Research Article

Peierls-type metal-insulator transition in carbon nanostructures

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1. Introduction

Zeleites are microporous crystalline aluminosilicates that have uniform porous structures. The pore diameters are in the range between 0.3 nm and 1.2 nm. The robust porous skeletal structure of zeolites has been widely used as catalysts, adsorbents, porous supports, and hosts for making nanomaterials [1,2]. In this work we use the calcined ZSM-5, a type of 10 member-ring zeolite with framework code MFI [3–5], as a template for forming carbon nanostructures in its pore network by using the chemical vapor deposition (CVD) method [6]. The skeletal structure of ZSM-5 is shown below in Fig. 1(a); it has straight channels along the b-axis and sinusoidal channels along the a-axis. Both channels have an inner diameter of ~5 Å and interconnected with each other with a segment distance ~10 Å. Each ZSM-5 crystal is about 2–3 μm across, as shown in Fig. 1(b). In contrast to previous works in which 4 Å carbon nanotubes [7–9] were formed inside the linear channels of AFI zeolite [6,10,11], here the nanocarbon@ZSM-5 has a three dimensional (3D) structure. Characterization by Raman spectroscopy indicates a clear radial breathing mode (RBM) peak at 805 cm−1 that agrees extremely well with that for the (3,0) carbon nanotube with a diameter of 3 Å. Four-probe electrical resistance measurement on a single zeolite crystal showed a metallic temperature dependence down to 3 K, with a sharp reversal below that temperature. Differential resistance measurements below 30 K showed the development of a quasigap at the Fermi level, which is a signature of the Peierls-type metal-insulator (M-I) transition. Electrical transport measurements on multiple few-micron-sized nanocarbon@ZSM-5 crystals showed metallic temperature dependence of resistance down to 30 K, at which point the resistance exhibited a sharp upturn that is accompanied by the opening of a quasigap at the Fermi level as indicated by the differential resistance measurements. Further Hall measurements have yielded both the sign of the charge carrier and its density. The latter demonstrated excellent consistency with the quasigap data. We employed first-principles calculations to verify that there can indeed be softening of the phonon modes in the (3,0) carbon nanotubes.

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magnetic field dependence up to 6 T of applied field.

Theoretical research on Peierls transition was widely studied in one-dimensional carbon materials, such as on single-wall carbon nanotubes CNT(5,5), CNT(3,3), CNT(5,0) [21–25], or in linear carbon chains [26]. In support of our experimental results, we have carried out first-principles calculations on (3,0) nanotubes and showed the existence of phonon soft modes as a result of electron-phonon coupling.

2. Experimental

The nanocarbon@ZSM-5 was grown by using the CVD method. The calcined ZSM-5 zeolite crystals were put in a quartz tube. Five atmosphere pressure of methane (CH₄) was heated to 800 °C for 10 h to grow the carbon nanostructures in the pores of ZSM-5. Subsequent to cooling down, nanocarbon@ZSM-5 was characterized by both Raman spectra and thermal gravimetric analysis (TGA). Results are detailed in the following section.

To measure the transport properties of nanocarbon@ZSM-5, we first deposit a thin layer of photoresist (950 PMMA 9 A) on a quartz substrate. Nanocarbon@ZSM-5 crystals were dispersed on the PMMA and heated on a hotplate at 180 °C for 90 s. This process was helpful to fix the dispersed crystals on the quartz substrate for the subsequent processing. A layer of adhesive Ti with a thickness of 5 nm was coated on the crystals by sputtering, followed by a layer of Au with a thickness of 60 nm. Focused ion beam (FIB) was used to select one crystal, on which the Ti/Au film was etched into a designed square geometric pattern as shown schematically in Fig. 2(a) with the four numbered electrical leads. A scanning electron microscope (SEM) image of the actual device is shown in Fig. 2(b). Due to the small size of the crystals, the traditional six-lead Hall bar geometry was not possible. To measure the longitudinal resistance, current was passed between leads 1 and 2 as shown in Fig. 2(a), and voltage was measured across leads 3 and 4. For the Hall measurements, current was passed between leads 1 and 3 under an applied magnetic field, and voltage was measured across leads 2 and 4.

Measurements of the fabricated device were carried out by using the Physical Property Measurement System (PPMS). A Keithley 6221 was used as the current source and a SR850 lock-in was used as voltmeter to measure the resistance and differential resistance of nanocarbon@ZSM-5.

3. Results and discussion

Measured Raman spectrum is shown in Fig. 3(a). The very high peak at 1604 cm⁻¹ is the G band which arises from the vibrations of C–C sp² bonds. The peak at 1388 cm⁻¹ is the D band which arises from the defects in the structure of nanocarbon@ZSM-5. A lower D band peak usually indicates a lower concentration of defects in the sample. We have tried to adjust the fabrication conditions to minimize the defects. The peak at 805 cm⁻¹ is the radial breathing modes (RBM) of carbon nanotubes. It is well known that the RBM originates from the coherent vibration of the carbon atoms along the radial direction, which is unique to carbon nanotubes. Normally \( \nu_{\text{RBM}} = \frac{4}{d} + \beta \) where \( \beta = 228 \), \( \beta = 16 \), with \( d \) the nanotube diameter in units of nm. Typical RBM range is 100–350 cm⁻¹. From the measured Raman breathing mode data we deduce \( d = 0.29 \) nm, indicating the nanocarbon@ZSM-5 structure comprises a network of (3,0) carbon nanotubes. From the ab initio calculations as that described in the Supplemental Materials, the RBM frequency of the (3,0) carbon nanotube is around 817 cm⁻¹, very close to the experimentally observed value of 805 cm⁻¹. The RBM of the (2,1) carbon nanotube, 0.236 nm in diameter, is noted to be on the order of 10% higher in frequency. Hence the identification of (3,0) carbon nanotube from its RBM is rather unique. The peak at 1192 cm⁻¹ can be due to the combination of RBM and D band modes, usually denoted the intermediate frequency modes (IFM) [8,27,28] that are composed of both first and second-order modes. For comparison, the Raman spectrum for the empty ZSM-5 template is also shown in Fig. 3(a) as the blue curve. It is seen that there are no visible peaks in the relevant frequency range. This comparison indicates that the Raman signal indicated by the black curve in Fig. 3(a) is from the nano–carbon structure.

Results of the TGA measurements on crystals of nanocarbon@ZSM-5 are shown in Fig. 3(b). The sample was placed in the TGA equipment Q5000 and heated in air from room temperature to 800 °C with a heating rate of 2 °C/min. The sample weight was monitored by a microbalance. By burning off the carbon inside the ZSM-5 crystals, we obtained the carbon’s weight content from the difference in weight before and during the heating process. As shown in Fig. 2(b) the carbon content of nanocarbon@ZSM-5 is 14.3 wt%. By assuming the carbon structure to be (3,0) carbon nanotubes in each segment of the structure, this TGA result translates into a pore occupation ratio of 35%. Detailed calculation that leads to this number is given in the Supplemental Materials, Section...
The derivative of the weight curve (blue) shows a sharp peak at around 600 °C, which indicates the decomposition temperature of nanocarbon structure inside the pores of ZSM-5.

Fig. 4(a) shows the temperature variation of the measured longitudinal resistance in nanocarbon@ZSM-5. Very good linear variation of the resistance, characteristic of metal, is seen from room temperature down to 30 K. However, when the temperature was lowered below 30 K, the resistance is seen to increase quickly. This phenomenon is robust as it appeared in multiple samples. A second sample showing the same metal-insulator transition is shown in the Supplemental Materials, Section B. Differential resistance measurements at four temperatures, plotted as a function of the driving current, is shown in Fig. 4(b). The appearance of a sharp peak at the Fermi level is indicative of the development of a quasigap driven by the soft phonon mode, i.e., a Peierls transition. The sample was measured by the four-terminal configuration shown in Fig. 2(a). (A colour version of this figure can be viewed online.)
function of the driving current, is shown in Fig. 4(b). It shows that the mechanism of the resistance upturn below 30 K is associated with the development of a quasigap centered at the Fermi level. It is seen that at 30 K, the flat differential resistance indicates a linear, Ohmic I–V behavior. However, as the temperature is lowered a clear nonlinear I–V behavior is seen that can be interpreted as the development of a quasigap with a decrease in the resistance at the Fermi level due to the depletion of charge carriers. The magnitude of the resistance upturn, however, is relatively small, which means that only part of the sample has undergone a Peierls transition. Therefore we should consider the measured resistance to comprise a background resistance that follows the downward linear trend as a function of temperature, shown by the red dashed line in Fig. 4(a), that is in series with the part that has undergone a Peierls transition.

In order to substantiate our interpretation that the upturn in resistance below 30 K is due to the depletion of charge carrier density at the Fermi level, we have carried out Hall measurements under an applied magnetic field. The knowledge of both the longitudinal and transverse resistance would enable us to separately determine the mobility and charge carrier density. The results are shown in Fig. 5(a). We know that the Hall resistivity $\rho_{xy} = \frac{B}{ne}$ where $B$ is the magnetic field, $n$ denotes the charge carrier density, and $e$ is the electronic charge. The slope of the Hall resistance is seen to increase with decreasing temperature, indicating a decrease in the charge carrier density at the Fermi level as the temperature is lowered. The data are plotted as black symbols in Fig. 5(b).

Since the longitudinal resistivity is given by $\rho_{xx} = \frac{1}{ne}$, where $n$ denotes the charge carrier density and $\mu$ the mobility. If we consider the sample as a Peierls transition component in series with a metallic series resistance (red dashed line in Fig. 4(a)), then we have $\rho_{xx} = \frac{1}{ne} + \left(aT + b\right)$, where $aT + b$ is the linear metallic resistance in series as shown by the (extrapolated) red dashed line in Fig. 4(a), with $a = 3.23 \times 10^{-3} \Omega^{-1}$ and $b = 10.80 \Omega$. By fitting the longitudinal resistance data at temperatures higher than 30 K, we obtain the mobility value to be $\mu = 13.06 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is lower than that in the plane of graphite, $\mu = 9.0 \times 10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [29]. By assuming the mobility value to be a constant over the relevant temperature range, the value of $n$ can be directly obtained from the peak value of the differential resistance data in Fig. 4(b) (as it corresponds to the Fermi level). The charge carrier density obtained in this manner is plotted as red symbols in Fig. 5(b). We can see that the agreement is excellent, which not only confirms our assumption that the mobility is constant over the relevant temperature range, but also leads to the conclusion that a Peierls-type M–I transition has indeed occurred through the opening of a quasigap in the Fermi level charge carrier density.

4. Theoretical considerations

Peierls-type M–I transition owes its origin in the electron-phonon coupling and the one-dimensional geometry. Since the ZSM-5 zeolite pores comprise intersecting one-dimensional channels with 5 Å inner diameter, (3,0) CNT can be accommodated. Here we would like to consider the nanocarbon@ZSM-5 to consist of (3,0) CNT segments, which is supported by the Raman RBM signal at 805 cm$^{-1}$. This value is very close to the ab-initio estimation of the RBM for the (3,0) CNT at 817 cm$^{-1}$. Our theoretical consideration is to see if the (3,0) CNT can have phonon softening, which is a necessary condition (but may not be sufficient) for the nanocarbon@ZSM-5 to exhibit a Peierls-type M–I transition [12,13].

In a Peierls process the lattice distorts (usually dimerizes) and opens a gap at the Fermi level, thereby makes the system transit from a metal to an insulator at zero temperature. In such a process the equilibrium positions of atoms change, causing an increase in the elastic energy. However, distortion of the atomic lattice simultaneously opens a gap in the electronic band structure at the Fermi level and lowers the electronic energy. As the latter more than compensates the increase in the elastic energy, hence this is an instability that can occur with especially high inelasticity in 1D metals. However, if the atomic bonding is strong, the Peierls transition temperature can be low. We have carried out ab-inito calculations on the (3,0) CNTs. The calculational details are given in the Supplemental Materials, Section C. Our estimation shows that the (3,0) CNT can indeed have phonon softening that undergoes a Peierls transition under $T_p \approx 273 K$. The relevant soft phonon mode of (3,0) CNT is illustrated in Fig. 6. We have to recognize, though, that the present nanocarbon@ZSM-5 is a 3D network of 1D segments, hence the theory necessarily over-estimate the Peierls transition temperature.

The existence of the Peierls-type transition in nanocarbon@ZSM-5 implies a reasonably large electron-phonon coupling. Since superconductivity is another consequence of electron-phonon coupling, in the earlier theoretical works [30,31] we have found that better screening of Coulomb interaction among the electrons, which is a negative element for superconductivity, can greatly suppress the Peierls transition while simultaneously enhance the superconductivity transition. As a result, our next experimental effort is along the direction of providing better Coulomb screening, with the intention to see if a superconducting ground state can be accomplished in this system.

![Fig. 5. (a) The temperature dependence of Hall resistance for nanocarbon@ZSM-5. (b) A comparison between the electronic charge carrier density obtained from by the Hall measurements (black symbols) and that obtained from fitting of the longitudinal differential resistance peak values vs. temperature in nano-carbon@ZSM-5 (red symbols). The red dashed curve is to guide the eye. (A colour version of this figure can be viewed online.)](image-url)
5. Conclusions

By making use of the ZSM-5 zeolite as the template we have successfully fabricated nano-carbon@ZSM-5 with a high pore filling factor (35%) 35. The Raman spectrum of nanocarbon@ZSM-5 exhibits a RBM peak around 805 cm\(^{-1}\), indicating the nanocarbon@ZSM-5 to display a metal to insulator transition at 30 K. This interesting phenomenon can be explained by the Peierls-type transition that opens a gap at the Fermi level. By carrying out resistance and Hall measurements we found consistency between the two registered layers in the back rotated 60\(^{\circ}\) with respect to the other layers, to facilitate easy visualization. The arrows shown in the figure indicate the magnitude and direction of the displacement for each atom in the soft phonon mode with \(q = 0.45/a\), where \(a\) is the length of the unit cell. (A colour version of this figure can be viewed online.)

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2020.10.037.

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Fig. 6. The unit cell of (3,0) CNT consists of four triangular layers of carbon atoms, with two registered layers in the back rotated 60° with respect to the two registered layers in the front. Here each layer is identified with a different color from the other layers, to facilitate easy visualization. The arrows shown in the figure indicate the magnitude and direction of the displacement for each atom in the soft phonon mode with \(q = 0.45/a\), where \(a\) is the length of the unit cell. (A colour version of this figure can be viewed online.)
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