Self-Consistent Charge Density Functional Tight-Binding Study of Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) Ammonia Gas Sensor

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Abstract

Geometric and electronic properties of 3,4-ethylenedioxythiophene (EDOT), styrene sulfonate (SS), and EDOT:SS oligomers up to 10 repeating units were studied by the self-consistent charge density functional tight-binding (SCC-DFTB) method. An application of PEDOT:PSS for ammonia (NH₃) detection was highlighted and investigated both experimentally and theoretically. The results showed an important role of H-bonds in EDOT:SS oligomers complex conformation. Electrical conductivity of EDOT increased with increasing oligomers and doping SS due to enhancement of π conjugation. Printed PEDOT:PSS gas sensor exhibited relatively high response and selectivity to NH₃. The SCC-DFTB calculation suggested domination of direct charge transfer process in changing of PEDOT:PSS conductivity upon NH₃ exposure at room temperature. The NH₃ molecules preferred to bind with PEDOT:PSS via physisorption. The most favorable adsorption site for PEDOT:PSS-NH₃ interaction was found to be at the nitrogen atom of NH₃ and hydrogen atoms of SS with an average optimal binding distance of 2.00 Å.

Keywords: PEDOT:PSS, Conducting polymers, Ammonia gas sensor, SCC-DFTB, QM/MD simulation

Background

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising π-conjugated polymers. Because of its unique properties such as low redox potential [1], low band gap (1.5–1.6 eV) [2], and good stability (below 150 °C) [3], PEDOT can be used in several applications such as transparent electrodes [4, 5], printing circuit boards [6, 7], OLED displays [8, 9], solar cell [10, 11], and textile fibers [12]. To improve the solubility and conductivity of PEDOT, poly(styrenesulfonate) (PSS) as a dispersant and a charge-balancing dopant is usually doped into PEDOT during the polymerization [10, 13–16]. Combination of PEDOT and PSS (PEDOT:PSS) provides the enhanced electrical conductivity (1–10 S·cm⁻¹) with solubility in water which allows the conductive polymer to be easily-processed as an electronic ink for practical applications in field of printed electronics [17].

In theoretical studies, structural and electronic properties of PEDOT and PEDOT:PSS have been investigated by many research groups, i.e., Dkhissi et al. used ab initio Hartree–Fock (HF/6-31G) and density functional theory (DFT/6-31G) methods to exhibit relative stability of the aromatic and quinoid forms of neutral PEDOT in the ground state [18, 19]. Aleman et al. reported structural and electronic properties of n-EDOT with n=1–8 [20]. Lenz et al. studied the influence of the degree of doping on the reflectivity and optical properties of PEDOT:PSS based on GGA PW91 functional [14]. Very recently, Gangopadhyay investigated the nature of the interaction between PEDOT and PSS using B3LYP/6-31G** [21]. However, to our best knowledge, there has been no report on theoretical studies of PEDOT:PSS for ammonia sensing applications.

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Ammonia (NH₃) is highly toxic gas that is naturally existed in the atmosphere at low-ppb to sub-ppb levels. It can be widely used in various applications such as production of fertilizer and chemicals, refrigeration systems, and clinical diagnosis [22]. However, at high concentration of NH₃, it can cause irritation the skin, eyes, nose, throat to respiratory tract due to its corrosive properties. Exposure to a massive concentration of NH₃ (>5000 ppm) may be fatal within minutes. Therefore, detection of NH₃ has attracted much attention for environment protection and human health. Recently, several research groups have reported the fabrication of NH₃ gas sensors based on inorganic, organic and hybrid materials. For example, Pang et al. synthesized cellulose/TiO₂/PANI composite nanofibers by electrospinning and polymerization for NH₃ detection at room temperature [23]. The response value of the composite nanofibers to 250 ppm NH₃ was found to be 6.335. Zhang et al. fabricated MoS₂/ZnO nanocomposite film sensor by layer-by-layer self-assembly technique. The MoS₂/ZnO nanocomposite film exhibited a high sensitivity to NH₃ with a normalized response value of 24.38% in gas concentration of 5 ppm at room temperature [24]. Moon et al. prepared Co₃O₄–SWCNT nanocomposites by arc-discharge method [25]. The Co₃O₄–SWCNT sensor was investigated to various reducing gases such as H₂S, NH₃, H₂, and CH₄. At the optimum operating temperature of 250 °C, the response value of Co₃O₄–SWCNT sensor was ~50% for 100 ppm NH₃ detection. Other current materials for NH₃ sensing application were summarized in Table 1. Although some materials with specific preparation methods exhibited excellent sensing performances towards NH₃, most of them did not support the preparation of sensing film on flexible substrate that is one of serious problems for future wearable gas sensing application. In addition, each of these methods suffers from several disadvantages such as high cost, high complexity, long operating time for sensing film preparation and high operating temperature in gas detection. Therefore, the development of NH₃ gas sensors on flexible substrate with high sensitivity, simplicity, low temperature processing, high productivity, low-cost, low material waste and room operating temperature for NH₃ detection is still an important task for low-cost high-performance wearable gas sensors. In this work, we have fabricated a PEDOT:PSS NH₃ gas sensor based on inkjet printing method. Theoretical studies of PEDOT:PSS for NH₃ detection have been performed for the first time by using Self-consistent charge density functional tight-binding (SCC-DFTB). The most favorite site of NH₃ adsorption on PEDOT:PSS have been systematically investigated. It should be noted that the SCC-DFTB method was derived from DFT by neglect, approximation, and parametrization of interaction integrals. It offers several advantages including rapid computation of large scale molecular systems (several thousands of atoms), reliable description of dispersions and weak interactions (Van der Waals and H-bonding), and good prediction for properties (geometry, electronics, and binding energies) [26–28]. Moreover, the SCC-DFTB method was used for investigation of NH₃ adsorption on sensing material, which is consistent with experimental observations [29]. The SCC-DFTB was therefore selected for PEDOT:PSS theoretical studies on NH₃ sensing application for this work.

### Methods

**SCC-DFTB Method and Models of PEDOT:PSS**

The SCC-DFTB method is based on a second-order expansion of the DFT energy with respect to density fluctuations around a reference density [30]. The SCC-DFTB utilizes the Kohn-Sham orbitals with the optimized linear combination of atomic orbitals (LCAO) Slater-type valence electron basis set. The total energy of SCC-DFTB can be written as

\[
E_{SCC-DFTB} = \sum_{\mu \nu} c_{\mu} c_{\nu} H_{\mu \nu}^{0} + \sum_{A \neq B} E_{AB}^{rep} + \frac{1}{2} \sum_{AB} \gamma_{AB} \Delta q_{A} \Delta q_{B}
\]

Where \( \mu \) and \( \nu \) denote atomic orbitals, A and B denote atoms, \( c_{\mu} \) are the expansion coefficients of molecular orbitals, \( H_{\mu \nu}^{0} \) is unperturbed Hamiltonian, \( E_{AB}^{rep} \) is the two-body repulsive energy term, \( \Delta q_{A} \) and \( \Delta q_{B} \) are the induced charge on each atom A and B, respectively, and \( \gamma_{AB} \) is a distance-dependent function describing charge interactions.

Regarding SCC-DFTB, this method has been called as a “basis-set independent” method [31, 32].

### Table 1: Comparison of sensing materials for NH₃ detection in the literatures with the present work

| Sensing material | Gas response | Operating temperature | Ref. |
|------------------|--------------|-----------------------|------|
| Reduce graphene oxide | 0.64% (ΔR/R₀) 1000 | 22 °C | [50] |
| Silver Nanocrystal- MWNTs | ~9% (ΔR/R₀) 1000 | RT. | [51] |
| PANI | 2.3% (ΔR/R₀) 750 | RT. | [52] |
| ZnO nanorods | 10.1 (R/R₀) 100 | ~300 °C | [53] |
| SnO₂ | 1.74 (R/R₀) 100 | 200 °C | [54] |
| Co₃O₄ crossed nanosheet (CNS) | 5.6 (R/R₀) 100 | 111 °C | [55] |
| Pristine PEDOT:PSS | 4.08% (ΔR/R₀) 500 | RT. | This work |
are no integrals calculated in the DFTB method, thus there cannot be a basis set superposition error (BSSE). In addition, different basis sets are usually derived for electronic and repulsive potential parameters, the effects of BSSE on PEDOT:PSS-NH₃ interactions is therefore neglected for this study. The bond lengths, bond angle, and torsion angle of PEDOT and PSS are defined as shown in Fig. 1. To verify the accuracy of the SCC-DFTB method, the structure and electronic properties of PEDOT, PSS, and PEDOT:PSS (n = 1 to 3) obtained from SCC-DFTB method implemented on DFTB⁺ [33] in conjunction with the mio-0-1 parameter set [30, 34] were compared with density functional theory [35] at B3LYP/6-31G* [36, 37] level using GAMESS [38]. It should be noted that B3LYP can be well used for the description of the geometric and electronic structures of π-conjugated polymers [18, 19, 21]. However, it fails to accurately represent dispersion/weak non-covalent interactions. This leads to a serious limitation for investigation of PEDOT:PSS-NH₃ interactions. The B3LYP was thus employed to study the geometric and electronic properties of PEDOT:PSS only. After validation of the SCC-DFTB accuracy, PEDOT, PSS, and PEDOT:PSS up to n = 10 were fully optimized and studied based on SCC-DFTB calculation. Geometries were optimized until the atomic forces were less than 1.0 × 10⁻⁴ Hartree/Bohr. The SCC tolerance was set to 10⁻⁶ au. The electron temperature was kept to 1000 K in order to improve SCC convergence and include the effect of thermal electronic excitation [39, 40].

**QM/MM Simulation of EDOT:SS in Ammonia**

The QM/MM simulation was performed under canonical ensemble. The system consists one EDOT:SS molecule and 250 NH₃ molecules in a periodic cubic box of 16.38 × 16.38 × 16.38 nm³ as shown in Fig. 2. Total numbers of atoms in the simulation box were 1034 atoms. A target nuclear temperature of 298 K was maintained using a Berendsen thermostat [41]. The equations of motion were integrated using the Velocity Verlet algorithm [42] with an integration time step of 1 fs. The total simulation time were 100 ps.

**Fabrication of PEDOT:PSS Gas Sensor**

The PEDOT:PSS aqueous solution (Clevios™ P VP AI 4083, solid content 1.3–1.7%, PEDOT:PSS weight ratio = 1:6) was purchased from Heraeus Precious Metals GmbH & Co., KG and used without any further purification. A PEDOT:PSS NH₃ gas sensor was fabricated based on ink-jet printing method [17]. Briefly, interdigitated electrodes with 1-mm interdigit spacing were deposited on PET flexible substrate by screen printing of silver conductive paste. The aqueous PEDOT:PSS was mixed with dimethyl sulfoxide (DMSO), glycol (EG) and triton x-100 in order to improve conductivity, viscosity and surface tension. The mixed PEDOT:PSS electronic ink was then deposited on interdigitated electrodes by a modified ink-jet printer. The thickness of PEDOT:PSS sensing film could be controlled by varying the number of printed layers. The fabricated PEDOT:PSS gas sensor was tested with ammonia, acetone, ethanol, methanol, and toluene at 500 ppm concentration to assess the response and selectivity of the sensor. All experiments were performed at room temperature (25 ± 2 °C) and the relative humidity of 58 ± 2%. Gas response of PEDOT:PSS gas sensor is defined as
where $R_{\text{air}}$ and $R_{\text{gas}}$ are the sensor resistance in pure air and in test gas, respectively.

**Results and Discussion**

**Structural and Electronic Properties of PEDOT:PSS**

List of bond lengths, bond angle, and torsion angle of EDOT, SS and EDOT:SS oligomers ($n = 1$ to 3) obtained at the SCC-DFTB and DFT methods is given in Additional file 1: Table S1–S3 in the supplementary data section. Root-mean-square deviations (RMSD) of bond lengths, bond angle and torsion angle of optimized structures ($n = 1$ to 3 units) between SCC-DFTB and B3LYP/6-31G* methods are shown in Table 2. The RMSD values were calculated by a simple equation: 

$$S(\%) = \left( \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \times 100 \right),$$

where $S$ is the sensor response.

The HOMO, LUMO and energy gap ($\epsilon_g$) of EDOT, SS and EDOT:SS with $n = 1$ to 3 units based on B3LYP/6-31G* and SCC-DFTB methods are shown in Table 3. One can be seen that the $\epsilon_g$ of EDOT, SS and EDOT:SS ($n = 1$ to 3 units) predicted by the SCC-DFTB is less than that of B3LYP/6-31G* about 1.31–3.49 eV. Although there is a big difference $\epsilon_g$ prediction, the SCC-DFTB still yields values directly comparable with experimental results. For EDOT with eight units, B3LYP/6-31G* estimated the $\epsilon_g$ of 2.75 eV [20] while SCC-DFTB predicts the $\epsilon_g$ of 1.17 eV (see Fig. 4) which is in good agreement with experimental investigations (1.5–1.7 eV) [2, 44–46]. The HOMO and LUMO energies for EDOT, SS, and EDOT:SS with $n = 1$ to 10 units based on SCC-DFTB method are reported in Additional file 1: Table S5 in the supplementary data section.

The HOMO and LUMO energies can imply to the ionization potential and electron affinities, respectively [47]. For EDOT oligomers, the HOMO and LUMO energies increase and decrease, respectively, with increasing oligomers ($n$). These cause from an increase of $\pi$ conjugation resulting to increase of electrical conductivity when number of oligomers increase (see Fig. 4). In case of SS oligomers, HOMO and LUMO energies do not increase/decrease linearly. These may come from variety of sulfonate functional groups conformation of SS oligomers. For EDOT:SS oligomers, it clearly shows enhancement of electrical conductivity in all $n$ as shown in Fig. 4. At $n = 10$, the $\epsilon_g$ of EDOT:SS is 0.35 eV which is three times greater than that of pristine EDOT (1.08 eV). The electrons prefer to transfer from EDOT to SS oligomers ranging from 0.007 to 0.444 [e] with increasing oligomers ($n$).

**Sensing Property of PEDOT:PSS Gas Sensor**

The gas response of pristine PEDOT:PSS gas sensor to various volatile organic compound (VOCs) such as toluene, methane, ethanol, acetone, and ammonia at room temperature is displayed in Fig. 5. It clearly shows that the pristine PEDOT:PSS gas sensor exhibited relatively high response and selectivity to ammonia compared with other VOCs. The gas responses to NH$_3$, acetone, methanol, ethanol, and toluene were 4.08, 2.41, 0.77, 0.58, and 0.49%, respectively. Sensing mechanism of PEDOT:PSS sensor to ammonia can be explained via direct charge transfer process and swelling process [17]. In this work, only direct charge transfer process has been investigated.

### Table 2 Root mean square deviations (RMSD) of bond lengths, bond angle and torsion angle of optimized EDOT, SS and EDOT:SS structures ($n = 1$ to 3 units) between SCC-DFTB and B3LYP/6-31G* methods

| $n$ | Bond length (Å) | Bond angle (°) | Torsion angle (°) |
|-----|----------------|---------------|------------------|
| 1   | 0.084          | 1.128         | -                |
| 2   | 0.077          | 1.960         | 2.218            |
| 3   | 0.075          | 0.621         | 0.771            |
in depth based on SCC-DFTB method. The results will be discussed in the next section.

**QM/MD Simulation**

In order to study the tendency and behavior of NH\textsubscript{3} orientation toward PEDOT:PSS, the QM/MD simulation of a EDOT:SS in 250 NH\textsubscript{3} molecules was performed in a periodic box at room temperature. Last 50 ps simulation times were used for radial distribution function (RDF) analysis. The RDFs from the atoms of EDOT to the H and N atoms of NH\textsubscript{3} molecules are shown in Fig. 6a and b, respectively. One can be seen that NH\textsubscript{3} molecules prefer to localize at H atoms of EDOT molecule with the first RDFs peaks of 1.94 and 2.04 Å for H and N atoms of NH\textsubscript{3} molecules, respectively. In case of SS, the probability of finding NH\textsubscript{3} molecules surrounding the O atoms of SS is higher than that of the other atoms as displayed in Fig. 6c and d. Based on the first RDFs peaks, the H atoms of NH\textsubscript{3} molecules turn toward the O atoms of SS at the position of 1.91 Å and the N atoms of NH\textsubscript{3} tends toward the H atoms of SS at the position of 2.30 Å. The results suggest that NH\textsubscript{3} molecules interact with both EDOT and SS and favor to bind at the sites of O and H atoms. To better understand the binding distances and interaction energies between EDOT:SS and NH\textsubscript{3}, four configurations (see Fig. 7) extracted from the first RDFs peaks were re-calculated with SCC-DFTB energy calculation including van der Waals dispersion corrections [48, 49].

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Model & n & \multicolumn{3}{|c|}{B3LYP/6-31G*} & \multicolumn{3}{|c|}{SCC-DFTB} \\
\hline & & HOMO & LUMO & \(\varepsilon_g\) & HOMO & LUMO & \(\varepsilon_g\) \\
\hline
EDOT & 1 & -5.71 & 1.90 & 7.61 & -5.38 & -1.26 & 4.12 \\
 & 2 & -4.77 & -0.71 & 4.06 & -4.55 & -1.96 & 2.59 \\
 & 3 & -4.33 & -1.03 & 3.30 & -4.2 & -2.21 & 1.99 \\
SS & 1 & -7.22 & -1.09 & 6.13 & -6.41 & -3.11 & 3.30 \\
 & 2 & -7.20 & -1.36 & 5.84 & -6.53 & -3.34 & 3.19 \\
 & 3 & -7.29 & -1.48 & 5.81 & -6.62 & -3.49 & 3.13 \\
EDOT:SS & 1 & -6.02 & -0.89 & 5.13 & -4.95 & -2.83 & 2.12 \\
 & 2 & -4.67 & -1.28 & 3.39 & -4.16 & -2.79 & 1.37 \\
 & 3 & -4.87 & -1.58 & 3.29 & -3.83 & -3.04 & 0.79 \\
\hline
\end{tabular}
\caption{HOMO, LUMO and energy gap (\(\varepsilon_g\)) in eV of EDOT, SS and EDOT:SS with \(n=1\text{-}3\) units obtained by B3LYP/6-31G* and SCC-DFTB methods.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Optimized structures of \(a\) EDOT, \(b\) SS, and \(c\) EDOT:SS oligomers with \(n=10\) units based on SCC-DFTB calculation.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Variation of energy gaps of EDOT, SS, and EDOT:SS oligomers obtained by SCC-DFTB method.}
\end{figure}
The interaction energy ($E_{\text{int}}$) can be calculated by the following equation:

$$E_{\text{int}} = E_{\text{tot}}(\text{EDOT:SS + NH}_3) - E_{\text{tot}}(\text{EDOT:SS}) - E_{\text{tot}}(\text{NH}_3),$$ (3)

where $E_{\text{tot}}(\text{EDOT:SS + NH}_3)$, $E_{\text{tot}}(\text{EDOT:SS})$ and $E_{\text{tot}}(\text{NH}_3)$ are the total energies of the EDOT:SS with NH$_3$, individual EDOT:SS and individual NH$_3$, respectively.

The interaction energy between EDOT:SS and NH$_3$ at different adsorption sites and NH$_3$ orientation configurations is shown in Fig. 8. The H$_{\text{SS}}$-N$_{\text{NH}_3}$ configuration exhibits the highest interaction energy (6.596 kcal/mol) with the binding distance of 2.00 Å. This result suggests that the NH$_3$ molecules prefers to interact with EDOT:SS via the lone pair on the N atom at H atoms of EDOT:SS. At this adsorption site, electron charge transfer was found to be from the NH$_3$ molecule to the EDOT:SS (0.032 e). The holes of EDOT:SS interact with the electron-donating NH$_3$. The delocalization degree of conjugated $\pi$ electrons of EDOT:SS is increased by charge transfer from the adsorbed NH$_3$ molecules. Formation of a neutral polymer backbone occurs and leads to decrease in charge carriers of EDOT:SS. It causes the increase in resistance of EDOT:SS in present of NH$_3$. This behavior is in good agreement with our experimental results as shown in Fig. 5.

**Conclusions**

The PEDOT:PSS conductive polymer for NH$_3$ detection was investigated both experimentally and theoretically. The structural and electronic properties of PEDOT:PSS oligomers were studied based on SCC-DFTB method and compared with B3LYP/6-31 g*. Calculations indicated that SCC-DFTB is indeed capable of reproducing the DFT-predicted features of PEDOT:PSS conductive polymer system (C-S-O-H bonding). Non-planar conformation in
PEDOT:PSS chain structure naturally occur due to the existence of repulsive interactions between the sulfur atoms and H-bond attractive interactions between EDOT and SS oligomers. The EDOT behaves as an electron donor for EDOT: SS composites. The electrical conductivity of EDOT increases with increasing oligomers and doping SS. The energy gap of EDOT: SS with 10 oligomers was found to be 0.35 eV based on SCC-DFTB. The printed PEDOT:PSS gas sensor exhibited good response and selective to NH₃ at room temperature over VOCs such as toluene, methanol, ethanol, and acetone. Theoretical investigation showed interaction between NH₃ and EDOT: SS via physisorption. The H atoms of SS are the most favorable adsorption site of NH₃. Direct charge transfer process dominates changing in conductivity of EDOT:SS upon NH₃ exposure at room temperature. The PEDOT:PSS sensor acts as an electron acceptor for NH₃ detection. It is hoped that this work will be useful for better understanding of the NH₃ interactions with PEDOT:PSS and can be used to confirm the direct charge transfer sensing mechanism of PEDOT:PSS gas sensors for NH₃ detection.

Additional Files

![Fig. 7 Orientations of NH₃ molecules around EDOT:SS based on the first RDFs peaks](image1)

![Fig. 8 EDOT:SS-NH₃ interaction energies at different adsorption sites and configurations as a function of the distance (d)](image2)

**Additional file 1: Table S1.** Average bond lengths, bond angle and torsion angle of EDOT, SS, EDOT of EDOT:SS (EDOT:SS₁) and SS of EDOT:SS (EDOT:SS₅) with n = 1 units optimized by B3LYP/6-31G* and SCC-DFTB calculation. **Table S2.** Average bond lengths, bond angle and torsion angle of EDOT, SS, EDOT of EDOT:SS (EDOT:SS₁) and SS of EDOT:SS (EDOT:SS₅) with n = 2 units optimized by B3LYP/6-31G* and SCC-DFTB calculation. **Table S3.** Average bond lengths, bond angle and torsion angle of EDOT, SS, EDOT of EDOT:SS (EDOT:SS₅) and SS of EDOT:SS (EDOT:SS₅) with n = 3 units optimized by B3LYP/6-31G* and SCC-DFTB calculation. **Table S4.** Average bond lengths, bond angle and torsion angle of EDOT, SS, EDOT of EDOT:SS (EDOT:SS₅) and SS of EDOT:SS (EDOT:SS₅) with n = 10 units optimized by SCC-DFTB calculation. **Table S5.** Energy of the HOMO and LUMO in eV of EDOT, SS and EDOT:SS oligomers optimized by SCC-DFTB calculation. (DOCX 29 kb)
Abbreviations
EDOT: 3,4-ethylenedioxythiophene; NH₃: Ammonia; PEDOT:PSS: Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate); RDF: Radial distribution function; RMSD: Root mean square deviations; SCC-DFTB: Self-consistent charge density functional tight-binding; SS: Styrene sulfonate

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Authors’ Contributions
AM performed the computational simulations. YS carried out the sensor fabrication measurements. CW conceived and designed the work. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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References
1. Dietrich M, Heinz J, Heywang G, Jonas F (1994) Electrochemical and spectroscopic characterization of poly(3,4-ethylenedioxythiophene). J Electroanal Chem 369:87–92
2. Pei Q, Zuccarello G, Ahsikog M, Ingaras O (1994) Electrochromic and highly stable poly(3,4-ethylenedioxythiophene) switches between opaque blue-black and transparent sky blue. Polymer 35:1347–1351
3. Kiebooms R, Aleshin A, Hutchison K, Wudl F (1997) Thermal and electromagnetic behavior of doped poly(3,4-ethylenedioxythiophene) films. J Phys Chem B 111:10137–10139
4. Ouyang J (2013) Secondary doping methods to significantly enhance the performance of PEDOT:PSS. J Mater Chem A 1:4325–4332
5. Li H, Xiao Y, Han G, Hou W (2017) Honeycomb-like poly(3,4-ethylenedioxythiophene) as an effective and transparent counter electrode in bifacial dye-sensitized solar cells. J Power Sources 342:709–716
6. Bokzurt A, Low A (2011) Low-cost flexible printed circuit technology based on layer-by-layer self-assembled molybdenum disulfide/zinc oxide nanocomposite film. J Alloys Compd 534:408–412
7. Popp J, Zhang Z, Chen Y, Zhang J, Wang Q, Wang F, Wei Q (2016) A room temperature ammonia gas sensor based on cellulose/CoOx/PANI composite nanofibers. Colloids Surf A Physicochem Eng Asp 494:248–255
8. Zhang D, Jiang C, Sun Y (2017) Room-temperature high-performance ammonia gas sensor based on layer-by-layer self-assembled molybdenum disulfide/zinc oxide nanocomposite film. J Alloys Compd 684:476–483
9. Moon S, Vuong NM, Lee D, Kim D, Lee H, Kim D, Hong SK, Yoon S-G (2016) CoOx/SWCNT composites for H2S gas sensor application. Sens Actuators B 222:166–172
10. Gau M, Cui Q, Elstner M (2011) DFTB3: extension of the self-consistent charge density-functional紧 binding method (SCC-DFTB). J Chem Theory Comput 7:931–948
11. Elstner M (2006) The SCC-DFTB method and its application to biological systems. Theor Chem Acc 116:316–325
12. Wongsombook C, Wang Y, Khodcharoen T, Lefe S (2014) Nonequilibrium quantum chemical molecular dynamics simulations of CoO/Pt heterofullerene conversion. Carbon 68:285–295
13. Feng X, Wee S, Witeh H, Morokuma K, Vidi C, Borgeuet E (2005) Sensitivity of ammonia interaction with single-walled carbon nanotube bundles to the presence of defect sites and functionalities. J Am Chem Soc 127:10533–10538
14. Elstner M, Porezag D, Junghnickel G, Elsner J, Haght M, Frauenshahn T (1998) Self-consistent charge density functional tight-binding method for simulations of complex materials properties. Phys Rev B 58:7260–7268
15. Popp J, Aghna-Chamanduty M, Sukh S (2003) BSSE-free description of intermolecular force constants in hydrogen fluoride and water dimers. Int J Quantum Chem 92:152–159
16. Gau M, Cui Q, Elstner M (2011) DFTB3: extension of the self-consistent charge density-functional tight-binding method (SCC-DFTB). J Chem Theory Comput 7:931–948
17. Araki H, Hayahime H, Fraunlein T (2007) DFTB+ a sparse matrix-based implementation of the DFTB method. J Phys Chem B 111:5678–5684
18. Niehaus TA, Elstner M, Frauenhahn T, Suhai S (2001) Application of an approximate density-functional method to sulfur containing compounds. J Mol Struc (THEOCHEM) 541:185–194
19. Tong X-M, Chu S-I (1997) Density-functional theory with optimized effective potential and self-interaction correction for ground states and autoionizing resonances. Phys Rev A 56:3406–3416
20. Cohen AJ, Handy NC (2000) Assessment of exchange correlation functional. Chem Phys Lett 316:401–407
21. Rives JT, Jorgensen WL (2008) Performance of BLYP density-functional methods for a large set of organic molecules. J Chem Theory Comput 4:297–306
22. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koscielny A, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) General atomic and molecular electronic structure system. J Comput Chem 14:1347–1363
23. Weinert M, Davenport JW (1992) Fractional occupations and density-functional energies and forces. Phys Rev B 45:13709–13712
24. Wentzcovitch R, Martins J, Allen P (1992) Energy versus free energy conservation in first-principles molecular dynamics. Phys Rev B 45:11372–11374
41. Berendsen HJC, Postma JPM, Van Gunsteren WF, Dinola A, Haak JR (1984) Molecular-dynamics with coupling to an external bath. J Chem Phys 81:3684–3690
42. Swope W, Andersen H, Berens P, Wilson K (1982) A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: application to small water clusters. J Chem Phys 76:637–49
43. Kim GH, Hwang DH, Woo SI (2012) Thermoelastic properties of nanocomposite thin films prepared with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) and graphene. Phys Chem Phys 14:3530–3536
44. Zotzing GA, Reynolds JR, Steel PI (1991) Poly(3,4-ethylenedioxythiophene) (PEDOT) prepared via electrochemical polymerization of EDOT, 2,2'-bis(3,4-ethylenedioxythiophene) (BiEDOT), and their TMS derivatives. Adv Mater 9:795–798
45. Huang H, Pickup PG (1998) A donor-acceptor conducting copolymer with a very low band gap and high intrinsic conductivity. Chem Mater 10:2212–2216
46. Sankaran B, Reynolds JR (1997) High-contrast electrochromic polymers from alkyl-derivatized poly(3,4-ethylenedioxythiophenes). Macromolecules 30:2582–2586
47. Ullah H, Ayub K, Ullah Z, Hanif M, Nawaz R, Shaha AHA, Bilal S (2013) Theoretical insight of polypyrrole ammonia gas sensor. Synth Met 172:14–20
48. Rappe AK, Casewit CJ, Colwell KS, Goddard WA III, Skiff WM (1992) Uff, A full periodic table force field for molecular mechanics and molecular dynamics simulations. J Am Chem Soc 114:10024–10035
49. Elstner M, Hobza P, Frauenheim T, Suhai S, Kaxiras E (2001) Hydrogen bonding and stacking interactions of nucleic acid base pairs: a density-functional-theory based treatment. J Chem Phys 114:5149
50. Wu J, Tao K, Miao J, Norford LK (2015) Improved selectivity and sensitivity of gas sensing using a 3D reduced graphene oxide hydrogel with an integrated microheater. ACS Appl Mater Interfaces 7:27502–27510
51. Cui S, Hu P, Lu G, Wen Z, Mattson EC, Hirschmugl C, Josifovska MG, Weinert M, Chen J (2012) Fast and selective room-temperature ammonia sensors using silver nanocrystal-functionalized carbon nanotubes. ACS Appl Mater Interfaces 4:4898–4904
52. Sengupta PP, Barik S, Adhikari B (2007) Polyaniline as a gas-sensor material. Mater Manuf Process 21:263–270
53. Chen T-Y, Chen H-I, Hsu C-S, Huang C-C, Wu J-S, Chou P-C, Liu W-C (2015) Characteristics of ZnO nanorods-based ammonia gas sensors with a cross-linked configuration. Sens Actuators B 221:491–498
54. Li Y, Chen N, Deng D, Xing X, Xiao X, Wang Y (2017) Formaldehyde detection: SnO2 microspheres for formaldehyde gas sensor with high sensitivity, fast response/recovery and good selectivity. Sens Actuators B 238:264–273
55. Zhang Z, Zhu L, Wen Z, Ye Z (2017) Controllable synthesis of Co3O4 crossed nanosheet arrays toward an acetone gas sensor. Sens Actuators B 238:1052–1059