

Supplementary Information

Defect-induced Strong Localization of Uranium Dicarbide on Graphene Surface

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Part 1. Definitions of binding, interaction and preparation energies

The calculated binding (E_{bin}), interaction (E_{int}) and preparation (E_{prep}) energies are defined as

$$E_{\text{bin/int}} = [E_{\text{iso/relaxed}}(\text{UC}_2) + E_{\text{iso/relaxed}}(\text{V6})] - E(\text{UC}_2+\text{V6}) \quad (1)$$

$$E_{\text{prep}} = E_{\text{int}} - E_{\text{bin}} = E_{\text{prep}}(\text{UC}_2) + E_{\text{prep}}(\text{V6}) = [E_{\text{relaxed}}(\text{UC}_2) - E_{\text{iso}}(\text{UC}_2)] + [E_{\text{relaxed}}(\text{V6}) - E_{\text{iso}}(\text{V6})] \quad (2)$$

where $E(\text{UC}_2+\text{V6})$ is the total energy of the UC_2 molecule trapped in the graphene with V6 defect, $E_{\text{iso}}(\text{UC}_2)$ and $E_{\text{iso}}(\text{V6})$ represent the total energies of the isolated UC_2 and graphene with V6 defect, respectively, and $E_{\text{relaxed}}(\text{UC}_2)$ or $E_{\text{relaxed}}(\text{V6})$ denotes the total energy of UC_2 or graphene with V6 defect in its relaxed geometry, with both the UC_2 and graphene being in the same atomic configurations as in the relaxed $\text{UC}_2+\text{V6}$ system. The E_{int} represents a measure of the strength of the chemical interaction between the UC_2 molecule and V6-defective graphene, a positive E_{int} means an attractive interaction; while the E_{bin} encompasses not only the energy gained due to the chemical interaction E_{int} , but also the energy paid to deform the UC_2 molecule and V6-defective graphene from their ideal configurations to the relaxed $\text{UC}_2+\text{V6}$ system (i.e., preparation energy, E_{prep}). The terms “binding energy” (“adsorption energy”) and “interaction energy” are often used ambiguously in the literature.

Part 2. Details of EDA for newly formed U-C bonds in I and V.

Table S1. EDA parameters for newly formed U-C bonds in I and V (energy in eV).

Configuration	Fragment	$\Delta E_{\text{int}}^{\text{a}}$	$\Delta E_{\text{Pauli}}^{\text{b}}$	$\Delta E_{\text{elestat}}^{\text{c}}$	$\Delta E_{\text{orb}}^{\text{d}}$
I	U//(V6+C2)	29.92	-65.13	31.03 (33%)	64.01 (67%)
V	UC ₂ //V6	14.86	-23.31	11.90 (31%)	26.27 (69%)

^a Interaction energy, $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elestat}} + \Delta E_{\text{orb}}$; ^b Pauli repulsion energy; ^c Electrostatic interaction energy; ^d Orbital interaction energy. (To be consistent with equations (1) and (2), we have taken positive sign for attractive interaction, which is opposite to the results of bond energy decomposition implemented in ADF.)

One might notice that different interaction energy values are presented in Table S1 and Table 1 for configuration V, despite the same method in dividing fragments. This originates from different calculation methods for E_{int} and ΔE_{int} . According to the equation (2), E_{int} is calculated by

$$E_{\text{int}} = E_{\text{bin}} + E_{\text{prep}} = E_{\text{bin}} + E_{\text{prep,geo}} \quad (3)$$

However, based on the energy decomposition method in ADF, ΔE_{int} is calculated by

$$\Delta E_{\text{int}} = E_{\text{bin}} + E_{\text{prep}} = E_{\text{bin}} + E_{\text{prep,geo}} + E_{\text{prep,el}} \quad (4)$$

where $E_{\text{prep,geo}}$ is the energy required to deform the separated fragments from their equilibrium geometry to the geometry in the compound, and $E_{\text{prep,el}}$ refers to the energy necessary to electronically excite the fragments from their electronic ground-states to their valence electronic configuration. Therefore, the origination of difference between E_{int} and ΔE_{int} can be derived from

$$\Delta E_{\text{int}} - E_{\text{int}} = E_{\text{prep,el}} \quad (5)$$

$E_{\text{prep,el}}$ has been taken into account in bond energy decomposition in ADF, but is not included in equation (3).

Part 3. Details of MOs information for configuration I

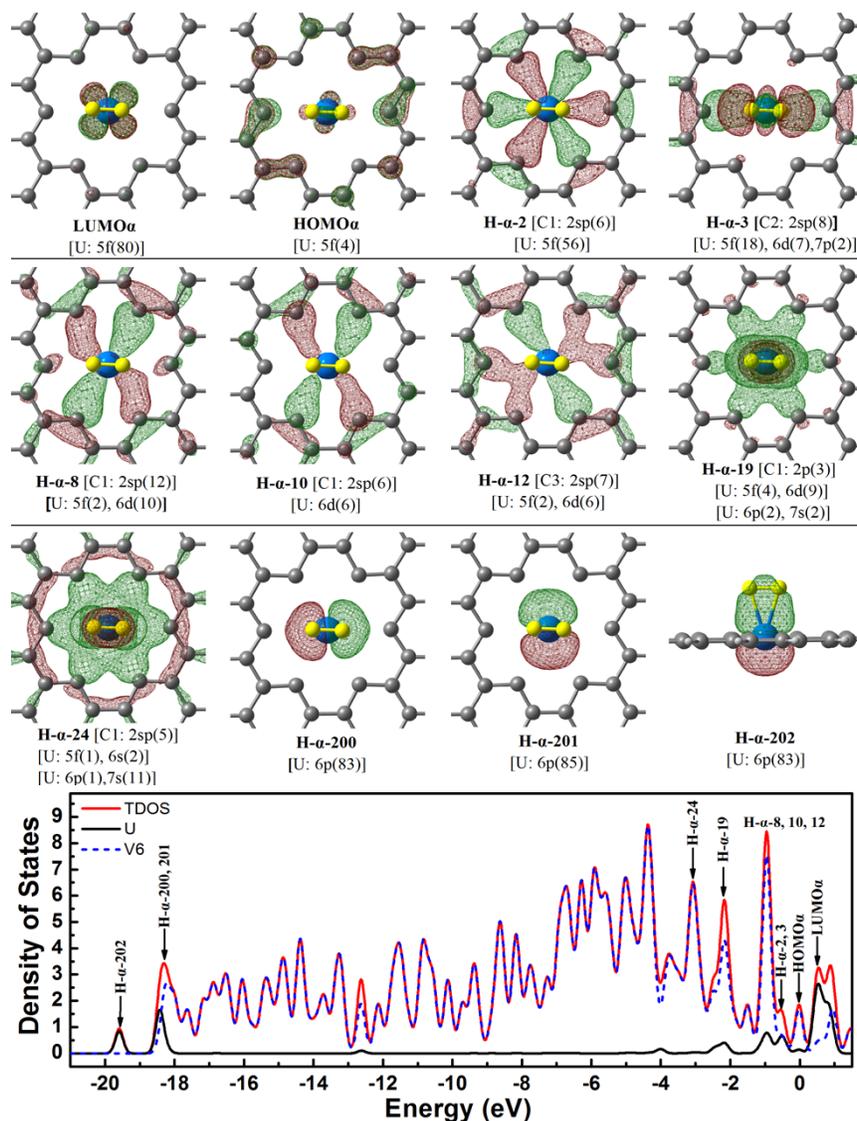
Table S2. Main contributions from AOs ($\geq 1\%$) to the MOs with uranium participation for configuration I, and contributions from MOs to selective U-C bonds*.

MOs	Orbital Energy (eV)	Contributions to bond (%)		U (%)				C(UC ₂) (%)		C1(V6) (%)	
		U-C(UC ₂)	U-C1(V6)	5f	6d	6p	other	2s	2p	2s	2p
HOMO	0.00			3							
HOMO-1	-0.02		4	6	2						2
HOMO-2	-0.41	12		15	3				6		
HOMO-3	-0.59	8		10	2				5		
HOMO-4	-0.71	3		4					3		
HOMO-5	-0.96			4							
HOMO-6	-1.06	-1	-2	25	4	3	7p: 1	1	7	1	5
HOMO-7	-1.08			2							
HOMO-8	-1.29		7	4	2						8
HOMO-9	-1.35			1	6						
HOMO-10	-1.37	6	2	16					6		2
HOMO-11	-1.47	2	1	9	1				2		2
HOMO-12	-1.53	6		16	5	1			7		4
HOMO-13	-1.61			2	3						
HOMO-20	-2.35			3	2		7s: 4				
HOMO-21	-2.55	11	11	5	5				6		7
HOMO-199	-18.99					93	5p: 2				
HOMO-200	-19.58	12	13			75	5p: 2	3	2	2	1
HOMO-201	-19.60	13	9			78	5p: 2	3	2	1	1

*Note: the contributions from MOs to U-C bonds are calculated from Mulliken bond order decomposition, ^[1-3] the negative values indicate contributions to antibonding. Because of the approximate symmetry of I, only information of one U-C(V6) or U-C(UC₂) bond is listed, “C1” in Figure 1 is denoted as C1(V6).

Part 4. MOs information for configuration V

Figure S1. Density of states (DOS) and characteristic Kohn–Sham MOs diagram with key percentage of AOs contributing to MOs for configuration V (isodensity value: ± 0.02 , only α orbitals). In DOS diagram, the red solid line represents total DOS (TDOS) for relaxed UC_2+V6 system (V), the black solid line and the blue dash line correspond to the local DOS (LDOS) for fragments of U atom and V6-defective graphene in V, respectively.



Part 5. References for Supplementary Information

- [1] R. S. Mulliken, *J. Chem. Phys.* 1955, **23**, 1841-1846.
- [2] R. S. Mulliken, *J. Chem. Phys.* 1955, **23**, 1833-1840.
- [3] R. S. Mulliken, *J. Chem. Phys.* 1955, **23**, 2338-2342.