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Coaxing graphene to be piezoelectric

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Several exotic characteristics and properties have made graphene a well-studied material from both a basic science viewpoint as well as tantalizing applications ranging from nanoelectronics, gas separation membranes to ultracapacitors. Graphene, however, is non-piezoelectric. This is obvious when graphene is in its metallic or semi-metallic state. However, even when graphene is in dielectric form—which can be engineered through porosity or by using nanoribbons—graphene is non-piezoelectric due to its centrosymmetric crystal structure. Using quantum mechanical calculations, we show that merely by creating holes of the right *symmetry*, graphene can be coaxed to act as a piezoelectric. We find that certain specifically tailored porous graphene sheets can "acquire" piezoelectricity coefficient that is nearly 72% of the well-known piezoelectric (quartz) or 36% of boron nitride nanotubes. © *2012 American Institute of Physics*. [doi:10.1063/1.3676084]

An infinite pristine graphene sheet exhibits unique zero band gap semi-metallic behavior.[1,2] Considered to be one of the strongest material, graphene can sustain strains up to 25% (Ref. 3), and its behavior can vary from metallic to semi-conducting depending on deformation, defects, and (if in ribbon form) surface termination.[1,4,5] Remarkably, high electron mobility and other exotic characteristics (e.g., pseudomagnetic field,[6] anomalous quantum hall effect, and spin transport[1]), have made graphene an intensely studied material from both basic science viewpoint as well as tantalizing applications ranging from nanoelectronics, gas separation membranes to ultracapacitors.[1,7]

In a piezoelectric material, an applied uniform strain can induce an electric polarization (or vice-versa). Crystallographic considerations restrict this technologically important property to non-centrosymmetric crystal systems,[8] and indeed, the latter is a necessary condition for a material to exhibit piezoelectricity. Formally, the polarization vector is related to the second order strain tensor through the third order piezoelectric tensor,

$$P_i = d_{ijk}\varepsilon_{jk}. \tag{1}$$

Tensor transformation properties require that, under inversion-center symmetry, all odd-order tensors vanish. Thus, most common materials, such as silicon and NaCl, are not piezoelectric, whereas ZnO and GaAs are.

Piezoelectricity is preferentially used where precise control of mechanical motion is required (e.g., in scanning probe microscopes) and have now found wide applications, such as next-generation energy harvesters,[9] artificial muscles,[10] sensors and actuators,[11] among others.

Due to the semi-metallic nature of pristine graphene, piezoelectricity is hardly a property associated with it. However, graphene nano-ribbons (GNRs) can be either metallic or semi-conducting depending on the width or edge termination conditions.[12] Likewise, porosity can also cause graphene to act as a dielectric.[13] Nevertheless, the crystal structure of graphene manifestly precludes the presence of piezoelectricity even when graphene is in dielectric form.

Can graphene be "coaxed" to act as a piezoelectric? In this letter, we attempt to answer this question through detailed quantum mechanical calculations and show that the interplay of symmetry, nanoscale size-effect, and an understudied property of graphene (-flexoelectricity) indeed allows such a possibility. The present arrays of piezoelectric ceramics are heavy, inherently brittle, and (some) pose significant environmental risk due to high lead content.[14] Piezoelectric polymers are light and environmentally benign, but usually have considerably smaller piezoelectric response in terms of actuation. Thus, nature has dealt humankind with a very limited choice of effective electromechanical materials often with electromechanical conversion efficiencies that are far from ideal. Design of graphene as a piezoelectric could potentially open new avenues for multifunctional materials and the attendant applications.

We preface the introduction of our central concept through a very simple observation. A *non-uniform strain* or the presence of *strain gradients* may potentially break the inversion symmetry and induce polarization even in *centrosymmetric* crystals. This is tantamount to extending relation (1) to include strain gradients,

$$P_i = \underbrace{d_{ijk}\varepsilon_{jk}}_{=0,\text{fornon-piezo materials}} + f_{ijkl}\frac{\partial \varepsilon_{jk}}{\partial x_l}. \tag{2}$$

Here f_{ijkl} are the so-called flexoelectric coefficients. While the piezoelectric property is non-zero only for select materials, the strain gradient-polarization coupling (i.e., flexoelectric coefficients) is, in principle, non-zero for all dielectric materials. This implies that, under a non-uniform strain, all dielectric materials are capable of producing a polarization. This is indeed true for graphene nanoribbons as well.[16,17]

The central concept behind our exploration is as follows.[15] Consider a material consisting of two or more

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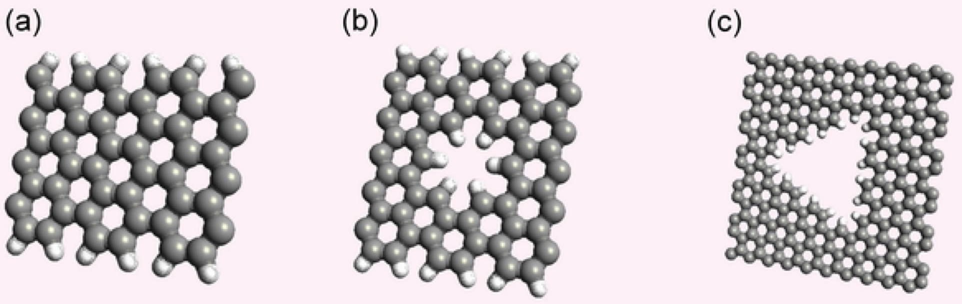

FIG. 1. (Color online) Geometries considered in the simulations (a) pristine GNR, (b) circular hole GNR, and (c) graphene sheet with triangular hole. The white colored atoms refer to H atoms which mark the termination of GNR.

different non-piezoelectric dielectric materials—one example is simply a (dielectric) graphene sheet with holes in which case air serves as the 2nd dielectric. Even under the application of uniform stress, differences in material properties at the interfaces will result in the presence of strain gradients. Those gradients will induce polarization due to the flexoelectric effect. As will be explained shortly, as long as certain symmetry rules are followed, the net average polarization will be nonzero. Thus, the nanostructure will exhibit an overall electromechanical coupling under uniform stress behaving like a piezoelectric material. The length scales must be nanoscale since this concept requires very large strain gradients, and those for a given strain are generated easily only at the nanoscale. Regarding symmetry, topologies of only certain symmetries can realize the central concept discussed in this paper. For example, circular holes distributed in a material will not yield apparently piezoelectric behavior even though the flexoelectric effect will cause local polarization fields. Due to circular symmetry, the overall average polarization is zero. A similar material but containing triangular shaped holes (or inclusions), for example, and aligned in the same direction, will exhibit the required apparent piezoelectricity.

The first requirement for any form of graphene to exhibit piezoelectricity is that it must be in semi-conducting or insulating state. We begin by exploring various graphene configurations. We consider three set of geometries: pristine GNR, GNRs with circular holes, and graphene sheet with triangular holes.

Edges and porosity can both result in dangling bonds. In our calculations, they were passivated using hydrogen. Using density functional theory (DFT), we first geometrically relax all the geometries both under the application of zero and finite strain conditions. Figure 1 shows the geometries. Once the system is fully relaxed, electronic band structure calculations are carried to ensure the semiconducting nature of the geometry (Figure 2).

In quantum simulations, the piezoelectric coefficient is calculated as[15]

$$d_{ijk} = \partial P_i / \partial \varepsilon_{jk}. \tag{3}$$

Here, the third order piezoelectric tensor d_{ijk} defines the linear response of an electric polarization P_i to the applied strain ε_{jk}.

Once the structure depicting dielectric behavior is obtained, the electronic polarization is obtained using the Berry-phase approach applied using the quantum package "Espresso."[18] All geometries were optimized to energy minimum state by ensuring that maximum force per atom is constrained to 0.05 eV/Å. The electronic ground state wavefunctions are collected using the grid value of $1 \times 1 \times 14$ for the k-points when performed for GNR, whereas the grid of $1 \times 6 \times 6$ k-points is used for graphene sheet. The Berry-phase approach is then applied to the obtained ground state configuration with dense mesh of k points in the desired direction for observation of polarization. The average polarization obtained from the simulations is defined by the following relation:

$$\langle P_x \rangle = P_o + d.\varepsilon + O(\varepsilon^3). \tag{4}$$

P_o is the pre-existing polarization due to surface effects present prior to application of the strain. Nonlinear effects are

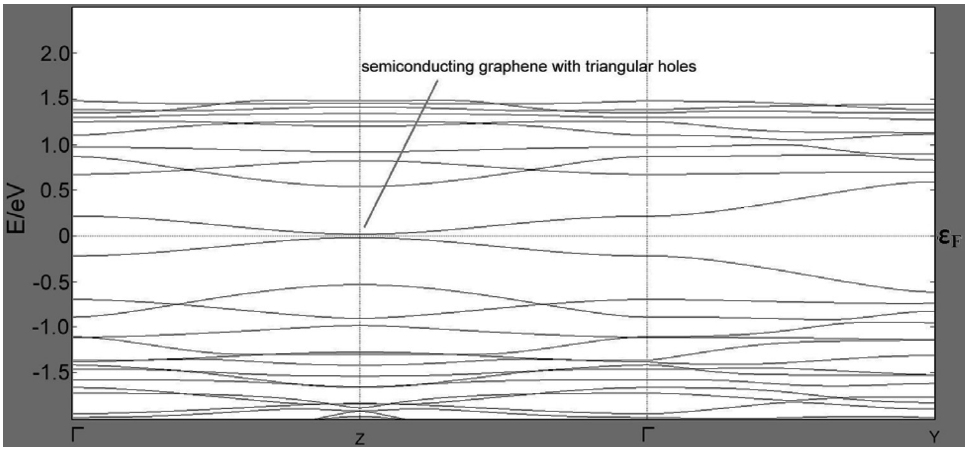

FIG. 2. Band structure of the GNR with triangular holes. The band gap highlights dielectric behavior. The other geometries taken under study displayed similar band openings.

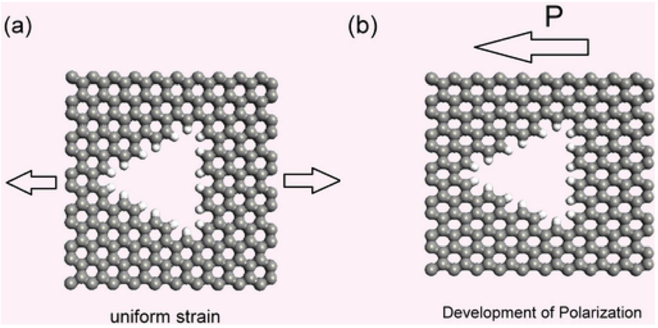

FIG. 3. (Color online) The development of polarization for triangular-hole-graphene sheet under the action of strain.

discarded ($O(\varepsilon^3)$) and ensured by the application of very small values of strain. As expected from the symmetry arguments used earlier, the pristine graphene and the circular porous GNR did not show any piezoelectric behavior.

The graphene sheet containing triangular holes, however, developed a large amount of polarization under the action of mechanical strain. The results are shown in Figure 3.

We obtain a piezoelectric coefficient of 0.124 C/m^2. The value for pristine GNR and GNR with circular hole is of course 0 (as expected). It is interesting to compare this result to some well-known natural piezoelectrics (Fig. 4), e.g., quartz (∼72%) and boron nitride nanotubes (∼36%).

Our results are easily interpreted within the context of flexoelectricity. Figure 5, based on linearized theory of elasticity calculations, shows the qualitative behavior of the strain distribution accompanying a hole in a thin sheet. As evident, average strain gradient (due to breaking of the reflection symmetry around the hole) is non-zero and flexoelectricity will cause both local polarization and non-vanishing average polarization.

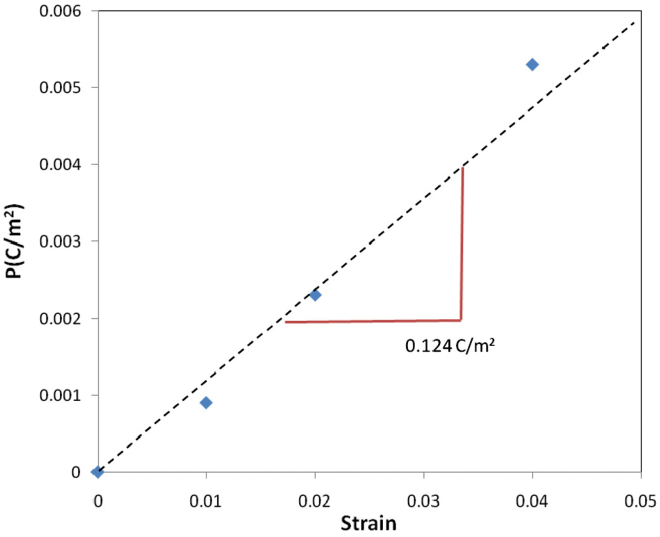

FIG. 4. (Color online) Average polarization as a function of applied strain. For comparison, identical curves are shown for well-know naturally piezoelectric materials.

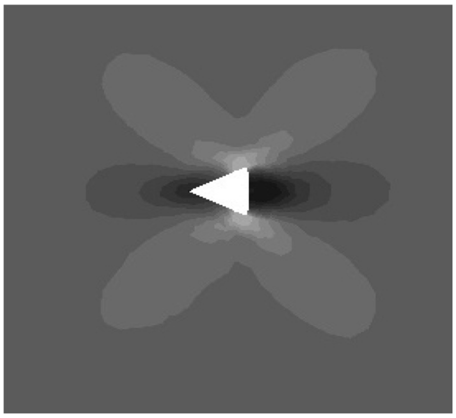

FIG. 5. A finite element model based on elasticity theory provides an indication of the qualitative nature of the strain distribution around the triangular hole.

In conclusion, simply by creating holes of the right symmetry in a dielectric graphene sheet will transform this manifestly non-piezoelectric material into a piezoelectric one. Tailored porosity may be induced in graphene through electron-beam irradiation providing a route to an experimental realization of the concepts described in this letter.

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