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PAPER

Defect-induced Strong Localization of Uranium Dicarbide on Graphene Surface

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Defects such as the most stable hexavacancy (V6) distribute widely on neutron-irradiated graphite surfaces, which play a dominant role in immobilizing radioactive products released from nuclear fuels. By performing DFT calculations, we explore the interaction of gaseous uranium dicarbide (UC_2) molecule on a graphene nanosheet with a V6 defect, in order to investigate the behavior of the representative vapor species of uranium carbide fuels in reactor cores. Results suggest that UC₂ can be trapped in the V6 defect with considerable binding energy of > 10 eV, with all the six dangling bonds of the V6 defect being saturated by UC₂. Bonding nature analyses also reveal that the U-C interaction lies in the synergistic interplay between electrostatic and covalent interaction with extensive participation of U valence electrons from 5f to 7p orbitals, which further stimulate polarization of semi-core 6p orbitals and their subsequent contributions to the bonding. This strong interaction leads to a favorable binding of UC₂ to the defective graphite surface, which reduces the capability of nuclear graphite to retain harmful fission products by the vacancies being filled with UC₂. These findings highlight substantial chemical reactivity and strong localization of UC₂ on the widespread V6 defects in nuclear graphite, and may provide an important reference in establishing modern nuclear reactor safety at atomic level.

Introduction

Graphite is a key component of modern nuclear reactors due to its exceptional capability in sustaining neutron irradiation as well as retaining radioactive products.^{1,2} Of particular interest is the study on the interaction of radioactive products with graphite, which is critical for the development of Gen-IV hightemperature reactors (HTR).^{1,3} When the radioactive products are released from nuclear fuels (including fission products, radioactive actinide products, etc.), they must be contained within HTR, where graphite plays an important role in serving as a barrier of these gaseous products.⁴ Previous experimental and theoretical studies have been primarily focused on the sorption of metallic fission product (Ag, Cs, Sr atoms, etc.) on graphite.^{1,3,5-7} Surprisingly, few studies concerned directly with the interaction of evaporated nuclear fuel molecules such as uranium dicarbide (UC_2) with graphite, albeit the existence of gaseous UC₂ in vapor above the solid state is known. The behavior of gaseous uranium carbides in reactors is considered to be significant for the safety aspects of HTR, and must be completely known when these molecules are prevalent at high temperatures, especially in a high temperature excursion accident.8,9

Uranium carbides are one of the most ideal candidates for nuclear fuel materials in the next generation reactors, in particular the HTR, due to their outstanding physical properties such as high linear power and high thermal conductivity.^{10,11} Previous studies indicated that vapor species of solid uranium carbides might be released during their use as nuclear fuels,^{12,13} in which UC₂ is the most abundant gaseous molecule identified by mass spectrometry¹⁴. Thus the gas phase UC₂ might be in direct contact with the coating graphite. In a previous study, we have found a strong chemisorption capability (binding energy: 2.27 eV) of UC₂ (symmetric triangular structure) on a pristine graphene surface, without significant damage to the graphene.⁹ These results obtained from the pristine structure may be viewed as a lower limit case for the adsorbability of nuclear graphite.

However, defects of the nuclear graphite are inevitable and widespread under neutron irradiation.^{2,15-17} These defects normally distribute near graphite surfaces^{16,18} and introduce chemical reactivity around them, where the behaviors of metallic fission products are very different from that on the pristine area.^{3,6,16} The defects on graphite surfaces are already suggested to play an important role in immobilizing the gaseous fission products, due to the high binding energies.^{3,6,16} Therefore, for the sake of reactor design and environmental safety, the defects will certainly need to be taken into account, in order to get more detailed insight into the behavior and influence of radioactive actinide products (such as evaporated

uranium carbide molecules) on neutron-irradiated graphite. On the other hand, there is great interest with respect to the nature of actinide bonding,¹⁹⁻²³ although recent theoretical research has provided valuable understanding on the bonding and structure of metallic functional materials, which are formed by actinides with pure sp² carbon.^{9,24-27} Little is known about the interaction mechanism of the actinides in direct binding with defective carbon materials. This has also inspired us to investigate the bonding nature between UC₂ and the defect sites of nuclear graphite at atomic level.

In this article, we use DFT calculations to study the interaction between the most stable UC₂ molecule (symmetric triangular structure) and a graphene nanosheet with a hexavacancy (V6) defect, which has been identified as the most stable and abundant vacancy defect distributed on heavily neutron-irradiated graphite surfaces.¹⁸ Taking into account that the radioactive product interaction on graphite is mainly effected by local structures, and the defects are favored adsorption sites,¹⁶ using a finite graphene model is suitable to investigate the local behavior of UC2 around the V6 sites on nuclear graphite surfaces. Our results indicate a clear tendency for graphene with a V6 defect to bind much stronger with UC₂ than the pristine structure. Interestingly, in the most stable structure, UC₂ is fully localized in the V6 defect, its robust C-C bond is dissociated to form pentagon carbon rings with the vacancy. Formation of new polarized U-C bonds also occurs to saturate the vacancy, with not only considerable contributions from the valence orbitals of U but unexpected participation of the core-like orbitals to the bonding. Our studies may provide realistic prediction for more general trends and properties of UC₂ on nuclear graphite under normal and accident conditions, which can be reference to further experiments and theoretical understanding on the bonding nature of the actinides with defective carbon materials.

Computational Methods

The graphite surface was modeled using a graphene cluster of 37 coronene ($C_{96}H_{24}$) with zigzag edges and hydrogen termination. Six adjacent carbon atoms in the central region of the graphene model were removed to give a V6 defect with six dangling sp^2 bonds. During relaxation, the terminal hydrogen and the outmost carbon atoms were fixed to reproduce the twodimensional planar-sheet configuration of the graphite surface. The finite graphene model has been found to be feasible to ensure the behavior of its center similar to the bulk graphite surface, especially for investigating strong local interaction.^{28,29} Furthermore, considering the interaction at defect sites is mainly a local behavior, the current setup can offer a reasonable model for investigating the bonding nature and local interaction of small molecules on bulk graphite with surface defects, with a much reduced computational cost.^{30,31} Here, the symmetric triangular UC₂ (quintet ground state)^{9,12,13,32} is taken to as the representative since it is the most energetically favorable structure.

Geometry optimizations and subsequent vibrational frequency calculations were carried out using the Gaussian09 programs.33 The spin-unrestricted gradient-corrected BP8634 exchange correlation functional was employed. The small-core quasi-relativistic pseudo-potential ECP60MWB and associated ECP60MWB-SEG valence basis sets^{35,36} were applied to the U atom to take into account the relativistic effects,¹¹ while the polarized 6-31G(d) basis set³⁷ was used for the light atoms. The approach has been successfully used in previous theoretical calculations for uranium encapsulated fullerene systems.^{25,38} Since defective graphene is substantially more reactive than pristine graphene plane for small molecules, the UC₂ molecules were initially placed at various possible configurations above the V6 defect. During optimization, the systems were fully relaxed without symmetry constraints. Frequency calculations were done at the same level to confirm the structures are true minima on their respective potential energy surfaces. Natural atomic orbital (NAO) and natural bond orbital (NBO)³⁹ analyses were performed to obtain contributions of various atomic orbitals (AOs) in molecular orbitals (MOs), as well as localized descriptions of the U-C bonds. Energy decomposition analysis (EDA)⁴⁰⁻⁴² was carried out in ADF2012.01 package,⁴³ in order to divide the interaction energy into three terms: Pauli repulsion, electrostatic interaction and orbital interaction, for a quantitative interpretation of newly formed U-C bonds. The EDA calculations were performed at BP86/TZP44 level of theory on the optimized structures, while scalar relativistic effects were accounted for using the zero-order regular approximation (ZORA).⁴⁵ The 1s shells of C atoms and 1s-4f shells of U atom were treated as froze core in EDA.

Results and Discussion

We obtained five representative stable configurations of the symmetric triangular UC₂ on the graphene nanosheet with a V6 defect. The ground state of each configuration is illustrated in Fig. 1a, with the total energies of relative spin states listed in Table 1. As shown in Fig. 1a and Table 1, UC₂ tends to bind directly to dangling carbon atoms. Formation of new C-C and U-C bonds makes these optimized states highly exothermic, from 7.74 to 13.82 eV, with respect to the symmetric triangular UC₂ in the gas phase, which also indicates that the graphene with a V6 defect can bind stronger with UC₂ than the pristine graphene (binding energy: 2.27 eV).⁹

It is worth noting that with a relative large deformation as occurring in our systems, the true bonding strength can be better understood from the interaction energies rather than the binding energies. The binding energy encompasses not only the stabilizing term gained due to the chemical interaction called interaction energy, but also the destabilizing term called preparation energy or deformation energy required to distort the individual fragments during the binding process (see Part 1 of the Supplementary Information for the definition and difference). As shown in Table 1, the preparation energy lies in the range of 1.85-6.67 eV, which is much higher than that of



Fig. 1 (a) Optimized configurations (only center region), relative energies (in eV) and key bond distances (in Å) of symmetric triangular UC₂ activated on graphene with a V6 defect. (b) Total bond order (BO), interaction (E_{int}) and binding energies (E_{bin}) between UC₂ and V6-defective graphene for the optimized configurations (also listed in Table 1).

 UC_2 on pristine graphene $(0.08 \text{ eV})^9$ due to the larger deformation. However, there is still a preference in the binding energy for V6-defecitve graphene, because the interaction energy can favorably compensate for the preparation energy. Subsequent analyses of the bond order reveal that the interaction energy (from 9.59 to 20.49 eV, Table 1) is roughly in linear correlation to the total Wiberg bond order⁴⁶ (from 6.79 to 10.74, Table 1) between UC₂ and V6-defective graphene of each configuration (Fig. 1b). The optimized configurations suggest that the U atoms are localized near the center of the V6 defects. Configuration I (singlet) is the most energetically favorable state, in which the robust C-C bond (between a double and triple bond)¹³ of UC_2 is dissociated to saturate four dangling bonds at the defect sites, forming two pentagon carbon rings. The U atom also binds to the other two dangling bonds with a bond order value of 1.27 for each U-C bond, and the formation of new pentagons and U-C bonds leads to an extremely stable closed-shell system (interaction energy: 20.49 eV). Configuration V (triplet) may seem like not involving the direct bind of UC₂ to the V6 defect, UC₂ binding with the defect (interaction energy: 9.59 eV) is also much weaker than that in I, but still significantly stronger than that for pristine graphene surface (interaction energy: 2.35 eV).9 Due to such a big difference in the interaction energies, it is also necessary to investigate the interaction mechanism in V.

The chemical interaction between two fragments can be understood qualitatively from electronic density distribution. In past work, UC_2 has been found to be chemically adsorbed on pristine graphene with intense charge transfer,⁹ shown in Fig.

2a. As displayed in charge density difference diagrams of I and V (Fig. 2b and 2c), charge transfer also occurs within the V6 defects when trapping UC₂. However, the charge transfer is found to be more obvious than UC₂ on pristine graphene, by comparing Fig. 2d-2f. Moreover, from the charge density difference diagrams of V and UC₂ on pristine graphene, we can see that they involve charge transfer mainly between U and six adjacent C atoms in the graphene, with much more intense charge transfer in V. This leads to a higher total Wiberg bond order value of 6.53 calculated between U and the V6-defective graphene than that of 2.83 between U and the pristine graphene.⁹ The above analysis further verifies the high chemical reactivity of the V6 defect, and illustrates the difference in the interaction with or without the V6 defect. More importantly, in both I and V, the electron density apparently increases (pink) at the intermediate region between UC₂ and six dangling bonds of the V6 defect, which demonstrates that covalent interaction due to molecular orbital overlaps plays an important role in the bonding.

To get more insight into the bonding nature between UC₂ and V6, the localized orbital locator (LOL) was calculated by using Multiwfn.⁴⁷ More specific, LOL (referred to as v) is a measure of the relative value of local kinetic energy, compared with that of the uniform electron gas when mapped onto the finite range (0, 1). For the uniform electron gas, LOL has a constant value of 0.5.⁴⁸ By comparing Fig. 2g-2h, one can see that the electrons around the six carbon atoms at V6 site are more localized after trapping UC₂. We can also find significant electron localization at the center of the C(UC₂)-C(V6) bond in

Table 1. Total energies (E, in a.u.) and relative energies (ΔE , in eV) of typical configurations with different spin multiplicities (\mathbf{M}) for the UC₂+V6 systems; binding (E_{bin}), interaction (E_{int}), and preparation (E_{prep}) energies (in eV), as well as total Wiberg bond order ($\mathbf{BO}(UC_2-V6)$) between UC₂ and V6 of the ground state for each configuration.

Configuration	М	E	ΔΕ	$oldsymbol{E}_{ ext{bin}}$	$oldsymbol{E}_{ ext{int}}$	$oldsymbol{E}_{ ext{prep}}$	$E_{\text{prep}}(\text{UC}_2)$	$E_{\text{prep}}(V6)$	BO (UC ₂ -V6)
I	1	-3997.72065	0	13.82	20.49	6.67	4.65	2.02	10.74
	3	-3997.70816	0.34						
п	1	-3997.68551	0.96						
	3	-3997.68607	0.94	12.88	13.99	1.11	0.21	0.91	9.35
	5	-3997.66893	1.41						
ш	1	-3997.63240	2.40(1)						
	3	-3997.63252	2.39(8)	11.42	18.60	7.18	4.26	2.92	9.54
	5	-3997.60798	3.07						
IV	1	-3997.60045	3.27						
	3	-3997.60149	3.24	10.57	12.38	1.81	0.07	1.73	8.02
	5	-3997.58361	3.73						
V	1	-3997.49701	6.09						
	3	-3997.49723	6.08	7.74	9.59	1.85	0.00(1)	1.85	6.79
	5	-3997.47861	6.59						



Fig. 2 Isosurfaces of electronic density difference for the UC₂ unit on different graphene nanosheets (a-f) and cutplane visualization of localized orbital locator (LOL) (g-i) around the V6 site for clean V6 defect, I and V. For electronic density difference diagrams, the pink color corresponds to accumulation, the blue represents depletion, isosurface value= ± 0.002 (a-c) and ± 0.01 (d-f), respectively); (a, d) UC₂ on pristine graphene (ref. [9]); (b, e) I; (c, f) V. For LOL diagrams, values of LOL > 0.5 (greenish-yellow) are associated with relatively slow electrons, indicating regions where the electrons are localized, such as in bonds or lone-pairs.

I, namely, typical non-polar covalent C-C bond. On the other hand, regions with v > 0.5 extend along U-C bonds in both configurations, with the local maxima occurring on C atoms. This electrons unequally shared situation caused by the large difference in electronegativity can be interpreted as a polar covalent nature, or as an indicator of non-negligible ionic contribution to the U-C bonds. To gain a more quantitative assessment of the newly formed U-C bonds, we performed EDA between U and V6+C2 fragments for configuration I, and UC₂ and V6 fragments for configuration V, respectively. The results are compiled in Table S1, which show that the electrostatic interactions and orbital interactions contribute about 33% and 67% to the total attractive energies for I, about 31% and 69% for V. Therefore, it is concluded that the newly formed U-C bonds are stabilized mainly by orbital (covalent) interaction, also with significant electrostatic (ionic) interaction.

These energetic and geometric results, as well as the electronic density distribution, give a first indication of very strong chemical bonding between UC₂ and the unsaturated C atoms at the V6 defect site, with the ionic and covalent interaction simultaneously involved in the U-C bonds. It will be further investigated below by the analyses of MOs information and charge population. Since the C-C sp²-hybridization bonding is already clear, the interaction mechanism could be clarified by investigating MOs with overlaps on U-C bonds of the systems.

The density of states (DOS) and MOs diagram along with U percentage are illustrated in Fig. 3 (I) and Fig. S1 (V). The local DOS (LDOS) of the U atom indicates that AOs of U contribute to amount of MOs in the systems (i.e., total DOS, TDOS). The lowest unoccupied molecular orbital (LUMO) in both configurations are dominated by U 5f AOs (87% and 80%,



Fig. 3 Density of states and Kohn–Sham frontier MOs diagram for I in defect region (isodensity value: ±0.02). Inner MOs with U 6p character are also shown below. Detailed components of MOs with U participation are listed in Table S2.

respectively), with a rather more U 5f character than occupied orbitals. One can also see obvious interaction of the central U AOs with $C(UC_2)$ or C(V6) 2sp AOs in frontier occupied MOs, for example, from HOMO-1 to HOMO-6 in I. 5f and 6d AOs are mainly involved in the bonding, usually with little hybridization of 7s and 7p. Although U 7s character presents in HOMO-20 of I, HOMO α -19 and HOMO α -24 of V, the contributions are negligible. The calculated NAO populations for U 7s are 0.18 and 0.40 in I and V, respectively, and both are smaller than that of isolated symmetric triangular UC_2 (7s: 1.04). In addition, significant 7s character appears in occupied MOs of symmetric triangular UC2,¹³ but it is found in unoccupied MOs such as LUMO+9 (7s: 20%) in I and LUMO α +86 in V (7s: 28%). Thus, it can be concluded that the U 7s electrons almost transfer to the C atoms in both systems, resulting into the electrostatic interaction. NBO analyses reveal that the U-C bonds in I and V contain about 30% uranium and 70% carbon composition, suggesting the highly polar nature, which is also in line with the LOL and EDA analyses.

For U-C systems, the participation of the valence 5f and 6d orbitals with partial mixing of 7s and 7p is fully reasonable and well accepted in the scientific community.^{26,49} Here, the participation of the valence orbitals can be also seen in HOMO-6 of **I** and HOMO α -24 of **V**. For both configurations, the high chemical reactivity of the V6 stimulates the valence electrons of uranium to participate in polarized U-C bonds, stabilizing the

systems. However, one can notice that U semi-core 6p AOs slightly hybridize with the valence orbitals to participate in the U-C bonds (see HOMO-6 of I and HOMOα-19, 24 of V). More interestingly, a careful examination of the MOs of I (HOMO-199~201) and V (HOMO α -200~202) with much lower energy than the HOMO region reveals considerable U AOs contributions, which have been found to be mainly 6p character. In V, the 6p AOs are not involved in U-C bonds, which is almost localized on the U atom. Conversely, the 6p AOs in I, interact with C sp^2 hybrid orbitals, contributing to the U-C bonds in HOMO-200 (6p: 75%) and HOMO-201 (6p: 78%). The total contributions of these two MOs with U 6p character to one U-C bond are about 20%, which are comparable to the MOs with U valence AOs character (Table S2). It is somewhat surprising that the normally core-like 6p filled orbitals are involved in the U-C bonds of I, which was not reported in previous theoretical work for UC2, but it can be by considering previous theoretical reasonable and experimental work on uranyl⁵⁰ and CUO²⁰. This is due to the electrostatic interaction between U and C atoms resulting in polarization on the 6p orbitals, which further leads to participation of the 6p orbitals via hybridization with the valence 5f orbitals.⁵¹ Similar hybridization can be also found in the case of 4f/5d in rare earth.⁵² This process produces a partial hole in the 6p orbitals (NAO population for U 6p is 5.76, reduced from the purely atomic value of 6.00), which could

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increase the orbital overlap with the C atoms because of the similar energy of U 6p and C sp^2 hybrid orbitals, as well as the effective radial extent and correct orientation of U 6p orbitals, as in the case of uranyl.⁵⁰

Conclusion

In summary, based on DFT calculations, we studied the interaction between UC₂ and graphene with a V6 defect, which results in a highly stable closed-shell structure (i.e., configuration I) with considerable binding energy, fully saturating the vacancy by disrupting the robust C-C bond in UC₂ and forming new U-C bonds between UC₂ and the defect sites. Furthermore, bonding analyses for I show that U-C bonds are polarized, and the mechanism of the interaction lies in the synergistic interplay between electrostatic and covalent bonding. In other words, the charge transfer between U and C atoms leads to polarization of the semi-core 6p orbitals, which is necessary for their mixing of the valence orbitals, sequentially interacting with C 2sp orbitals to make a significant contribution to the energetic stabilization of U-C bonds. Since the V6 defects are expected to have particular stabilities in other carbon materials such as carbon nanotubes and fullerenes¹⁸ inducing V6 defects might enhance the adsorbability of such materials, which subsequently facilitate applications in nuclear fuel reprocessing and nuclear waste disposal.

Our calculations suggest that UC₂ tends to interact stronger with V6-defective graphite surface than with pristine graphite surface with much higher binding energy.⁹ The irradiated graphite, therefore, can be considered as an effective barrier to the release of UC2 from reactor cores. It is also worth noting that the binding energies from DFT calculations between the metallic fission products and graphite with vacancies are more consistent with the experimental values than those with the pristine structures³ thus we believe our current results are also more reliable when compared to future experimental data. However, this strong interaction may weaken the sorption of other detrimental radioactive products such as metallic fission products. Since a graphite surface has limited sorption sites, variety of gaseous radioactive products are competing for sorption sites with high binding energy like vacancies in HTR,^{16,53} and UC₂ is likely to be more powerful in the competition, especially in a high temperature excursion accident. The present study provides not only comprehensive understanding of the bonding nature between actinide compounds and carbon nanomaterials with dangling C atoms, but also an important reference to the behavior of gaseous UC₂ on heavy-irradiated nuclear graphite during nuclear cycle.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Definitions of binding, interaction and preparation energies; Details of EDA for newly formed U-C bonds in I and V; Details of MOs information for configuration I; MOs information for configuration V; References for Supplementary Information. See DOI: 10.1039/b000000x/

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The strong localization of UC_2 in V6-defective graphene stabilizes the system extremely and stimulates participation of semi-core orbitals in bonding.