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Short communication

Screening of ions in carbon and gold nanotubes — A theoretical study

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ABSTRACT

We examine the insertion of alkali ions into narrow nanotubes of graphite and gold by density functional theory. The surrounding tubes screen the ionic charge very effectively; the resulting image energy compensates well for the loss of solvation. In addition, ion–ion interactions are strongly reduced. These effects are stronger for gold than for graphite tubes. Our results explain at an atomic level, why narrow tubes store charge so effectively.

1. Introduction

Supercapacitors store electrical energy very efficiently, and are therefore at present the subject of intensive research. Since the capacity should be roughly proportional to the surface area, porous electrodes are particularly attractive. At a first glance, one would expect that the optimum pore size is such that the ions can enter the pores without shedding their solvation shells. However, experimentally it has been observed that pores with smaller radii, such that the fully solvated ions cannot enter, store energy even more efficiently [1,2]. Kondrat and Kornyshev [3] were quick to point out that this increase in the capacity per unit area is caused by the image interaction of the ions with the pore walls. The image charge effectively screens the Coulomb potential of the ions, and thus reduces the strengths of the ion–ion interaction and allows a denser packing of the excess charge.

Quantitatively this effect has been explored within simple models in which the electrode material was described either as a perfect metal or on the Thomas–Fermi level [4]. While these undoubtedly catch the essential physics, a more detailed and atomistic description is called for. In this work, we take a first, and as we believe important, step in this direction and investigate by density functional theory (DFT) the interaction of two different ions, Na^+ and Cs^+, with two different kind of nanotubes, carbon and gold tubes, in order to explore how the screening depends on the chemical nature of the materials. Besides the Coulomb effects we also calculate the energetics of ion insertion into the tubes, an aspect which so far has received scant attention.

2. Details of the investigated systems

As has been pointed out recently [5], performing DFT calculations with ions is not easy; solvated protons in front of a metal electrode acquire at best a partial positive charge of the order of 0.5. Fortunately the situation with tubes is more favorable: in the cases we investigated, Na and Cs atoms placed inside small tubes of carbon and gold, automatically take up unit positive charge. However, this effect is restricted to tubes with diameters of the order of 10 Å or less; in thicker tubes the charge on the ion becomes fractional. Therefore, we have performed calculations for narrow SWNT (single-wall nanotubes): for (6,6) gold NT (see [6,7]), and for (8,0) and (10,0) CNT (carbon nanotubes) (see Fig. 1). We have used cyclic boundary conditions in the axial direction, to represent infinitely long gold NT. We have considered CNT with a finite size in the axial direction (see Fig. 1).

The CNTs by themselves are not stable, therefore we saturated the dangling bonds with hydrogen atoms. All the systems used are neutral, but we confirmed the loss of a charge in the alkali atom by using the Bader method [8]. For the technical details of the DFT calculation and

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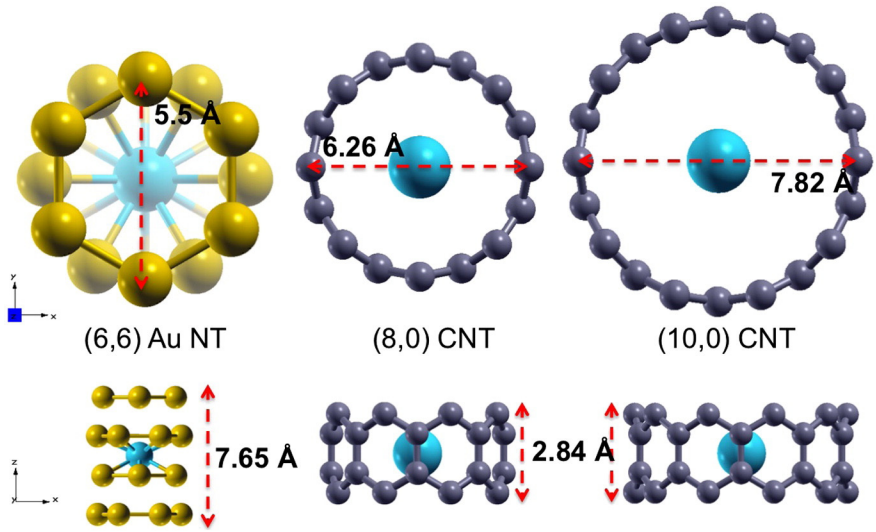

Fig. 1. Gold nanotube (left) and carbon rings (center and right) with a Na^+ in the center. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the relaxation of the geometries, we refer to [9] for the calculations with gold, and to [10] for graphite.

3. Results and discussions

3.1. Distribution of the image charge

Real metals screen external charges better than semimetals like graphite [11,12], and we expected to see the same effect in the present calculations. To illustrate the position of the image charge, we calculated charge difference plots, which show the excess of the charge in the system tube containing Na with respect to the empty tube and the isolated Na atom. Fig. 2 compares the situation for Na in a carbon nanoring with 8 hexagons (8,0) CNT, and in the gold nanotube. Both systems have roughly the same diameter, the carbon ring being slightly larger. In the center of both plots, we see the fully ionized Na^+. The image charge (red) resides on the atoms and extends in the form of a lobe toward the ion. In the case of gold, the image charge is closer to the ion than in the carbon ring; in addition, it is more delocalized on gold. As expected, gold screens better than carbon.

3.2. Energetics

In all cases the equilibrium position of the ion is on the central axis, as indicated in Fig. 1. For reasons of symmetry, this is perhaps not surprising for narrow tubes, but obviously this cannot hold for very wide rings, which appear almost flat on an atomic scale. It would be interesting to see, at what ring diameter the central axis ceases to be the most favorable position, but for reasons pointed out above this cannot be explored with DFT.

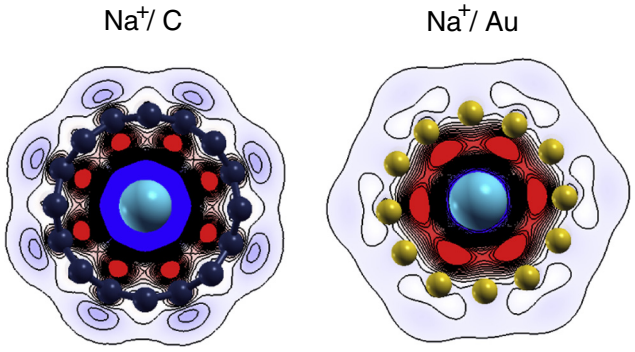

Fig. 2. Charge difference plots for a sodium ion in a (8,0) carbon ring with 8 hexagons (left) and in a gold tube (right). Red (blue) indicates an excess of negative (positive) charge. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For all cases considered we have calculated the energy required to insert the atom into the tube:

$$E_{\text{ins}} = E(\text{tube} + \text{ion}) - E(\text{tube}) - E(\text{alkali atom}) \quad (1)$$

where all energies refer to the relaxed systems. With the exception of Cs in the gold nanotube, which is too big to fit in, insertion is exothermal, see Table 1. Let us first discuss the insertion of Na, which fits into all three tubes without distortion. The insertion can then be decomposed into three steps: (1) ionization of the Na atom; (2) transfer of the electron into the tube; (3) insertion of the ion into the tube with a concomitant gain of image energy. This gives:

$$E_{\text{ins}} = I_1 - \Phi + E_{\text{im}} \quad (2)$$

where I_1 denotes the first energy of ionization, Φ is the work function of the tube, and E_{im} is the gain in image energy upon insertion of the ion. The energies of ionization are freely available in the literature; for the work function of the (6,6) Au NT we obtained a value of 5.5 eV, not too far from the value for Au(111) (5.2 eV). The workfunctions of carbon nanotubes are notoriously difficult to determine; we took the values from a careful study by Su et al. [13]: 4.8 eV for (8,0) CNT, and 4.6 eV for (10,0) CNT. So we are able to estimate the image energies for the sodium ion, and we have included them in our table. As expected, they are lowest (more favorable) on the Au NT, and highest on the (10,0) CNT.

For Cs the situation is more complicated, because it does not fit well into the Au NT nor into the (8,0) CNT. Both these tubes are deformed,

Table 1
Energies of insertion for Cs and Na, and image energies for the corresponding ions. All values are in eV; in the case of the CNT they are for the hydrogenated tubes. The energies E_{ins} refer to the insertion of a single atom according to Eq. (1), the energies $E^{\text{b}}_{\text{ins}}$ to the insertion of an atom from the bulk metal according to Eq. (3).

	Atom	Au NT	(8,0)CNT	(10,0) CNT
88	Na	−3.58	−1.24	−0.64
	Cs	0.52	−1.75	−2.00
E_{im}	Na^+	−3.19	−1.58	−1.18
	Cs^+	–	–	−1.29
$E^{\text{b}}_{\text{ins}}$	Na	−2.47	−0.13	0.47
	Cs	1.31	−0.45	−0.21

which costs a sizable amount of energy. Without this deformation the insertion energies for Cs and Na should differ by their energies of ionization, so that the energies for Cs should be about 1.25 eV lower (more favorable) than for Na. However, this is only true for the (10,0) CNT, into which Cs^+ fits without deformation. In this ring the two ions have, within DFT error, the same image energy, which shows the consistency of our calculations.

The image energy is the energy that the ion gains from the tube when it is inside. This has to be compared with the energy that the ion gains from its environment when it is in the bulk of the solution, which is its free energy of solvation. In typical solvents the solvation energies for Na^+ are of the order of 3–4 eV, and for Cs^+ of the order of 2–2.5 eV, so they are generally greater than the image energies. However, the ions do not shed all of their solvation shell when they enter the tubes; as a minimum they can keep two solvent molecules. So the energies that the ions gain from their environments are of the same order of magnitude in the nanotubes and in the bulk of the solution.

A referee has suggested to refer the insertion energies not to a single alkali atom but to an atom in the bulk:

$$E^{b}_{ins} = E(\text{tube} + \text{ion}) - E(\text{tube}) - E(\text{alkali atom in bulk}). \quad (3)$$

The latter energy can be obtained from the former by adding the energies of atomization (1.11 eV for Na, 0.79 eV for Cs). The referee suggested that a positive value of E^{b}_{ins} would indicate that bulk deposition of the alkali metal would take place before ion insertion, making the respective tube unsuitable for ion storage. However, this argument ignores entropy effects, and also ion–ion interactions within the tube. Further, during insertion the ions could take one or two water molecules with them, and thus lower their energies. Nevertheless, these energies are of some interest, and we have therefore included them in Table 1.

The energy required to transfer an ion from the solution to the tubes involves the difference in the electrostatic potential between the two positions. Thus, by changing the electrode potential the energy, and hence the concentration, of a particular ion in the tube can be raised or lowered.

The energies presented in this paragraph are for a single ion. If we want to charge the nanotubes as highly as possible by packing many ions of the same sign into them, ion–ion interactions become important, to which we shall turn next.

3.3. Screened Coulomb potential

In order to investigate the effect of the image charge on the ion–ion interaction within tubes, we calculated the electrostatic potential along the axis of the tube. As has been rightly pointed out by Kondrat and Kornyshev [3], this potential is strongly screened by the image force, so that ion–ion interactions are weakened, and more ions of the same sign can be packed into narrow tubes, an effect which they called the *superionic state*.

The potentials, as calculated from DFT, have a physical meaning only outside the range of the pseudopotentials. Fig. 3 shows the results for Na^+ on the left; as expected from our discussion above, the screening becomes better in the order (10,0)CNT < (8,0)CNT < Au NT; the difference between Au and (8,0)CNT, which have similar diameters, is quite notable. For comparison we also show the screened potential for a perfect metal tube whose surface coincides with the position of the atoms of (8,0)CNT. Obviously, this simple model severely underestimates the screening. However, the principle difficulty of this model is the position of the effective surface. For a three-dimensional crystal, the nominal surface lies half a lattice spacing in front of the first plane of atom cores. For a metal surface, the effective image plane lies even 0.3–0.4 Å in front of the nominal surface [14], while for graphite it lies well behind the nominal surface, its position depending strongly on the applied electric field [11]. For tubes, not even the nominal surface plane is defined, so there is no obvious rule where one should place the effective image plane. Therefore we have refrained from comparing our calculations with the results of a Thomas–Fermi model [4], which suffers from the same problem.

On the r.h.s. of Fig. 3 we compare the potentials for Na^+ and Cs^+. In the (10,0) CNT, into which both ions fit equally well, we obtained practically the same potential, which shows that in this case the screening is a purely Coulombic effect. This is in line with the image energies calculated in the previous paragraph. The situation is different for the Au tube, into which only Na^+ fits without deforming the tube. At short distances, the potential of Na^+ is screened better, while at larger distances the potentials for the two ions merge. So the deformation has only a short-ranged effect on the screening. Finally we note that far outside of the tube, the potential drops to zero; this shows that the screening of the charge in this region is complete.

4. Conclusions

In this work we have investigated the screening of ions in very thin nanotubes by DFT, choosing Na^+ and Cs^+ as model ions, and comparing gold and carbon tubes. In all cases the image energy compensates well for the partial loss of the solvation sheath, and the Coulomb potential is strongly screened. These effects are always stronger on gold than on the semi-metallic carbon tubes, which is in accord with their double-layer properties [11,12]. As long as the ions fit well into the nanotubes, these effects are the stronger, the smaller the tubes. Thus our

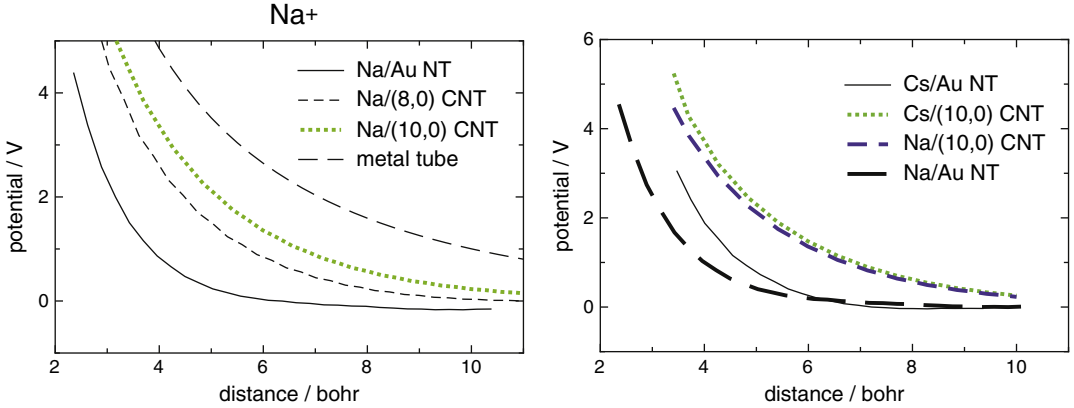

Fig. 3. Screened Coulomb potential along the axis of the tube as a function of the distance from the ion.

calculations explain on an atomic level, why narrow tubes store charge more efficiently than wider tubes.

Conflict of interest

There is no conflict of interest.

Acknowledgments

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