

Poster Session 1

T1

Coherent phonon spectra of G band in single wall carbon nanotubes

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In ultrafast (femtosecond) pump-probe spectroscopy, coherent phonons have been known to be observed in terms of oscillations of the change in optical constants (e.g. reflectivity and transmittance) as a function of delay time between pump and probe pulses, in which these oscillations are directly related to the modulations of absorption coefficient. For a single wall carbon nanotube (SWNT), Fourier power spectra of the differential reflectivity or transmittance as a function of phonon frequency show several peaks that correspond to the SWNT's coherent phonon modes, such as the radial breathing mode (RBM), G band, and even acoustic modes.^[1,2] In the case of RBM, oscillations of optical constants are already understood as a result of a diameter-dependent band gap.^[3,4] However, this mechanism cannot be used for the other phonon modes. In particular, if we consider the same mechanism for the G-band, it was previously predicted that the modulations of absorption coefficient due to G-band phonons are about 1000 times smaller than those caused by the RBM.^[5] However, recent experiments showed that the coherent G-band signal is comparable to, and almost on the same order as, the RBM signal.^[6]

In this work, we present an origin of the strong coherent G-band signal. Instead of the energy gap modulations as in the RBM, here we expect that the modulations of electron-photon interaction as a function of time should be relevant to the coherent G-band intensity. We also compare the coherent G-band intensity with the other coherent phonon modes in a specified SWNT chirality. We expect that there might be a common origin of the coherent phonon spectral line shapes of any materials due to changes of phase in the coherent oscillations. This theory could be a significant progress for understanding a general and systematic behavior of coherent phonons.

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Quantum interference effect in Raman spectra of metallic nanotubes

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In graphene and metallic single wall carbon nanotubes (m-SWNTs), the existence of gapless linear energy bands (Dirac cones) modify the G band (in-plane optical phonon modes) Raman spectra. One of the well-known phenomena is the Kohn anomaly effect, in which the phonon energy (lifetime) becomes lower (shorter) due to the interaction between the G phonon and an electron-hole pair in the linear energy band.^[1] The other phenomenon is the asymmetric spectral shape of the G band, also known as Breit-Wigner-Fano (BWF) line shape, which long been observed in m-SWNTs^[2] and recently observed in graphene.^[3] However, the origin of this BWF lineshape asymmetry remains a question. In this presentation, the origin of BWF line shape is explained by means of quantum interference of phonon G band spectra and electronic Raman spectra (ERS).^[4] The ERS are electronic spectra whose origin comes from an electron-hole pair excitation in the vicinity of the Dirac cone.^[5]

In this work, we calculated the exciton-exciton interaction between a photo-excited exciton and an exciton in the linear band of a m-SWNT which is relevant to the ERS. We calculated ERS spectra as a function of laser excitation energy and we reproduced the experimental BWF spectral shape for all laser excitation energies. The Coulomb potential, generally, gives a maximum value at momentum transfer $q=0$ but surprisingly, we found that the direct Coulomb interaction between the two excitons vanishes at $q=0$. The absence of the direct Coulomb interaction is due to the symmetry of the two sub-lattices of SWNTs unit cell. Using the same method, we extend the story in graphene and reproduce the experimental result of the G band asymmetry as a function of Fermi energy. We also predict that the radial breathing phonon mode (RBM) spectra in m-SWNTs exhibit the opposite BWF asymmetry to that of the G band, by showing the laser energy dependence of RBM spectra.

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Spontaneous formation of O₈ clusters and chains within nanostructures

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We perform first principles calculations based on the density functional theory to show that the building blocks of the oxygen ϵ -high pressure solid phase spontaneously form when oxygen molecules are enclosed within fullerenes and small diameter nanotubes. We observe that the stability increases with the enclosure diameter. The building blocks consist in O₈ clusters, which are able to self-assemble into periodic arrays inside nanotubes. Such chains are semiconductors when isolated or when encapsulated in boron nitride nanotubes, and become doped when confined in carbon materials. In the same way as we observe a magnetic collapse in oxygen ϵ solid phase, these O₈ clusters maintain this property when encapsulated. Molecular dynamics simulations confirm the formation and stability of the clusters and chains in ambient conditions.

Wave propagation along coplanar transmission line covered with inkjet printed multi-walled carbon nanotubes network

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The trend of device minimization in size, weight and cost for use in commercial wireless communication systems has resulted in an increasing demand for highly integrated system-on-chip solutions. To shrink the size of interconnections and passive devices, many researchers have proposed the use of slow-wave propagation mode in order to reduce the effective electrical wavelength of the RF signals.^[1]

On the other hand, carbon nanotubes (CNTs) are emerging as novel nanomaterial for a large variety of applications, particularly as electronic material owing to their amazing mechanical, thermal and unique electrical properties.^[2] Thin films of CNTs networks/arrays, a planar topology is usually preferred, with in view the application to CNT-based interconnects and carbon-based circuits.^[3] The use of CNTs network could bring solutions to reduce the size of microwaves circuits in addition to the benefit of short-time and low-cost fabrication using inkjet printing. Furthermore, this technique gives the possibility to readily control the pattern geometry, location, film thickness, and uniformity of the films.

In this present study, we aim at investigating the mode propagation when multi-walled carbon nanotubes (MWCNTs) ink is used to print films on coplanar waveguides (CPWs) lying on glass substrate. The extracted line characteristics from measured S-parameters offer an accurate analysis of the propagation mechanism, revealing the existence of a slow-wave mode regime. A good master of this property is appropriate for exploiting the slow-wave phenomenon in order to scale down the size of passive integrated structures. Thus, the impact of geometry and the number of alternate deposited CNTs networks are experimentally tested.

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Phase diagram of Ni-C nanoparticles from computer simulation

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Carbon nanotube synthesis critically depends on the chemical and physical states of the catalyst particle from which they grow. In the typical temperature range (600-1000 °C) of SWNT synthesis, pure isolated Ni nanoparticles are solid although atomic diffusion can lead to significant shape changes. Under growth conditions, these nanoparticles are exposed to reactive carbon. Depending on temperature, carbon chemical potential and nanoparticle size, carbon can either stay adsorbed on the surface, or diffuse to subsurface or in the core of the nanoparticle, thereby inducing a partial or complete melting.

On the basis of the tight binding model developed for the Ni-C system coupled with grand canonical Monte Carlo simulations,^[1] we try and calculate size dependent liquid/solid phase diagrams for Ni-C alloys. We thus extend our previous calculations^[2,3] and rationalize our findings using suitable order parameters, as proposed by Steinhardt et al.^[4]

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Is exciton BEC possible in individual carbon nanotubes? A theoretical prospective

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I will tell about one interesting possibility that we have lately theoretically demonstrated to exist for the 1D exciton Bose-Einstein condensation (BEC) phenomenon in individual small-diameter ($\sim 1\text{--}2$ nm) semiconducting carbon nanotubes (CNs).^[1] This originates from the strong coupling of excitons and low-energy inter-band plasmons enabled via the quantum confined Stark effect by using an external electrostatic field applied perpendicular to the CN axis. The perpendicular electrostatic field mixes excitons and inter-band plasmons of the same band,^[2] to result in strongly coupled hybridized excitations-exciton-plasmons in one individual CN.^[3] Such hybridized excitations are strongly correlated collective Bose-type quasi-particles and, therefore, could likely be condensed under appropriately created external conditions — in spite of the well-known statements of the BEC impossibility in ideal 1D/2D systems^[4] and experimental evidence reported earlier for no exciton BEC effect in CNs.^[5] Possibilities for achieving BEC in 1D/2D systems are theoretically demonstrated earlier in the presence of an extra confinement potential.^[6] The correlated exciton-plasmon system in a CN presents such a special case. The effect requires fields ~ 1 V/nm and temperatures below 100 K that are experimentally accessible.^[7] The effect offers a testing ground for fundamentals of 1D condensed matter physics and opens up perspectives to develop a tunable highly coherent polarized light source with CNs.

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The influence of the curvature of surface and π electrons on adsorption of nanocarbons

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Nano carbons structures as CNTs, graphenes, fullerene, Mackay crystal and their composite have been attracting scientists and engineers to finding of novel functional materials for water technology and electronics. We have investigated the adsorption of nanocarbons as adsorbent with varying their surface curvature at adsorption point by use of ab initio simulation. The adsorption of CNTs, fullerene, graphene and Mackay crystals, has been simulated for Cesium, Cs, as adsorbate. The results show commonly that π -electron extending beyond the surface of carbons plays important role for catching the valence 6s electron of alkali metal Cs. The valence 6s electron of Cs flows into nanocarbon's π orbitals. It helps for nanocarbons to adsorb Cs stably by the charge transfer interaction. The surface curvature of the adsorption point clearly influences on the adsorption strength. The adsorption becomes more stable if curvature radius of CNTs increases. For the negative Gaussian curvature of Mackay crystals, the adsorption is enhanced around octagonal rings among the hexagons. This result points out that such a sophisticated configuration by the spread of π electrons contributes to the adsorption strength. The feature is useful for nanocarbon filter or film in novel water technology or future carbon electronic materials.

Detection mechanisms in carbon-nanotube-based molecular sensors

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Carbon Nanotubes (CNTs) are highly promising for chemical and biological sensing applications, owing to their high chemical and mechanical stabilities, high surface areas and unique electronic properties. We report the results of theoretical studies of detection mechanisms of both pristine and receptor-functionalized CNTs. The calculations use density functional theory (DFT) combined with Keldysh non-equilibrium Green's function (NEGF) method to examine changes in conductance and current due to attachment of analyte molecules. These include ammonia, nitrogen dioxide, glucose and ethylene. For nitrogen dioxide, which chemisorbs on the CNT, we show that the attachment produces significant differences in both transmission and Current-Voltage (I-V) curve. For ammonia, we find that it can be either physisorbed or chemisorbed depending on its position relative to the metallic leads. The chemisorbed case shows detectable differences in transmission and I-V curves. For glucose detection, we investigate the sensing mechanism of CNTs functionalized with pyrene-1-boronic acid. Glucose attachment results in formation of an anion complex, which decreases conductivity through the CNT. For ethylene detection, the sensing mechanism of CNT functionalized with a copper(I)-based receptor is investigated. We find that ethylene binding to the receptor results in detectable changes in both conductance and current. For all cases, the calculated changes in conductance and current are consistent with experiments.^[1-4]

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Focusing of low energy electrons by Carbon Nanotubes

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The trajectories of low kinetic energy electrons, in the range of a few eV, are strongly modified by the interaction with the polarization charges they induce on a surface. We show how this effect is relevant in inverse photoemission spectroscopy (IPS) data analysis from carbon nanotubes (CNTs). IPS from CNTs exhibit two main resonances, located around 2.5 eV and 12.5 eV above the Fermi level. The intensity of the first resonance is dependent on the average tube diameter and the second one has a distinctive spectral shape, which can be related to the graphitization level of the CNTs' external walls.

In order to analyze the origin of these resonances, a phenomenological reconstruction of an IPS spectrum from a CNTs' array was performed. This reconstruction successfully reproduces the spectral shape of the 12.5 eV resonance. However, the intensity is lower than the actual measurements in the initial energy range of the spectrum. The analysis of these results, using graphite's electronic band structure, suggests the additional intensity required to reproduce the experimental data, could have its origin in an electronic focusing mechanism, induced by the CNTs' image charge potential. Calculations of the electronic trajectories close to the tubes show this focusing effect is significant for both low energy electrons and small diameter tubes.

Theoretical Limits to Suspended Graphene Varactors and Tunneling Relays

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The high yield strength, low flexural rigidity and low mass density of suspended graphene membranes are potentially promising for nanoelectromechanics applications. We have explored the theoretical limits to graphene varactor and tunneling relay performance. The suspended graphene varactor, where capacitance is tuned by electrostatic actuation of membrane deflection, provides a capacitor tuning range of ~76%, with a membrane pull-in voltage V_p as low as ~1V. An intrinsic electrical quality factor as high as 200 is predicted at 1 GHz for these devices [M. AbdelGhany et al. Appl. Phys. Lett. 101, 153102 (2012)]. Nonlinear currents arising from capacitance modulation under sinusoidal drive are predicted to appear at odd harmonics, with amplitude proportional to $(V_{ac}/V_p)^{(5/3)}$. We have also considered the theory of the tunneling relay, where the electrostatic actuation of a graphene membrane is combined with the exponential dependence of tunneling current through a vacuum gap. Sub-threshold swings as steep as 10 mV/decade are predicted, breaking the thermionic limit of 60 mV/decade at room temperature [M. AbdelGhany et al. Appl. Phys. Lett. 104, 013509 (2014)]. The predicted performance suggests that a significant reduction in dynamic energy consumption over conventional field effect transistors is physically achievable. We will report on our recent experimental progress towards realizing graphene nanoelectromechanical devices with large area graphene.

Electronic properties of bilayer β -graphyne

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Among the large variety of carbon allotropes there are some graphene-like structures which can be constructed by replacing some bonds $=C=C=$ in graphene by acetylenic linkages $-C\equiv C-$, called graphynes (GYs),^[1] or by diacetylenic linkages $-C\equiv C-C\equiv C-$, called graphdiynes (GDYs)^[2]. These non-natural carbon allotropes include both, sp^2 - and sp^1 -hybridized carbon atoms. After the theoretical prediction of these flat structures, with exceptional electronic, thermal and mechanical properties, several experimental studies have been performed to achieve their large-scale synthesis.^[3] Due to their intrinsic semiconducting properties, GYs and GDYs have been proposed as promising candidates in many electronic and photoelectronic applications and also with potential applications as membranes to separate molecules, hydrogen storage media, and anode materials in lithium-ion batteries.^[4,5]

According to first-principles electronic structure calculations^[6] some particular types of graphynes-like networks also possess Dirac cones as the case of graphene. One of these structure, β -graphyne, has a Dirac cone not located at the K and K' points of the Brillouin zone, but on lines between the high symmetry Γ and M points. In this work we show a theoretical study based on DFT of the electronic properties of bilayers of β -graphyne, for different stacking configurations. Our results show that the bilayer is semimetal or semiconductor, depending on the stacking mode. The system changes from a metal, for A-A stacking, to a semiconductor with a small gap of 0.15 eV, for A-B stacking, being this most stable configuration according to the study of total energy and stability.

By applying an electric field perpendicular to the layers, the gap of the semiconductor can be closed and a metallic state is obtained. This behavior is contrary to that reported for the case of α -graphyne^[7] for which the semi-metallic systems become semiconductor with a gap that increases with the field intensity.

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Computational Modeling of Channel Length Modulation in Carbon Nanotube Field Effect Transistors

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Single walled carbon nanotube (CNT) field effect transistors (FETs) are unique devices because of their intrinsically one-dimensional transport, tunable band gap, and high mobility. They also offer potential performance advantages such as high-linearity in analog RF amplifiers, high surface-to-volume ratio, which is useful for chemical sensors, high frequency mechanical oscillations for RF NEMs devices, and high cutoff frequencies in the THz region. Several research groups have used theoretical and computational methods to analyze electrical transport in CNT FETs, and there are several software tools available for this. Studies have focused on improving numerical methods or modeling for process and circuit design, or specific aspects of transport in CNT FETs, such as multiband effects, carrier velocity saturation, Schottky barrier effects, and electron-phonon scattering. The vast majority of these studies and tools, however, assume a uniform voltage, resistance, and Fermi energy along the length of the CNT. This assumption is not valid because the gate, source and drain capacitances vary spatially, which requires a spatial solution of Poisson's equation. Also, this assumption precludes modeling of pinch-off and channel length modulation, effects that strongly influence electrical transport in FET devices. Here we report computational modeling and characterization of quasi-ballistic electrical transport in semiconducting carbon nanotube field effect transistors, and fit experimental electrical transport data from both suspended and on-substrate single-walled carbon nanotube transistors fabricated using chemical vapor deposition. Numerical modeling is performed using finite element methods within the Landauer framework while explicitly including spatial inhomogeneity by calculating the voltage, resistance and Fermi energy at discrete points along the CNT channel. These spatial variations play an important role in several high voltage effects that are important in the quasi-ballistic transport regime where most present day devices operate. We show the relationship between device geometry and pinch-off, current saturation, and channel length modulation in the quantum capacitance regime, and discuss computational modeling issues. This model can be used for extraction of device properties from experimental data and as a design tool for device processing optimization and CNT based circuitry. Such analysis is urgently needed in order to gain a more complete understanding of CNT FET operation.

Ab initio molecular dynamics study of bond dissociation mechanism of ethanol during carbon nanotube growth via CVD process

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The growth mechanism of carbon nanotubes and graphenes has been widely discussed their discovery. At present, most of the computational studies focusing on the growth process of these materials starts using isolated carbon atoms and therefore ignores the initial dissociation process.^[1] Under such circumstance, we have investigated the dissociation of carbon source molecules on the flat and curved metal surfaces by ab initio molecular dynamics (MD) simulation to discuss the initial stage of formation process.^[2-4] Especially, dissociation of ethanol on a nickel cluster has been closely investigated.^[3,4] From our latest simulation,^[4] it is confirmed that C–C bonds in only CH_xCO fragments are dissociated on the nickel cluster, whereas there is no preferential structure among the fragments for C–O bond dissociation. The dissociation preference is not correlated with the bond dissociation energy of corresponding bonds in freestanding molecules but is correlated with the energy difference between fragment molecules before and after dissociation on the nickel surface. In the presentation, our recent results will be introduced with relevant calculation results on this matter.

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Origins of carbon nanotube helicity and preference for (n, n–1) tubes

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The future fate of many practical applications of carbon nanotubes hangs on the capability to selectively produce CNT with required chirality. Despite all the progress in exploration of CNT nucleation and growth, the understanding of the origins of nanotube chirality is still missing. Thermodynamically, the energetics of CNT–catalyst interface^[1] appear to favor achiral armchair or zigzag CNT, and although the structures of CNT caps differ for different tubes, there is no additional “intrinsic” bias from cap energetics^[2] that could favor other chiralities. Yet neither achiral type is frequently produced in CVD growth. Simple arguments based on the screw dislocation model^[3] outline an explanation of the overall trend towards larger chiral angles. But a more in-depth look at the experimental results finds crucial “fine details” that seemingly contradict expectations, e.g., the almost complete absence of purely armchair CNT. To resolve these issues, we’ve developed a comprehensive theory of CNT nucleation and growth (with termination easily added to the picture) that includes the different factors shaping the chirality distribution of CNT yield, including nanotube–catalyst interface^[1], the energetic landscape of CNT caps,^[2] and growth kinetics,^[3] building upon our “nanoreactor” framework developed for graphene synthesis.^[4] Our study reveals how the aggregate state of the catalyst particle can substantially alter the equations governing nucleation and growth rate, in such a way that jointly they provide a CNT type distribution that is sharply peaked at the minimally chiral CNT types, thus explaining the abundance of near-armchair tubes such as (6, 5) in recent experimental studies (e.g.,^[5]) yet little or no pure armchair.

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SWCNT Growth from Organic Precursors Without a Catalyst: Possibilities and Limitations Revealed by Theoretical Simulations

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Our recent simulations of catalyst-free, chirality-controlled growth from cycloparaphenylene (CPP) precursors are presented. We will show that different chemical routes for chirality-controlled growth exist, and depend on the nature of the growth agent. We demonstrate this phenomenon using acetylene (C_2H_2) and the ethynyl radical (C_2H) as growth agents, at temperatures ranging from 300 to 800 K. In the case of the ethynyl radical, we observe a strong dependence of the SWCNT growth rate on the chiral angle. This is consistent with a previously proposed screw-dislocation-like model of transition metal-catalyzed SWCNT growth. However, the absence of a catalyst in this case indicates that the SWCNT growth rate is an intrinsic property of the SWCNT edge itself. Additionally, the ability of a SWCNT to avoid defect formation during growth is also an intrinsic quality of the SWCNT edge, one that is maximized at lower temperatures. However, using the ethynyl radical as the growth agent, the SWCNT diameter does not influence the growth rate; acetylene-based growth is, on the other hand, strongly diameter-dependent. We therefore predict the existence of a maximum local growth rate for a particular (n,m) SWCNT at a given acetylene/ethynyl ratio.

Spontaneous origami in multi-phase 2D phosphorus

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Similar to graphitic carbon, phosphorus monolayers, dubbed phosphorene,^[1] can be exfoliated from layered black phosphorus. Phosphorene is a p-type semiconductor with a significant band gap. It is stable, flexible, and displays a high carrier mobility,^[1] suggesting its potential use in 2D electronics. Most interesting, based on ab initio density functional calculations, we found that phosphorus can form four different 2D structural phases that are almost equally stable and may be inter-connected. Connection of two planar phases resembles a sharp origami-style fold, displayed in Fig. 1. This fold occurs naturally in this multi-phase system, whereas in single-phase systems like graphene it requires the presence of defect lines or lines of adsorbed atoms. We also find the possibility of moving this fold by structural transformation from one allotrope to another, with an unusually low activation barrier of <0.5 eV per bond. Since the electronic properties of multi-phase phosphorene may also be tuned by in-layer strain, including a semiconductor-to-metal transition, we postulate that origami-style folded phosphorene should display an unprecedented richness in its electronic behavior.

[1]. H. Liu et al. ACS Nano 8 (2014)

[2]. Z. Zhu and D. Tomanek, Phys. Rev. Lett. (2014)

Polygonal nanotubes of multi-phase layered phosphorus

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Similar to graphite, black phosphorus is a layered structure that can be exfoliated to monolayers dubbed phosphorene^[1] Similar to carbon nanotubes, which are related to few-layer graphene, we propose the existence of phosphorus nanotubes formed of phosphorene. Different from graphite, besides the black allotrope, layered phosphorus has three stable structural phases, called blue-P^[2], γ -P and δ -P, which can be connected naturally. The fact that connected structures do not lie in a plane allows us to design nanotubes by connecting laterally nanoribbons of different phases. Unlike single-phase nanotubes consisting of a layer rolled up to a cylinder, multi-phase phosphorene nanotubes will have a polygonal cross-section, as shown in Fig. 1. Both single-wall and multi-wall phosphorene nanotubes may be constructed in this way. The availability of more than one structural phase offers much larger structural richness than the carbon counterpart with one single phase. Consequently, we find that the electronic properties of phosphorene nanotubes depend not only on the chiral vector that defines the edge structure, but also the presence of the individual phosphorene phases. In analogy to the successful synthesis of carbon nanotubes by ball milling of graphite, we believe that phosphorene nanotubes may be formed in the same way in an inert atmosphere.

[1]. H. Liu et al. ACS Nano 8 (2014)

[2]. Z. Zhu and D. Tomanek, Phys. Rev. Lett. (2014)

Adsorption of NH₃ and BH₃ on the Surface of Boron Nitride Nanotubes – A DFT Study

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Adsorption of NH₃ and BH₃ on the surface of different boron nitride single-wall nanotubes (BNNTs) have been investigated using density functional theory (DFT-B3LYP). The optimized geometries and density difference plots are obtained using 6-31+G* basis set and the characterization techniques such as Infra-red (IR) studies, X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance studies (NMR) were determined using 6-31G* basis functions. Adsorption sites and chemisorption energies of NH₃ and BH₃ on the BNNTs surface depends on the chirality of BNNT. Electron deficient BH₃ forms stronger chemisorbed complex than NH₃. As expected, about 0.3e charge is transferred from NH₃ to BN nanotube and it is confirmed by the density difference plot. However, electron density gain or loss by BNNT depends on the structure of BH₃-BNNT complexes. Major changes in B(1s) and N(1s) binding energies and chemical shifts of 11B and 15N are found at the vicinity of adsorption sites, and these theoretical results may be useful in characterizing such complexes experimentally.