FIELD EMISSION PROPERTIES OF BN/C and BN@C HYBRID NANOTUBES

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ABSTRACT

We demonstrate that boron-nitride (BN) doping in carbon nanotubes can greatly improve the field emission properties of these systems. The intrinsic electric field associated with the polarity of the B-N bond enhances the emitted current density through a reduction of the work function at the tip. Using state-of-the-art, large-scale *ab initio* calculations, we show that this effect is present in both coaxial (BN@C) and linear (BN/C) nanotubular assemblies. While in the coaxial geometry the improvement amounts to a factor of five, the current density is predicted to increase by up to two orders of magnitude in BN/C superlattices.

INTRODUCTION

One decade after their discovery[1], it has been shown that carbon nanotubes possess outstanding potential for their mechanical and electrical properties[2]. The advent of carbon nanotubes, together with recent progress in nanomaterials design and processing, has led to a quest for other novel graphene-based materials with technologically desirable properties. The closely-related boron nitride (BN) nanotubes and mixed BN-C systems[3, 4, 5, 6, 7, 8], which are now produced in macroscopic quantities, have electronic properties that are complementary to pure carbon nanotubes and could therefore be useful in a variety of novel electronic devices. For instance, an early theoretical study predicted that BN/C junctions may well be a practical way to realize stable, nanoscale heterojunctions[9].

In this paper, we investigate BN/C heterojunctions and BN@C coaxial systems using large-scale *ab initio* simulations[10]. Our calculations show that the polarity of the B-N bond in BN/C heterostructures and related coaxial BN@C systems do dramatically enhance field emission properties, and lead to attractive electronic devices. Although carbon nanotubes are already considered to be good emitters, these desirable properties may be further enhanced by making use of the electronic properties of BN-doped carbon systems. The idea here is to make use of the dipole field as means to *reduce* the work function at the tips, thereby enhancing the extraction of electrons from the system.

The orderly introduction of BN in pure carbon nanotubes may be obtained with two different techniques: either by substituting one CC pair by one BN pair in the hexagonal lattice and therefore mixing the C and BN phases (Fig. 1a), or by creating a system that presents two coaxial homogeneous phases of C and BN (Fig. 1b).

The synthesis of pure BN nanotubes through a substitution reaction from a pure C nanotube offers a potentially new route for the design of BN/C heterostructures[11]. The method involves three basic steps: (1) the coverage of portions of a carbon nanotube by a *c*hemical

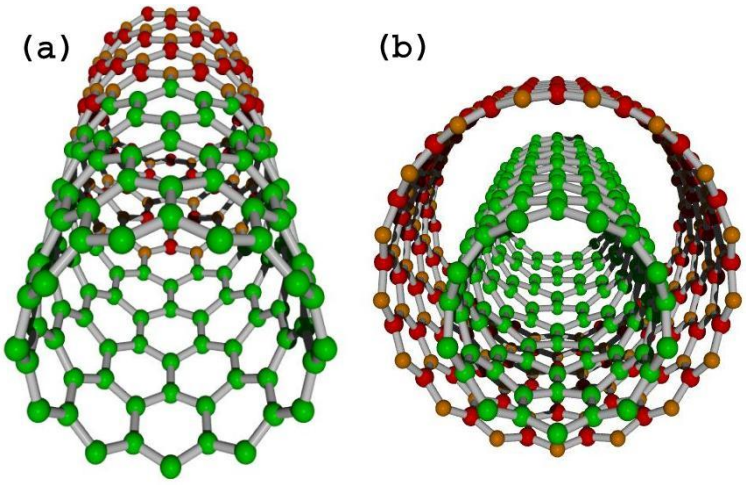

Figure 1: Prototypes of BN-C hybrids: (a) a BN/C heterojunction based on the (11,0) nanotube and (b) a $C_{(9,0)}@BN_{(17,0)}$ biwalled system.

mask (2) the $C_2 \rightarrow$B-C substitution reaction of the unmasked system and, (3) the removal of the chemical mask, leaving the untouched carbon chemically bounded to BN. This idealized scheme may be subject to practical difficulties. The most significant is undoubtedly the diffusion of the reactants inside, or through the mask. It is worth noting that a similar idea has already been successfully applied to the design of p-n junctions in the K-doping of a carbon nanotube partially masked by PMMA[12]. We also note that earlier attempts at synthesizing BN-C tubular systems from a B-C-N powder have not led to the formation of heterostructures as depicted in Fig. 1a, but rather to biwalled systems in which the BN and C materials are segregated into individual, nested shells, as shown in Fig. 1b[5]. Nevertheless, all of these systems represent potentially interesting structures for materials investigations.

$(BN/C)_n$ SUPERLATTICES and HETEROJUNCTIONS

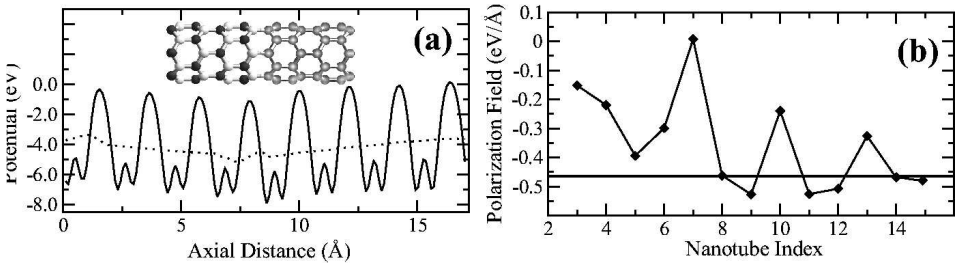

Figure 2: (a) Average electrostatic potential (full line) and macroscopic average (dotted line) along a BN/C $(6,0)$ superlattice (insert) and (b) macroscopic dipole field for zigzag $(l,0)$ tubes as a function of the helicity index. The asymptotic value for planar BN/C in the zigzag direction is represented by the horizontal line.

The majority of BN/C nanotube superlattices are characterized by an axial dipolar electric field, which is a direct consequence of the polar nature of the B-N bond. In a periodic

superlattice of polar and non-polar materials (such as BN and C) any polarization field will manifest itself in the behavior of the total electrostatic potential of the system. In fact, the latter displays a typical sawtooth behavior that is the signature of the presence of the field superimposed onto the periodic crystalline potential[14]. For convenience, we have computed the planar average of the electrostatic potential along the nanotube axis, as shown in Fig. 2a. This average, which is over the directions perpendicular to the tube axis, displays strong oscillations due to the varying strength of the ionic potentials. To subtract out this effect, we have implemented the averaging procedure of Ref. [13], and thereby calculated the one-dimensional *macroscopic* average of the electrostatic potential of the system. The value of the dipole field is then obtained from the slope of the macroscopic average potential[14] and is shown in Fig. 2b.

From simple geometric considerations, it is clear the strongest effects will be observed in the $(l, 0)$ zigzag nanotubes, since this geometry maximizes the dipole moment of the B-N bond. Hence, we have primarily concentrated on zigzag nanotubes, and the flat sheet as the limit for large diameter tubes. The corresponding electric fields are summarized in Fig. 2b. In contrast, the (l, l) armchair nanotubes are not expected to display any dipole field. This is because any individual nanotube ring must be charge neutral, so that no field is possible. Chiral nanotubes will have fields that are between the zigzag and armchair values and will depend on the individual terminations.

From Fig. 2b, it is clear that the magnitude of the macroscopic electric field for the various

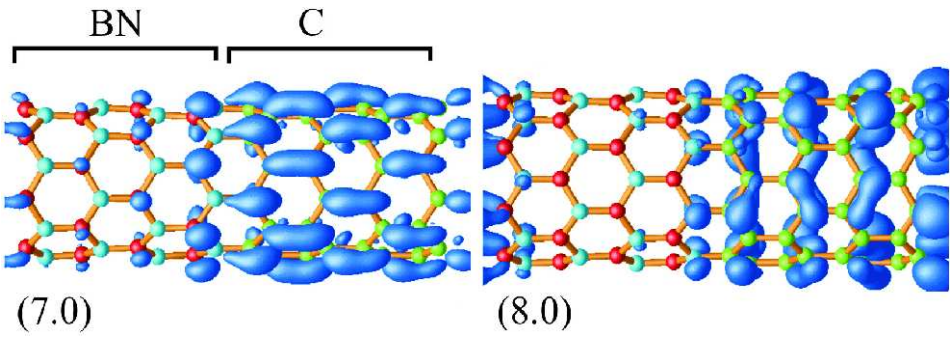

Figure 3: 3D plots of the valence state for (7,0) and (8,0) BN/C superlattices.

superlattices has strong oscillatory character. Nanotubes with helicity indices 7, 10,... $3n+1$ are characterized by a substantially smaller field. This effect originates from the fact that the carbon sections effectively screen the macroscopic dipole field with an efficiency that depends on the nanotube helicity. BN/C band offset calculations have shown that the valence state of the BN/C superlattices is always spatially localized in the carbon region[15]. This state plays an important role in determining the response to the macroscopic electric field induced by the BN section. For small diameter nanotubes the valence state displays either a longitudinal or a transverse symmetry as exemplified by the (7,0) and (8,0) tubes on Fig. 3[16]. Specifically, for $(l = 3n + 1, 0)$ nanotubes, such as the (7,0) tube, the valence state always assumes longitudinal character. The axial distribution of valence electrons therefore induces a *depolarization* field that is *opposite* to the one induced by the BN section. This field is very effective in small diameter nanotubes, so that for the (7,0) nanotube the screening is almost total and the observed macroscopic field is close to zero. For larger diameter nanotubes, the symmetry of the valence state gradually loses its peculiar axial or longitudinal character and

the macroscopic field asymptotically approaches the value found for a flat BN/C sheet in the "zigzag" direction.

Despite the screening by the valence electrons which are distributed over the carbon portion of the BN/C superlattices, a net electric field is built up along any zigzag structure. The existence of such a macroscopic field clearly influences the extraction of electrons from BN/C systems. Qualitatively, a good electron emitter is characterized by a large geometrical field enhancement factor β and a small work function ϕ. the latter is of course an intrinsic property of the emitter material. Quantitatively, the current at the emitter tip is calculated from the well-known Fowler-Nordheim relationship[17].

To assess the efficacy of BN/C systems as emitters, we have computed the field enhancement factor for tubes of length 15.62 Å in an applied field of 0.11 $V/$Å. As expected, the applied field is very well screened inside the system and a local field enhancement factor of ~ 2.1 is obtained for the different BN/C systems. Since the field enhancement factor increases *linearly* with the size of the nanotubes, large enhancement factors are clearly possible for long nanotubes[18].

To examine this effect quantitatively, we have built up a set of finite sized (6,0) zigzag structures using B, N, and C in various combinations. The work functions were then computed as the difference between the vacuum level and the Fermi energy of the system. The former was obtained by the previously discussed potential average procedure, while the latter was simply given by the highest occupied eigenstate of the system. In order to avoid any spurious effects arising from the periodic calculation, we have used the so-called *dipole correction* in a unit cell surrounded by a vacuum of at least 15 Å[19].

Turning to the heterostructures, we consider a finite NB/C (6,0) system consisting of four alternating N and B layers followed by 8 C layers, giving a total of 96 atoms. Due to the intrinsic electric field experienced by the electron, the work function is reduced to 5.04 eV at the C tip and increased to 7.52 eV at the N tip. The same trend is observed for the BN/C system, where the work function at the B tip is equal to 5.00 eV while at the C tip it equals 6.45 eV. The work function is reduced by 1.40 eV, a significant decrease as compared to the pure carbon system. This large difference leads to significant macroscopic effects. According to the Fowler-Nordheim relationship, the logarithm of the current density (J) depends upon the work function ϕ as $\ln J \sim -\phi^{3/2}$. It follows that the insertion of BN segments in C nanotubes will increase the current density by up *to two orders in magnitude* as compared to pure carbon nanotube systems.

BN@C BIWALLED HYBRIDS

It is clear from the previous discussion that the presence of BN atoms induces a remarkable improvement of the field emission properties at the carbon tip in a NB/C heterojunction. However, the use of such devices as *performant* field emitters is limited by the issues surrounding their synthesis. From a practical point of view, the related nested BN@C or C@BN systems offer a more direct way to take advantage of the polarity associated with the BN phase.

To assess the field emission properties of BN@C devices, we have performed calculations of the field enhancement factor and of the work function. In particular, we investigated the effect of the presence of a finite BN nanotube shell surrounding a C nanotube–the C$(5,5)$@BN$(18,0)$, as shown on Fig. 4. As expected from classical electrostatics, the field enhancement factor is not modified by the presence of the BN shell, since the insulating BN layer does not disturb the screening properties of the underlying C tube. On the contrary, the dipole field induced

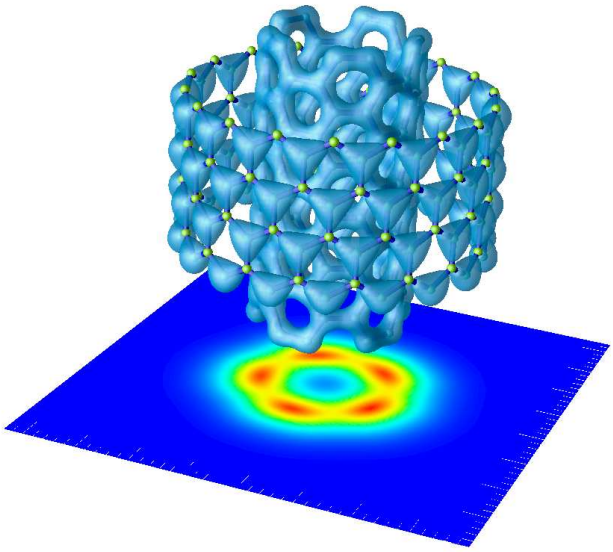

Figure 4: Electron density 5 Å from the tip of a C$(5,5)$@BN$(18,0)$ biwalled system.

by the BN shell produces a net decrease of the work function ($\sim$ 0.5 eV) and a subsequent increase of the emitted current (up to a factor of 5), as compared to the current emitted by a bare (5,5) carbon nanotube.

SUMMARY

We have demonstrated that ordered BN-C systems are characterized by the presence of a dipolar electric field, whose value is highly sensitive to the helicity of the underlying nanotubes. This macroscopic field can reduce the work function of the C nanotube tips, thereby increasing the field emitting properties of carbon nanotube tips by up to two orders of magnitude for the linear BN/C nanotube and a factor of five for BN@C biwalled systems.

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