Tunable charge transfer on selectively functionalised diamond nanoparticles

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A B S T R A C T

For applications in nanomedicine, it has been shown that charge transfer properties are fundamental to the efficient loading and release of therapeutic agents, though it is not always clear whether intrinsic surface reconstructions and chemical conditions will encourage or suppress electron donation or acceptance. In this study we have investigated the relationship between the localised surface charge transfer, the ionization potential and the electron affinity of a model diamond nanoparticle, as a function of the distribution of important intrinsic surface terminations: H, O and OH. The detailed results reveal that diamond nanoparticles can act as electron donors or electron acceptors, depending on the type of surface terminations that are applied, the efficiency of the surface passivation (coverage) and the orientation of the facets where binding occurs. The results suggest that incomplete passivation is not necessarily undesirable, and that by driving charge transfer in different directions (to, or from, the host nanoparticle) by changing the surface chemistry new methods for more tailored applications such as drug delivery may be explored, based on post synthesis processes that do not necessitate modifications to the formation and purification processes already in place.

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1. Introduction

Undoubtedly one of the most exciting applications for colloidal nanoparticles is in the field of nanomedicine [1–3]. Although there are still many challenges in realising this potential [4,5], there are some cases where research is progressing well toward the clinic [6,7], and others were even at the early stages we are beginning to see how the intrinsic properties of the nanoparticle are playing a crucial role [8,9]. Nanoparticles are useful for imaging [10], detection [11] and drug delivery [12]; provided their surfaces are dressed appropriately [13].

One example in this domain is diamond nanoparticles [14–17], which are already showing great promise for a range of therapies [19–21]. Benefits include increased selectivity [23,24] and sensitivity [22], the ability to more effectively moderate dosage [25] and provide more long term, sustained treatments without burst effusion [26]. It is now possible to produce stable suspensions of nanodiamonds with a hydrodynamic diameter of ~3.0 nm, with a narrow size distribution [27], which provides an even greater specific surface area for carrying therapeutic agents, biomarkers and ligands [28,29]. In each case, charge transfer properties are important to interactions of molecules with the surfaces of nanoparticles, including the loading and release of therapeutic agents, and will therefore impact the dose and dose rate during treatment. For example for the positively charged doxorubicin ions ($NH3+$)

to be attracted to diamond nanoparticles the surfaces must be negatively charged, so that one needs to consider variations in the charge equilibrium on the surface sites and the amine group on doxorubicin to control the capture and release, as determined by solvent cations or anions [30]. In short, drugs may be bound to, and released by, the nanoparticle *via* charge transfer; which is well known in many other drug delivery platforms as well [31–34].

In general, the direction and efficiency of charge transfer depends on whether the underlying diamond nanoparticle acts as a donor or an acceptor, and can be characterized using the sign and value of the ionization potential (the donation of an electron) and the electron affinity (the accepting of an electron). It is possible to make direct measurements, and in the case of the H-terminated diamond surfaces it is well known that the electron affinity is negative [35,36]; though the exact value depends on a variety of factors [37–39]. This includes the type of interface [40,41], and species of surface terminations [43] or atmospheric conditions [42,44]. In addition to this, specific mixtures of surface groups (including H and OH) may result in NEA [45]. Similarly, recent studies have also shown that charge transfer at the nanodiamond surface depends sensitively on the types of particles, surfaces and surrounding medium [46–48]. Given these relationships, it is logical to assume it is possible to use them to our advantage. If the charge transfer reactions occurring at the surfaces could be tuned, it may be possible in the future to tailor these particles to various applications, including (but not limited to) nanodiamond-based drug nanomedicines to the individual needs of patients.

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In this study we have investigated the relationship between the localised surface charge transfer on a model diamond nanoparticle, as a function of the distribution and coverage of important intrinsic surface terminations: H, O and OH. We find that there are likely to be definite advantages to attempts to selectively passivating certain surface of diamond nanoparticles, depending on the type of reactions one wishes to encourage or suppress.

2. Computational methods

Selective passivation of specific facets of nanoparticles is still challenging experimentally, so we have elected to use electronic structure simulations to model a range of different configurations, and compare the results. Specifically, we have used the self-consistent charge density functional tight-binding method (SCC-DFTB) [49] implemented in the DFTB+ code [50], which is an approximate quantum chemical approach where the Kohn–Sham density functional is expanded to second order around a reference electron density obtained within the generalised gradient approximation (GGA). In this approach a confinement potential is optimised to anticipate the charge density and effective potential in both molecules and solids, and a minimal valence basis set is used to account explicitly for the two-centre tight-binding matrix elements within the DFT level. The double counting terms in the Coulomb and exchange–correlation potential, as well as the intra-nuclear repulsion are replaced by a universal short-range repulsive potential. In all the calculations, the "PBC" set of parameters is used to describe the contributions from diatomic interactions of carbon, hydrogen and oxygen [51]. This method has proven very successful in the past for modeling the absorption of oxygen containing groups on the surfaces of nanodiamond [52–54].

The diamond nanoparticle we have chosen in this case is a rhombitruncated-octahedron, as it is known to be a stable, low energy morphology, with a convenient combination of {100}, {111}, and {110} surfaces [55]. In particular, the (110) facets play an important role in the environmental stability and aggregation of diamond nanoparticles, and are resistant to the persistent graphitization that is characteristic of the bare (111) facets [56]. In this study, a 705 carbon atoms structure is used (denoted C_{705}), which is 2.2 nm in average

diameter, and to provide consistency with previous works [57], and a set of facet-dependent configurations have been considered. The configurations include structures where passivation is restricted to facets in a particular crystallographic orientation (denoted as {100}:X, {110}:X, and {111}:X, where X is the surface termination), and particles where passivation is suppressed on facets in a particular crystallographic orientation (denoted by the remaining facets that are passivated: {100}/{110}:X, {111}/{110}:X, and {100}/{111}:X). The fully passivated ($C705H228$) particle has also been included for the purposes of comparison. All structures have been fully relaxed with a conjugate gradient methodology, without constraints, until forces on each atom were minimized to be less than 10^{-4} a.u. (i.e. ≈ 5 meV/Å). In the absence of surface terminations, this relaxation invokes surface reconstructions, to eliminate unpaired electrons where possible (see Fig. 1).

At this point it is prudent to point out that the binding energy (and overall stability) of each type of surface termination depends on the surrounding thermochemical conditions [57], and the presence of excess charges [58]. This includes variations in temperature and the supersaturation of each species, and alternative species, in the bath. This issue has been treated in detail, using *ab initio* thermodynamics, and considering the impact of varying the partial pressure of water, in Ref. [59].

Following the relaxation of each structure the relative charge on the passivated carbon atoms and the attached atoms or molecules was extracted. There is no unique and definitive way of calculating charges, which are not strictly observable quantities, regardless of the method used. For this reason, it is preferable to compare the difference between charges on surfaces and molecules, again, regardless of the method used. In our particular case the Mulliken charges form an integral part of the energy functional in DFTB which expresses local density fluctuations around a given atom. The Mulliken charge fluctuations are calculated from the eigenvalue coefficients, and are algorithmically independent from bonding considerations and spatial partitioning schemes.[60] Therefore, although they generally have limited quantitative value, they are generated consistently and in a meaningful way (rather than using a separate method, *a posteriori*) and the relative differences are useful in illustrating *trends*, making them entirely suitable for comparing the impact of the different configurations included here.
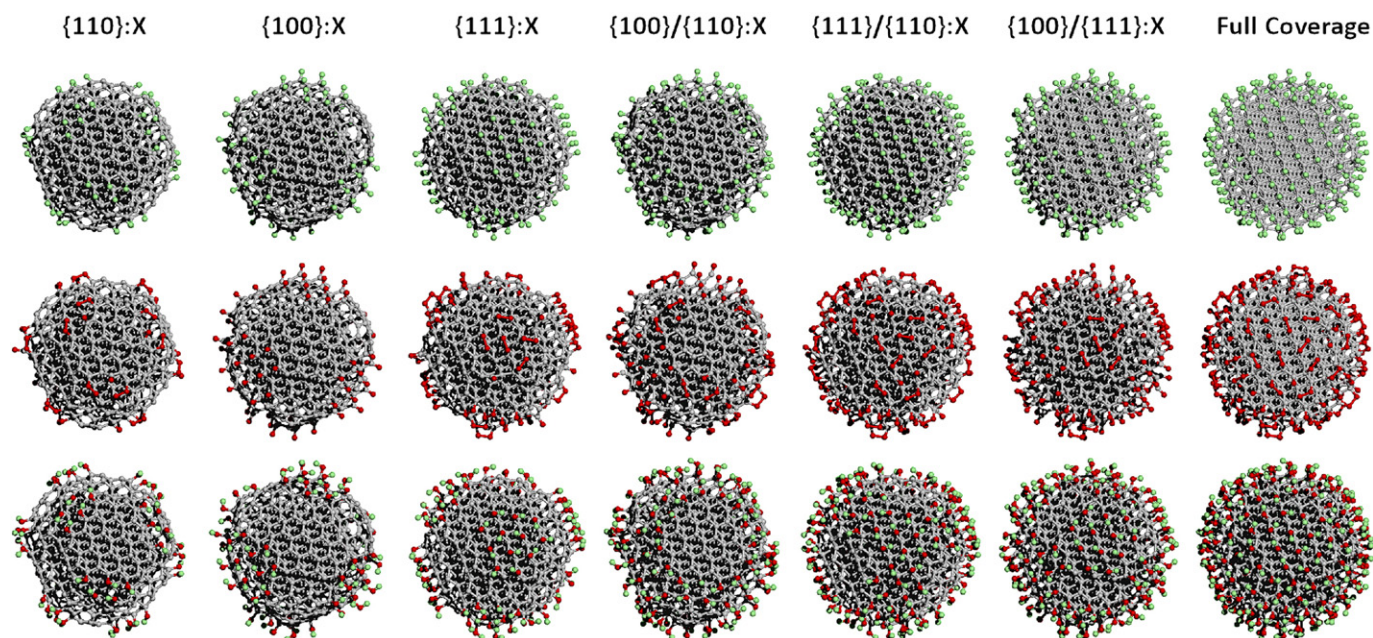

Fig. 1. Schematic representation of the selectively passivated diamond nanoparticles used in this study. The orientation of the passivated facets is labelled, for hydrogen (top), oxygen (centre) and hydroxyl (bottom). The configurations are shown in increasing order of passivation (coverage) from left to right. Carbon atoms are shown in grey, oxygen in red, and hydrogen in pale green for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)