

Designing multifunctional chemical sensors using Ni and Cu doped carbon nanotubes

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We demonstrate a “bottom up” approach to the computational design of a multifunctional chemical sensor. General techniques are employed for describing the adsorption coverage and resistance properties of the sensor based on density functional

theory and non-equilibrium Green’s function methodologies, respectively. Specifically, we show how Ni and Cu doped metallic (6,6) single-walled carbon nanotubes may work as effective multifunctional sensors for both CO and NH₃.

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1 Introduction Detecting specific chemical species at small concentrations is of fundamental importance for many industrial/scientific processes, medical applications, and environmental monitoring [1]. Nanostructured materials are ideally suited for sensor applications because of their large surface to volume ratio, making them sensitive to the adsorption of individual molecules. Specifically, single-walled carbon nanotubes (SWNTs) [2] work remarkably well as detectors for small gas molecules, as demonstrated for both individual SWNTs [3–8] and SWNT networks [9, 10]. Previous studies have shown that SWNTs are highly sensitive to most molecules upon functionalization [11–19]. However, the difficulty is determining which specific molecules are present. In this study, we show how changing the functionalization provides “another handle” for differentiating the SWNTs’ response to different gases/molecules.

Recent experimental advances now make the controlled doping of chirality selected SWNTs with metal atoms a possibility. Specifically, these include (1) photoluminescence, Raman, and XAS techniques for measuring the fraction of various SWNT chiralities in an enriched sample [20–22]; (2) the separation of SWNT samples by chirality using DNA wrapping [23–25], chromatographic separation

[26, 27], and density gradient ultracentrifugation (DGU) [28]; (3) SWNT resonators for measuring individual atoms of a metal vapor which adsorb on a SWNT [29, 30]; and (4) the next generation of monochromatic aberration corrected low energy ($\lesssim 50$ kV) transmission electron microscopes (TEMs) [31, 32]. The latter will provide control over the formation of defects *in situ* by adjusting the energy of the electron beam above and below the threshold energy for defect formation at a specific location in the SWNT. Combined with the strong binding energies of Ni and Cu in SWNT and graphene vacancies [13, 19, 33], it may soon be possible to take a specific SWNT chirality and dope the structure with individual metal atoms at a chosen location by “electron-beam engineering.”

At the same time, theorists are now able to embrace a “bottom up” approach to the design of nanosensors, harnessing the thermodynamics of self-assembly to find useful sensing systems *in silico*. With recent advances in both computational power and methodologies, theorists can now efficiently and accurately screen hundreds of candidate sensor designs using a combination of density functional theory (DFT) for energetics of adsorption and stability, and non-equilibrium Green’s function (NEGF) methodologies for the electrical response [33].

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In general, any nanosensing system consists of the following four main components: (1) a “target molecule” to be detected, (2) an “active site” where the target molecule may adsorb on the sensor, (3) a property of the sensor which changes upon adsorption of the target molecule, and (4) a “background” of adsorbing molecules which make up the background signal, as depicted in Fig. 1. For the sensor to be effective, the active site must be designed so that adsorption of the target molecule in the presence of the background is sufficient to change the sensing property.

In this study, we shall consider Ni and Cu doped metallic (6,6) SWNTs as our active sites, specifically when Ni replaces two C atoms in a divacancy structure, and Cu replaces a single C atom in the monovacancy structure, as shown schematically in Fig. 2. Of the two possible orientations for a divacancy in an armchair SWNT, we here consider the one in which Ni adsorption has been shown to be more favorable. These two active sites have previously been shown to be both stable, and somewhat resistant to oxidation under standard atmospheric pressure and room temperature [33]. As such, we shall consider the background to have a standard atmospheric composition with an absolute humidity of 4%, shown in Table 1.

2 Methodology All DFT calculations have employed the PBE exchange correlation (XC)-functional [34]. Adsorption energies and structural minimization calculations have been performed using the real-space projector-augmented-wave method DFT code GPAW [35], with a grid spacing of 0.2 Å, taking spin polarization into account. NEGF transport calculations [36] have employed the electronic Hamiltonian obtained from the DFT code SIESTA [37], with a double zeta polarized (DZP) localized basis set.

Vacancies in the (6,6) metallic carbon nanotube have been modeled using six repeated minimal unit cells, with a supercell of $15 \text{ \AA} \times 15 \text{ \AA} \times 14.622 \text{ \AA}$. Such a large supercell was necessary to both minimize interactions between defects and adsorbates and to ensure the Hamiltonian of the nanotube layers adjacent to the cell boundaries was converged to within 0.1 eV of that for the pristine nanotube. For such a large supercell, a Γ -point calculation was found

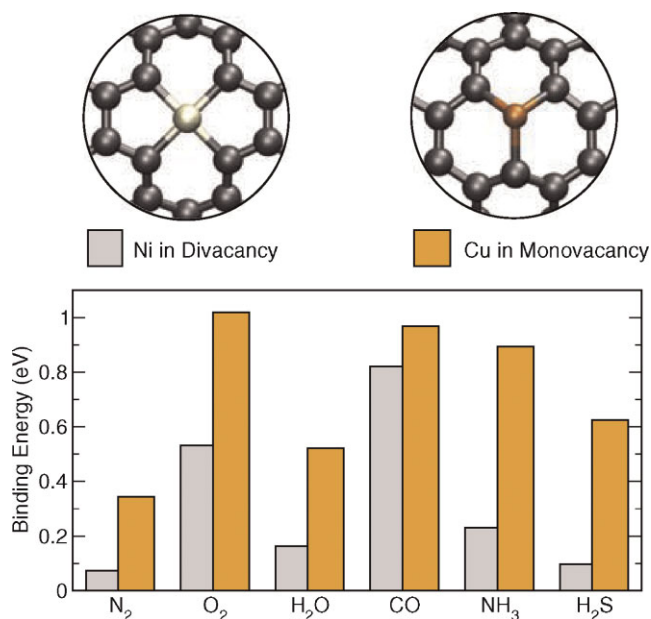


Figure 2 (online color at: www.pss-b.com) Binding energies in eV for N₂, O₂, H₂O, CO, NH₃, and H₂S on a Ni atom occupying a divacancy site (gray) and on a Cu atom occupying a monovacancy site (orange) in a (6,6) carbon nanotube. Schematics of the two active sites are shown above.

sufficient to obtain convergence of adsorption energies with respect to k -point sampling.

Binding energies E_{bind} are defined as the difference in total energies between a gas phase target/background molecule with a clean active site and a target/background molecule adsorbed on an active site. As seen in Fig. 2, CO has a strong binding energy to both active sites, while NH₃ binds only to Cu in a monovacancy site. We shall use this in our design of a multifunctional sensor for CO and NH₃.

3 Results and discussion For a sensor containing hundreds, if not thousands of sites, the fractional coverage of sites is reasonably described by the fractional coverage in thermodynamic equilibrium θ at standard temperature and pressure in terms of the target molecule concentration. Specifically for a sufficiently large ensemble of active sites, the fractional coverage of sites by a given adsorbate

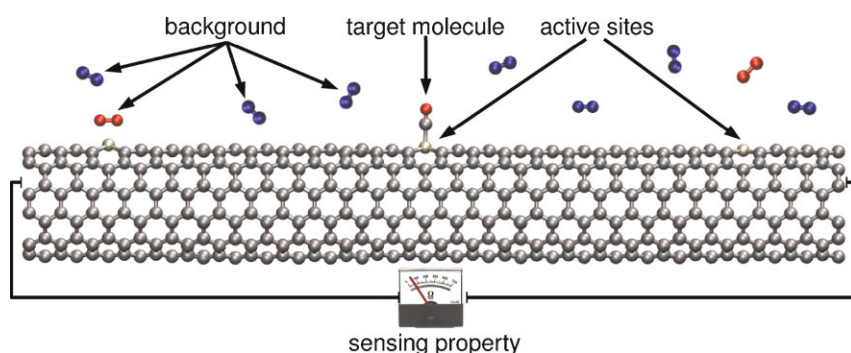


Figure 1 (online color at: www.pss-b.com) Schematic of a chemical sensor consisting of active sites (metal dopants in a (6,6) carbon nanotube), a target molecule (CO), a background (atmospheric air), and a sensing property (resistance).

Table 1 Equilibrium atmospheric concentrations at 4% absolute humidity.

background	concentration (%)	target	concentration (ppb)
N ₂	74.96	CO	96.00
O ₂	20.11	NH ₃	16.32
H ₂ O	4.00	H ₂ S	0.96

X in a background set of molecules \mathcal{B} at equilibrium is given by

$$\Theta[X] = \frac{K[X]C[X]}{1 + \sum_{Y \in \mathcal{B}} K[Y]C[Y]}, \quad (1)$$

where $K = k_+/k_-$ is the ratio of forward and backward rate constants for the adsorption reaction. This may be expressed as

$$K[X] = \exp \left[\frac{E_{\text{bind}}[X] - TS_{\text{gas}}[X]}{k_B T} \right], \quad (2)$$

where $S_{\text{gas}}[X]$ is the gas phase entropy of species X [38], k_B is Boltzmann's constant, and T is the temperature.

In Fig. 3, we see the coverages of both Ni and Cu active sites as a function of CO and NH₃ concentration. Clearly, both Cu and Ni active sites will be sensitive to the adsorption of CO. On the other hand, the coverage of the Cu active sites is sensitive to NH₃ concentration, while Ni active sites are not. This suggests that by combining the response of Cu and Ni active sites, we may obtain a multifunctional sensor for both CO and NH₃.

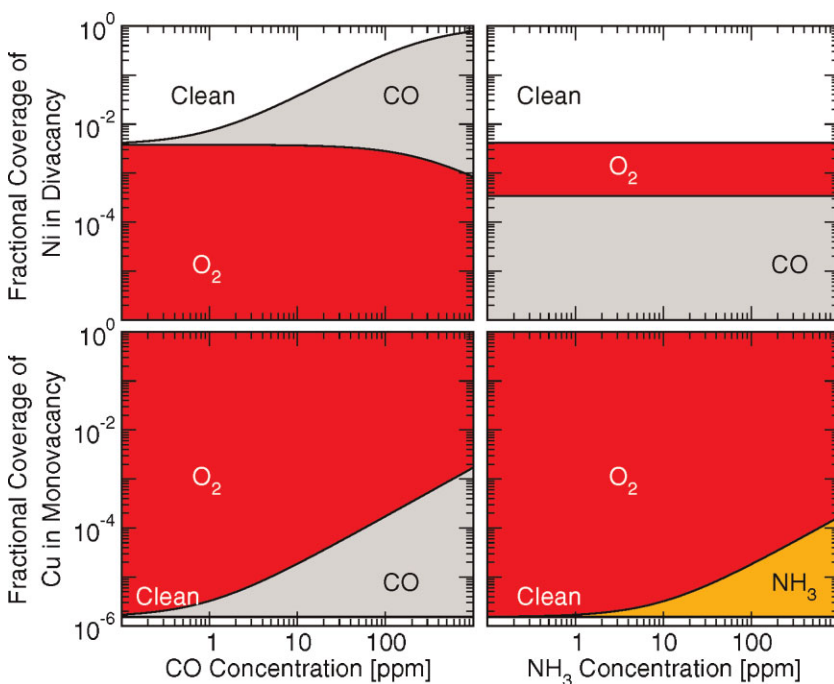


Figure 3 (online color at: www.pss-b.com) Fractional coverage in thermal equilibrium of Ni in a divacancy (top) and Cu in a monovacancy (bottom) versus CO concentration (left) and NH₃ concentration (right) in a background of air at room temperature and 1 bar of pressure.

However, although molecules may adsorb on the active sites, the sensing property of the SWNT resistance must change significantly for the sensor to be useful. In Fig. 4, we show both the density of states (DOS) and transmission probability $T(\epsilon)$ for an electron of a given energy ϵ to travel past an active site as calculated within the NEGF method. Since the energy levels of a given molecule may be thought of as its electronic “finger print,” so long as there is sufficient binding between the molecule and active site, this “finger print” is evidenced in the DOS of the system. Furthermore, the peaks of the DOS due to the molecule tend to form Fano anti-resonances in the transmission, as electrons are scattered off these states (cf. Fig. 4). In this way, any adsorbed molecule tends to leave its “finger print” in the transmission probability through an active site. For this reason, conductance/resistance is generally an effective sensing property.

Finally, we may estimate the average change in resistance ΔR of an active site as a function of target molecule concentration. As discussed in Ref. [33], this change in resistance is reasonably well described by

$$\Delta R \approx \sum_X R_s(X) (\Theta[X, C] - \Theta[X, C_0]), \quad (3)$$

where C is the concentration, C_0 is the concentration at standard temperature and pressure, $R_s(X) = G_0(1/T(\epsilon_F, X) - 1/2)$, $G_0 \equiv 2e^2/h$, is the quantum of conductance, and $T(\epsilon_F, X)$ is the transmission probability at the Fermi level through an active site with species X adsorbed.

In Fig. 5, we show ΔR for a single active site (Ni or Cu) as a function of target molecule concentration (CO or NH₃). Keeping in mind that a change in concentration from 1 to 50 ppm amounts to a change from allowable to

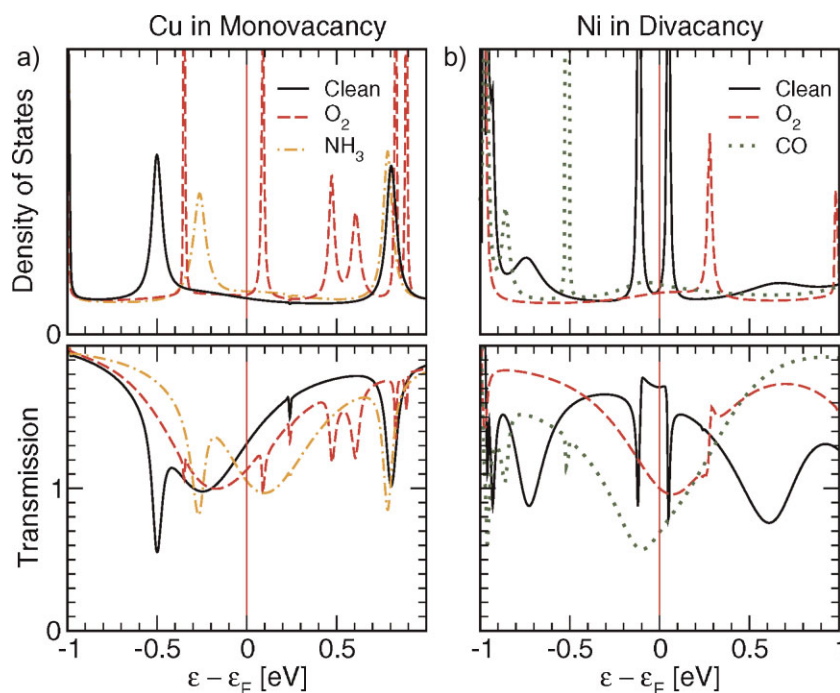


Figure 4 (online color at: www.pss-b.com) Density of states (top) and transmission function (bottom) versus energy ε relative to the Fermi level ε_F in eV for clean (solid line; black), O_2 occupied (dashed line; red), NH_3 occupied (dash-dotted line; orange), and CO occupied (dotted line; green) (a) Cu in monovacancy and (b) Ni in divacancy II of a (6,6) carbon nanotube.

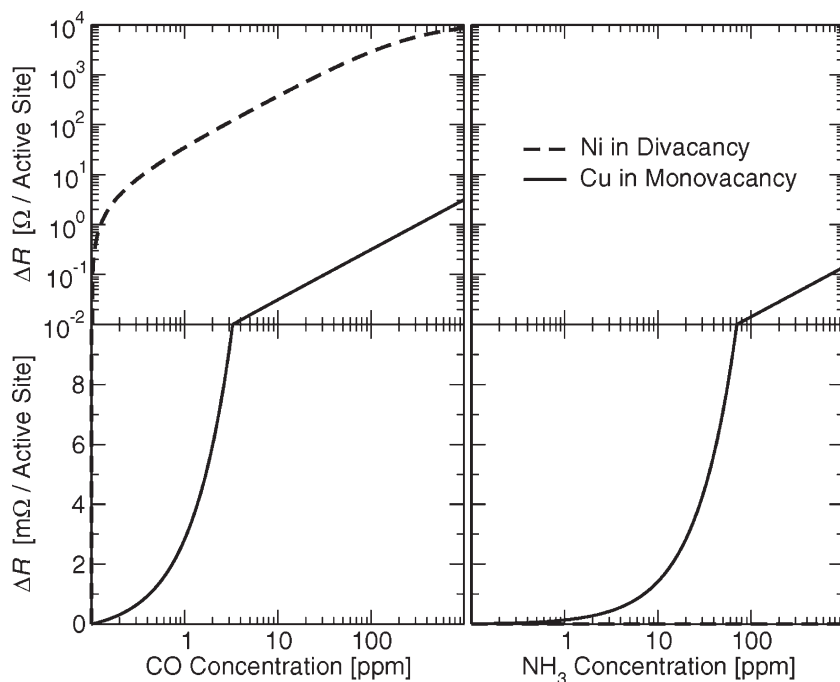


Figure 5 Change in resistance ΔR in Ω (top) and $m\Omega$ (bottom) per active site versus CO (left) and NH_3 (right) concentration in ppm for Ni in a divacancy II (dashed line) and Cu in a monovacancy (solid line) of a (6,6) carbon nanotube. The reference concentrations of CO and NH_3 are 0.1 and 0.01 ppm, respectively, in a background of air at room temperature and 1 bar of pressure.

toxic concentrations for both CO and NH_3 , we see that this sensor design should work effectively for both target molecules.

4 Conclusions In conclusion, we have demonstrated *in silico* how a combined Cu and Ni doped metallic SWNT device may work effectively as a multifunctional sensor for both CO and NH_3 . The methodology employed is applicable

to other sensor designs and different environments. Also, by varying the metal dopant, we obtain “another handle” for tuning the sensitivity of our sensor.

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