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Enhanced detection of volatile organic compounds (VOCs) by caffeine modified carbon nanotube junctions

Alton Turner [a], Tyler McCoy [a], Wei Cao [b], Abdennaceur Karoui [c], Waleed M. Maswadeh [d], Branislav Vlahovic [c], Hani E. Elsayed-Ali [b], Brenna Daniel [a], Mickael Castro [e], Kishor Kumar Sadasivuni [f], Mehran Elahi [a], Adetayo Adedeji [a], Bijandra Kumar [a,*]

[a] Department of Mathematics, Computer Science and Engineering Technology, Elizabeth City State University, Elizabeth City, NC 27909, United States of America
[b] Old Dominion University, Department of Electrical and Computer Engineering, 12050 Jefferson Ave., Newport News, VA 23606, United States of America
[c] North Carolina Central University, CREST, Department of Mathematics and Physics, 1801 Fayetteville Street, Durham, NC 27707, United States of America
[d] US Army, RDECOM, ECBC, Edgewood, MD, United States of America
[e] IRDL UMR CNRS 6027, Université de Bretagne Sud, Lorient, France
[f] Center for Advanced Materials, Qatar University, Qatar

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ABSTRACT

Detection of vapor phase analytes and gas molecules is primarily essential for numerous applications including medical diagnostic, environmental monitoring, chemical threat detection, food quality control, and chemical warfare agents. Here, we developed Caffeine functionalized carbon nanotubes (CNTs) random network based vapor quantum resistive sensors (vQRSs) for volatile organic compounds (VOCs) detection. The localized transmission electron microscopy (TEM) image and energy dispersive X-ray spectroscopy (EDS) confirm migration of caffeine to CNT–CNT junction (CNTj). We have recorded more than one order of magnitude higher sensitivity and unique selectivity towards selective VOCs (e.g., acetone, toluene, ethanol, methanol, etc.) with short response time (few seconds) for caffeine modified CNT junction (Caf-CNTj) vQRSs. Molecular dynamics (MD) calculations suggest that the sensitivity of the sensor is diffusion limited, with an advective contribution for ethanol. The designed Caf-CNTj sensors can potentially be important candidate to be a part of electronic nose used for various application such as breath analysis and food quality monitoring.

1. Introduction

Healthy human body generates 1840 type of volatile organic compounds (VOCs) excreted from several bodily fluids such as breath, urine and skin secretions [1]. The generated VOCs profile can potentially be used for early stage detection of numerous invasive diseases. [2–4] In particular, VOCs profile of exhaled breathe characterized using electronic nose (e-nose) designed by combining multiple individual sensors together, have attracted immediate attention for early stage lung cancer detection and other diseases (e.g., tuberculosis, diabetes) [3,5–10]. However, the performance of e-nose is highly dependable on use of individual sensors assembled in an array [11,12]. The key challenges in designing individual sensor include, but not limited to the detection limit, selectivity, drift in signal, etc., when tested in practical conditions. Therefore, major efforts are directed towards designing new sensors able to function in more realistic conditions (e.g., humidity, temperature) with high sensitivity and specific sensing pattern [9,11,13].

One-dimensional carbon nanotubes (CNTs) offer exceptional electrical and physical properties essential for sensing application [14–26]. The electrical properties of CNTs abruptly transformed due to variation in physical and chemical state of surrounding environment [25,27]. However, pristine CNT based sensors exhibit poor sensitivity and selectivity to different analytes due to lack of strong affinity to the CNT's surface [25]. The sensitivity and selectivity of the CNTs devices can be enhanced by multiple ways e.g., modifying surface of CNTs ("key/lock" principle) or fabricating CNTs random network based vapor quantum resistive sensors (vQRS). The sensing mechanism of CNT random network consisting multiple CNTs junctions based vQRS differs from individual CNT based sensors as in first case tunnel junctions are modulated by the presence of VOCs rather than modulation of electron/hole

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* Corresponding author.
E-mail address: bkumar@ecsu.edu (B. Kumar).

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transport properties and by charge transfer phenomena in the latter case. Additionally, vQRS are more practical as the impact of tube length, diameter, adventitious doping from the ambient and deposition method [28–30] are eliminated. Another major advantage of vQRS [5,31–35] over individual CNT based device [23,24,36–38] is that it can be easily fabricated using simple fabrication procedures such as drop casting and layer by layer spray deposition, without requirement of cutting-edge fabrication techniques. The selectivity and sensitivity can preferably be introduced in vQRS by functionalization (covalent/noncovalent) of CNTs with functional molecules or tuning the chemical properties of CNT junction (CNTj) [31–33,39–45]. In particular, biomolecules (e.g., amylose) noncovalently bind to surface of CNTs due to pi–pi interaction and allows fabricating of CNTs random network based vQRS consisting sensitive CNT junctions [32].

Caffeine (1,3,7-trimethyl-xanthine) is a biomolecule widely used in developing hetero-atomic nanocatalysts or alone for various applications such as oxygen evolution reaction, drug delivery and others [46–50]. Caffeine has been selected as a functional element because it can non-covalently bind to the CNT surface via pi–pi interaction and also consists heteroatomic structure with unique chemical and electronic properties. Thus, it may potentially enhance the selectivity and sensitivity developed sensory system towards VOCs detection by modulation of CNT junctions' properties. In fact, our results show that the close encounter of caffeine with CNT junctions not only enhances the sensitivity by order of magnitude for selective VOCs (toluene, methanol, ethanol, and acetone and chloroform) but also significantly improves selectivity patterns. Element diffraction scattering (EDS) with transmission electron microscopy (TEM) at nanoscale confirm the presence of caffeine molecules that are mainly embedded in groves of CNTs junctions. We suggest that the modulation CNT junctions due to absorption of analytes molecules at embedded caffeine originate higher sensitivity and selectivity. Additionally, the designed sensors are able to detect down to one ppm concentration of analyte with sub-second response time. Molecular dynamics (MD) calculations allowed characterization of the junction behavior, the mechanisms of adsorption of caffeine by a CNT homojunction, and suggest that the sensitivity of the sensor is diffusion limited.

2. Materials and experimental methods

2.1. Chemicals and techniques

Multiwall carbon nanotubes (MWCNTs, Outer Diameter: 20–30 nm, Inside Diameter: 5–10 nm Ash: <1.5 wt%, Purity: >95 wt%, Length: 10-30 μm, Specific Surface Area: 110 m^2/g, Electrical Conductivity: >100 S/cm, Bulk density: 0.28 g/cm^3, True density: ∼2.1 g/cm^3), were purchased from Cheap Tubes Inc (Brattleboro, Vermont) and used without any further purification process. Caffeine and used solvents (toluene, methanol, ethanol, acetone, and chloroform, purity $\geq$ 99.9%) were obtained from Sigma-Aldrich and used as received. All sensing experiments were carried out using Biologic SP-200 potentiostat in static and dynamic mode (Supplementary Data Section S1 & S2). Transmission electron microscopic (TEM) imaging of specimen were done using a high resolution transmission electron microscope JEOL JEM-2100F. Element diffraction scattering, known as Energy-dispersive X-ray spectroscopy (EDS) data were collected using an Oxford INCAx-sight EDS detector. Raman spectra were recorded using a Renishaw InVia Raman Microscope and Spectrometer.

Some aspects of the experimental finding have been verified by molecular modeling of the CNT junction pristine, functionalized with Caffeine, and exposed to VOC molecules. Different geometries of the junction have been tested, but reported results are only for 90°X-junction built off two long (5-5) CNTs, a more complete study will be reported elsewhere. Both bonded and unbonded junction are built and analyzed with molecular dynamics, and exposed to caffeine and thereafter to methanol molecules.

2.2. Fabrication of CNTj chemiresistive sensors

Caf-CNTs and CNTs solutions were prepared sonication methods. CNTs (2 mg) were dispersed in methanol at a concentration of 0.2 mg/ml, using ultra-sonication (40 kHz, 120 V) bath for 30 min under controlled condition (temperature −25 °C). In order to prepare Caf-CNTs, caffeine was dissolved in the suspension with a concentration of 0.2 mg/ml followed by further sonication for another 20 min. The sensors were fabricated using 100 nF ceramic multilayer capacitors with radial configuration, voltage rating of 50 vdc, dimensions of 4 mm × 4 mm × 2.5 mm and weighing 0.15 g. The metallic electrodes within the capacitor were exposed using established polishing protocols [33,34]. This was followed by chemically cleaning involving 10 min sonication in ethanol followed by 10 min sonication in DI water. Using drop casting, 10 microliter (μL) solution was carefully deposited on the electrodes and the samples were then dried in air at room temperature for two hours. To remove excessive caffeine, fabricated sensors were softly washed with DI water and again dried at room temperature overnight.

2.3. VOCs sensing characteristics

Sensing studies were performed by exposing sensors to saturated VOCs in static- and dynamic-mode (Supplementary Data Section S1 & S2). In static mode, the holder with the mounted sensors was quickly transferred into an air tight 1 L conical flask (in thermostatically controlled cabinet) filled with saturated vapors of the VOCs being tested. The volume of the VOC sample is fixed to 150 mL, located at the bottom of the flask. After 5 min being in saturated vapor, the sensors were promptly transferred from the flask and placed in open environment. Only long term experiments were performed in dynamic mode. The *current vs. time* signals were recorded using the potentiostat by applying 0.1 V constant potential. It should be noted that the testing experiments have been conducted at atmospheric pressure, at 25 °C, and with the relative humidity (RH) levels of 40%, to mimic realistic application conditions of the sensor. The response of the sensors has been represented by the relative amplitude (A_r) calculated using Eq. (1):

$$A_r = \frac{(R - R_0)}{R_0} \tag{1}$$

where R_0 is the initial resistance of sensors in air and R is the resistance in the presence of VOCs. Sensing experiments were also performed by injecting 1 μL, 5 μL, 10 μL, 100 μL and 1000 μL methanol in similar chamber under the same experimental conditions as discussed above.

2.4. Atomistic modeling of CNT 90° X-junction

To explain our experimental observations and data, computational modeling of the core part of CNT based sensors has been done through molecular and atomic calculations. Although quantum mechanics calculations are the most rigorous, they cannot be utilized to study the atomic structure and thermodynamics of our systems for they are extremely large. Existing quantum mechanics software are capable of handling 120 atoms in relatively acceptable time, but 200 atoms require days or weeks of CPU time. The hybrid molecular dynamics-quantum Car–Parinello is computationally efficient and more rigorous than MD, but

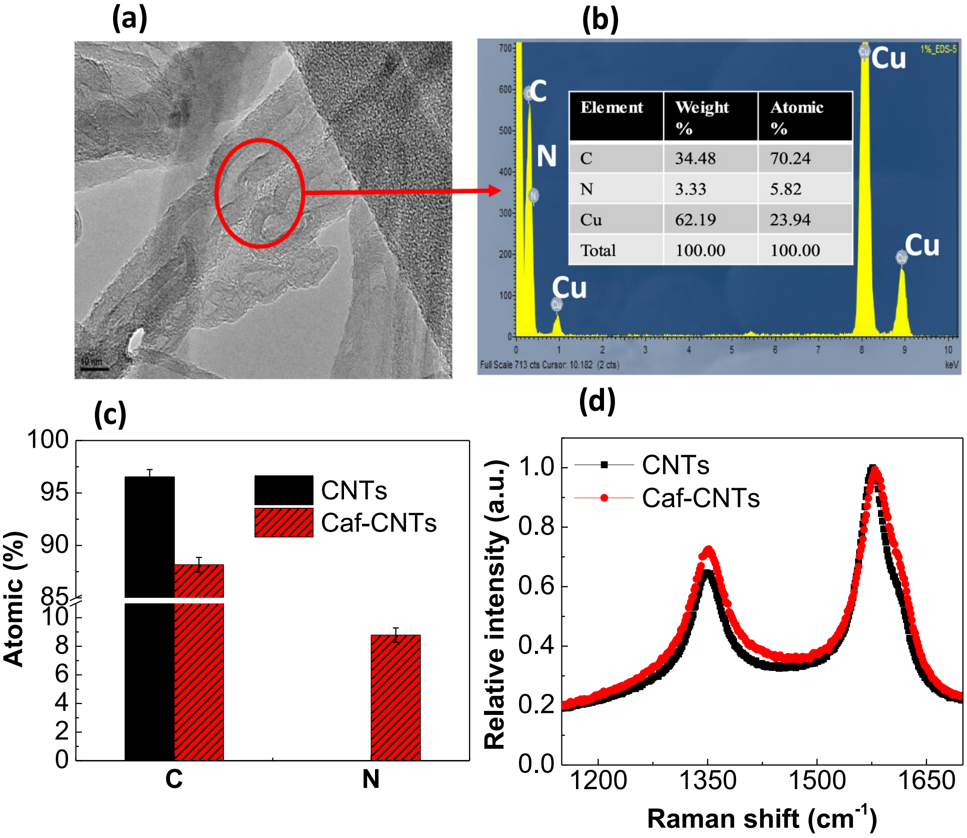

Fig. 1. Characterization of Caf-CNTj: (a) High Resolution TEM and (b) corresponding EDS spectra and elemental table (in-set) of Caf-CNTs, (c) composition histogram and (d) Raman spectra for CNTs and Caf-CNTj.

also requires significant computation time [51]. Thus, we limited our study to classical mechanics based MD. To explain the electric signal of the sensor, electronic properties based on electron density properties and electron energy levels is investigated using the semi-empirical quantum approach incorporated in VAMP (Datasheet VAMP, Biovia/Accelrys Materials Studio), and ab-initio in CASTEP and will be published elsewhere. Our MD investigation has been done in three phases, which are:

(i) finding the atomistic structure and thermochemical properties of each molecule, when isolated, as well as when these molecules intermingle, as unraveled by HR-TEM imaging,
(ii) determining the chemical and physical properties of CNT junction through its energetics, and
(iii) investigating in details interaction dynamics of these molecules: isolated CNT, interaction CNT–CNT, CNTj with caffeine, and CNTj-Caf (CNTj sensitized with caffeine) with methanol. Other volatile organic molecules will be tested in later phases of this work.

Forcite MD software package (*Biovia Materials Studio Forcite Plus datasheet)* has been utilized to characterize the ability of CNTj-Caffeine to detect solvents, and to explain the above described experimental observations. Specifically, we calculated (i) the equilibrium atomic structure of H-terminated CNT, (ii) interactions of CNTs resulting in homojunctions (CNTj), (iii) the junction thermochemical properties, (iv) the interaction of various molecules of interest with various configurations of CNTjs, (v) the diffusion of caffeine molecules in medium that contains CNTs and CNTjs, and (vi) the affinity of caffeine molecules to CNTj. The effect of chirality on the physical properties of CNTj and wall multiplicity were explored, and will be published elsewhere.

At this point, we have analyzed the case of methanol, and will continue with a series of VOCs that the authors have experimentally tested. The overall goal being to evaluate the ability of detection of solvents by the CNTj-Caffeine material system, and how to improve our understanding of the observed phenomena; this is useful for maximizing the sensing performance. The type of studied MD parameters include atom coordinate, total energy and its components, temperature, mean square displacement (MSD), and space–time correlation function. The molecular prototyping and utilized methods are given in the supporting document (Supplementary Data Section S2).

3. Results and discussion

3.1. Characterization of caffeine functionalized CNTs

The caffeine modified CNT junction (Caf-CNTj) and pristine CNTs based vQRSs were fabricated by dispersing the CNTs in caffeine media or methanol respectively. Transmission electron microscopy (TEM) images of entangled CNTs random network, suggest well dispersion of CNTs in methanol after 15 min sonication (SI Fig.S3). High resolution TEM image further confirms presence of multi carbon layers and clean surface of CNTs (SI Fig.S3). In case of pristine CNTs random network, CNTj remains untainted. However, morphology of CNTs in Caf-CNTj sensors is more robust suggesting physically adsorption of caffeine molecules on tube surface. More importantly a cloud of host material, most probably, accumulated caffeine is clearly noticed at CNT junction in Caf-CNTj network (Fig.S3). Here, it should be noted that such small molecules not only non-covalently bind to the surface of CNTs due to pi–pi interaction but also can accumulate due to inter-hydrogen bonding [52]. We also performed localized EDS

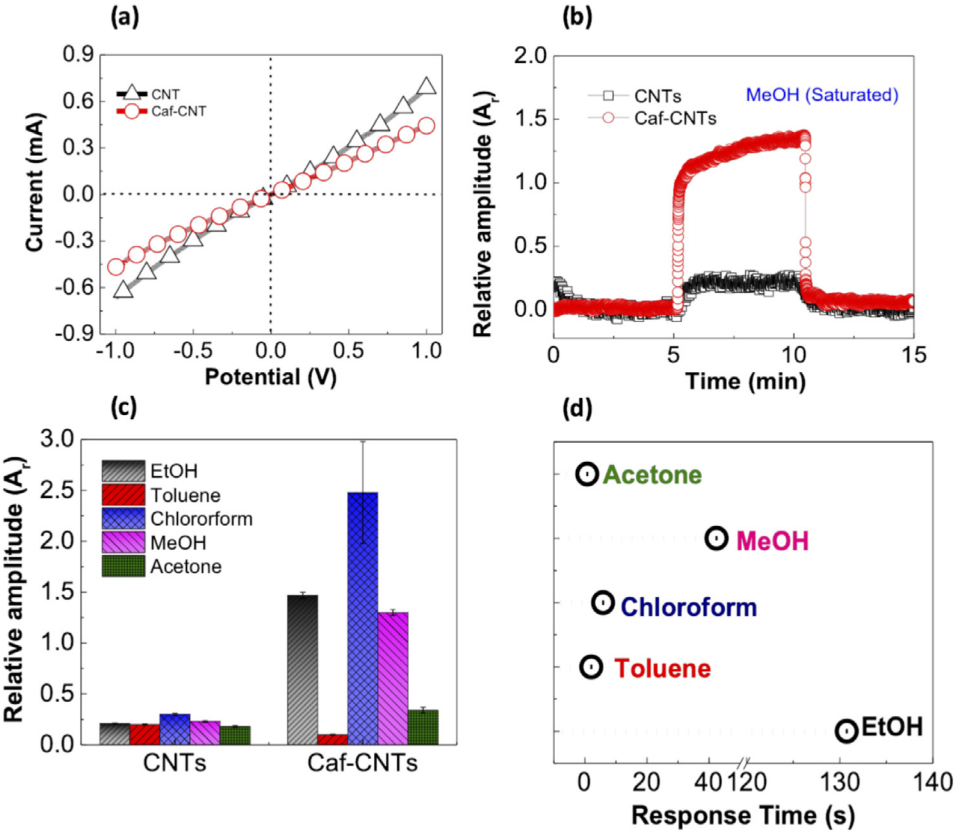

Fig. 2. VOCs sensing characterization of fabricated sensors: (a) I–V curve for CNTs and Caf-CNTj vQRSs, (b) Sensing curve for Caf-CNTj vQRSs and CNTs vQRSs for saturated methanol vapors. (b) Sensing signal for different VOCs for Caf-CNTj vQRSs, (c) relative sensing pattern for CNTs and Caf-CNTj vQRSs, and (d) Extracted response time for Caf-CNTj vQRSs.

at the junction of CNTs (Fig. 1a–b). The corresponding elemental analysis suggests presence of more than 5% atomic nitrogen atoms. These results strongly confirm that caffeine molecules are not only non-covalently adsorbed on the surface of CNTs but also conceivably accumulate at CNTj of random network.

We also performed molecular simulation and our results confirm that attraction forces between CNTj and caffeine are rather strong enough to make the caffeine motion bound to the junction (SI file - S2). The details are discussed in supplementary information. We further performed EDS experiments on bulk samples for both CNTs and Caf-CNTj. The results suggest absence of nitrogen atom in pristine CNTs (SI file S3). However, in case of Caf-CNTj, approximately 8% atomic nitrogen was observed confirming the presence of caffeine molecules (Fig. 1C). Raman spectroscopy results also show presence of two characteristic peaks at "∼1348 cm^{-1}" and "∼1576 cm^{-1}" that are associated with D and G bands (Fig. 1d) [53–55]. The appearance of D peak confirms that used CNTs are defective. However, variation in I_D/I_G ratio — for CNTs and Caf-CNTj is negligible suggesting that binding of caffeine does not introduce any additional defects.

3.2. Analysis of sensing properties of fabricated sensors

Fig. 2(a) suggests that both CNTs and Caf-CNTj exhibit linear current vs potential relationship confirming ohmic contact between CNTs random network and electrodes. However, the average resistance of Caf-CNTj (∼200 kΩ) was slightly higher in comparison to the pristine CNTs (∼180 kΩ) random network sensing electrodes. This can be attributed to the presence of Caffeine molecules at the surface of CNTs and CNTj as evidenced by TEM image. Fig. 2(b) shows the sensing behavior of CNTs and Caf-CNTj vQRSs towards saturated methanol vapors. Here it should be noted that all reported sensing curves represent measured data, without any treatment such as base-line correction, or alignment of the gas switching. They have been collected by performing experiments in realistic environmental conditions (environmental temperature, pressure and humidity) [56]. Interestingly, Caf-CNTj vQRS exhibits four times higher relative amplitude in comparison to the pristine CNTs based sensors for methanol confirming superior sensitivity of Caf-CNTj vQRSs. These results suggest that caffeine plays a significant role in enhancing sensitivity of the CNT sensors. These sensors were also examined for other VOCs including ethanol, toluene, acetone and chloroform. Each of these VOCs is unique in terms of chemical properties (e.g., solubility parameter, polarity, partial vapor pressure) [31,32,39]. The selected solvents can be subcategorized in three section: polar (methanol, ethanol, and acetone), borderline (chloroform) and nonpolar (toluene). The order or relative magnitude of sensitivity for tested VOCs is as follows chloroform, ethanol, methanol, acetone, and toluene. In case of methanol, and ethanol we observed almost complete recovery of Caf-CNTj vQRS within the time interval provided during sensing experiments (SI Fig.S4). Fig. 2(c) shows the sensing pattern of CNTs and Caf-CNTj vQRS. Close encounter of caffeine enhances the sensitivity and selectivity of vQRS significantly. Here it should be noted that caffeine is highly soluble in chloroform followed by acetone, methanol, ethanol and toluene at room temperature and atmospheric pressure [18]. Thus, relative magnitude should be in similar trend as sensitivity can be directly related to solubility parameters [32,57]. However, this is not the case as caffeine solubility is higher in acetone, but the magnitude of the signal is lower in comparison to the methanol and ethanol. Even after normalization with respect to the number of molecules calculated via Antoine's equation [58],

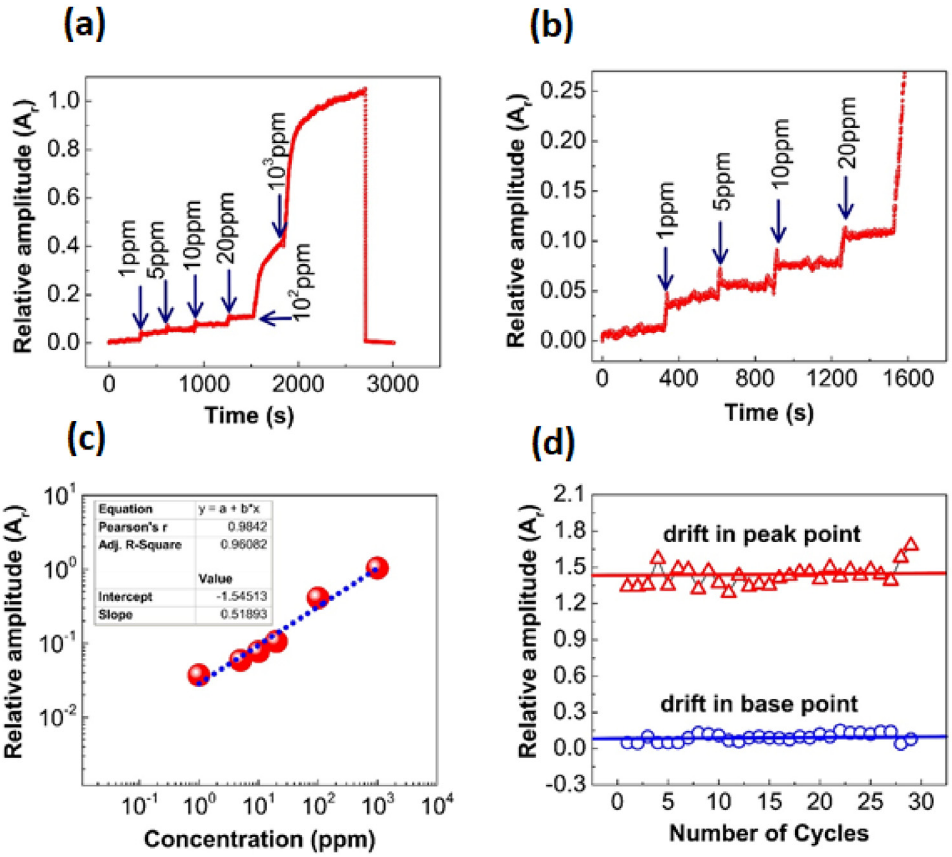

Fig. 3. Identification of detection limit and long-term stability: (a) Response for varying concentration of methanol, (b) magnified signal, (c) concentration vs relative amplitude at log scale, and (d) variation in the peak intensity and baseline. All results were collected for Caf-CNTj vQRSs against methanol vapor.

the magnitude for acetone remains significantly lower (Table S3). These results strongly suggest that solubility itself is not the only parameter to explain the sensing pattern of Caf-CNTj vQRSs. The extracted response time, which is determined at 90% of sensor final amplitude after analytes exposure, also varies significantly for tested solvents (Fig. 2d). The shortest response time recorded for acetone is only 0.78 s suggesting quick response of CNTj in Caf-CNTj vQRS (Fig. 2d). In contrast, for methanol and ethanol response times are 40 and 130 s respectively.

In the first environmental experimental conditions, the Caf-CNTj vQRSs did not show visible drift in baseline and peak of the relative amplitude for methanol. Thus, we focused on studying the detection limit and long-term stability of Caf-CNTj vQRSs against methanol vapor (SI Fig.S5).

Fig. 3(a) shows the response of Caf-CNTj vQRSs towards different concentrations varying from 1ppm to 10^3 ppm (volumetric) of the methanol vapors. At every injection, we observed a sharp jump in relative amplitude. Even at 1ppm, a magnitude of 0.03 relative amplitude was recorded (Fig. 3b). However, when the concentration reaches to 100 ppm the response increased significantly. At 1000 ppm concentration the relative magnitude is close to the magnitude recorded for saturated methanol vapors. The linear curve of the relative amplitude versus concentration (in ppm) in the log–log chart in Fig. 3(c) demonstrates a power relationship; it has a ~-1.55 intercept and $\sim$0.52 slope. The extrapolation of relative amplitude–concentration relation and the strength of detected signal suggest the possible application for sub ppb methanol detection ability of developed sensors. We also examined the stability of the sensors by exposing continuously for 30 cycles (Fig. 3d) and testing again after 30 days. During 30 cycles we observed only an insignificant drift in peak and baseline of the signals (Fig. 3d). Interestingly, the Caf-CNTj vQRS exhibits similar sensitivity after 30 days as evidenced by similar type of sensing curve and range of relative magnitudes. The results strongly suggest the long-term stability of Caf-CNTj vQRSs.

3.3. Molecular dynamic study

To explain the observed sensing capability of VOCs by pristine CNTj and by CNTj with embedded caffeine (Caf-CNTj vQRSs), MD has been performed (SI Fig. S6–S21). The focus of the MD calculations in this paper is on interpreting the sensing properties based only on the CNTj atomic structure and the chemical interactions of the sensed analytes with the CNTj. Intentionally, we reported on metallic tubes (5,5) CNTs, as extreme case. The purpose is to show that CNTj of these metallic tubes still show the minimal requirement for sensing. MD calculations cannot be used to characterize the electronic properties and the conductivity of the molecules and the CNTj, but did clearly show atomic structure variations and adsorption of tested analytes by the (5,5)-(5,5) CNTj and that the adsorption and diffusion of the analytes are correlated to the responsivity of the CNTj. The effect of such molecular interactions on the conductivity of the junction is being studied with ab-initio and semi-empirical methods and will be published elsewhere, where we will include the effect of the tube type, whether metallic or semiconductor.

Fig. 4a shows the position of special points in a caffeine molecule (labeled Caff-1) relative to the center of the junction. These points are the center of five- and six-atom rings (Ring-5 and Ring-6, respectively) within the caffeine molecule (SI Fig. S.12–S.15). First conclusive output of our MD study is that the attraction forces between CNTj and caffeine are rather

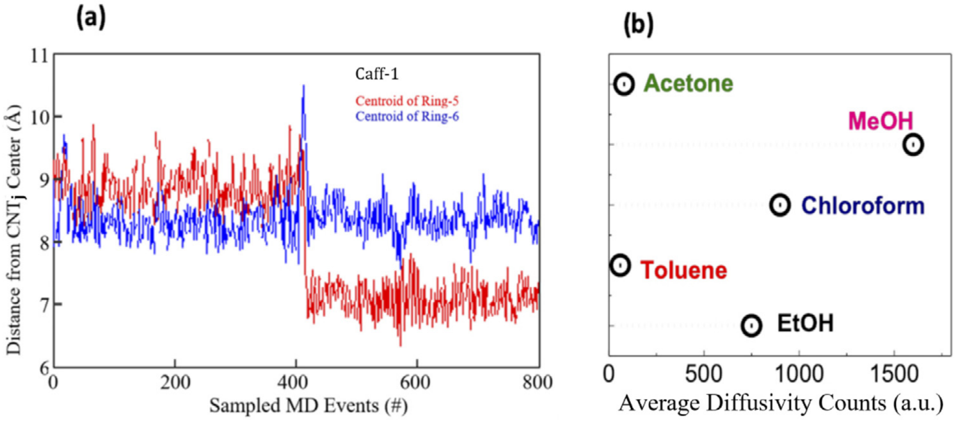

Fig. 4. Molecular dynamic study of the system. (a) Relative position of the caffeine molecule 1 (relative to the junction center), and (b) mean squared displacement (MSD) obtained by MD of five analytes, while interacting with caffeine adsorbed at CNTj.

strong enough to make the caffeine motion bound to the junction (Fig. 4a) as observed in our TEM analysis. MD has also been performed with pristine CNTj and by CNTj with embedded caffeine (Caf-CNTj vQRSs) simultaneously interacting with several methanol molecules (Fig S.16). The positions of 4 methanol molecules, selected for the variety of properties they represent have been presented in SI file. For simplicity, the molecule position is given as the distance from the CNTj center to the oxygen atom in each of the methanol molecules. Various cases appear, either a physisorption binding is established, or breaking away from the two CNTs or the CNTj, or an alternated behavior between these two. Once the methanol molecule breaks free from the CNT or the CNTj vicinities, the motion becomes globally linear modulated with tiny fluctuations. The first molecule (Meth-1) has departed away from the CNTj at the start of the MD, whereas Meth-2 bounced and returned to the CNTj then later totally broke away from the CNTj. In contrast, Meth-4 (b) appeared to be bound with the CNT, a very week bonding due to a physisorption, which does not stop the methanol from moving. One can notice that VOC molecules either break away from the CNTj and may come back, or oscillate around the junction, on a surface whose center is that of the junction and radius is 55 Å with spikes that extend up to 8 to 10 Å. This simplified description describes the nature of the bonding of VOCs to the CNTj.

We have experimentally determined that the sensitivity of Caf-CNTj vQRSs to tested VOCs decreases in the following order: chloroform, ethanol, methanol, acetone, and toluene. We also determined dissimilar response times of the sensor as shown in Fig. 3(d). We believe that these findings can be correlated to the VOC molecule motions during their interactions with CNTj. To that end, we calculated the mean squared displacement (MSD) of the centroid of each of the VOC molecule during MD runs. The MSD is defined as:

$$\left\langle (x - x_0)^2 \right\rangle \text{ that is } \frac{1}{N}\sum_{i=1}^{N}(x_i - x_0)^2 \qquad (2)$$

where i indexes the time-dependent position. It is a measure of the molecule position changes relative to its initial positions x_0. It is commonly utilized to quantify the extent of random motion.

In atomistics, the MSD is measured over time to determine the extent of an atom spreading, solely by diffusion, or to verify if an advective force is also contributing to motions of atoms and molecules [59]. The MSD is also used in studying transport and mixing phenomena in various engineering problems [60]. Further, it quantifies vibrations within solid state phases (Debye–Waller factor) and it is employed in the Langevin equation that describes Brownian diffusion of particles [61].

We suggest that the response time for Caf-CNTj vQRS, presented in Fig. 2(d), can be interpreted based on the nature of motion of the VOC analytes, while in the proximity of the CNTs and CNTj, whether pristine junction or functionalized by caffeine. To that end the diffusion of the 5 experimentally tested VOCs has been evaluated by calculating the MSD of the VOC(s) during MD runs made in the same thermodynamics conditions, in particular at the same temperature.

Fig. 4b clearly shows a similar tendency of MSD of the VOCs with the measured response time for acetone, methanol, chloroform, and toluene and to less extent ethanol. In light of this data, the diffusion of these analytes, appeared to have contributed in the signal and the sensitivity of the sensor. The only found discrepancy was with ethanol, in which case, diffusion seems not to be the only phenomenon responsible on the sensor signal. We propose that advective motions were involved in ethanol and CNTj interactions. Advection is the transport of a substance by bulk (or group) motion. Advection does not include transport of substances by molecular diffusion, and requires currents, which in this case could be due to electrostatic forces. Conserved properties during advection are transferred with the moved substance. These include the energy, enthalpy, and momentum, which are extensive quantities.

The sensing mechanism at the molecular level: The sensing of the CNT junction (CNTj) is associated to the capture of analyte molecules, Captured molecules affect the CNTj electronic properties, including the conductivity. MD calculations was utilized to check if the capture of the analyte could result in direct bonding, that is gas-surface chemisorption, or indirectly via physisorption. However, MD has not provided any evidence for covalent chemical bonding of VOC molecules with the CNTj; this means that the device is not altered by the analyte, which is practically relevant for the sensor. MD has shown that physisorption rather takes place along the bodies of the two CNTs and the junction. Ultimately, the analyte gets trapped in the junction vicinity. The conductivity of CNT and CNTj are significantly changed. In contrast, analytes that are not adsorbed, do not effect at all the conductivity of the CNTj.

The physisorption process is characterized by a long residence time, well beyond 100 ps and even ns, a low binding energy in the order of 50 meV, and a separation gap of 4 Å between the analyte and the CNT and CNTj surfaces. The adsorption is dominated by either single molecule surface diffusion, or advective group diffusion involving both the pair of CNTs and the analyte. The nature of diffusion depends on the analyte, among the studied species. Also these analytes were found to diffuse differently from each others, and their diffusion was found tightly correlated to the response time for Caf-CNTj vQRSs.

Sensitivity and Selectivity of CNTj relative to the studied VOCs: The obtained surface diffusion time-range, before the analyte molecule breaks away from the CNTj, and the surface diffusivity (at the CNT surface) are found to vary from one type of molecule to another, among the studied VOC molecules. The diffusivity has been characterized by the MSD rate. The given order of the CNTj sensitivity is in direct correlation with MSD.

4. Conclusions

To conclude, we have shown that caffeine adsorbed at CNTj in random network enhances the selectivity and sensitivity of the CNTs vQRSs. High-resolution TEM image, Raman spectroscopy and localized EDS analysis confirm that caffeine noncovalently interacts with CNTs and preferably aggregates at the CNTj. The non-covalent bonding is largely supported by MD calculations. All MD runs, which span 200 ps with 1 fs time steps, demonstrated that the caffeine molecules do not bound to the CNTs, do not diffuse along the CNT bodies, but rather remain in the vicinity of the CNTj. This is contrast to the tested VOCs which often escape from the CNT junction. A closer look into the trajectories of the tested VOC molecules unravels strong aggregation in some particular zones of the CNTj.

The Caf-CNTj vQRSs exhibit significantly improved sensitivity i.e., more than one order of magnitude higher than CNTs sensors, for most of the studied VOCs vapors. TEM and EDS results suggest that caffeine embedded at CNTj is primary responsible for high sensitivity, which has been largely confirmed by our MD calculations. MD suggests that diffusion plays a major role in the sensing functionality. Other mechanisms, such as advective motion for polar VOC molecules when localized fields appear in certain configurations of CNTj could come to play. Thus, further study is essential to deconvolute the role of these potential mechanisms.

Caffeine molecules not only enhance the sensitivity but also offer distinctive selective pattern. The developed sensors were able to detect methanol down to 1 ppm and maintain long-term measurement constancy. The robustness, short response time and long–term stability of caffeine sensors can be used for developing electronic noses for cancerous breaths analysis.

CRediT authorship contribution statement

Alton Turner: Prepared the sensors and perform all sensing experiments, Write the manuscript, Read and approved the final manuscript. **Tyler McCoy:** Prepared the sensors and perform all sensing experiments, Write the manuscript, Read and approved the final manuscript. **Wei Cao:** Perform TEM, EDS and Raman spectroscopy experiments, Reviewed the manuscript, Read and approved the final manuscript. **Abdennaceur Karoui:** Performed MD simulation experiments, Reviewed the manuscript, Read and approved the final manuscript. **Waleed M. Maswadeh:** Performed MD simulation experiments, Reviewed the manuscript, Read and approved the final manuscript. **Branislav Vlahovic:** Performed MD simulation experiments, Reviewed the manuscript, Read and approved the final manuscript. **Hani E. Elsayed-Ali:** Write the manuscript, Read and approved the final manuscript. **Brenna Daniel:** Prepared the sensors and perform all sensing experiments, Reviewed the manuscript, Read and approved the final manuscript. **Mickael Castro:** Designed and supervised manuscript, Reviewed the manuscript, Read and approved the final manuscript. **Kishor Kumar Sadasivuni:** Reviewed the manuscript, Read and approved the final manuscript. **Mehran Elahi:** Designed and supervised manuscript, Reviewed the manuscript, Read and approved the final manuscript. **Adetayo Adedeji:** Designed and supervised manuscript, Write the manuscript, Read and approved the final manuscript. **Bijandra Kumar:** Designed and supervised manuscript, Write the manuscript, Read and approved the final manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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