Tetracyanoethylene oxide- functionalized graphene and graphite characterized by Raman and Auger spectroscopy.

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ABSTRACT: The tetracyanoethylene oxide (TCNEO) functionalization of chemical vapor deposition grown large area graphene and graphite was performed using reaction of TCNEO with carbon surface in chlorobenzene. The successful functionalization has been confirmed by Raman and Auger spectroscopy, and by numerical modeling of the structure and vibrational modes of TCNEO-functionalized graphene. Raman spectra of TCNEO-functionalized graphene and graphite show several groups of lines corresponding to vibrations of attached carbonyl ylide. One of key signatures of TCNEO attachment is the high intensity Raman band at $\sim 1450\text{ cm}^{-1}$, which represents the C-C=C in plane vibrations in functionalization-distorted graphene. Raman spectra indicate the existence of central (pristine) attachment of TCNEO to graphene surface.

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1. Introduction.

Graphene, a single or few-layer graphite, emerges as a promising material with many applications in electronics, materials engineering, and in chemistry [1]. Chemical functionalization of graphene expands the spectrum of possible graphene applications. In particular, covalent modification of graphene is an important mechanism to enable control over graphene properties. To date, there are only a handful of experimentally demonstrated reactions leading to covalent functionalization of graphene [2,3,4]. It includes the Diels-Alder reactions of graphene with tetracyanoethylene, maleic anhydride, 9-methylantracene, and 2,3-dimethoxy-1,3-butadiene [2], the reaction with formation of benzyne-graphene [3], and the reaction of graphene with tetracyanoethylene oxide (TCNEO) [4]. Recently, Cao and Houk [5] reported on the elegant computational investigation of reactions of 1,3-dipolar cycloaddition of azomethine ylide and carbonyl ylide with graphene. For azomethine ylide, the modeling [5] shows that its pristine attachment to graphene is energetically unfavorable due to significant distraction of conjugated system. At the same time, according to calculations [5], the 1,3-dipolar cycloaddition of carbonyl ylide with graphene is energetically allowed as for corners and edges, so as for pristine attachment to graphene.

In this work, we report the experimental and numerical modeling investigation of features of Raman and Auger spectra of TCNEO-functionalized graphene and graphite. Among other results, we provide verification of Cao-Houk's prediction [5].

2. Material and Growth Setup

Graphene samples were grown in a CVD reactor (a more detailed description of used

CVD setup may be found in the Ref. 3). A Thermo Scientific Lindberg Blue M furnace was used along with Lindberg 58434 power control unit. Copper foils (25 μm -thick, Alfa Aesar #10950), used as catalytic substrates for graphene growth, were cleaned with Acetic acid and deionized (DI) water. Cu foil substrates were annealed at temperatures 960-990°C under flow of 1000 sccm Ar and 500 sccm H_2 for 45 minutes. The growth was carried out via supplying ultra high purity Methane gas (CH_4) at the rate of 50-100 sccm along with a flow of Ar at 1000 sccm and H_2 at 500 sccm for 2-10 minutes. After growth, the samples were rapidly cooled down by sliding the quartz tube out of the furnace while under high flow of Ar gas. A highly oriented pyrolytic graphite (HOPG) sample (Structure Probe Inc., SPI-I) was used for testing the utilized functionalization reaction with bulk graphite.

All chemical reagents were acquired from Sigma Aldrich and Fisher Scientific. 0.1 mM of tetracyanoethylene oxide (TCNEO) was dissolved in 3 ml of chlorobenzene. A graphene sample (0.5 cm x 0.5 cm area) was added into the solution and refluxed during 48h. Following this treatment, the sample was washed three times by acetonitrile, dried by argon, and stored in inert atmosphere.

3. Chemical reaction: generation of carbonyl ylide from tetracyanoethylene oxide, and attachment of carbonyl ylide to graphene and graphite.

In this work, we used chemical vapor deposition-grown large area graphene on Cu foil substrates [6]. A HOPG sample (Structure Probe Inc., SPI-I) was used for testing the

functionalization reaction with bulk graphite. For functionalization, graphene and graphite samples were heated with TCNEO for 48 hours in chlorobenzene at 150-160°C (see the Figures 1 and 2 for details of the process). It is well known that the ring structure of TCNEO opens up at temperatures of about 100°C, leading to the formation of a carbonyl ylide (see the Figure 1 for details) [4,7]. This property of TCNEO was used for 1,3-dipolar cycloaddition of TCNEO to fullerenes in toluene [8,9]. However, graphene is much less reactive than fullerenes and it requires modification of the reaction conditions. In our work, we adjusted the procedure parameters for covalent modification of large area CVD-grown graphene and graphite.

Figure. 1. Formation of carbonyl ylide from TCNEO.

Figure. 2. Functionalization of graphene by TCNEO. The scheme shows both edge (shown at the upper right corner of the scheme) and pristine attachments to graphene.

Successful functionalization was confirmed using Raman and Auger spectroscopy, supported by detailed modeling of phonon modes and reaction energies for TCNEO-functionalized CVD-graphene. In addition, we also tested the TCNEO-based functionalization reaction with HOPG, and obtained TCNEO-functionalized graphite.

4. Characterization methods

Thicknesses and structural properties of carbonyl ylide-functionalized graphene and graphite samples before and after functionalization were analysed using a Horiba Jobin-Yvon Aramis micro-Raman spectrometer with a cooled CCD detector (Jobin Yvon's Synapse camera). A frequency doubled Nd:YAG laser was used for excitation (emission wavelength 532 nm, radiation power ~5 mW).

Auger spectroscopy is a powerful tool for analyzing graphene, capable of determining thickness of graphene up to six layers, and detecting the dopant or defect species [10]. In our work, Auger analysis (Perkin-Elmer PHI 600 Scanning Auger Multiprobe with RBD Digital Acquisition) was used to confirm the successful functionalization of the CVD grown graphene samples. Auger measurements were done with a 3keV beam over an area of 200 X 200 μm and samples were tilted 30° off electron beam normal towards the ion gun. Spectra were collected on “as received” surfaces (not shown), and on surfaces after three seconds sputtering with a 3Kev Ar ion beam to remove atmospheric contamination. Point analysis of different thicknesses of graphene show differences in relative peak heights for the substrate (Cu) versus graphene layer peaks (C,N,O), but consistent ratios

between the C and N. Area scans were therefore employed due to the non-uniform thickness of the graphene, since the intent was to confirm functionalization.

5. Results of functionalization

5.1. Raman spectra of TCNEO-functionalized graphene and graphite.

Figure 3. (Color online) Raman spectra of graphene and TCNEO-functionalized graphene. (a) The spectra of a CVD-grown graphene sample taken before (bottom curve in (a)) and after (upper curve in (a)) the 48 hours-long functionalization reaction of graphene with tetracyanoethylene oxide in chlorobenzene, with numerically extracted background from Cu substrate. For the discussion of new lines appearing in the spectrum (shown by arrows with indicated spectral positions in cm^{-1}) after treatment see the text. The shape of 2D line in our graphene sample before treatment: single Lorentzian at 2700 cm^{-1} , is shown in the inset. (b) and (c): The low- and mid- frequency parts of the Raman spectrum of 48 hours- treated graphene layer on Cu. The excitation wavelength $\lambda_{\text{exc}}=532 \text{ nm}$.

The results of Raman measurements of one of our graphene layers are shown in the Figure 3. The Raman spectra for the selected area before and after treatment are shown in Fig. 3(a) after background subtraction of the Raman spectrum of the underlying Cu substrate (see Ref. 3 for details). The Raman spectra of untreated graphene (see the bottom curve in Fig. 3(a)) show the typical set of major lines: the D-line at 1330-1350 cm^{-1} , the G-line at 1582 cm^{-1} , and the 2D line at about 2700 cm^{-1} [11]. The 2D/G intensity ratio is about 0.8. It is worth noting that the position and the symmetric single-Lorentzian shape of 2D line (the inset of Fig. 3(a)), as well as the results of optical and SEM microscopy, show that we use a few-layer turbostratic graphene as starting material, which is rather typical for the selected growth parameters [12]. After chemical treatment of our sample (and following washing of sample three times in acetonitrile), the Raman spectra demonstrated significant modifications. The new lines occur at different frequency regions: the band around 1450 cm^{-1} (see Fig. 3(a)), the high frequency lines at 2231 cm^{-1} and the band at 2943 cm^{-1} , the mid-frequency bands at 665 and 744 cm^{-1} (see Fig. 3(a) and Fig. 3(c)), and the low frequency lines/bands around 226 cm^{-1} , 188 cm^{-1} , and at 117 cm^{-1} . The chemically modified graphene shows a significant increase in the intensity of the graphene D band at 1340-1350 cm^{-1} (upper curve in Fig. 3(a)) [11], and the appearance of a broad fluorescence background. The appearance of these lines and features clearly indicates the successful modification of graphene surface. The observed fluorescence background indicates that the system of graphene with attached carbonyl ylide has electron states with energy spacing and hierarchy of relaxation times allowing radiative recombination in visible region.

The line at 2231 cm^{-1} (Fig. 3(a)) is the well known signature of C-N stretching modes,

which indicates that the attached structure contains cyano-groups [4]. The band at 1340-1350 cm^{-1} , and the band with peak near 2943 cm^{-1} , correspond to functionalization reaction-generated defects-related modes (where 1340-1350 cm^{-1} feature represents the D-band, and the high frequency modes near 2900-3000 cm^{-1} are the combination modes close to D+G combination frequency) [13]. Finally, the observed fluorescent background, together with significant suppression of (double-resonance-enhanced) 2D line in modified graphene ($I_{2D}/I_G \sim 0.2$ instead of ~ 0.8 before functionalization), indicates significant modification of electron band structure in TCNEO-functionalized graphene.

5.2 Auger Spectroscopy of TCNEO-functionalized graphene.

Figure 4 shows the Auger spectra of CVD graphene before functionalization (bottom curve) and after 48 hours-long reaction with TCNEO in chlorobenzene. The Cu substrate signals (the three peaks between 750 and 920 eV) were included in Figure 4 to show the relative signal ratios of graphene and Cu. As one can see, the spectra of functionalized graphene show more intense carbon peak (C1 peak at 290 eV [14]), and the Nitrogen (N1, ~ 380 eV [14]) and Oxygen (O1, ~ 510 eV [14]) peaks. Auger spectra confirm successful functionalization of graphene.

Figure 4. The Auger spectra of CVD-grown large area graphene before (bottom curve) and after 48-hours long functionalization reaction with TCNEO in chlorobenzene.

5.3. TCNEO-functionalized graphite

We also used the TCNEO-based functionalization reaction with bulk HOPG, and obtained TCNEO-functionalized graphite. Figure 5 shows the Raman spectra of HOPG before and after functionalization. The changes in the spectrum are similar to that for CVD graphene. The Raman spectra of TCNEO-functionalized HOPG graphite demonstrated the similar behaviour with a very clear appearance of the D line, the intense band around 1450 cm^{-1} , the C-N line at 2232 cm^{-1} , and the distinct fluorescence background.

Figure 5. Raman spectra of highly ordered pyrolytic graphite before (bottom curve) and after (upper curve) 48 hour –long functionalization reaction with tetracyanoethylene oxide in chlorobenzene. Excitation wavelength 532 nm.

6. Computational Methods and Results

6.1. Structure of TCNEO-functionalized graphene

The structure of graphene sheets functionalized with TCNEO were analyzed using *ab initio* computational methods based on density functional theory [15,16]. Our calculations were carried out using the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [17,18] electronic structure code. We employed the Kleinman-Bylander form [19] of norm-conserving Troullier-Martins pseudopotentials [20]. The exchange-correlation energy functional was evaluated using the generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof [21]. To improve the

accuracy of the computed binding energies between graphene and TCNEO, all calculations were conducted using the split-valence double zeta plus polarization basis sets [22]. The energy mesh cut-off was set to 250 Rydberg.

We examined the reactions of cycloaddition of TCNEO to the surface of pristine graphene and to the edge of an H-terminated graphene sheet. Pristine graphene was modeled by a rectangular periodic supercell containing 72 C atoms. The edge of a graphene sheet was modeled by a supercell containing a stripe of 42 C atoms passivated with H atoms along its sides. The calculated structures of tetracyanoethylene oxide attached to the surface of pristine graphene and to the edge of an H-terminated graphene sheet are shown in Figs. 6(a) and 6(b), respectively. The dimensions of the supercells were selected to be sufficiently large to minimize the effects of artificial periodicity on the studied systems. The Brillouin zone was sampled with a Monkhorst-Pack k-point mesh of 6x6x1 for pristine graphene and 6x1x1 for the graphene edge. Structural optimization was performed via the conjugate gradient method. The residual forces acting on all atoms were required to be smaller than 0.03 eV/Å.

Figure 6. Calculated structures of (a) the surface of pristine graphene and (b) the edge of an H-terminated graphene sheet functionalized with TCNEO. (c) Calculated vibrational spectra of pristine graphene and an H-terminated graphene edge functionalized with TCNEO. The spectra are broadened by 10 cm^{-1} using a Gaussian function.

6.2. Energetics of chemical reaction and vibrational modes of TCNEO-functionalized graphene.

6.2.1 Energetics of chemical reaction for different attachments of carbonyl ylide.

The binding energies, E_b , between graphene and TCNEO were evaluated as $E_b = E_{G+TCNEO} - E_G - E_{TCNEO}$, where $E_{G+TCNEO}$ was the total energy of graphene functionalized with TCNEO, E_G was the total energy of graphene, and E_{TCNEO} was the total energy of an isolated TCNEO molecule. To eliminate the localized basis set superposition error in SIESTA calculations, the binding energies were computed using the counterpoise correction method proposed by Boys and Bernardi [23]. Our calculations demonstrated that the reaction of cycloaddition of TCNEO to the surface of pristine graphene was endothermic with the binding energy of $E_b = + 1.85$ eV. In contrast, the reaction of cycloaddition of TCNEO to the edge of graphene sheet was found to be exothermic with the binding energy of $E_b = - 0.60$ eV. These results were consistent with a previous theoretical study of dipolar cycloadditions of azomethine ylides and carbonyl ylides to graphene clusters carried out by Cao and Houk (See Ref. 5). The study of Cao and Houk indicated that the outer layer of graphene clusters were significantly more reactive toward cycloadditions than the center areas. Specifically, the reactions on the corner and edge bonds of graphene clusters were found to be exothermic for both azomethine ylide and carbonyl ylide, whereas the reactions on the center bonds were found to be either endothermic or had close to zero reaction energy [5].

It is worth to point that our calculations have been made for components in a gas phase. The actual reaction between TCNEO and graphene goes under different conditions, in a solution. The effect of solvent, which has been not included into modelling, can be a very significant help in promotion of the TCNEO-graphene reaction.

At the same time, despite of just-mentioned applicability limitations, we expect some correlation between estimated values and actual results of the reaction. Our expectations

are based on the results of previous research. Earlier, the same TCNEO-utilizing modification was made with fullerene C60, a rather close “relative” of graphene [24]. In the Ref. 24, the reaction mixture was refluxed during 15 hours in toluene (boiling point 111°C). For graphene, these conditions did not work. Therefore, we tried different solvents, and ended up with a more polar solvent, chlorobenzene, with the higher boiling point (131°C), and a longer duration of reaction (48 hours). As one can see, the conditions for the modification of graphene are harder than that for C60.

We tested our numerical model with the TCNEO-C60 reaction. From our calculations, the cycloaddition of TCNEO to C60 is exothermic. Comparing it with the results for graphene, where the cycloaddition of TCNEO to graphene is exothermic for edges and endothermic for the surface, we see the clear correlation with the observed significant difference in the experimental conditions of the reaction for similar systems. The higher temperature and a specific interaction of more polar solvent with a substrate make the energetically-unfavorable process (of central carbonyl ylide attachment) possible.

6.2.2. Vibrational modes in carbonyl ylide-functionalized graphene.

The vibrational spectra of graphene sheets functionalized with TCNEO were calculated using the VIBRA package distributed with the SIESTA code. The phonon frequencies were computed at the Γ point using the method of finite differences. The finite atomic displacements were set to ± 0.04 atomic units. The forces on each atom within the supercell were evaluated using the Hellmann-Feynman theorem.

In the case of edge attachment to graphene, for low- and mid-frequency parts of

the vibrational spectrum, the calculations predict several attachment-related modes: vibrations around 121 cm^{-1} (114, 121, 125, 129 cm^{-1}) associated with bending of CN groups; 145 cm^{-1} mode corresponding to the up-down motion of the TCNEO molecule; 241 cm^{-1} mode related to sideways (toward the edge) tilt of TCNEO; 189 and 293 cm^{-1} modes related to C-O-C bending; modes at 648 and 656 cm^{-1} representing sideways tilt (or twist) of the TCNEO's 5-member ring; and modes at 691 and 751 cm^{-1} related to stretch modes of the 5-member ring.

In case of pristine (central) graphene attachment, for low and mid-frequency ranges, calculations predict vibrations around 121 cm^{-1} (118, 121, 126, 130 cm^{-1}) associated with bending of CN groups; the up-down motion of the TCNEO molecule at 153 cm^{-1} ; 197 and 219 cm^{-1} modes related to C-O-C bending; modes at 630 and 644 cm^{-1} representing sideways tilt (or twist) of the TCNEO's 5-member ring; and 695 and 753 cm^{-1} modes related to stretch modes of the 5-member ring. It should be noted that the computed frequencies of the vibrational modes do not take into account the Raman selection rules, so some theoretical lines may not show up in the experimental Raman spectra.

At the higher vibrational frequencies, the clear signature of successful functionalization for both pristine and edge attachment of graphene functionalized with TCNEO is, according to our calculation, the line corresponding to the stretch $\text{C}\equiv\text{N}$ bonds at $2211 - 2228\text{ cm}^{-1}$. The calculations show no vibrations associated with the TCNEO molecule attached to either pristine graphene or to the graphene edge in the range of $1400\text{-}1500\text{ cm}^{-1}$, or at the higher frequencies. All vibrational modes associated with the TCNEO molecule (except for the triple $\text{C}\equiv\text{N}$ bonds) are located below $1100\text{-}1200\text{ cm}^{-1}$.

The higher frequency modes (except the $\text{C}\equiv\text{N}$ modes at $\sim 2230\text{ cm}^{-1}$), according to calculations, in TCNEO-functionalized graphene come from the graphene layer. In particular, several modes in the range between $1410\text{-}1460\text{ cm}^{-1}$ are associated with different C-C=C in-plane vibrations (see Fig. 7). We see similar vibrational modes in pristine neat graphene and in pristine (defect-free) graphene functionalized with TCNEO. These modes are usually not visible in Raman spectra of pristine perfectly-periodic graphene due to selection rules. *It is important to point out that these modes provide a significantly higher contribution to the phonon density of states (and, therefore, to the Raman spectra) in the case of central, pristine attachment of TCNEO to graphene layers (see Fig. 6(c), upper curve).*

The results of vibrational spectra calculations for edge attachment of carbonyl ylide to graphene show peaks around $3000\text{-}3200\text{ cm}^{-1}$ (see Fig.6 (c), bottom curve) These peaks correspond to the C-H stretching modes. These modes are here because the modeled edge of graphene is passivated with Hydrogen atoms. The C-H stretching modes are absent in the calculated spectrum of "pristine graphene + TCNEO" (Fig.6(c), upper curve), because there are no Hydrogen atoms in our model of pristine graphene.

6.3. Interpretation of Raman spectra

Comparison of experimental observations (see Fig. 3) and results of numerical modeling allow us to attribute the observed Raman low frequency lines in the following way: the line at 117 cm^{-1} presumably represents bending of CN bonds, the line at 188 cm^{-1} is related to C-O-C bending of attached carbonyl ylide, the line at 226 cm^{-1} may correspond either to the sideways (toward the edge) tilt of TCNEO in case of edge attachment, or

may be related to C-O-C bending in TCNEO in case of pristine/central attachment. For the mid-frequency modes, the line at 665 cm^{-1} is most likely the sideways tilt (or twist) of the TCNEO's 5-member ring, the line at 744 cm^{-1} belongs to the stretch modes of the 5-member ring. In the high-frequency range, the line at 2231 cm^{-1} is caused by the stretch modes of triple C $\equiv$ N bonds. The increase after functionalization of the D-line, the new strong band between D and G lines with center near 1450 cm^{-1} , and the increased D+G band [13] (together with combinations of G and $\sim 1450\text{ cm}^{-1}$ -modes), are due to attachment induced distortions of the graphene layer, that destroyed the selection rules and made otherwise forbidden lines visible in Raman spectra.

Figure 7. (Color online) Vibrational modes with frequencies locating between 1340 and 1582 cm^{-1} in TCNEO-functionalized graphene in case of (a) (left column) central (pristine) attachment and (b) (right column) edge attachment. For the accuracy of modeling, the edge bonds in case of edge attachment of TCNEO are assumed to be passivated with hydrogen.

In TCNEO-modified large area CVD grown graphene (where the possible contribution from edges is significantly smaller compared to the commonly used graphene suspensions), and in TCNEO-modified HOPG (where edges play only a minor role due to the high structural uniformity of the HOPG surface), the observation of successful modification indicates the existence of central (pristine) attachments to graphene. The high intensity and position of the new high intensity band at $\sim 1450\text{ cm}^{-1}$ (comparable in intensity to both D and G bands) provides further evidence of central attachment of TCNEO.

7. Summary.

To summarize, we have performed the covalent cycloaddition of tetracyanoethylene oxide to epitaxial graphene and graphite. The Raman and Auger spectra of TCNEO-functionalized graphene and graphite show the signatures of successful attachment. In particular, Raman spectra of TCNEO-functionalized graphene and graphite show several signs of functionalization: the appearance of CN line at 2231 cm^{-1} , the growth of intensity of defects-related D band at $1340\text{-}1350\text{ cm}^{-1}$, the raise of D+G band near 2940 cm^{-1} , the appearance of low frequency lines corresponding to vibrations in attached carbonyl ylide, and of the new high intensity Raman band at $\sim 1450\text{ cm}^{-1}$. The numerical modeling reveal that the 1450 cm^{-1} line represents the C-C=C in plane vibrations in functionalization-distorted graphene and indicates the existence of central (pristine) attachment of TCNEO to graphene surface.

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