UV activation, sorption/desorption kinetics, and electronic properties of carbon nanostructures described in terms of electronic band structure

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Abstract

Nanotubes, fullerenes, and graphene belong to a family of carbon allotropes that show promise for application in a wide range of flexible thin film electronic devices including photovoltaics, LEDs, transistors, biointerfaces, and sensors. However, surface doping of carbon-based materials by gas adsorption can cause dramatic changes in the optoelectronic properties of different nanostructures. At CNMS at ORNL, my research group will soon be conducting experiments to investigate the effect of UV light on the sorption/desorption kinetics of oxygen and water on different carbon allotropes. Here, I use topics from MSE 674 class to relate photo-induced and sorption-induced changes in the electronic properties of carbon nanomaterials to band structure concepts, including the Fermi level, density of states, and bandgap. Surface activation by UV light and sorption-induced metal/semiconductor/insulator transitions are described in terms of the formation of surface depletion regions and p-type and n-type doping by oxygen and water. UV-induced desorption is discussed in relation to plasmon excitations. By relating the results of our future measurements to band structure concepts and DFT calculations, it is possible to combine theoretical and experimental descriptions of the effect of UV activation on the gas sorption kinetics of different carbon nanostructures.

Nanotubes (CNTs), fullerenes, and graphene belong to a family of carbon allotropes that are being explored for application in a wide range of thin film devices including photovoltaics [1], LEDs [2], transistors [3], biointerfaces [4], and gas sensors [5]. Their unique optoelectronic properties, low cost, and compatibility with roll-to-roll processing have propelled carbon-based materials to the forefront of nanoscience research over the past two decades [6]. The high

bandgap tunability of carbon allotropes allows films to be made semiconducting or metallic by the introduction of intrinsic and extrinsic dopants [7]. However, the environmental stability of carbon nanomaterials and may present a fundamental limitation to reliable device performance. The high surface area of nanostructures allows for gas sorption that can cause unpredictable changes in a film's optoelectronic properties. Even exposure to sub-ppm analyte concentrations can dramatically alter band gap, work function, local density of states, and induce charge transfer and semiconductor-metal transitions in carbon nanostructures [1, 8-10].

The perfect sp2 hybridization in defect-free graphene makes it electronically stable and generally prevents chemisorption of atmospheric gases [9]. However, the curvature of C_{60} and CNT structures causes hybridization of the planar derived trigonal orbitals that introduces some sp3 character to the dominant sp2 planar bonding [7]. This disrupts the sp2 network and allows for higher reactivity with ambient gases. Many of the intrinsic properties of carbon films are compromised upon exposure to air due to charge transfer reactions with adsorbed oxygen and water [8-13]. Desorption of O_2 and H_2O from carbon surfaces is critical for the activation of gas sensors, modification of surface wetting characteristics, and tuning of band structure [8-10]. While thermal treatment is often used for the removal of physisorbed gases, Miyamoto et al. report that some thermal treatment methods targeting the removal of oxygen show preferential desorption of CO and CO_2 rather than O_2 [14]. The displacement of carbon atoms from the film surface disrupts sp2 bonding and leads to the formation of locally electron-rich and electron-deficient regions which increase the probability of irreversible gas chemisorption at the carbon vacancy sites [9, 15].

As an alternative to thermal treatment, UV activation can be used to remove adsorbed gas molecules, tune electronic properties, and induce hydrophobic-hydrophilic transitions in carbon films [9, 13]. For sensing applications, continuous UV illumination of nanostructures can improve gas response by more than an order of magnitude [16]. During UV activation, the gas response of carbon structures results from sorption-induced and photoinduced defects in the adsorbent material [13], electronic photoexcitations in the gas molecules and adsorbent [15], and photoinduced plasmons in the film and substrate [17, 18]. The combination of optoelectronic and chemical processes taking place at the film surface makes it difficult to identify the underlying mechanisms controlling photoinduced sorption/desorption processes on carbon structures. Here, we perform in situ electronic and quartz crystal microbalance (QCM) measurements to study the effect of UV activation on the gas response and sorption kinetics of H_2O and O_2 on C_{60}, semiconducting single wall nanotubes (s-SWNTs), metallic single wall nanotubes (m-SWNTs), and multiwall nanotubes (MWNT). We compare mass loading, reversibility, response time, and their effect on the conductivity of different carbon allotropes by characterizing films under a variety of humid and oxygen-rich conditions.

Extrinsic doping of carbon nanostructures under atmospheric conditions occurs primarily as a result of O_2 sorption [8, 12]. DFT calculations show that physisorbed O_2 molecules can settle at the top sites of carbon atoms with the O=O bonds parallel to the carbon surface [13]. This leads to hybridization between the valence bands in the adsorbent material and O_2 molecule, which increases the density of states at the Fermi level [12] and results in hole doping behavior [14]. On SWNT, O_2 molecules physisorb with a binding energy of ~0.25 eV and withdraw ~e/10 charge per molecule [19]. Sorption-induced charge transfer with O_2 is responsible for p-type behavior in SWNT [9, 12] and can result in conductivity changes of up to 50% in SWNT films [8]. Similar sensitivity to oxygen has been observed in C_{60} [20-22] and graphene [23, 18].

The desorption of O_2 by UV activation can alter charge carrier density in SWNT [15] and graphene [23, 17] and carrier mobility in C_{60} [22]. Photodesorption is mediated in part by photoinduced π-electron surface plasmons [15]. Plasmon lifetime in SWNTs is on the order of 1 fs, after which plasmons decay into single-particle hot electron and hole excitations [24]. Hot carrier injection from the carbon surface to the adsorbate molecule can penetrate the energy barrier between and result in molecular desorption. In this way, UV-induced plasmon excitation energy is dissipated by gas desorption [17, 19]. The plasmon-adsorbate interaction has been proposed as a primary mechanism for UV-induced O_2 desorption from SWNT [15] and graphene [18].

UV activation can also result in chemisorption of O_2 on carbon surfaces. Both interactions between between physisorbed spin-triplet oxygen and photoexcited carbon and the absorption of UV photons by O_2 can lead to the formation of singlet oxygen [15]. This significantly lowers the activation energy (E_A) required for charge transfer between the adsorbed molecule and nanostructure and enhances oxidation of the carbon surface [21, 25]. During dissociative chemisorption of oxygen, each O atom rests above a C-C bond bridge site to form a C-O-C complex which destroys the perfect π-bonding between carbon atoms. It remains unclear whether this enhances further photooxidation at other C-C bridge sites [13, 14] or leads to chemical stabilization of nanostructures by trapping local photoinduced charges [15, 20]. In this study, we investigate this question by measuring sorption/desorption kinetics and their effect on electrical conductivity when carbon films are exposed to O_2 in the dark and in the presence of UV light.
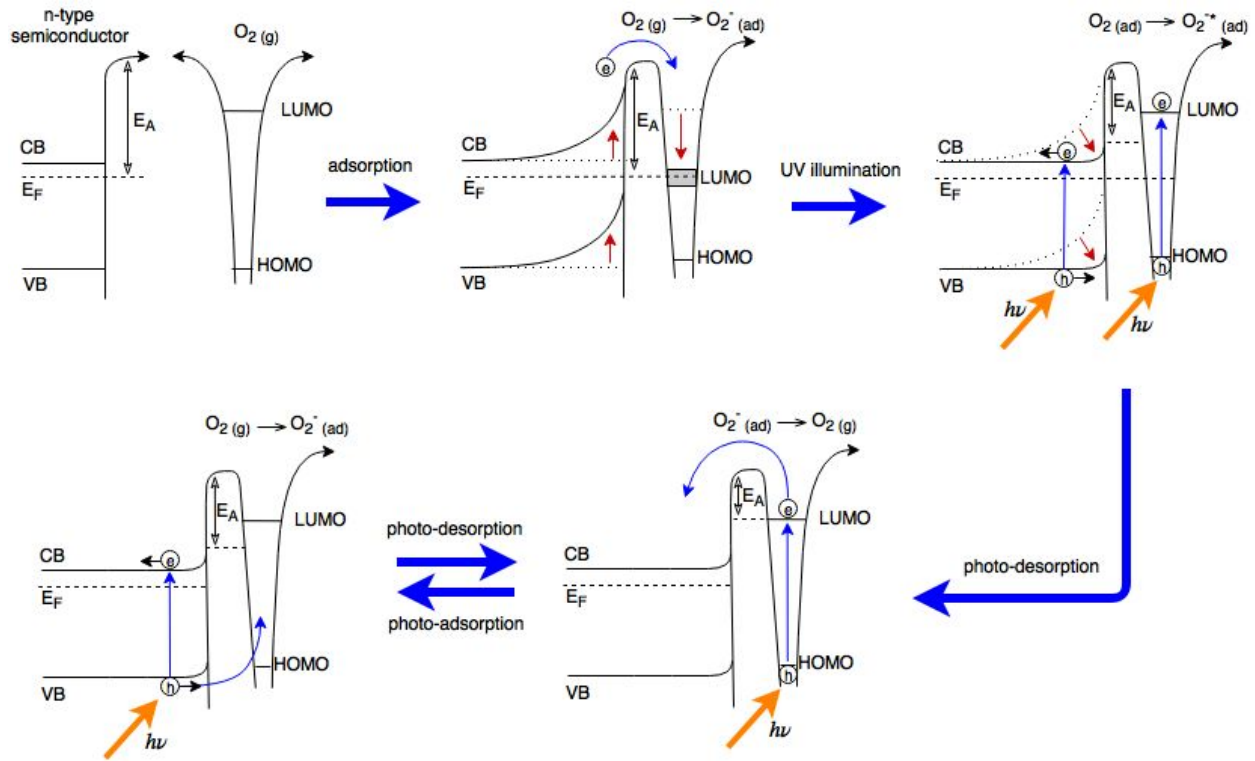
Figure 1. Mechanisms for photo-induced sorption/desorption processes. Adsorption of a charge accepting molecule (O_2) on an n-type semiconductor causes upward band bending in the adsorbent material, broadening of the LUMO level of the adsorbate molecule, and pinning of the LUMO level to the semiconductor E_F level. Upon UV illumination, photo-generated charge carriers, SPV, and singlet oxygen formation decrease the size of the charge transport barrier E_A, which facilitates charge transport between the adsorbent and adsorbate. This increases the rate of both UV-induced chemisorption of O_2 and photoinduced desorption of O_2.

Photoinduced sorption/desorption processes can be described in terms of the electronic structure of the adsorbent material and the molecular orbitals of O_2, as shown in Figure 1 for an n-type semiconducting adsorbent such as C_{60} [7]. The activation energy E_A represents the charge transfer energy barrier between O_2 and the carbon surface. Before physical gas adsorption, EA corresponds to the work function of the carbon surface, which is roughly 4.8 eV for SWNT bundles [29] and 4.7 eV for C_{60} [30]. The O_2 molecule approaches the carbon surface in its spin triplet ground state, where the O-O bond has a binding energy of 5.2 eV and the HOMO is the π^*_{2p} level and the LUMO is the σ^*_{2p} level [28]. During van der Waals-induced physical sorption/desorption processes, O_2 remains in its spin triplet state and $E_A = 0$. At room temperature, primarily because of structural defects, chemisorption of O_2 occurs on C_{60} with $E_A \approx$ 0.7 eV [20] and SWNT and other carbon structures with $E_A \approx 1.2$ eV [15, 31]. Upon chemisorption, negative charge transfer from the carbon structure to O_2 reduces the carrier density near the film surface and results in the formation of a surface depletion region. This

causes upward bending of the conduction (CB) and valence bands (VB) (downward band bending in p-type structures), broadening of the LUMO level of the O_2 molecule, and pinning of the O_2 LUMO level to the Fermi level (E_F) of the adsorbent material [26]. Without UV activation, desorption by electron transfer from O_2 back to n-type C_{60} requires roughly 0.7 eV [20]. Absorption of UV photons at the surface can produce electron-hole pairs which migrate in opposite directions due to the bent bands. As electrons move toward the bulk material and holes migrate toward the surface, excess charge in the depletion region is neutralized and band flattening occurs as a result of the surface photovoltage (SPV). In p-type adsorbents, UV absorption increases the downward band bending because the SPV transports negative charge to the film surface [27]. The SPV effect narrows the effective width of the E_A barrier, which increases the probability of charge transport through the barrier. Excitation in the adsorbed O_2 molecule can occur from singlet quenching by the carbon nanostructure or from absorption of UV photons [15]. The excitation in O_2 decreases the height of E_A for charge transfer from the O_2 to the carbon surface, which increases the probability of electron transport across the barrier and results in desorption of O_2. However, photoexcitations in the carbon nanostructure also lower the height of the energy barrier, so charge transfer back to the O_2 molecule may occur. Since the presence of UV light lowers the energy barrier between the adsorbed O_2 molecule and the carbon surface, the rates of both sorption and desorption are increased in the presence of light.

While O_2 is the most common environment-induced dopant present on carbon structures, dissociative H_2O sorption is becomes favored when oxygen or other defects are present on film surfaces. C-H and C-OH group formation allows for reversible hydrophobic-hydrophilic transitions in carbon structures, which strongly influences the adsorption isotherm [13]. After dissociative H_2O sorption, the OH moiety behaves as the acceptor in a charge transfer reaction with the carbon surface, and so may be treated as O_2 was described in Figure 1 [9]. Charge transfer to H2O or OH occurs in C_{60} [20] and SWNT [12] and can lead to an opening in the bandgap of graphene by up to 0.2 eV [10, 13].

In the experiment to be performed for this study, we will expose different carbon nanostructures, including C_{60}, s-SWNT, m-SWNT, MWNT, and graphene, to varying concentrations of O_2 and H_2O vapor and perform in situ measurements of conductivity and mass loading using a QCM. I will use band bending models to help explain differences in the gas response of n-type, p-type, and metallic materials. It is expected that the gas response of semiconducting films will be significantly higher than that of metallic films, as charge transfer on semiconducting surfaces will induce depletion regions which can be identified by surface conductivity measurements. Quantitatively understanding the kinetics behind UV activation on carbon materials will allow for improvements in surface cleaning methods, development of reversible gas sensors, and finer control over the wettability of nanostructured surfaces.

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