

## Supplementary Information

### Formation of nickel-carbon heterofullerenes under electron irradiation

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#### Modified potential

The same as in the original Brenner potential,<sup>1</sup> the energy of the system is represented as<sup>2</sup>

$$E_b = \sum_i \sum_{j(>i)} E_{ij}, \quad (1)$$

where the energy  $E_{ij}$  of the bond between atoms  $i$  and  $j$  separated by the distance  $r_{ij}$  is given by the sum of repulsive and attractive terms

$$E_{ij} = V_R(r_{ij}) - \bar{b}_{ij} V_A(r_{ij}). \quad (2)$$

The repulsive interaction is determined by the two-body function

$$V_R(r_{ij}) = f_{ij}(r_{ij}) A_{ij} \exp(-\lambda_{1,ij} r_{ij}), \quad (3)$$

where the cut-off function  $f_{ij}(r)$  has the form

$$f_{ij}(r) = \begin{cases} 1, & r < R_{ij}^{(1)} \\ \frac{1}{2} \left[ 1 + \cos \left[ \frac{\pi(r - R_{ij}^{(1)})}{(R_{ij}^{(2)} - R_{ij}^{(1)})} \right] \right], & R_{ij}^{(1)} \leq r \leq R_{ij}^{(2)} \\ 0, & r > R_{ij}^{(2)} \end{cases} \quad (4)$$

The attractive interaction is described by the two-body function

$$V_A(r_{ij}) = f_{ij}(r_{ij}) B_{ij} \exp(-\lambda_{2,ij} r_{ij}) \quad (5)$$

multiplied by the function  $\bar{b}_{ij}$  which describes the dependence of the interaction energy on the local coordination. The empirical bond order function  $\bar{b}_{ij}$  is given by the sum of the average of the terms  $b_{ij}$  and  $b_{ji}$  corresponding to each atom in the bond and of the additional correction function  $F_{ij}$ , which is used to account for conjugated versus non-conjugated bonding and to avoid the overlapping of radicals,

$$\bar{b}_{ij} = (b_{ij} + b_{ji}) / 2 + F_{ij}(N_{ij}^C, N_{ji}^C, N_{ij}^{\text{conj}}), \quad (6)$$

where  $N_{ij}^C$  is the number of carbon atoms bonded to atom  $i$  in addition to atom  $j$  and  $N_{ij}^{\text{conj}}$  is used to determine whether the bond between atoms  $i$  and  $j$  is a part of a conjugated system. The function  $F_{ij}$  is non-zero only for bonds between two carbon atoms.

The bond order function  $b_{ij}$  for each atom in the bond is determined by

$$b_{ij} = \left[ 1 + \sum_{k(\neq i,j)} G_{ijk}(\theta_{ijk}) f_{ik}(r_{ik}) \exp \left[ \alpha_{ijk} \left( (r_{ij} - R_{ij}^{(e)}) - (r_{ik} - R_{ik}^{(e)}) \right) \right] + H_{ij}(N_i^{\text{Ni}}, N_i^{\text{C}}) \right]^{-\delta}, \quad (7)$$

where  $R_{ij}^{(e)}$  is the equilibrium distance between atoms  $i$  and  $j$ ,  $\theta_{ijk}$  is the angle between the bonds between atoms  $i$  and  $j$  and atoms  $i$  and  $k$  and  $\delta$  is taken equal to 0.5 for all atoms. The function  $H$  in this expression depending on the numbers  $N_{ij}^{\text{Ni}}$  and  $N_{ij}^{\text{C}}$  of nickel and carbon neighbors of atom  $i$  in addition to atom  $j$  was present also in the original Brenner potential<sup>1</sup> but it was taken equal to zero for the previous version of the Ni-C potential.<sup>2</sup> Here non-zero values of this function are introduced to improve description of low-coordinated nickel atoms.

The function  $G_{ijk}(\theta)$  is taken in the form

$$G_{ijk}(\theta) = a_{ijk} \left[ 1 + \frac{c_{ijk}^2}{d_{ijk}^2} - \frac{c_{ijk}^2}{d_{ijk}^2 + (1 + \cos \theta)^2} \right]. \quad (8)$$

As opposed to the original Brenner potential,<sup>1</sup> we assume that the parameters of the function  $G_{ijk}(\theta)$   $a_{ijk}$ ,  $c_{ijk}$  and  $d_{ijk}$  depend on types of all three atoms  $i$ ,  $j$  and  $k$ .

The numbers  $N_{ij}^{\text{C}}$  and  $N_{ij}^{\text{conj}}$  are found as

$$N_{ij}^{\text{C}} = \sum_{\text{C } k(\neq j)} f_{ik}(r_{ik}), \quad (9)$$

$$N_{ij}^{\text{conj}} = 1 + \sum_{\text{C } k(\neq i,j)} f_{ik}(r_{ik}) F_0(N_{ki}^{\text{C}}) + \sum_{\text{C } l(\neq i,j)} f_{jl}(r_{jl}) F_0(N_{lj}^{\text{C}}), \quad (10)$$

where

$$F_0(x) = \begin{cases} 1, & x \leq 2 \\ [1 + \cos(\pi(x-2))] / 2, & 2 < x < 3 \\ 0, & x \geq 3 \end{cases} \quad (11)$$

In the modified Ni-C potential, the values of the function  $F_{ij}$  are corrected according the original Brenner potential. In addition,  $F_{\text{CC}}(1,2,2) = F_{\text{CC}}(2,1,2)$  are changed to  $-0.0630$  to improve the graphene edge energies. The correct energies of carbon structures on the Ni (111) surface are kept by adjusting the parameters  $a_{\text{CCNi}}$  and  $a_{\text{CNiC}}$ . The parameters of the modified potential are given in Table 1, Table 2 and Table 3. The parameters that are changed as compared to the previous version<sup>2</sup> are shown in bold. The function  $H$  now takes non-zero values only in the case of  $H = H_{\text{NiC}}(N^{\text{C}}, N^{\text{Ni}})$  for  $N^{\text{Ni}} \leq 5$  and  $N^{\text{C}} \geq 1$ . Namely,  $H_{\text{NiC}}(N^{\text{C}} \geq 1, N^{\text{Ni}} \leq 3) = 1.3$  and  $H_{\text{NiC}}(N^{\text{C}} \geq 1, N^{\text{Ni}} = 4, 5) = 2.5$ .

**Table 1.** Two-body parameters of the potential.

Parameters	C-C	C-Ni	Ni-Ni
$A$ (eV)	2606	1866	1473
$B$ (eV)	1397	184.6	61.24
$\lambda_1$ ( $\text{\AA}^{-1}$ )	3.2803	3.6768	3.2397
$\lambda_2$ ( $\text{\AA}^{-1}$ )	2.6888	1.8384	1.2608
$R^{(1)}$ ( $\text{\AA}$ )	1.7	2.2	3.0
$R^{(2)}$ ( $\text{\AA}$ )	2.0	2.5	3.3
$R^{(e)}$ ( $\text{\AA}$ )	1.3900	1.6345	2.0839

**Table 2.** Three-body parameters of the modified potential.

Parameters	CCC	CCNi	CNiC	CNiNi	NiNiNi	NiNiC	NiCNi	NiCC
$\alpha$ ( $\text{\AA}^{-1}$ )	0	0	0	0	4.40	0	4.01	0
$a$	$2.08 \cdot 10^{-4}$	<b>0.115</b>	<b>0.602</b>	$3.29 \cdot 10^{-3}$	$9.28 \cdot 10^{-2}$	0	$1.86 \cdot 10^{-4}$	$1.22 \cdot 10^{-5}$
$c$	330	0	0	5.72	7760	0	7410	240
$d$	3.50	1.00	1.00	0.348	69.0	1.00	7.75	1.00

**Table 3.** Values of function  $F_{CC}(i, j, k)$  for integer values of  $i, j$  and  $k$ . Between integer values of  $i, j$  and  $k$ , the function is interpolated by a cubic spline. All parameters not given are equal to zero,  $F_{CC}(i, j, k > 2) = F_{CC}(i, j, k)$ .

	$F_{CC}$
(0,1,1), (1,0,1)	<b>0.0996</b>
(0,2,1), (2,0,1)	<b>0.0427</b>
(0,2,2), (2,0,2)	<b>-0.0269</b>
(0,3,1), (3,0,1)	<b>-0.0904</b>
(0,3,2), (3,0,2)	<b>-0.0904</b>
(1,1,1)	0.1264
(1,1,2)	0.0108

(1,2,1), (2,1,1)	0.0120
(1,2,2), (2,1,1)	-0.0630
(1,3,1), (3,1,1)	-0.0903
(1,3,2), (3,1,2)	-0.0903
(2,2,1)	0.0605
(2,3,1), (3,2,1)	-0.0363
(2,3,2), (3,2,2)	-0.0363

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## REFERENCES

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2. I. V. Lebedeva, A. A. Knizhnik, A. M. Popov and B. V. Potapkin, *J. Phys. Chem. C*, 2012, **116**, 6572.