessing. These dynamic behaviors rely on the reversible reactions of breaking or reforming of strong covalent bonds within molecules, endowing materials with adaptivity in response to stimuli and variation of ambient conditions. However, the dynamic reactions usually require harsh conditions and take a long time to reach the thermodynamic equilibrium, which is presumably attributed to the high reaction barrier. Thus, searching for feasible dynamic reactions within a reasonable system is the key step to realizing the dynamic covalent materials. Interestingly, we have found that with the water molecules being adsorbed, the dominated hydroxyl and epoxy groups on GO can spontaneously migrate and the GO is converted to a dynamic covalent material with structural adaptivity to the biomolecule adsorption. However, how to maintain this dynamic oxygen migration on GO under a dry environment without water remains unclear.

The metal/GO composite as the promising building blocks of engineering materials and electronic devices, shows superior mechanical strength, high electronic and thermal conductivity, and sensitive reaction activity. The presence of metal substrates introduces the metal-GO interaction and the lattice match. In particular, the (111) surface of the copper substrate has been found to assist the epitaxial growth of graphene and show a better lattice match with the honeycomb plane of GO in experiments. Here, we performed the density functional theory (DFT) calculations to investigate the dynamic oxygen migrations on GO supported by a copper substrate (GO@copper).

Unexpectedly, we find that the copper substrate remarkably enhances the dynamic properties of oxygen groups on GO without water, leading to the para-oxygen and new meta-oxygen migrations with barriers less than or comparable to thermal fluctuations. Besides,
the hydroxyl can migrate between the para- and meta-positions on an aromatic ring of GO via the combination of these two migration paths. To the best of our knowledge, this is the first report of copper-substrate-enhanced dynamic oxygen migrations on GO under a dry environment.

Method

The DFT calculations are carried out using the Vienna Ab-initio Simulation Package (VASP). The exchange-correlation energy is described by the local density approximation (LDA). The convergence accuracy for energy and force in the geometry optimization and transition state (TS) search are $10^{-5}$ eV and 0.01 eV/Å, respectively. The projector augmented wave (PAW) is used with the plane wave cutoff of 500 eV. The Monkhorst-Pack mesh in the k-space is $1 \times 1 \times 1$. The system consists of a GO sheet supported on a four-layers (111) surface of the copper substrate, including 100 Cu atoms and 50 C atoms, in a periodic $5 \times 5$ supercell. The GO is stretched about 3.7 % to match the lattice of the copper substrate. The vacuum layer in the $z$-axis direction is set to 15 Å to avoid interactions between periodic images. The Cu atoms in the bottom-most layer of the substrate are fixed in all the calculations. The TSs are searched via the climbing image-nudged elastic-band (CI-NEB) method.

Results and discussion

The oxygen groups on the basal plane of GO, such as hydroxyl and epoxy groups, are distributed in correlation instead of a random distribution, according to our previous DFT calculations. As shown in Fig. 1(a), we choose a pair of hydroxyl and epoxy groups as a typical configuration to represent the correlated distribution of oxygen groups for simplicity. Considering the lattice match between GO and (111) surface of the copper substrate, we denote the hydroxyl-occupied carbon atom on the top of a Cu atom and the face-centered
Figure 1: (a) Top view of GO@copper with the correlated distribution of a pair of hydroxyl and epoxy groups. (b) Zoomed-in snapshots of two different reactant configurations led by the lattice match between GO and copper substrate. Top site: Hydroxyl-occupied carbon atom is on the top of a Cu atom; Fcc site: Hydroxyl-occupied carbon atom is on the face-centered position of Cu atoms.

position of a Cu atom by top site and fcc site, respectively (see Fig. 1(b)).

Figure 2 presents the oxygen migration pathways and state configurations on GO and GO@Cu. The oxygen migration assisted by the hydroxyl includes two successive reactions: the C-O bond breaking reaction and the proton transfer between the dangling oxygen and neighboring hydroxyl for the exchange. Without the Cu(111) substrate, the C-O bond breaking reaction has a lower energy barrier of 3.9 kcal/mol whereas there is a relatively high barrier of 14.7 kcal/mol for the proton transfer, indicating that it is difficult for oxygen groups to migrate by proton transfer at ambient conditions. However, for GO@Cu, the barrier for C-O bond breaking reduces to 1.3 kcal/mol (top site). Especially for the proton transfer, we can see a significant decrease of the barrier from 14.7 kcal/mol to 0.6 kcal/mol. These values of barriers lower than or comparable to the order of thermal fluctuations, can also be found for the fcc sites (3.1 kcal/mol and 1.7 kcal/mol), suggesting that the migration of oxygen groups can be achieved through C-O bond breaking reaction and proton transfer on GO@Cu at ambient conditions. For both GO and GO@Cu, the dangling C-O bond and the hydroxyl in the intermediates and products are at the para-positions of an aromatic ring, we thus name this type of oxygen migration as “Para-Oxygen Migration”.

The intermediate (M) becomes more stable than the reactant (R) due to the presence
Figure 2: Reaction pathways and state configurations for oxygen migration on GO and GO@Cu. The hydroxyl-assisted oxygen migration includes the C–O bond breaking reaction and the proton transfer between the dangling oxygen and neighboring hydroxyl for the exchange on GO without substrates (black lines), on top site of GO@Cu (red lines) and fcc site of GO@Cu (blue lines). Notations: reactants (R), intermediates (M), transition states (TS), and products (P). The energy levels of R on GO and GO@Cu(top site) are shifted for a better comparison. We name this type of oxygen migration on GO and GO@Cu as “Para-Oxygen Migration” since the dangling C–O bond and the hydroxyl in M and P states are at the para-positions of an aromatic ring.

Figure 3 compares the variation of bond length on GO and GO@Cu. In comparison to bond lengths on GO, the C–O bond of epoxy in R on GO@Cu is slightly shortened. In M, the C–O bonds in hydroxyl and the dangling C–O bond are significantly shortened, from 1.416 Å to 1.355 Å. The shorter C–O bond in M on GO@Cu suggests the stronger strengthen of the C–O bond, explaining the stability of M with the dangling C–O bond.

of Cu(111) substrate. On GO, M is 1.2 kcal/mol higher than R, indicating that the epoxy configuration with two C–O bonds is more stable than the dangling C–O bond. Whereas on GO@Cu, the energy of M is 6.8 kcal/mol (top site) and 2.0 kcal/mol (fcc site) lower than that of R. This demonstrates the important role of Cu(111) substrate on stabilizing the M, as the dangling C–O bond in M assists the subsequent proton transfer.
Figure 3: (a, b) Illustrations of distances for C–O bonds ($d_{CO1}$, $d_{CO2}$, and $d_{CO3}$), O–H bond ($d_{OH}$), and two oxygen atoms ($d_{OO}$) in reactants (R) and intermediates (M). (c) Lists of various distances in R and M on GO, fcc site, and top site of GO@Cu.

GO@Cu, the O–O distance in M becomes shorter and the O–H bond is a little elongated, indicating that the proton transfer is more favorable, consistent with the decreased energy barrier of proton transfer on GO@Cu.

Figure 4: Reaction pathways and state configurations for "Meta-Oxygen Migration", which occurs at the meta-positions of an aromatic ring, on the top site (red lines) and fcc site (blue lines) of GO@Cu.

Surprisingly, we have observed a new oxygen migration path, named "meta-oxygen migration", where the dangling C–O bond and the hydroxyl are at the meta-position on an aromatic ring on GO@Cu. Generally, the dangling C–O bond and the hydroxyl cannot co-
exist at the meta-position due to the steric effects. This is the case for oxygen migration we found on GO. In this new migration path, the C–O bond in epoxy breaks, and a dangling C–O bond is formed at the meta-position of the hydroxyl (see M in Fig. 4(a)), followed by a proton transfer reaction. The barriers for C–O breaking reaction and proton transfer are 3.3 kcal/mol and 0.1 kcal/mol for the top site, 2.4 kcal/mol and 0.6 kcal/mol for the fcc site. These values are all less than or comparable to thermal fluctuations, an indication of feasible oxygen migration on GO@Cu. In particular, the barrier of the proton transfer is only 0.1 kcal/mol, indicating that the proton can transfer very easily within the meta-oxygen migration. We also noted that the hydroxyl can migrate between the para- and meta-positions of an aromatic ring of GO@copper, via the combination of para- and meta-oxygen migrations. This new migration route of hydroxyl enriches our understanding of the dynamic behavior of oxygen groups on GO@copper.

Conclusions

In summary, we have shown the enhancement of dynamic oxygen migration on GO@copper based on the DFT calculations. The para-oxygen migration and a novel meta-oxygen migration are all achieved by the C–O bond breaking reaction and proton transfer between the oxygen atoms in water and dangling C–O bond, which are attributed to the relative low energy barrier as well as the stable dangling C–O bond. These findings confirm the local correlated distribution of oxygen groups and are informative for the understanding of the selective functionalization and reduction of GO. Besides, the existence of stable dangling C-O bond assists the proton transfer on GO, which may be broadly applied into areas such as electrolysis, capacitors, fuel cells, sensors and so on.

Our work elucidates the modulation of copper substrates on the innate dynamic behavior of oxygen groups on GO. The dynamic oxygen migration exhibited on GO@copper is more profound than that on the freestanding GO. On the one hand, the negligible energy
barrier and more migration paths will inevitably alter the interfacial activity,\textsuperscript{20,22} permit the breaking/reforming of covalent bonds finally enable the structural adaptivity in response to the biomolecular stimuli; on the other, benefiting from the numerous researches,\textsuperscript{13,14,28} high-quality and stable growth of GO on metal substrates have been experimentally achieved. Therefore, it is worth looking forward to metal-substrate supported GO applied to the design of performance-enhanced (bio)sensors, biomedical devices, and electronic equipment in the future.

**Author Contributions**

Yusong Tu conceived, designed and guided the research; Zihan Yan, Wenjie Yang, Hao Yang, and Chengao Ji performed the simulations; Zihan Yan, Shuming Zeng, Liang Zhao and Yusong Tu analyzed the data; Zihan Yan and Liang Zhao wrote the paper; All the authors participated in discussions of the research.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgement**

We are thankful for the helpful suggestions given by PhD candidates Zhijing Huang (Yangzhou University), Guangyu Du (The Hong Kong Polytechnic University), and Xiaoxue Liu (Jilin University). This work was funded by the National Natural Science Foundation of China (Nos. 12075201, 11675138), the Natural Science Foundation of Jiangsu Province (No. BK20201428), the Special Program for Applied Research on Supercomputation of the NSFC-Guangdong Joint Fund (the second phase), and Jiangsu Students’ Innovation and Entrepreneurship Training Program (No. 202111117008Z).
References

(1) Zou, W.; Dong, J.; Luo, Y.; Zhao, Q.; Xie, T. Dynamic covalent polymer networks: from old chemistry to modern day innovations. Adv. Mater. 2017, 29, 1606100.

(2) Zhang, Y.; Qi, Y.; Ulrich, S.; Barboiu, M.; Ramström, O. Dynamic covalent polymers for biomedical applications. Mater. Chem. Front. 2020, 4, 489–506.

(3) Zheng, N.; Xu, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: A Molecular Platform for Designing Functions beyond Chemical Recycling and Self-Healing. Chem. Rev. 2021, 121, 1716–1745.

(4) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R.; Sanders, J. K.; Stoddart, J. F. Dynamic covalent chemistry. Angew. Chem. Int. Ed. 2002, 41, 898–952.

(5) Otsuka, H. Reorganization of polymer structures based on dynamic covalent chemistry: polymer reactions by dynamic covalent exchanges of alkoxyamine units. Polym. J. 2013, 45, 879–891.

(6) Perera, M. M.; Ayres, N. Dynamic covalent bonds in self-healing, shape memory, and controllable stiffness hydrogels. Polym. Chem. 2020, 11, 1410–1423.

(7) Jin, Y.; Yu, C.; Denman, R. J.; Zhang, W. Recent advances in dynamic covalent chemistry. Chem. Soc. Rev. 2013, 42, 6634–6654.

(8) Tu, Y.; Zhao, L.; Sun, J.; Wu, Y.; Zhou, X.; Chen, L.; Lei, X.; Fang, H.; Shi, G. Water-Mediated Spontaneously Dynamic Oxygen Migration on Graphene Oxide with Structural Adaptivity for Biomolecule Adsorption. Chinese Phys. Lett. 2020, 37, 066803.

(9) Ovid’Ko, I. Metal-graphene nanocomposites with enhanced mechanical properties: a review. Rev. Adv. Mater. Sci. 2014, 38.

(10) Xu, H.; Wu, X.; Li, X.; Luo, C.; Liang, F.; Orignac, E.; Zhang, J.; Chu, J. Properties of graphene-metal contacts probed by Raman spectroscopy. Carbon 2018, 127, 491–497.
(11) Goyal, V.; Balandin, A. A. Thermal properties of the hybrid graphene-metal nanomicro-composites: Applications in thermal interface materials. *Appl. Phys. Lett.* 2012, *100*, 073113.

(12) Khalil, I.; Rahmati, S.; Julkapli, N. M.; Yehye, W. A. Graphene metal nanocomposites—Recent progress in electrochemical biosensing applications. *J. Ind. Eng. Chem.* 2018, *59*, 425–439.

(13) Frank, O.; Vejpravova, J.; Holy, V.; Kavan, L.; Kalbac, M. Interaction between graphene and copper substrate: The role of lattice orientation. *Carbon* 2014, *68*, 440–451.

(14) Gao, L.; Guest, J. R.; Guisinger, N. P. Epitaxial graphene on Cu (111). *Nano Lett.* 2010, *10*, 3512–3516.

(15) Kresse, G.; Hafner, J. Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium. *Phys. Rev. B* 1994, *49*, 14251.

(16) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1996, *54*, 11169.

(17) Perdew, J. P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* 1981, *23*, 5048.

(18) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, *13*, 5188.

(19) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* 2000, *113*, 9901–9904.

(20) Yang, J.; Shi, G.; Tu, Y.; Fang, H. High correlation between oxidation loci on graphene oxide. *Angew. Chem. Int. Ed.* 2014, *126*, 10354–10358.
(21) Kida, T.; Kuwaki, Y.; Miyamoto, A.; Hamidah, N. L.; Hatakeyama, K.; Quitain, A. T.; Sasaki, M.; Urakawa, A. Water vapor electrolysis with proton-conducting graphene oxide nanosheets. *ACS Sustainable Chem. Eng.* **2018**, *6*, 11753–11758.

(22) Gao, W.; Singh, N.; Song, L.; Liu, Z.; Reddy, A. L. M.; Ci, L.; Vajtai, R.; Zhang, Q.; Wei, B.; Ajayan, P. M. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nat. Nanotechnol.* **2011**, *6*, 496–500.

(23) Pandey, R. P.; Shukla, G.; Manohar, M.; Shahi, V. K. Graphene oxide based nanohybrid proton exchange membranes for fuel cell applications: An overview. *Adv. Colloid Interface Sci.* **2017**, *240*, 15–30.

(24) Gao, W.; Wu, G.; Janicke, M. T.; Cullen, D. A.; Mukundan, R.; Baldwin, J. K.; Brosha, E. L.; Galande, C.; Ajayan, P. M.; More, K. L., et al. Ozonated graphene oxide film as a proton-exchange membrane. *Angew. Chem. Int. Ed.* **2014**, *53*, 3588–3593.

(25) Karim, M. R.; Hatakeyama, K.; Matsui, T.; Takehira, H.; Taniguchi, T.; Koinuma, M.; Matsumoto, Y.; Akutagawa, T.; Nakamura, T.; Noro, S.-i., et al. Graphene oxide nanosheet with high proton conductivity. *J. Am. Chem. Soc.* **2013**, *135*, 8097–8100.

(26) Cheng, X.; Wu, H.; Zhang, L.; Ma, X.; Zhang, X.; Yang, M. Hydroxyl migration disorders the surface structure of hydroxyapatite nanoparticles. *Appl. Surf. Sci.* **2017**, *416*, 901–910.

(27) Wang, X.; Zhang, L.; Zeng, Q.; Jiang, G.; Yang, M. First-principles study on the hydroxyl migration from inner to surface in hydroxyapatite. *Appl. Surf. Sci.* **2018**, *452*, 381–388.

(28) Hidalgo-Manrique, P.; Lei, X.; Xu, R.; Zhou, M.; Kinloch, I. A.; Young, R. J. Copper/graphene composites: a review. *J. Mater. Sci.* **2019**, *54*, 12236–12289.
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