Comparative Study on the Formation and Oxidation-Level Control of Three-Dimensional Conductive Nanofilms for Gas Sensor Applications

Kyung Hee Cho, Jyongsik Jang,* and Jun Seop Lee*

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ABSTRACT: Investment in wearable monitoring systems is increasing rapidly for realizing their practical applications, for example, in medical treatment, sports, and security systems. However, existing wearable monitoring systems are designed to measure a real-time physical signal and abnormal conditions rather than harmful environmental characteristics. In this study, a flexible chemical sensor electrode based on a three-dimensional conductive nanofilm (3D CNF) is fabricated via facile polymerization with temperature control. The morphology and chemical state of the 3D CNF are modified via electrochemical doping control to increase the carrier mobility and the active surface area of the sensor electrode. The sensor electrode is highly sensitive (up to 1 ppb), selective, and stable for an analyte (NH3) at room temperature owing to the three-dimensional morphology of polypyrrole and the oxidation-level control.

INTRODUCTION

Flexible electronics have attracted much considerable attention because of their excellent potential for application in portable devices and displays.1−4 In particular, investment in wearable monitoring system research has been rapidly increasing for realizing applications, for example, in healthcare, sports, and security systems.5−7 However, conventional wearable monitoring systems are specialized for physiological measurements to track real-time health status and abnormal conditions rather than hazardous environmental situations. The ability to detect harmful and flammable substances has recently emerged as another technical problem for sensor devices in preventing diseases because of perilous chemicals.8−11 Therefore, it is necessary to develop small, simple, and accurate sensing materials with low detection limits (down to ppb level) for wearable chemical sensor systems. Considerable research has been performed on nanosized semiconducting materials owing to their favorable characteristics, such as their high surface-to-volume ratio and small size, which lead to amplified signals.12−16

Among the semiconducting materials, conducting polymer nanomaterials are used as sensing transducers because of their attractive inherent transport properties (i.e., electrical conductivity and energy migration at room temperature) originating from their conjugated backbone structure.17−20 Additionally, the oxidation levels of the conducting polymers can be changed via doping processes to facilitate a sensitive and rapid response to specific chemical species.21−23 Moreover, studies have been performed on the morphology control of conducting polymer nanomaterials in sensor transducers to maximize the interactions with target analytes. For example, Park et al. fabricated a multidimensional carboxyl poly(3,4-ethylenedioxythiophene) nanotube membrane-based biosensor using electrospinning and modified vapor deposition polymerization to detect dopamine molecules.24 Sakar et al. formulated poly(3,4-ethylenedioxythiophene) polystyrene sulfonate films with quasi-periodic parallel cracks, which had a high charge carrier mobility for use in alcohol and humidity sensors.25 However, the synthesis steps for morphology control at the nanoscale are complex.

Even though conducting polymer nanomaterials exhibit high performance as sensing transducers, there is a lack of methods for integrating sensor components into flexible electronic circuits, limiting the mass production of devices.26,27 In addition, the uniform diffusion of nanosized sensing materials is an obstacle for their application to flexible sensor devices.28−30 Several approaches have been proposed to achieve integration with a uniform distribution.31−35 One of the most promising approaches involves the direct generation of a conducting polymer nanostructure on a flexible substrate as a sensing transducer. This method allows the uniform
installation of nanostructures on devices at low cost without an integration step.

Herein, we describe the formation of a three-dimensional conductive nanoﬁlm (3D CNF)-based chemical sensor consisting of vertically aligned polypyrrole nanowires on a graphene substrate, through an electrodeposition process with temperature control. The morphology of the polypyrrole nanostructures is controlled by changing the synthesis temperature because the micelle size and the diffusion area increase with the temperature. Moreover, the doping level of the 3D CNF is changed using an electrochemical oxidation process to enhance the charge-transfer rate during the detection of the target analyte (NH₃). The 3D nanostructure and electrochemical doping enhance the active surface area and charge-carrier (hole) transfer of the nanoﬁlm, respectively. Thus, the electrochemically doped nanoﬁlm-based chemical sensor exhibits a high sensitivity to NH₃ gas, with low detection limits (down to ppb level) and fast response and recovery times. Additionally, the sensing ability of the chemical sensor electrode is retained after various bending cycles because of the ﬂexibility of the substrates [polyethylene naphthalate (PEN) and graphene] and the polypyrrole nanoﬁlm.

**RESULTS AND DISCUSSION**

**Formation Control of 3D CNF.** Figure 1a shows the overall process for the formation of 3D CNFs via the electropolymerization method. As a template of the conducting polymer nanostructures, monolayer graphene was introduced onto a PEN substrate using the wet transfer method. Figure 1b shows the illustrative formation mechanism of polypyrrole nanostructures with different temperatures on the graphene substrate.
decorate the surface with polypyrrole nanostructures. In the electrolyte solution, a phosphate buffer maintains the pH of the electrolyte during the polymer synthesis to prevent the influence of the generated hydrogen ions. Additionally, p-toluenesulfonic acid functions as not only a dopant but also a soft template of the pyrrole to form pyrrole-containing micelles. In the polymerization process, the pyrrole-containing micelles are adsorbed on the graphene surface, acting as templates at the beginning of the polymerization (i.e., nucleation sites). The generated nucleation sites inhibit the growth of polypyrrole in directions other than the vertical direction owing to the steric hindrance of adjacent nanostructures. The steric hindrance effect is enhanced with the growth of the polypyrrole nanostructure.

The morphology of the generated polypyrrole nanostructures changes from a nanowire to a micrograin with temperature variations (Figures 2 and S1). At a low synthesis temperature (5°C), nucleation sites with a diameter of 50 nm are uniformly formed on the surface, and vertically aligned polypyrrole nanowires (ca. 1 μm long, with a diameter of ca. 70 nm) are formed after the growth process. The nucleation sites and nanowires increase in size and become irregular with the increasing synthesis temperature, up to 70°C. Temperatures higher than 70°C result in thick-coated polypyrrole films rather than nucleation sites and nanowires on the graphene surface. In particular, at 90°C, the thickness of the aggregated part of the 3D CNF increases from 55 to 245 nm, and the diameter of the nanostructures enhances to 210 nm (Figure 3). Additionally, at the macroscale, the generated polypyrrole exhibits irregular surfaces at synthesis temperatures higher than 5°C (Figure 3). In a moderate temperature range (45–70°C), the films display micropores, and the size of the pores increases with the temperature. A synthesis temperature higher than 70°C yields a bumpy surface rather than pores.

The morphology change of the polypyrrole nanostructures originates from the following mechanism (Figure 1b). First, the size of the micelles in the electrolyte increases at higher reaction temperatures owing to the enlargement in the hydrodynamic radius. Then, the larger containers increase the size of the nucleation sites and enlarge the diffusion area of each nucleation site. The extended diffusion areas of the nucleation sites cause the overlap of the nuclei, resulting in the formation of a mass film on the substrate during the growth process. In addition, the Brunauer–Emmett–Teller (BET) surface areas of the films are decreased with increasing temperatures (33.9 m² g⁻¹ for 5°C, 29.9 m² g⁻¹ for 45°C, 24.2 m² g⁻¹ for 70°C, and 18.2 m² g⁻¹ for 90°C), owing to the fact that the number of nanowires per unit area is reduced at higher temperatures (Figure S3).

**Oxidation-Level Control of 3D CNF.** The 3D CNF polymerized at 5°C presents different chemical states and morphologies with an electrochemical oxidation-level control. During the oxidation control, transformations of the polymer chains (such as neutral, polaron, bipolaron, and overoxidation) occur with an increasing applied potential (Figure S4). Figure 4a shows the electrical conductivity of the 3D CNF with different oxidation levels (ranging from −1.4 to +1.4 V). The electrical conductivity increases with the oxidation level because a more positive potential improves the carrier density (0.2 × 10¹⁸ to 1.31 × 10¹⁹ cm⁻³) in the polymer chains. There are two improvements of the electrical conductivity—from −1.4 to −1.0 V and from 0 to 0.6 V—because of the changes in the charge-transfer property from neutral to polaron and from polaron to bipolaron, respectively. The highest value of the electrical conductivity is 101.8 S cm⁻¹ for an applied potential of +1.0 V. High applied voltages (from +1.3 V) cause overoxidation of the films, with a reduction of the electrical conductivity (to 1.3 × 10⁻³ S cm⁻¹ at 1.4 V) despite the high carrier densities. Additionally, the carrier mobility (μ), which originated from the electrical conductivity (σ) and carrier density (n₀), differs with the increasing applied potential. The carrier mobility rapidly decreases in the overoxidation region.
change the polymer chains to quinoid structures. Positive voltages increase the amount of (bi)polarons and defects and form the quinoid structure. Therefore, more species (polarons or bipolarons) are located on geometrical structure to a quinoid structure. Specifically, positive-doped species (polarons or bipolarons) are located on geometrical defects and form the quinoid structure. Therefore, more positive voltages increase the amount of (bi)polarons and change the polymer chains to quinoid structures.

Furthermore, the chemical composition of the 3D CNF was characterized using X-ray photoelectron spectroscopy (XPS). Figure 5 presents the new bond of the polymer chains in the N 1s region with different applied voltages. Peaks at ca. 400 eV [related to the neutral amine N of the pyrrolic unit (−NH−)] and ca. 398 eV (related to imine (−N═)) are observed in all cases. For a potential of −0.2 V, there is a peak corresponding to the positively charged N (−NH2−) at 401.4 eV, indicating the formation of polarons. For more positive potentials (+1.0 and +1.4 V), there is a bipolaron N peak (==NH−−) at 403.0 eV. Thus, increasing the oxidation level of the 3D CNF enhances the amount of positively charged N in the structure.

The morphology of the 3D CNF is reversibly changed for different oxidation levels using the osmotic effect of the counterion (bis(trifluoromethanesulfonyl)amide anion) (Figure 6). When electrochemical oxidation occurs, electrons are ejected from the 3D CNF, and a positive charge is developed on the structure. Enlarged pores are observed as the oxidation levels increase (7 nm for −1.2 V, 10 nm for −0.2 V, 15 nm for +1.0 V, and 30 nm for +1.4 V) (Figure S7). The BET surface area also increases, that is, from 33.9 m² g⁻¹ for −1.2 V to 41.5 m² g⁻¹ for +1.4 V at more positive potentials on account of the fact that polymer structures are more expanded at higher oxidation levels.

Sensor Application. The real-time responsive resistance changes were measured for different concentrations of gases at room temperature. The 3D CNF-based sensor electrodes consist of three parts, namely, the substrates (PEN and graphene), the source/drain electrodes (silver paste), and the transducer (3D CNF) (Figure S8). To confirm the sensing performance of 3D CNF, a bare chemical vapor deposition (CVD) graphene-based electrode shows a small response at a high concentration of NH₃ gas, but it cannot detect at a low concentration. Therefore, the sensing ability of the electrode at low concentrations originated from the 3D CNF layer. First, the effect of the synthesis temperature on the sensing performance was examined by exposing the sensor electrodes to NH₃ gas, which is a reducing gas. As shown in Figure 7, the response decreases with the increasing reaction temperature because of the reduced active surface area, caused by the larger nanowires and thicker aggregated part in the 3D CNF structure. The sensing performance with respect to the oxidation level is investigated for the 3D CNF polymerized at 5 °C.

Figure 8a shows the sensing performance of the electrodes with respect to the oxidation level. The sensor electrode oxidized at +1.0 V exhibits the highest sensitivity (down to 1 ppb) to NH₃ on account of the high carrier density (hole) and the additional inner channel in the nanowire structure. In contrast, despite the improved active sites in the structure, the electrode oxidized at +1.4 V shows no response to the NH₃ gas, owing to the destruction of the conjugated polymer chains. A highly sensitive electrode is achieved in the bipolaron state.

![Figure 6](https://dx.doi.org/10.1021/acsomega.9b03947)
significantly repeated bending deformation (up to 500 cycles) has no
success. The transducer for detecting NH3 and MeOH gases at various
concentrations. oxidized at +1.0 V can effectively utilize as a signal
detachment of the target molecule is related to the applied
behavior range is larger for the electrode oxidized at +1.0 V (1
ppb to 102 ppm for NH3 and 0.1 to 103 ppm for MeOH) than
The selectivity of sensor electrodes is also important for practical applications. Figure 8i presents the normalized resistance changes of the electrode oxidized at +1.0 V under exposure to various volatile gases at low concentrations (1 ppm for NH3 and MeOH; 100 ppm for others). Even though it has a lower concentration than the other gases, NH3 yields a signal change more than 10 times larger. Therefore, NH3 can be distinguished from other chemicals according to the extent and direction of the resistance changes. Thus, the sensing performance of the 3D CNF-based electrode is higher than that of other conventional conducting polymer-based sensor electrodes (Table 1).

CONCLUSIONS

3D CNFs were formed through a facile polymerization method with synthesis temperature control as transducers for a chemical sensor. The chemical states and morphologies of the 3D CNFs are changed using an electrochemical oxidation method. The 3D CNF oxidized at 1.0 V exhibits the highest charge carrier density (1.31 × 1019 cm−3), as well as an inner channel that enhances the interaction with the target analyte and increases the charge-transfer rate in the sensor electrode. The 3D CNF-based sensor shows a high sensitivity (down to 1 ppb) to NH3 gas and fast response times (<20 s) at room temperature. Moreover, the chemical sensor displays flexibility, cycle stability under various deformations, and selectivity to NH3 gas. Thus, the function of conductive nanostructures is optimized through the shape and chemical-state control, and the proposed method is effective for developing electrical devices and sensor systems.

EXPERIMENTAL SECTION

Materials. Pyrrole, sodium p-toluenesulfonate (pTSA), and bis(trifluoromethane)sulfonimide lithium salt (LiBis) were purchased from Sigma-Aldrich. Sodium phosphate dibasic dodecahydrate (Dibasic) and sodium phosphate monobasic dihydrate (Monobasic) were purchased from Junsei Chemical Co. All chemical reagents were used as received, without further purification.

Formation of 3D CNF. A 3D CNF was prepared on a graphene–PEN film via an electrodeposition reaction in a 100 mL aqueous solution containing 0.1 mol of pyrrole, 0.2 mol of sodium phosphates (1:1 molar ratio of Dibasic/Monobasic), and 0.1 mol of pTSA. The graphene–PEN film was prepared by CVD and a wet transfer method, as described in previous reports. Electrodeposition was performed at different temperatures under a constant potential of +0.8 V for 15 min in a three-electrode cell consisting of a Pt wire, Ag/AgCl, and the CVD graphene–PEN film as the counter, reference, and working electrodes, respectively. After the electrodeposition, the 3D CNF was rinsed with deionized (DI) water and dried at room temperature.

Oxidation-Level Control of 3D CNF. Oxidation-level control of the 3D CNF was conducted in the potentiostat mode using a three-electrode cell with 50 mL of a 0.1 M LiBis aqueous electrolyte. A Pt wire, Ag/AgCl, and the 3D CNF were used as the counter, reference, and working electrodes, respectively. A constant voltage was applied to the 3D CNF electrode for 3 min, and the voltage was changed from −1.6 to +1.4 V stepwise, with 0.2 V intervals. The electrical resistance
was measured via a four-probe method using a source meter immediately after each voltage application phase. The oxidation-level-controlled 3D CNF was rinsed with DI water and dried at room temperature.

**Electrical Sensing Measurement of Volatile Organic Compound Gases.** Gas sensor electrodes were prepared by painting each end of the 3D CNF with Ag paste and attaching a Cu wire to the ends at a distance of 1 cm. The sensor electrode was placed inside a vacuum chamber (100 Torr) and connected to a source meter to monitor the resistance change using a computer. In this experiment, a bubbler was used to vaporize different gases and to mix the vapors with N2 gas using a mass flow controller to modify the concentration of the analytes. The sensor electrode was exposed to various concentrations (1 ppb to 100 ppm) for 100 s and purged with N2 gas for the conductance to recover. The measurement was conducted by applying a constant current of $10^{-6}$ A to the electrode, and the response was calculated by measuring the normalized electrical resistance change $\Delta R / R_0 = (R - R_0) / R_0$, where $R$ and $R_0$ represent the measured real-time resistance and initial resistance, respectively. The response time was defined as the time taken for the resistance to reach 90% of the saturated value after the gas exposure, and the recovery time was defined as the time taken for the resistance to reach 90% of the initial value after purging with N2 gas.

**Characterization.** FE-SEM images were obtained using a JSM-6701F (JEOL Ltd., Japan). Raman spectra were obtained using a DXR2xi (Thermo, USA) installed at NCIRF at Seoul National University. XPS data were acquired using a Sigma Probe (Thermo, USA). The electrical conductivity was measured via a four-probe method using a source meter immediately after each voltage application phase. The oxidation-level-controlled 3D CNF was rinsed with DI water and dried at room temperature.

**Table 1. Summary of Representative Sensors for NH3 Detection**

| Sensing material | Sensing signal | Working temperature (°C) | Limit of detection | Response/recovery time | References |
|------------------|----------------|--------------------------|--------------------|------------------------|------------|
| PEDOT:PSS/FeCl3  | Resistance    | 25                       | 0.1 ppm            | 20 s/5 min             | 22         |
| PPy/rGO          | Resistance    | 25                       | 1 ppm              | 1 min/5 min            | 45         |
| PANI + rGO       | Resistance    | 25                       | 20 ppm             | 18 min/2 min           | 46         |
| ZnO/rGO          | Resistance    | 25                       | 10 ppm             | 84 s/216 s             | 47         |
| TiO2/rGO         | Resistance    | 25                       | 5 ppm              | 114 s/304 s           | 48         |
| 3D CNF           | Resistance    | 25                       | 1 ppb              | 18 s/56 s             | this work  |

Figure 8. Reversible and reproducible responses are measured at a constant current value ($10^{-6}$ A) of the 3D CNF with different oxidation levels.

(a) Normalized resistance changes upon sequential exposure to various concentrations of NH3. (b) Response and (c) recovery times of the 3D CNF toward 1 ppm of NH3. (d) Normalized resistance changes to different MeOH concentrations. (e) Calibration lines of the 3D CNF as a function of NH3 and MeOH concentrations. Each applied voltage is as follows: black for $-1.2$ V, red for $-0.2$ V, blue for $+1.0$ V, and pink for $+1.4$ V. (f) Periodic exposure of the $+1.0$ V applied 3D CNF to 1 ppb of NH3 gas. Normalized resistance changes of the $+1.0$ V applied 3D CNF under (g) various bending angles and (h) repeated bending cycles. (i) Sensing performance histogram of the $+1.0$ V applied 3D CNF to different oxidizing and reducing volatile gases. The concentrations of gases are as follow: 1 ppm for NH3 and MeOH and 100 ppm for others.
measured using a Keithley 2400, and the amount of charge was recorded using an electrochemical workstation (WBCS3000, WonAtech, Korea). The electrodeposition and oxidation-level control were performed using WBCS3000. The electrical conductivity, charge carrier mobility, and charge carrier density were calculated using the following equations.

The electrical conductivity was calculated as

\[ \sigma = \frac{L}{RA} \]  

(1)

where \( L \) represents the length, \( A \) represents the area of the CNF, and \( R \) represents the resistance measured by the source meter.

The charge carrier mobility was calculated as

\[ \mu = \frac{\sigma}{n_0 e l} \]  

(2)

where \( n_0 \) represents the charge carrier density and \( e l \) represents the electrical charge of the carrier.

The charge carrier density was calculated as

\[ n_0 = \frac{q}{V} \]  

(3)

where \( q \) represents the amount of charge and \( V \) represents the volume of the nanofilm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03947.

Various images of the 3D CNF at 25 °C polymerization; size change of the 3D CNF with temperature variation; surface area of the CNFs with different temperatures; different polypyrrole chain structures with changing oxidation levels; large-scale FE-SEM images as a function of the oxidation level; size deformation of the 3D CNF as a function of the oxidation level; surface area and pore distribution of the 3D CNF with voltage variation; structure of the sensor electrode; sensing performance of CVD graphene; and real bending images of the sensor electrode (PDF)

AUTHOR INFORMATION

Corresponding Authors

Jyongsik Jang — School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea; orcid.org/0000-0002-0415-802X; Phone: +82-2-880-7069; Email: jsjang@plaza.snu.ac.kr; Fax: +82-2-880-1604

Jun Seop Lee — Department of Materials Science and Engineering, Gachon University, Seongnam-Si, Gyeonggi-Do 13120, Republic of Korea; orcid.org/0000-0002-7350-2875; Phone: 82-31-750-5814; Email: junseop@gachon.ac.kr; Fax: +82-31-750-5389

Author

Kyung Hee Cho — School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03947

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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