Supplementary Material (ESI) for Nanoscale

Modeling the Thermostability of Surface Functionalisation by Oxygen, Hydroxyl, and Water in Nanodiamonds

Lin Lai*, Amanda S. Barnard

CSIRO Materials Science and Engineering, Clayton, VIC, 3168, Australia

E-mail: lin.lai@csiro.au

Models

To establish a frame of reference, we first studied the bare nanodiamond structures. In the case of the bare C_{705} nanodiamond, there are ~19.3% of sp^2-bonded, ~52.9% of sp^3-bonded, and ~27.8% of sp^{2+x}-bonded C atoms. The average C−C bond length was found to be 1.52 ± 0.06 Å. For the bare C_{837} nanodiamond, the fraction of sp^2-, sp^3-, and sp^{2+x}-bonded C atoms is ~33.0%, ~37.4%, and ~29.6%, respectively. The average C−C bond length was found to be 1.50±0.06 Å. All structural variations presented below will be compared with these values, and all adsorption configurations will be described as being stable or unstable with respect to these structures. As demonstrated in previous studies, adsorption and/or desorption will invoke a structural response, corresponding to changes in the structure of different facets (and possibly the particle as a whole), which will in turn influence the type of chemical character of the C atoms exposed to their surroundings.

Oxygen (O) Adsorption

The results of coordination and bond length variations are presented in Table 1. We can see that, in general, covalent O-adsorption invokes dramatic structural changes in the coordination of the C atoms, as well as a slight variation in their shapes. Compared with bare nanodiamonds, the O-{100}-functionalisation of the C_{705} nanodiamond (Figure 2(a) of main text) results in a dramatic increase in the fraction of the sp^2-bonded C atoms and a great decrease in the fraction of the sp^{2+x}-bonded C atoms, while the fraction of sp^3-bonded C atoms remains unchanged. In contrast, the O-{111}-functionalisation generates a dramatic

increase in the fraction of the sp^3-hybridised C atoms and a great decrease in the fraction of the sp^2- and sp^{2+x}-bonded C atoms. This is expected, since surface graphitization is known to be largely restricted to the {111} facets. Like the O-{111}-functionalisation, a similar trend is found in the O-{110}-functionalised C_{705} nanodiamond, although the coordination changes are moderate. In the configurations of the C_{705} nanodiamond with unsaturated {100}, {110}, or {111} facets, there are a significant increase in the fraction of the sp^3-hybridised C atoms and a great decrease in the fraction of the sp^2- and sp^{2+x}-bonded C atoms. Moreover, full O-termination results in nearly 100% of sp^3-hybridised C atoms.

In case of the C_{837} nanodiamond, we find that O-{100}-functionalisation induces a significant increase in the fraction of the sp^2-bonded C atoms, a slight decrease in the fraction of the sp^{2+x}-bonded C atoms, and a dramatic decrease in the fraction of the sp^3-bonded C atoms, compared with bare C_{837} nanodiamond. In contrast, the O-{111}- and full-O-functionalisation generate more dramatic structural changes, particularly in the fraction of sp^3-bonded C atoms, as surface graphitization is prevented.

The average length of the C−O bonds in the O-{100}-functionalised nanodiamonds is much shorter than those in alternative configurations. Given the typical bond length of C−O single and double bonds, we attribute the C−O bond on the {100} surfaces to be double bonds and attribute those on the {111} and {110} facets to be single bonds. This is further supported by the existence of the oxygen dimers on the nanodiamond surfaces (mostly on the {111} and {110} facets, see Figure 2 of main text) after geometrical optimization. These dimers saturated the unpaired electrons in the adsorbed O atoms forming a C−O−O−C connection and further stabilize the configuration. The structural changes are found to differ distinctly between the O-{100}- terminated C_{705} and C_{837} nanoparticles, although the two nanoparticles have a same number of adsorption sites on the {100} facets. Complete lack of passivation of the {111} facets allows for bucky-diamond surface reconstructions, which are

known to be more efficient when the {111}|{111} edges are present (see Ref 20 in main text).

Hydroxyl (OH) Adsorption

The results of coordination and bond length variations are presented in Table 2. We can see that, generally, the OH-functionalisation of the {100} and {110} facets induces only a slight structural changes, while the passivation of the {111} facets gives rise to a significant increase in the fraction of sp^3-bonded C atoms and a dramatic decrease in the fraction of sp^2-bonded C atoms. For example, we find nearly 100% of sp^3-bonded C atoms in the OH-{111}-functionalised C_{837} nanodiamond, which is due to the existence of large number of adsorption sites on the {111} facets of C_{837} nanoparticle, as well as the lack of the {110} facets.

Water (H_2O) Adsorption

The results of coordination and bond length variations in the H_2O-functionalised C_{705} and C_{837} nanodiamonds in the decomposition case and the physisorption case are presented in Table 3 and Table 4, respectively. In the first instance, the obtained results are actually from the OH-terminated nanodiamonds, and we can see they are in good agreement with data for OH-functionalisation (Table 2). The only different is that the error for the C−O bond length is larger for decomposed than for OH-functionalisation. This indicates a larger variation in length distribution of the C−O bonds, which possibly is arose from the H_2 molecules surrounding the nanodiamond, and their residual long ranged interactions with the remaining OH groups. This also indicates that OH-functionalisation of nanodiamonds is nearly unperturbed (except changes in bond length) by the presence of excess H_2 gas. On the other hand, we find little structural changes (C atom hybridisation and average C−C bond length) in H_2O-physisorbed nanodiamonds, as well as a larger C−O average distance than that in O- and OH-terminated nanodiamonds, confirming the assignment of physical adsorption.

Table 1. Fraction (%) of sp^1-, sp^2-, sp^3-, and sp^{2+x}-bonded C atoms and the average C−C and C−O bond lengths in C_{705} and C_{837} nanodiamonds with O-functionalisation.

Termination Sites	sp^1 [%]	sp^2 [%]	sp^3 [%]	sp^{2+x} [%]	*r* (C−C) [Å]	*r* (C−O) [Å]
C_{705} {100}	0.0	32.3	52.9	14.8	1.519±0.050	1.195±0.004
C_{705} {110}	0.0	13.3	65.1	21.6	1.528±0.049	1.422±0.084
C_{705} {111}	0.0	3.4	79.0	17.6	1.538±0.043	1.432±0.069
C_{705} {110}&{111}	0.6	2.3	85.8	11.3	1.542±0.040	1.420±0.089
C_{705} {100}&{111}	1.7	11.6	77.3	9.4	1.540±0.025	1.332±0.137
C_{705} {100}&{110}	1.7	17.6	69.5	11.2	1.539±0.055	1.300±0.133
C_{705} full coverage	0.7	5.4	91.3	2.6	1.549±0.041	1.395±0.101
C_{837} {100}	0.1	56.4	29.4	14.1	1.498±0.065	1.193±0.008
C_{837} {111}	0.6	2.3	86.3	10.9	1.543±0.041	1.406±0.096
C_{837} full coverage	0.7	7.8	90.9	0.6	1.547±0.029	1.377±0.118

Table 2. Fraction (%) of sp^1-, sp^2-, sp^3-, and sp^{2+x}-bonded C atoms and the average C−C and C−O bond lengths in C_{705} and C_{837} nanodiamonds with OH-functionalisation.

Termination Sites	sp^1 [%]	sp^2 [%]	sp^3 [%]	sp^{2+x} [%]	*r* (C−C) [Å]	*r* (C−O) [Å]
C_{705} {100}	0.0	22.6	63.1	14.3	1.522±0.057	1.412±0.009
C_{705} {110}	0.0	10.8	61.4	27.8	1.529±0.053	1.386±0.027
C_{705} {111}	0.0	1.6	77.6	20.9	1.539±0.041	1.411±0.023
C_{705} {110}&{111}	0.0	0.0	89.8	10.2	1.549±0.037	1.424±0.009
C_{705} {100}&{111}	0.0	2.6	81.8	15.6	1.543±0.039	1.409±0.020
C_{705} {100}&{110}	0.0	5.2	82.4	12.3	1.545±0.053	1.411±0.016
C_{705} full coverage	0.0	0.0	100.0	0.0	1.557±0.032	1.422±0.013
C_{837} {100}	0.0	46.2	39.8	14.0	1.502±0.062	1.415±0.011
C_{837} {111}	0.0	0.0	91.4	8.6	1.547±0.028	1.424±0.011
C_{837} full coverage	0.0	0.0	99.8	0.2	1.552±0.018	1.425±0.017

Table 3. Fraction (%) of sp^1-, sp^2-, sp^3-, and sp^{2+x}-bonded C atoms and the average C−C and C−O bond lengths in C_{705} and C_{837} nanodiamonds with H_2O decomposition (OH-termination and H_2 desorption).

Termination Sites	sp^1 [%]	sp^2 [%]	sp^3 [%]	sp^{2+x} [%]	*r* (C−C) [Å]	*r* (C−O) [Å]
C_{705} {100}	0.0	20.6	63.3	16.2	1.523±0.058	1.434±0.026
C_{705} {110}	0.0	12.2	60.3	27.5	1.525±0.051	1.465±0.031
C_{705} {111}	0.0	0.9	76.5	22.7	1.536±0.039	1.463±0.024
C_{705} {110}&{111}	0.0	0.0	88.4	11.6	1.547±0.034	1.440±0.016
C_{705} {100}&{111}	0.0	0.4	88.8	10.8	1.546±0.038	1.436±0.033
C_{705} {100}&{110}	0.0	11.6	72.2	16.2	1.534±0.059	1.437±0.027
C_{705} full coverage	0.0	0.0	100.0	0.0	1.557±0.032	1.421±0.017
C_{837} {100}	0.0	47.0	35.5	17.6	1.497±0.058	1.444±0.026
C_{837} {111}	0.0	0.0	90.8	9.2	1.545±0.026	1.436±0.015
C_{837} full coverage	0.0	0.0	100.0	0.0	1.552±0.020	1.423±0.013

Table 4. Fraction (%) of sp^1-, sp^2-, sp^3-, and sp^{2+x}-bonded C atoms and the average C−C and C−O bond lengths in C_{705} and C_{837} nanodiamonds with H_2O-physisorption.

Termination Sites	sp^1 [%]	sp^2 [%]	sp^3 [%]	sp^{2+x} [%]	r (C−C) [Å]	r (C−O) [Å]
C_{705} {100}	0.0	20.9	53.5	25.7	1.515±0.058	1.452±0.039
C_{705} {110}	0.0	19.3	52.9	27.8	1.515±0.062	N/A
C_{705} {111}	0.0	19.0	53.0	27.9	1.516±0.061	1.484±0.000
C_{705} {110}&{111}	0.0	19.4	53.0	27.5	1.515±0.062	1.445±0.000
C_{705} {100}&{111}	0.0	20.4	54.2	25.4	1.516±0.056	1.464±0.039
C_{705} {100}&{110}	0.0	21.4	52.8	25.8	1.516±0.058	1.456±0.047
C_{705} full coverage	0.0	20.9	54.2	25.0	1.516±0.057	1.468±0.048
C_{837} {100}	0.0	32.7	43.6	23.7	1.509±0.059	1.490±0.015
C_{837} {111}	0.0	27.2	45.9	26.9	1.511±0.059	1.487±0.006
C_{837} full coverage	0.0	24.4	49.7	25.9	1.514±0.055	1.491±0.008