Electronic transport in defective carbon nanotubes functionalized with gold clusters on CO gas exposure

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Abstract. We investigate the time-dependent electronic transport in single-walled carbon nanotubes (SWCNTs) functionalized with Au clusters during CO gas adsorption. Using a tight-binding Hamiltonian and the nonequilibrium Green’s function (NEGF) formalism the time-dependent zeroth and first order contributions to the current are calculated. The zeroth order contribution is identified as the time-dependent Landauer formula in terms of the slow time variable, whereas the first order contribution is found to be small. The conductance is explicitly evaluated by considering a form for the hopping integral which accounts for the effect of dopants on the charge distribution and the carbon-carbon distance. The effect of dopants is also studied in terms of fluctuations by calculating the autocorrelation function for the experimental and theoretical data. These calculations allow direct comparison with the experiment and demonstrate how the presence of dopants modifies the experimentally measured conductance of the SWCNT and provide the only study of fluctuations in the sensor response in terms of the autocorrelation function.
1. Introduction

Since the discovery of carbon nanotube (CNT) in 1991 [1], CNT has achieved a special identity in the field of nanoscience. CNT has emerged as a promising nanostructure material with a range of extraordinary properties [2]. The unique 1D structure of SWCNTs gives rise to electrical and chemical properties that have led to keen interest in many research communities and sensor industries. This has led to the development of CNT-based chemical sensors that can result in many societal benefits and daily life applications ranging from healthcare, environment to industry. The chemical sensing capabilities of CNT sensors can be improved by their functionalization. Studies have shown CNTs functionalized with metal nanoparticles (NPs) exhibit unique sensitivity toward various gases [3, 4, 5, 6, 7, 8, 9, 10]. It is observed that the sensing capability of metal NP-decorated CNTs is based on the changes in their electronic properties induced by charge transfer from gas molecules upon adsorption on the NP surface. Such changes can be easily detected by measuring electron current signals, and these properties make CNTs a miniature sensor sensitive to their chemical environment. Despite path breaking experiments on CNTs for gas sensing applications [3, 4, 5, 6, 7, 8, 9, 10], the underlying mechanism of gas detection in experiments still needs to be understood properly.

This work is focused on the theoretical understanding of the electronic transport in Au functionalized SWCNT during CO gas adsorption. The work addresses how the functionalization of SWCNTs with Au$_{20}$ cluster affects their electronic transport properties when used for CO gas detection. Electronic transport in such systems is divided into stationary and time-dependent phenomena. The results of stationary transport in low-dimensional systems using the nonequilibrium Green’s function (NEGF) formalism have been reported in the literature [11, 12, 13, 14]. Wingreen et al. [15] introduced a general formulation for time-dependent transport through mesoscopic structures by applying external time-dependent voltages. Kienle et al. [16] studied the time-dependent quantum transport through a ballistic CNT transistor in the presence of a time harmonic signal, while Hernandez et al. [17] presented their study of time-dependent electronic transport through a quantum dot using the NEGF formalism. But these studies have never dealt with functionalized CNT sensors. The present work distinguishes from previous studies [15, 16, 17] in that an analytical treatment is chosen to study the sensing behaviour of the functionalized CNTs. In this work, the time-dependence arises because of the interaction of CO molecules with the Au-SWCNT at each instant of time, not because of externally applied time-dependent potentials. The microscopic understanding of the experiment [10], i.e., the sensor response of the Au-decorated SWCNT as a function of CO gas exposure time involves building up a theoretical model of the Au-SWCNT to study its electronic transport properties, and develop a connection between the theoretical predictions and experimental observations.

The experiment was performed for many Au clusters (of different dimensions) with 30 minutes of exposure to 2500 ppm CO gas at room temperature and a bias voltage of 0.5V [10]. To model the electronic transport through the Au-SWCNT system on CO
adsorption, the calculations are performed for a defective (14,0) SWCNT decorated with a Au$_{20}$ cluster. The model considered in the calculations is based on the tight-binding (TB) Hamiltonian which describes electrons in SWCNT. The Au$_{20}$-SWCNT system is a nonequilibrium system because of the different chemical potentials on the left and right electrodes and the interaction of CO molecules with the Au-SWCNT complex at different times. Thus, we use the NEGF formalism to study the electronic transport in the system. In this formalism, we consider two time scales, a slow time scale ($\tilde{t}$) of the CO gas flow and a fast time scale ($t - t'$) of electron transport inside the SWCNT. Hence, an adiabatic expansion with respect to $\tilde{t}$ and Fourier transform with respect to ($t - t'$) are made in the calculations to compute the current. The zeroth order current is identified as the time-dependent Landauer formula in terms of $\tilde{t}$, whereas there is a first order contribution which is found to be small for this system. We derive an explicit formula for the transmission function and calculate the conductance in terms of the time-dependent hopping integral. The sensor response is explicitly calculated and compared with the experiment by choosing a form for the hopping integral which includes the effect of the Au and CO molecules on the conductance of the carbon nanotube. Our theoretical result is in agreement with the experimental result. As far as we know, there has not been much effort to microscopically model the functionalized CNT sensors to study the time-dependent quantum transport. The autocorrelation function (ACF) is also calculated using the conductance formula and the experimental data to study the fluctuations in the sensor response. Hence, this manuscript represents an important contribution to the field.

2. Tight-binding model and its operation

Figure 4(d) of [10] shows the adsorption configuration of nine CO molecules attached to an Au$_{20}$ cluster on a semiconducting (14,0) SWCNT with a missing carbon atom defect. The adsorption configuration demonstrates that the Au atoms of the cluster affect only a few nearest-neighbour carbon atoms of the defective SWCNT. As the changes in conductance are due to the Au cluster and the nearest-neighbour carbon atoms, we present a tight-binding model of the Au$_{20}$-SWCNT system (C) sandwiched between two semi-infinite (14,0) left (L) and right (R) nanotube electrodes as shown in figure [11]. In this model, we consider only four nearest-neighbour carbon atoms $A_1$, $B_1$, $B_2$ and $A_3$ which are affected by the cluster ‡ (the missing carbon atom site $A_2$ is occupied by the Au atom) and present a simplified picture of the model and its operation. As a result, the “effective length” of the nanotube which is involved in transport is a few nanometers.

The operational principle of the model is based on the changes in its conductance when the Au$_{20}$-SWCNT system is exposed to CO gas for 30 minutes. On exposure to CO gas a CO molecule interacts with the Au$_{20}$ cluster at an instant of time $\tilde{t}_1$

‡ If we consider more carbon atoms that are beyond the nearest-neighbour Au cluster then there will be no significant change in the result as only these four nearest-neighbour carbon atoms contribute to the changes in the conductance.
which affects the hopping of electrons from the π orbital of one carbon atom \( A_1 \) to the neighbouring carbon atom \( B_1 \). Tunnelling of the electron from \( A_1 \) to \( B_1 \) is an elastic process with the corresponding integral referred to as the hopping integral \( \gamma_{11}(\tilde{t}_1) = \gamma_0 \) (the hopping integral of pristine SWCNT). Then, the electron hops from \( B_1 \) to \( A_2 \) (Au) with the hopping integral \( \gamma_{12}(\tilde{t}_1) \), from \( A_2 \) to \( B_2 \) with \( \gamma_{22}(\tilde{t}_1) \), from \( B_2 \) to \( A_3 \) with \( \gamma_{23}(\tilde{t}_1) = \gamma_0 \), figure 1. In a similar way, the hopping integral changes when other CO molecules interact with the Au\(_{20}\) cluster at the next instants of time \( \tilde{t}_2, \tilde{t}_3, \ldots, \tilde{t}_n \) where \( n \) denotes the number of CO molecules interacting with the Au\(_{20}\)-SWCNT system. This is how the time-dependence arises here. The time-dependent hopping integral leads to time-dependent Hamiltonian and Green’s functions for the SWCNT. Thus, to study time-dependent transport through such a nano-hybrid model the time-dependent NEGF formalism is well suited.

3. Nonequilibrium Green’s function formalism

Wingreen et al. \[15\] have studied the time-dependent electronic transport through a small interacting region connected to two non-interacting leads using the NEGF formalism where the time-dependence arises because of externally applied time-dependent voltages. In the present model system, figure 1, the time-dependence arises because of the interaction of different CO gas molecules with the Au\(_{20}\)-SWCNT system at different times. We start with the general expression for the time-dependent current, equation (6) of \[15\] and modified it according to the present TB model. The time-dependent current flowing from the left/right electrode into the SWCNT is

\[
I_{L/R}(t) = -\frac{2e}{\hbar} \int_{-\infty}^{t} dt' \int \frac{d\varepsilon}{2\pi} \text{Tr}\left\{ e^{i\varepsilon(t-t')} \Gamma_{L/R}[G_C^r(t, t') + f_{L/R}(\varepsilon)G_C^a(t, t')] \right\},
\]

where \( G_C^r(t, t') = i \int dt_1 \int dt_2 G_C^r(t, t_1) \left[ \sum_{L,R} \int \frac{d\varepsilon}{2\pi} e^{i\varepsilon(t_2-t_1)} f_{L/R}(\varepsilon) \right] G_C^a(t_2, t') \) is the lesser Green’s function of the SWCNT, \( G_C^{r,a} \) are the retarded and advanced Green’s functions and \( f_{L/R}(\varepsilon) = \frac{1}{\sqrt{2\pi}} \) are the Fermi distribution functions in the left (L) and right (R) electrodes. Here the coupling functions \( \Gamma_{L/R}(\varepsilon) = 2\pi \sum_{\alpha,n} \rho_{\alpha,n} V_{\alpha,n} V_{\alpha,n}^* \) are considered to be energy and time-independent. In this model, we have a slow time scale \( \tilde{t} = (t + t')/2 \) of the CO gas flow (minutes) and a fast time scale \( t - t' \) of electron transport inside the SWCNT (\( \sim 10^{-15} \text{ s} \sim 10^{-17} \text{ s} \)). So we expand equation (1) by expanding the Green’s function up to linear order in the slow time variable \( \tilde{t} \) using adiabatic expansion \[14\] \[17\]. Then, taking the Fourier transform with respect to the fast time variable \[17\] we find that the zeroth and first order contributions to the total current in terms of \( \tilde{t} \) is \( I(\tilde{t}) = I^{(0)}(\tilde{t}) + I^{(1)}(\tilde{t}) \) with the Green’s functions:

\[
G^{r,a}(t-t', \tilde{t}) = G^{(0)r,a}(t-t', \tilde{t}) + G^{(1)r,a}(t-t', \tilde{t}),
\]

where \( G^{(0)r,a}(t-t', \tilde{t}) = G^{r,a}(t-t', \tilde{t}) \) and \( G^{(1)r,a}(t-t', \tilde{t}) = (t-t') \frac{dG^{r,a}(t-t', \tilde{t})}{dt} \) are the zeroth and first order Green’s functions. After taking the Fourier transform with respect to \( t - t' \) the Green’s functions become \( G^{r,a}(\varepsilon, \tilde{t}) = G^{(0)r,a}(\varepsilon, \tilde{t}) + G^{(1)r,a}(\varepsilon, \tilde{t}). \)

\* as (i) the time-dependence arises as different number of CO molecules interact with the Au\(_{20}\)-SWCNT complex at different times and (ii) the applied potential is time-independent.
Electronic transport in carbon nanotubes decorated with gold clusters

The time-dependent Green’s function for the complete electrode-(Au$_{20}$-SWCNT)-
electrode system, figure 1 is given by $G(\epsilon, \bar{t}) = [\epsilon - H(\bar{t})]^{-1}$, where $\epsilon = \epsilon \pm i \eta$ with $i \eta$ an infinitesimal imaginary term. $H(\bar{t})$, the Hamiltonian at time $\bar{t}$ corresponding to the 
Au$_{20}$-SWCNT system and the two SWCNT electrodes L and R is given by

\[
H(\bar{t}) = \begin{pmatrix}
H_L & h_{LC} & 0 \\
h_{LC}^\dagger & H_C & h_{CR} \\
0 & h_{CR}^\dagger & H_R
\end{pmatrix},
\]

(2)

where $H_{[L,R]}$ are the electrode Hamiltonians and $H_C$ is the time-dependent TB Hamiltonian for the SWCNT with matrix elements: $H_{A_iA_i} = \varepsilon_{A_i}(\bar{t})$, $H_{B_iB_i} = \varepsilon_{B_i}(\bar{t})$, on-site energy and $H_{A_iB_i} = H_{B_iA_i} = \gamma_{ii}(\bar{t})$ [2], $H_{B_{i+1}A_i} = \gamma_{i,i+1}(\bar{t})$, hopping integrals. $h_{LC}$ and $h_{CR}$ are the coupling matrices between the left, right electrodes and the SWCNT.

Using the Hamiltonian $H_C(\bar{t})$ the time-dependent nonequilibrium retarded and advanced Green’s functions for the SWCNT can be derived as $G_{C,a}^{r,a}(\epsilon, \bar{t}) = [\epsilon - H_C(\bar{t}) - \Sigma_L - \Sigma_R]^{-1}$, where $\Sigma_L = h_{LC}^\dagger g_L(\epsilon, \bar{t}) h_{LC}$ and $\Sigma_R = h_{CR}^\dagger g_R(\epsilon, \bar{t}) h_{CR}^\dagger$ are the self-energy terms due to left and right electrodes with $g_{[L,R]}(\epsilon, \bar{t}) = [\epsilon - H_{[L,R]}(\bar{t})]^{-1}$ the Green’s functions of the electrodes.

4. Results and discussion

4.1. Zeroth order time-dependent Green’s function for the SWCNT

For the Hamiltonian $H_C(\bar{t})$, we explicitly calculate the zeroth order time-dependent retarded Green’s function in a $5 \times 5$ matrix form

\[
G_C^{0,r}(\epsilon, \bar{t}) = \begin{pmatrix}
\varepsilon - \varepsilon_{A_1} - \Sigma_L & \gamma_0 & 0 & 0 & 0 \\
\gamma_0 & \varepsilon - \varepsilon_{B_1}(\bar{t}) & \gamma_{12}(\bar{t}) & 0 & 0 \\
0 & \gamma_{12}(\bar{t}) & \varepsilon - \varepsilon_{A_2}(\bar{t}) & \gamma_{22}(\bar{t}) & 0 \\
0 & 0 & \gamma_{22}(\bar{t}) & \varepsilon - \varepsilon_{B_2}(\bar{t}) & \gamma_0 \\
0 & 0 & 0 & \gamma_0 & \varepsilon - \varepsilon_{A_1} - \Sigma_R
\end{pmatrix}^{-1}.
\]

(3)

Here we assume that the coupling to the electrodes effectively gives rise to a finite imaginary term in the self-energies which is larger than $i \eta$ [12] at all times. Therefore, we drop the term $i \eta$ in the Green’s function matrix for the SWCNT. The self-energy terms $\Sigma_{[L,R]}$ are related to the coupling functions hence are also energy and time-independent.

4.2. Zeroth order time-dependent Landauer formula

The zeroth order Green’s functions ($G_{C,a}^{0,r,a}$) give the zeroth order current. Applying the adiabatic expansion to equation [11] the expression for the zeroth order current is

\[
I_{L/R}^{(0)}(t - t', \frac{t + t'}{2}) = -\frac{2e}{\hbar} \int_{-\infty}^{t} dt' \int \frac{d\varepsilon}{2\pi} \text{Im} \text{Tr} \left\{ e^{i\varepsilon(t-t')} \Gamma_{L/R} \left[ 1 \int dt_1 \int dt_2 G_{C}^{(0)r}(t - t_1, \frac{t + t_1}{2}) \right] \right\}.
\]
After taking the Fourier transform and using \( I^{(0)}(\tilde{t}) = x I^{(0)}_{L} - (1 - x) I^{(0)}_{R} \) with \( \Gamma_L = \lambda \Gamma_R \) and fixing the arbitrary parameter \( x = 1/(1 + \lambda) \), where \( \lambda \) is the constant of proportionality \[14\], a simple expression for the total current through the SWCNT is derived as

\[
I^{(0)}(\tilde{t}) = \frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} Tr(\Gamma_L G_C^{(0)r}(\varepsilon, \tilde{t}) \Gamma_R G_C^{(0)a}(\varepsilon, \tilde{t})) [f_L(\varepsilon) - f_R(\varepsilon)],
\]

where \( I^{(0)}(\tilde{t}) \) is identified as the Landauer formula \[11, 14, 18\] that depends on the slow time variable with \( T(\varepsilon, \tilde{t}) = Tr(\Gamma_L G_C^{(0)r}(\varepsilon, \tilde{t}) \Gamma_R G_C^{(0)a}(\varepsilon, \tilde{t})) \) the transmission function of the system and \( \Gamma_{\{L,R\}} = i[\Sigma_{\{L,R\}} - \Sigma_{\{L,R\}}^\dagger] \) describe the electrode-SWCNT coupling. Considering only the first element of the \( \Gamma_L \) matrix \( (\Gamma_{L,11}^{(0)}(\tilde{t})) \) and the last element of the \( \Gamma_R \) matrix \( (\Gamma_{R,55}^{(0)}(\tilde{t})) \) the transmission function is found to depend only on one off diagonal element of the \( G_C(\varepsilon, \tilde{t}) \) matrix \( (G_C^{(0)r,a}(\varepsilon, \tilde{t})) \) and is given by

\[
T(\varepsilon, \tilde{t}) = \Gamma_{L,11}^{(0)}(\tilde{t}) G_{C15}^{(0)}(\varepsilon, \tilde{t}) \Gamma_{R,55}^{(0)}(\tilde{t}) G_{C15}^{(0)*}(\varepsilon, \tilde{t}).
\]

To derive an explicit expression for the conductance, we consider linear response \[12\] as the experiment is performed with low bias. In linear response, equation \[5\] becomes \( \delta I^{(0)}(\tilde{t}) = \frac{e}{\hbar} \int \frac{d\varepsilon}{2\pi} T(\varepsilon, \tilde{t}) \delta [f(\varepsilon - \mu_L) - f(\varepsilon - \mu_R)] \) where \( \mu_{\{L,R\}} \) are the chemical potentials associated with the left and right electrodes \[12\]. This equation leads to the conductance given by: \( G^{(0)}(\tilde{t}) = \frac{\delta I^{(0)}(\tilde{t})}{(\mu_L - \mu_R)/e} = \frac{e^2}{\hbar} \int \frac{d\varepsilon}{2\pi} T(\varepsilon, \tilde{t}) (\frac{\delta f}{\delta \varepsilon}) = \frac{e^2}{\hbar} T(\varepsilon_f, \tilde{t}) \) on using \( \delta [f(\varepsilon - \mu_L) - f(\varepsilon - \mu_R)] = (\mu_L - \mu_R)(\frac{\delta f}{\delta \varepsilon}) \) and \( (\frac{\delta f}{\delta \varepsilon}) = \delta(\varepsilon_f - \varepsilon) \) where \( \varepsilon_f \) is the Fermi energy.

To calculate the transmission function we use \( \Gamma_{L,11}^{(0)}(\tilde{t}) = -2Im(\Sigma_{L,11}(\tilde{t})) = -2Im \Sigma_L(\tilde{t}) \) and \( \Gamma_{R,55}^{(0)}(\tilde{t}) = -2Im(\Sigma_{R,55}(\tilde{t})) = -2Im \Sigma_R(\tilde{t}) \), and the explicit value of \( G_{C15}^{(0)r,a}(\varepsilon, \tilde{t}) \) can be obtained from equation \[3\]. Hence the expression for the transmission function for the Au20-SWCNT system in the presence of CO molecules is derived as

\[
T(\varepsilon_f, \tilde{t}) = \frac{4 Im \Sigma_L Im \Sigma_R \gamma_0^2 \gamma_2^2(\tilde{t}) \gamma_0^2}{|G_C^{(0)r}(\varepsilon_f, \tilde{t})|^2_{5 \times 5}}.
\]

Equation \[6\] gives an explicit formula for the transmission function indicating the dependence of the transmission function and conductance on the time-dependent hopping integrals and on-site energies.

4.3. First order contribution to the current

Using the adiabatic expansion and substituting the equation for \( G_C^{(1)}(\varepsilon, \tilde{t}) \) we also derive the first order contribution to the current

\[
I^{(1)}_{L/R}(t - t', \tilde{t}) = -\frac{2e}{\hbar} \int_{-\infty}^{t} dt' \int \frac{d\varepsilon}{2\pi} Im Tr \left\{ e^{i\varepsilon(t - t')} \left[ \Gamma_{L/R}(t) \int dt_1 \int dt_2 G_C^{(0)r}(t - t_1, \tilde{t}) \right] \right\}.
\]
Taking the Fourier transform the expression for the first order current becomes

\[
\times \sum_{L,R} \left\{ \frac{d\varepsilon}{2\pi} e^{i\varepsilon(t_2-t_1)} f_{L/R}(\varepsilon) \Gamma_{L/R} G_C^{(1)a}(t_2-t',\bar{t}) + \int dt_1 \int dt_2 G_C^{(1)r}(t-t_1,\bar{t}) \right. \\
\left. \times \sum_{L,R} \frac{d\varepsilon}{2\pi} e^{i\varepsilon(t_2-t_1)} f_{L/R}(\varepsilon) \Gamma_{L/R} G_C^{(0)a}(t_2-t',\bar{t}) + \Gamma_{L/R} f_{L/R}(\varepsilon) \right. \\
\left. \times G_C^{(1)r}(t-t',\bar{t}) \right\}. 
\] (7)

Taking the Fourier transform the expression for the first order current becomes

\[
I_{L/R}^{(1)}(\bar{t}) = -\frac{e}{\hbar} \text{Im} \text{Tr} \left\{ \Gamma_{L/R} \left[ i \sum_{L,R} \frac{d\varepsilon}{2\pi} f_{L/R}(\varepsilon) \left( G_C^{(0)r}(\varepsilon,\bar{t}) \Gamma_{L/R} G_C^{(1)a}(\varepsilon,\bar{t}) + G_C^{(1)r}(\varepsilon,\bar{t}) \right) \right. \\
\left. \times \Gamma_{L/R} G_C^{(0)a}(\varepsilon,\bar{t}) \right] + \int \frac{d\varepsilon}{2\pi} f_{L/R}(\varepsilon) \Gamma_{L/R} G_C^{(1)r}(\varepsilon,\bar{t}) \right\}. 
\] (8)

The contribution of equation (8) is small compared to \( I^{(0)}(\bar{t}) \) as \( G_C^{(1)r,a}(t-t',\bar{t}) \sim (t-t')^{15} \) and the fast time variable \( t-t' \sim 10^{-15} \text{ s} - 10^{-17} \text{ s} \). Therefore, we have not included the first order contribution to the final result. Hernandez et al. \cite{17} have also calculated the time-dependent zeroth and first order contributions to the current for a quantum dot where they have found a relevant contribution of the first order term. Hence, there could be future experiments in which the first order term is enhanced (e.g., when \( \frac{\partial G_C^{r,a}}{\partial \varepsilon} \sim 1/(t-t') \)) and equation (8) becomes significant.

\subsection*{4.4. Theory and Experiment}

To compare theory and experiment we explicitly calculate the average values of the normalized conductance \( \langle G^{(0)}(\bar{t}) / G_0 \rangle \) for Au clusters with CO molecules where \( G_0 \) is the conductance for the bare system for a 5 × 5 matrix using equation (6). The hopping integral is defined as \( \gamma = \langle \varphi_A(r-R_A)|H_C|\varphi_B(r-R_B) \rangle \), where \( \varphi_A \) and \( \varphi_B \) are the atomic wavefunctions of the carbon atoms A and B, and \( R_{A(B)} \) are their position vectors. Using the standard wavefunctions, \( \gamma \) can be found to have the form \( \gamma(\Delta a(\bar{t})) = \gamma_0 \exp(-\Delta a(\bar{t})/a_0) \), where the parameter \( \gamma_0 = 2.0 \text{ eV} \) is the hopping integral without the Au and CO molecules and \( a_0 = 0.33 \text{Å} \). Similar parameterization was done by Sood et al. in \cite{19}. In the experiment \cite{10}, the calculations show that adsorption at the Au_{20} corner sites is the most energetically favourable configuration for the adsorption of CO molecules than the edge sites. However, the experimental result (figure 4(c) of \cite{10}) is for an ensemble of larger Au clusters. At any instant of time the CO molecules can be on a combination of corner and edge sites of the Au clusters hence the different changes in the conductance arising due to the CO molecules at the edge and corner sites is neglected and is assumed to be an average value. \( \Delta a(\bar{t}) \) is a parameter which includes the effects of the CO and Au molecules on the charge distribution and the nearest-neighbour carbon-carbon distance of the SWCNT. \( \gamma(\Delta a(\bar{t})) \) is the modified hopping integral due to the interaction of CO molecules with the Au-SWCNT system at each \( \bar{t} \). As we are interested in electronic transport properties (conductance), the effect of the hopping integral, i.e., hopping of electrons between the adjacent carbon atoms is
more significant than the on-site energy. Hence, the contribution of the on-site energy to the conductance is suppressed. In the calculation, we fix the parameters $\Delta a(\bar{t})$ and $\varepsilon_f(\bar{t})$ for each interaction time. A set of the values of these parameters is chosen which best fits the experimental result. These parameters carry the information about the dopants, Au and CO molecules. The effect of these molecules on the conductance can be seen from the variation of these parameters with time, figure 2, causing a decrease in the conductance. The interaction of CO molecules with Au-decorated SWCNT at each $\bar{t}$ causes charge redistribution in the system, leading to a partial charge transfer from the Au-CO complex to the SWCNT. This deforms SWCNTs which changes the carbon-carbon distance and affects the wavefunctions and the hopping integral, and hence changes the sensor response. This charge transfer and the resulting changes in C-C distance increase ($a_{cc}$ becomes more negative) with time as more and more CO molecules interact with the Au-SWCNT, as indicated by increasing negative values of $\Delta a(\bar{t})$ with time $\bar{t}$ in figure 2(a). This enhances the hopping integral $\gamma_{ij}(\Delta a(\bar{t})) = \gamma_0 \exp(\Delta a(\bar{t})/a_0)$ as shown in figure 2(b), which represents the variation of the hopping integral with respect to the CO exposure time and the inset shows its variation as a function of the parameter $\Delta a(\bar{t})$. As a result, the energy bands of the SWCNT change locally which shifts the position of the Fermi level away from the valence band of the central SWCNT (as also reported in Ref. [20]), indicated by increasing values of $\varepsilon_f$ with $\bar{t}$ in figure 2(c) and with $\Delta a(\bar{t})$ in the inset. This reduces the hole carrier concentration and hence the conductance of the SWCNT, which is consistent with the experiment. Figure 3 compares the plot between the normalized electrical conductance, calculated by fixing $\Delta a(\bar{t})$(Å) and $\varepsilon_f(\bar{t})(eV)$, and the experimental conductance with respect to exposure time of CO molecules. Hence, the formula reproduces the normalized electrical conductance plot of the experiment. This direct connection between theory and experiment represents an important effort towards conceptual understanding of the experiment, i.e., the effect of dopants on the electronic transport in the system.

4.5. Autocorrelation function

We find a novel way of studying the sensor response by calculating the fluctuations, autocorrelation function (ACF) [21], of sensor response shown in figure 3. The autocorrelation function is defined as

$$ACF = \frac{\sum_{i=1}^{n-k}(G(i) - \bar{G})(G(i+k) - \bar{G})}{\sum_{i=1}^{n}(G(i) - \bar{G})^2},$$

where $G(\bar{t}) = G^{(0)}(\bar{t})/G_0$ is the normalized conductance at time $\bar{t}$ and $\bar{G} = \frac{1}{n} \sum_{i=1}^{n} G(\bar{t})$ is the mean of the conductance. $n$ is the total number of observations and $k = 1, 2, 3 \cdot \cdot \cdot K$ is the time lag, where $K < n$.

The autocorrelation is a mathematical tool which is used for finding patterns and degree of randomness in a series of values (e.g., time series). It represents the correlation of a variable with itself at two different times [21]. Figure 4 shows ACF plot which starts with a positive autocorrelation that decreases and becomes negative as the time
lag increases. The ACF plot gives a pattern for the conductance which is a signature of strong correlation between the data points indicating non-randomness in the sensor response and signifies the sensitivity of the sensor. Hence, ACF is useful in finding the pattern of the sensor response. Again we find that theory reproduces experiment in the ACF plot. This result suggests that ACF can be useful to study and compare the sensitivity of the same device for various other toxic gases by comparing the pattern of the sensor response for different gases (here the result is shown for CO gas) and may also be useful for other low-dimensional systems such as sensors based on graphene.

5. Conclusions

We present theoretical understanding of the electronic transport in Au-decorated SWCNTs during CO gas adsorption. We derive an explicit formula for the transmission function in terms of the time-dependent hopping integrals and the on-site energy using the time-dependent NEGF formalism and report on the calculation of conductance by considering a form for the hopping integral as shown in figure 3. The set of equations (5), (6) and (8) are the major results of this manuscript and have been reported for the first time for the Au-SWCNT system used for CO gas detection. Equation (5) is the zeroth order current which is the time-dependent Landauer formula. The dependence of the transmission function and conductance on $\gamma(t)$ and $\varepsilon_{A/B}(t)$ has been given by equation (6). Equation (8) represents the first order contribution to the current which is small. Hence this phenomena of electronic transport is essentially described by the Landauer formula evaluated at each time $t$. The formula for the transmission function is then used to compare the theoretical results with the experiment. We find the formula quantitatively reproduces the experimental result [10]. The model gives a set of parameters that best fits the experiment. We also calculate and compare the ACF for the sensor response of the theory and experiment and find the results are in agreement, figure 4. We observe a strong correlation in the sensor response indicating the sensitivity of the Au-decorated SWCNT sensor. Hence, ACF is found useful in recognizing the pattern of the sensor response.

This work is an attempt at a microscopic study of time-dependent quantum transport in Au-decorated SWCNT sensors using the NEGF formalism and presents an important contribution towards a conceptual understanding of how the Au and CO molecules change the experimentally observed conductance of the nanotube. Such a detailed investigation of these nanostructures is needed which will give insight into a microscopic understanding of the fundamental science of molecule-CNT nanohybrids that will be useful to tailor the properties of CNTs for beneficial applications. This theoretical approach can be applied to other low-dimensional structures such as CNT, graphene and systems functionalized with DNA [22, 23] for sensing applications.
Acknowledgments

This work has been supported by the Council of Scientific and Industrial Research (CSIR) and the University Faculty R & D Research Programme.
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Figure 1. Schematic view of adsorption of CO molecules at the Au$_{20}$ cluster surface on a semiconducting (14,0) SWCNT with a missing carbon atom defect at site $A_2$. Au atoms are yellow solid circles, C atoms are blue solid circles with outline, and O atoms are red empty circles. L, R indicate the left and right nanotube electrodes and C denotes the Au$_{20}$-SWCNT system. The arrow indicates the path of transmission.

Figure 2. Variation of (a) $\Delta a(\bar{t})(\text{Å})$ with time $\bar{t}$ (min), (b) $\gamma_{ij}(\Delta a(\bar{t}))(\text{eV})$ with time $\bar{t}$ (min) and $\Delta a(\bar{t})$ (inset) and (c) $\varepsilon_f(\bar{t})(\text{eV})$ with time $\bar{t}$ (min) and $\Delta a(\bar{t})(\text{Å})$ (inset).
Figure 3. The average sensor response for Au-decorated SWCNTs with CO molecules adsorbed at the Au surface. The experimental data are reproduced with permission from Nano Lett. 10 (2010) 958. Copyright 2010 American Chemical Society.

Figure 4. Experimental (empty bars) and theoretical (solid bars) autocorrelation function plots.