Determination of toxic carbonyl species including acetone, formaldehyde, and phosgene by polyaniline emeraldine gas sensor using DFT calculation

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A B S T R A C T

Detection of toxic carbonyl gases such as acetone, formaldehyde, and phosgene by polyaniline emeraldine salt (PANI ES) was theoretically investigated using the UB3LYP/6-31G(d) level of theory. Sensing potentials of nPANI ES ($n = 2$, 4, 6, and 8) complexed with toxic carbonyl gases were described in terms of structural, electronic, and optical properties. We found that HOMO-LUMO gaps of PANI ES after response to toxic carbonyl compounds are decreased, revealing higher electron delocalization and conductivity along backbone of PANI ES complexes compared with bare PANI ES. Phosgene shows the highest conductivity followed by formaldehyde and acetone, respectively, while reverse tendency was detected for interaction energies. UV–vis-NIR spectra estimated by means of TD-UB3LYP/6-31G(d) method of PANI ES complexes are all blue-shifted compared to their intrinsic structures, confirming the n-type doping process. The amount of blue-shift for acetone sensing is distinctly higher than those observed for formaldehyde and phosgene. These obtained results not only revealed a conductivity enhancement of polyaniline emeraldine salt sensing with toxic carbonyl gases but also demonstrated an ability to determine such toxic gases by utilizing optical measurement.

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1. Introduction

Carbonyl compounds such as acetone, formaldehyde, and phosgene are well-known as toxic volatile species. Acetone has colorless, volatile, and flammable liquid, which is used as solvent and precursor in several industries. In human body, acetone is a product obtained from fatty acid metabolism, which is an important biomarker gas for diabetes diagnosis. It was reported that diabetes patients have acetone in expired breath (1800 ppb) more than healthy persons (300–900 ppb) about 2–6 times [1]. Formaldehyde is also known as a serious toxic volatile compound for organisms, which is cause of dermatitis, cancer, watery eyes, asthma, pulmonary edema, and respiratory irritation [2]. Formaldehyde is also utilized as another essential precursor in many materials and chemical compounds. Similar to formaldehyde, phosgene ($COCl_2$) is a highly toxicity gas employed in plastic and pesticide industries. Phosgene was used as combat gas in World War I since its vapor is cause of severe lung injury [3].

Detection of toxic volatile gases has been an interesting subject for both experimental and theoretical investigations. Conducting polymers (CPs) have been introduced as an attractive material in electronic devices such sensors, batteries, solar cells, fuel cells, displays, electromagnetic shielding, actuators, and etc. [4–10]. Among conducting polymers, polyaniline (PANI) is recognized as a low cost material with high efficiency for determining various volatile gases since it has high stability, portable, high sensitivity at room temperature, short time response and easy preparation [11–14]. In addition, solubility of PANI ES is easily modified by substituting hydrogen atoms on phenyl rings with electron donor/acceptor groups [15–17] as compared to functionalization of other nanomaterials such as fullerene and carbon nanotube [18–20]. According to chemically synthesized, PANI exhibits three base forms i.e. leucoemeraldine base (LEB; fully reduction), emeraldine base (EB; semioxidized), and pernigraniline base (PNB; fully oxidized), resulting in low conductivity. To significantly improve its conductivity, PANI was doped into the conductive form of emeraldine salt (ES) by protonic acids [21]. PANI ES has been proved to be one of the most attractive chemiresistive and optical sensor in the field of conducting polymers for detecting analyte gases [8,22–34]. For former operation, change of conductivity of PANI ES

is a key factor to determine analytes, while major advantages of optical measurements are unaffected to environmental interference and more selectivity [32,35]. Recently, PANI ES and modified PANI ES have been employed as sensing material for detecting ammonia gas studied by experimental and theoretical methods [36–38]. Only few experiments were investigated for formaldehyde [26] and acetone [27,34] sensing with PANI ES based chemiresistive sensors. It was reported that resistance along PANI ES after interacting with acetone vapor was decreased [27]. Similar result was also obtained for formaldehyde, showing that the resistance along PANI ES continuously measured by observing voltage over the load resistor and applying the Ohm's law was decreased as concentration of formaldehyde [26]. Unfortunately, no optical measurement of such carbonyl volatile species sensed by PANI ES was exhibited. The literature shows that only optical sensing potentials of PANI ES were examined for ammonia, dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), methanol, and acetonitrile [8,31–33]. Interestingly, theoretical investigation on the sensing potential and selectivity of polyaniline emeraldine salt for toxic carbonyl gases such as acetone, formaldehyde, and phosgene is not demonstrated.

In the current study, we choose toxic volatile gases consisting of carbonyl group, which are greatly different in electron donating/withdrawing substituent abilities including acetone, formaldehyde, and phosgene. Density functional theory was performed to elucidate the response mechanism and selectivity of such carbonyl species sensed by PANI ES. Several structural properties were evaluated in terms of bond distances, bond angles and dihedral angles, while interaction energies, charges, HOMO, LUMO, HOMO-LUMO gaps, ionization potential (IP), electron affinity (EA), vertical IP (VIP), and vertical EA (VEA) of bare PANI ES and PANI ES complexes were calculated to see how toxic carbonyl compounds affect changes in electronic descriptions. UV-VIS-NIR spectra with respected to time-dependent DFT (TD-DFT) technique of such complexes were also estimated and discussed in order to demonstrate optical sensing power of PANI ES. To our best knowledge, these issues have not been addressed.

2. Theoretical methods

Geometries of the parent nPANI ES, where n is number of repeating unit and nPANI ES-X complexes, where X is acetone (Ace), formaldehyde (For), and phosgene (Pho), were fully optimized using the unrestricted hybrid B3LYP functional, consisting of Becke's three-parameter hybrid exchange functional (B3) and the correlation functional of Lee, Yang, and Parr (LYP) in conjunction with 6-31G(d) basis set. The UB3LYP/6-31G(d) method was chosen since it has been proven to accurately examine the open-shell π-conjugated systems [39,40] without spin contamination [41–43]. This level of theory was successfully applied for describing structural and electronic properties of the relevant conducting polymer system [44]. All calculations were performed using Gaussian 09 package [45] with the default temperature and pressure of 298.15 K and 1.00 atm, respectively, while the frontier molecular orbital plots were displayed by Jmol program [46]. In this study, a single molecule of toxic carbonyl gases was added to PANI ES structures since in the case of conducting polymer multiple absorbed molecules exhibited a slightly different result in structural, energetic, and electronic properties [47], while conductive property of single-walled SiC nanotubes becomes a metal at a concentration of 30% for HCHO, HCN, and CO [48]. Charges of bare nPANI ES and their complexes were set to +1 with doublet spin. It is well-known that positive charge in PANI ES is localized at the N—H site and the carbonyl toxic gases are electron donating group. Consequently, only configurations of oxygen atom of analytes directly

bound to the N—H site of nPANI ES are evaluated. Optimized structures of PANI ES dimer, tetramer, hexamer, and octamer sensing with acetone (nPANI ES-Ace), formaldehyde (nPANI ES-For), and phosgene (nPANI ES-Pho) were obtained when the stationary point was located. To ensure true minima of such complexes, no imaginary frequencies were confirmed by the frequency analysis. Since interaction in our system is relatively weak, the basis set superposition error (BSSE) can be a major contribution to the interaction energy. Therefore, all interaction energies (ΔE) between nPANI ES and analytes were calculated with and without BSSE correction by applying counterpoise (CP) method. The interaction energy (ΔE) and counterpoise corrected energy (ΔE_{CP}) are defined in Eqs. (1) and (2), respectively.

$$\Delta E = E_{complex} - E_{nPANI} - E_{analyte} \tag{1}$$

$$\Delta E_{CP} = \Delta E - E_{BSSE} \tag{2}$$

To correctly determine the dispersion interaction in a weakly bound system, several different degrees of empiricism have been applied in the DFT calculation [49]. Therefore, additional single-point calculations based on optimized 2PANI ES-X (X = Ace, For, and Pho) structures obtained from the UB3LYP/6-31G(d) method were performed by applying dispersion corrected CAM-UB3LYP/6-31G(d) and UB3LYP-D3/6-31G(d) methods, including benchmark interaction energies obtained from CCSD/6-31G(d) calculations. According to CCSD interaction energies (ΔE) listed in Table 1, the ΔE values of 2PANI ES sensing with acetone, formaldehyde, and phosgene are −16.13, −12.50, and −8.78 kcal/mol, respectively. Without the dispersion correction the B3LYP functional provides the underestimated values of ΔE, while dispersion corrected interaction energies obtained from CAM-UB3LYP method are in good agreement with the results calculated from CCSD. In our systems UB3LYP-D3 shows a stronger interaction energy in comparison with CCSD about 1–2 kcal/mol. As the results, the CAM-UB3LYP method was utilized to accurately examine all interaction energies of nPANI ES-X complexes obtained from the UB3LYP method (CAM-UB3LYP/6-31G(d)//UB3LYP/6-31G(d)).

To describe electronic properties of nPANI ES complexes, charge transfer effects, HOMO, LUMO, HOMO-LUMO gaps (E_g), ionization potential (IP), electron affinity (EA), vertical IP (VIP), vertical EA (VEA), density of states (DOS), and UV–vis-NIR spectra were elucidated by the B3LYP method since it was demonstrated that in the case of conjugated polymer the CAM-B3LYP method predicted overestimated values of electronic properties including HOMO, LUMO, HOMO-LUMO gap, whereas the B3LYP method shows a better estimation as compared to the experimental observation [50]. According to Koopman's theorem, IP and EA of substances are negative of HOMO and negative LUMO, energies, respectively. However, such approximation provide large error values of estimated IP and EA when dealing with the electron correlation systems [51]. Consequently, the vertical IP and EA of intrinsic nPANI ES and nPANI ES sensing with analytes were evaluated using ΔSCF method [52]. UV-VIS-NIR spectra of nPANI ES before and after response to analytes were simulated using the TD-UB3LYP/6-31G(d) level of theory. Properties of infinite polyaniline such as interaction energies, charges, HOMO, LUMO, and E_g were estimated from second order polynomial fits of the plots of these parameters versus $1/n$.

3. Results and discussion

3.1. Structural properties

As in the case of conducting polymers, alteration in geometries of polyaniline emeraldine salt leads to change of conductive properties. The planar structure evaluated by dihedral angle between the two phenyl rings is a key parameter to estimate the