Talanta 115 (2013) 713–717

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Design of interpenetrated network MWCNT/poly(1,5-DAN) on interdigital electrode: Toward NO_2 gas sensing

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ARTICLE INFO

Article history:
Received 4 April 2013
Received in revised form
8 June 2013
Accepted 14 June 2013
Available online 24 June 2013

Keywords:
Poly-diaminonaphthalene
Polymer conducting
Room temperature gas sensors

ABSTRACT

In this paper, poly(1,5-diaminonaphthalene) was interpenetrated into the network made of multiwalled carbon nanotubes (MWCNT) on platinum interdigital electrode (IDE) by electro-polymerization of 1,5-diaminonaphthalene (1,5-DAN). The electro-polymerization process of 1,5-DAN on MWCNT was controlled by scanning the cyclic voltage at 50 mV s^{-1} scan rate between −0.1 V and +0.95 V vs. saturated calomel electrode (SCE). The results of voltammetric responses and Raman spectroscopy represented that the films MWCNT/poly(1,5-DAN) were successfully created by this polymerization process. The films MWCNT/poly(1,5-DAN) were investigated for gas-sensing to NO_2 at low concentration level. The gas-sensing results showed that the response–recovery times were long and strongly affected by thickness of the film MWCNT/poly(1,5-DAN). Nevertheless, these films represented auspicious results for gas sensors operating at room temperature.

1. Introduction

NO_2 produced from the combustion processes must be carefully monitored because it is colorless, flammable, and dangerous, even at very low concentration. Gas sensors based on metal oxides sensing layers (In_2O_3, SnO_2, WO_3, etc.) have been known to be widely used for NO_2 detection [1]. They could detect low concentration levels (typical 0–100 ppm), but often require high operating temperatures—approximately 300–500 °C. Furthermore, metal oxide sensors, due to their close molecular structure with that of detected gases, show similar responses and lack of selectivity [2]. Recently, the introduction of semiconductor organic polymers has opened several advantages for gas sensors: high selectivity, high sensitivity, room temperature operation, easy thin film process and low cost [3,4]. For example, the interdigital electrodes (IDE) coated with electrochemically synthesized conducting polymers (polypyrrole, polyaniline, polythiophene) have been used to fabricate chemiresistive sensors promising applicability in gas detection [5–10]. However, when exposed to chemically aggressive electron withdrawing vapors like SO_2, Cl_2, NO_2, etc., these polymers usually provoke irreversible resistance change that is believed to be due to over-oxidation of the polymer backbone [11,12].

Poly(diaminonaphthalene) (PDAN) synthesized from aromatic diamine is a new type of multifunctional electroactive polymer which has attracted considerable attention in recent years. Besides electroconductivity, electroactivity, electrochromism and electrocatalysis, PDAN has exhibited very interesting properties originated from chemical reactivities of preserved amino groups on the macromolecular structure [13,14]. It is well known that NO_2 as strong oxidizing gas could be absorbed by the basic amino group. Thus, PDAN can be expected to be a sensing material for NO_2 detection. However, PDAN presents relatively low electrical conductivity and dense morphology that could diminish the sensor performances and increase the response–recovery times. This effect is expected to be exacerbated by using the 3D conductive electrode substrate based on carbon nanotubes [15].

In this paper, we describe the preparation of a network made of multiwalled carbon nanotubes (MWCNT), dispersed by interaction with Nafion® on the IDE [8]. The network can be then interpenetrated with an electroactive polymer by electropolymerization of 1,5-diaminonaphthalene. We obtained the conductive sensor IDE/MWCNT/poly(1,5-DAN) which showed good performance upon exposure to low concentration of NO_2 gas at room temperature. These results of the sensor IDE/MWCNT/poly(1,5-DAN) have been our primary results on conducting polymer-based gas sensors that could be possible for gas sensor operating at room temperature.

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http://dx.doi.org/10.1016/j.talanta.2013.06.025

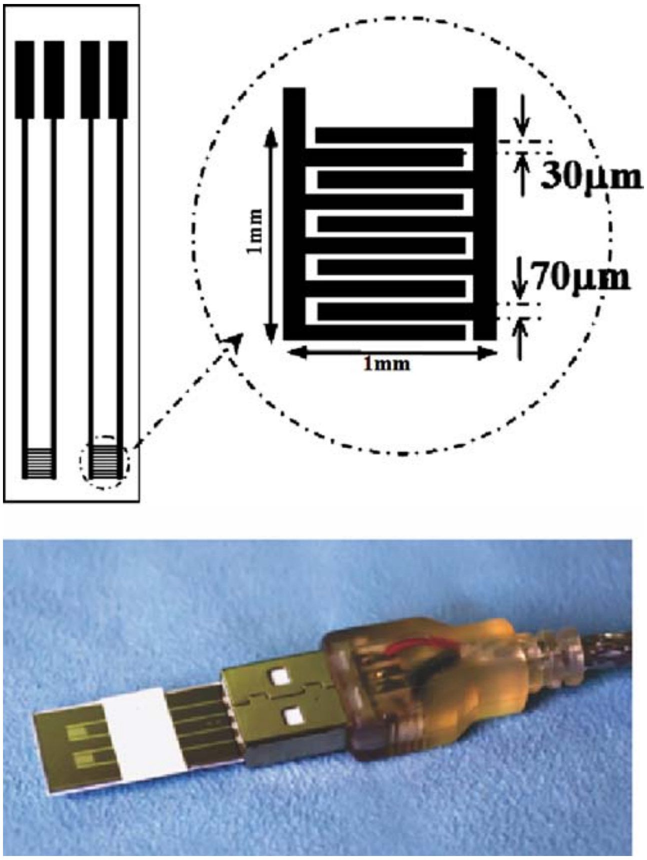

Fig. 1. Structure of the IDE electrode.

2. Experimental

2.1. Preparation of the gas-sensing film

The platinum interdigital electrode was prepared by a lift-off process with typical photolithography technique followed by sputtering of platinum on SiO_2 wafer [16]. The Pt interdigital electrode (IDE) on the SiO_2 wafer with six-finger configuration (the finger width of 70 μm and gap size of 30 μm) is shown in Fig. 1. The Pt-electrode thickness on the SiO_2 wafer was about 200 nm.

To fabricate the MWCNT layer, MWCNT (Shenzhen Nanoport Company, China) were dispersed in 1.25% Nafion® solution prepared by dilution of 5% Nafion® solution (Aldrich) in absolute ethanol [8]. The MWCNT–Nafion® mixture (10 μL) was drop-coated onto the platinum electrode IDE through evaporation of dispersion aliquot in air.

1,5-diaminonaphthalene (1,5-DAN) and $HClO_4$ were obtained from Merck as precursors for fabricating the sensing-layer. 1,5-DAN with concentration 5 mM in a 1 M aqueous $HClO_4$ solution was used as the solution to interpenetrate the poly(1,5-DAN) into the MWCNT network in electro-polymerization process. The electrochemical apparatus was a classical three-electrode set-up using an electrochemical analyzer system (AUTOLAB EcoChemie PGSTAT-30*)*. The network IDE/MWCNT was used as the working electrode. The reference electrode was saturated calomel electrode (SCE) and the counter-electrode was platinum grid. The interpenetrated networks IDE/MWCNT/poly(1,5-DAN) were obtained by operating the electrochemical process when scanning the cyclic voltage at 50 mV s^{-1} scan rate between −0.1 V and +0.95 V vs. SCE.

2.2. Characterization of the film IDE/MWCNT/poly(1,5-DAN)

The interpenetrated networks IDE/MWCNT/poly(1,5-DAN) were characterized by exalted Raman spectroscopy (Labram-HR 800) using a 514 nm He–Ne laser of 0.16 mW. Morphologies of the interpenetrated networks IDE/MWCNT/poly(1,5-DAN) were examined by a high-resolution scanning electron microscope (SEM-HITACHI S4800).

To investigate gas-sensing properties, an analytical gas source (100 ppm NO_2 in N_2 balance) from Air Liquide America Specialty Gases LLC was blended with the carrier gases (20% O_2 and 80% N_2) by flow-through mixing principle [17] to obtain the desired gas concentrations. The gas responses (S) of the sensor based on interpenetrated networks IDE/MWCNT/poly(1,5-DAN) were defined with the following equation: $S=((R-R_o)/R_o)\times 100$, where R and R_o are the resistances respectively of the sensor exposed in environment containing NO_2 gas and in pure air. The resistances of the sensor were measured by data acquisition (Keithley, Model 2700). The gas-sensing characteristics of the sensors were investigated in a chamber with 1000 mL in volume. The total flow rate of gases through the testing-chamber was fixed at 1000 mL/min.

3. Results and discussion

3.1. Electrosynthesis of poly(1,5-DAN) on the IDE/MWCNT

Electrochemical polymerization of poly(1,5-DAN) was performed by cyclic voltammetry (CV) from the aqueous solution containing 5 mM 1,5-DAN and 1 M $HClO_4$ onto the platinum interdigital electrode modified with MWCNT layer. Fig. 2 displays the cyclic voltammograms between −0.15 and +0.95 V vs. SCE at a scan rate of 50 mV s^{-1} taken during the electrochemical polymerization. This characteristic agrees well with the results published by Pham et al. [13]. In detail, the anodic peak at around 0.64 V on the first scan, indexed (I) in Fig. 2, corresponds to the 1,5-DAN oxidation. In subsequent cycles, this peak seems to disappear. At lower potentials (E), two typical redox systems were formed at the assigned positions (II-1, II-2) and (III-1, III-2) in Fig. 2 and the electrical current continuously increased during scans reflecting the growth of the conductive polymer film on the IDE/MWCNT. This CV behavior shows that it is possible to electropolymerize 1,5-DAN inside the MWCNT network.

To confirm the successful polymerization of 1,5-DAN on surface of MWCNT, redox responses of the above synthesized films

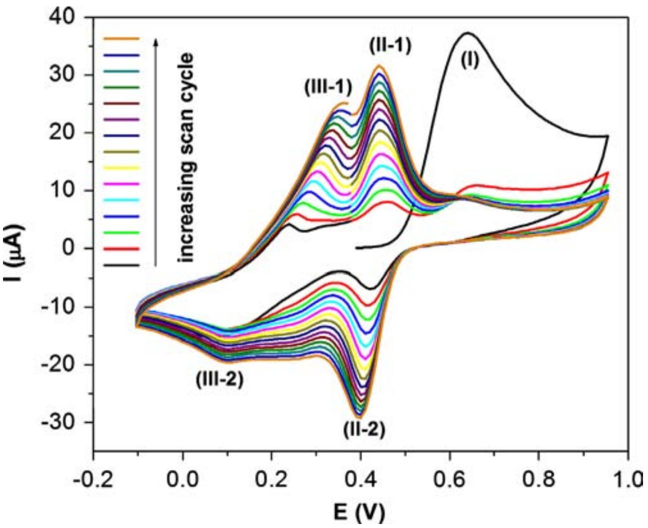

Fig. 2. Cyclic voltammetric curves during poly(1,5-DAN) film growth onto IDE/MWNT-Nafion®; solution: 5 mM 1,5-DAN in 1 M $HClO_4$; scan rate$=$50 mV s^{-1}.

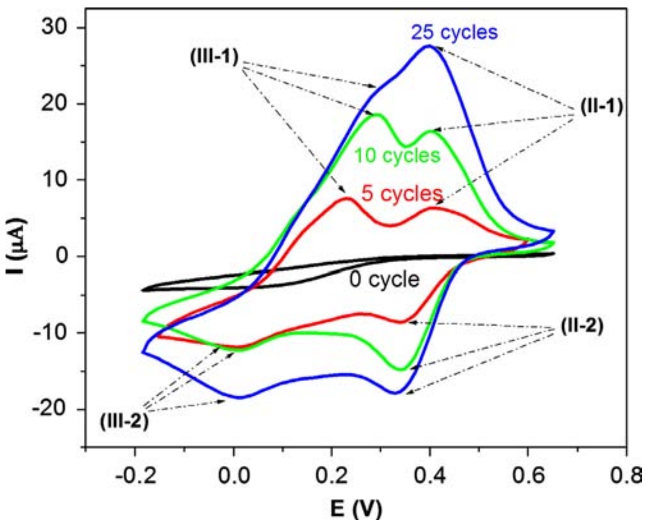

Fig. 3. Voltammetric responses of the interpenetrated network IDE/MWCNT/poly (1,5-DAN) formed by various scans during electro-polymerization: 5, 10 and 25 cycles; solution: 0.1 M $HClO_4$; scan rate: 50 mV s^{-1}.

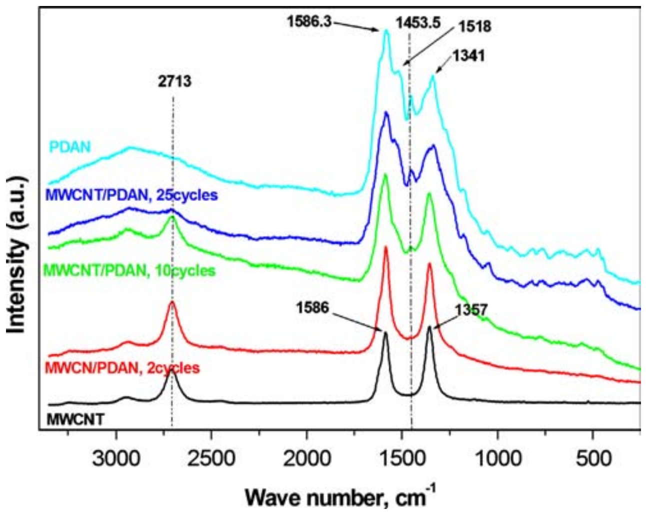

Fig. 4. Raman spectra of MWCNT, poly(1,5-DAN) and the interpenetrated networks MWCNT/poly(1,5-DAN).

IDE/MWCNT/poly(1,5-DAN) after scanning 0, 5, 10 and 25 cycles were obtained by scanning the cyclic voltammograms of these films in 0.1 M $HClO_4$ solution. Two typical redox couples of the poly(1,5-DAN) [13] clearly seen in Fig. 3 at positions assigned (II-1, II-2) and (III-1, III-2) indicate that poly(1,5-DAN) was successfully deposited on the nanotubes network. Furthermore, the current increasing with the scan number indicates that the film thickens.

3.2. Raman spectra of the synthesized films IDE/MWNT/poly(1,5-DAN)

Raman spectra of the pure MWCNT, the poly(1,5-DAN) and the interpenetrated network MWCNT/poly(1,5-DAN) with different numbers of electro-polymerization cycles (2, 10, and 25) are shown in Fig. 4. The spectrum of the pure carbon nanotubes shows the *D*-band (1357 cm^{-1}) and the *G*-band (1586 cm^{-1}) which are due to the sp^2 sites from carbon structures such as diamond-like, amorphous carbon and graphite, and the corresponding second-order harmonic *D*-band is present at 2713 cm^{-1} [18]. For pure poly(1,5-DAN), the vibrations of naphthalene ring are detected at 1586.3, 1518 and 1453.5 cm^{-1}. The band at 1341 cm^{-1} region corresponds to C–N stretching vibration of polaronic units [19]. In the case of interpenetrated network MWCNT/poly(1,5-DAN), the 1453.5 and 1518 cm^{-1} bands of poly(1,5-DAN) are present, and their intensity increases with increasing number of polymerization cycles. On the contrary, the band at 2713 cm^{-1} of the carbon nanotubes decreases its intensity when the number of poly(1,5-DAN) polymerization cycles increases (Fig. 4). All these results evidence that the carbon nanotubes are coated with the poly(1,5-DAN) in the polymerization process.

3.3. Morphological characteristics

Morphologies of the MWCNT, the poly(1,5-DAN) and the synthesized films IDE/MWCNT/poly(1,5-DAN) were characterized by scanning electron microscopy as shown in Fig. 5. The MWCNT are uniform tubes with diameters 40–60 nm (Fig. 5a). Pure poly (1,5-DAN) presents a particle-like structure (Fig. 5b). Poly(1,5-DAN) was developed and covered on the IDE/MWCNT as seen in Fig. 5c whereas Fig. 5d and e shows SEM images of surface morphologies of the MWCNT/poly(1,5-DAN) with electroactive polymerization of 10 and 25 cycles, respectively. The results indicated that the porosity of the MWCNT/poly(1,5-DAN) films decreased with increasing the number of polymerization cycles.

3.4. Gas sensing of the films IDE/MWCNT/poly(1,5-DAN)

In order to evaluate the number of polymerization cycles on performance to NO_2, the films IDE/MWCNT/poly(1,5-DAN) with 0, 5, 10, and 15 cycles were exposed to 5 ppm NO_2 at room temperature (28 °C). The initial resistances of the films IDE/MWCNT/poly(1,5-DAN) with 0, 5, 10, and 15 cycles are 8.12, 6.21, 4.65 and 2.38 kΩ, respectively. Upon exposure to NO_2, the film MWCNT (without polymerization) had inconsiderable change in its resistance while the large resistance changes of the films IDE/MWCNT/poly(1,5-DAN) with polymerization were observed. Fig. 6 shows the response and recovery of the films IDE/MWCNT/poly(1,5-DAN) with different polymerization cycles of 5, 10 and 15 to 5 ppm NO_2. The results in Fig. 6 indicate that all the sensors have similar behavior in which the resistance of the sensor decreased dramatically upon exposure to NO_2 gas, and then recovered in pure air. To explain the gas-sensing mechanism, it could be suggested that NO_2 gas removes unoccupied electrons from the "NH_2" groups in the poly(1,5-DAN) backbone, inducing the formation of NO_2^- ions and radical cations (polarons) on the polymer. When the radical cations were created, new double bonds by electron jumping from a neighboring position can be formed, that allow charges to migrate. The creation of polarons and bipolarons mobile charges across the backbone of the polymer (PDAN) reduced the resistance of the films IDE/MWCNT/poly(1,5-DAN). Fig. 6 also indicates the lower sensitivity of the film IDE/MWCNT/poly(1,5-DAN) formed with a small number of polymerization cycles (5 and 10), but they show better response and recovery times in comparison to that of large polymerization cycles (15). The effect can be explained by reduced film porosity when the polymerization cycles increased. Furthermore, resistance signal of the film IDE/MWCNT/poly(1,5-DAN) with 10 cycles was found to be more stable than that of 5 cycles. Thus, the film IDE/MWCNT/poly(1,5-DAN) with 10 cycles was selected for investigation to various NO_2 concentrations. Fig. 7 shows response of the film IDE/MWCNT/poly (1,5-DAN) with 10 cycles to 2, 6, and 10 ppm NO_2. These results show that the resistance of this film reduces with increasing NO_2 concentration. However, similar to characteristics shown in Fig. 6, the resistance of the film IDE/MWCNT/poly(1,5-DAN) didnot recover to initial value in the tested interval. It might take a very long time for this film to completely recover after being exposed to NO_2.

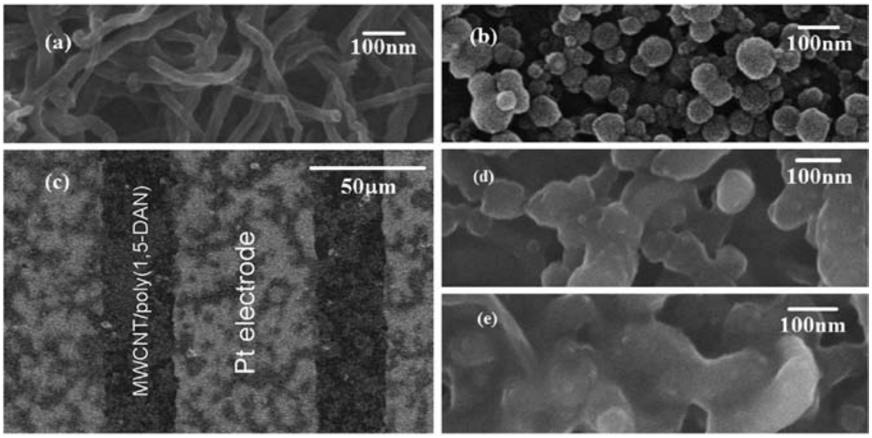

Fig. 5. SEM images: MWCNT (a), poly(1,5-DAN) (b), surface of the film IDE/MWCNT/poly(1,5-DAN) (c), and surface morphologies of MWCNT/poly(1,5-DAN) at 10 cycles (d) and at 25 cycles (e).

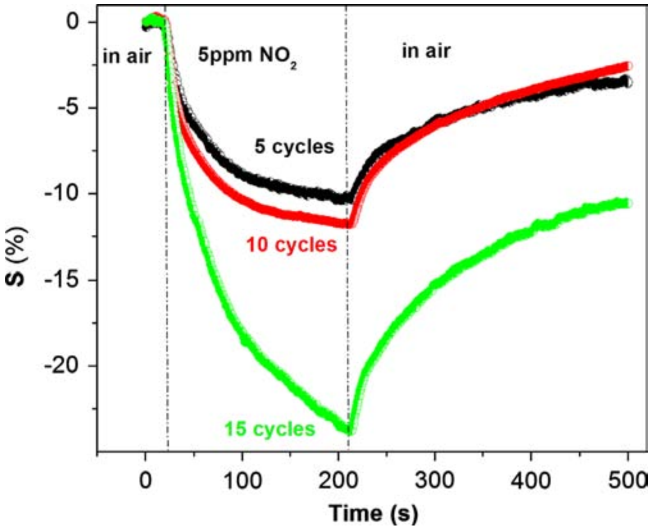

Fig. 6. Response curves of the film IDE/MWCNT/poly(1,5-DAN) with 5, 10 and 15 polymerization cycles after exposure to 5 ppm NO_2.

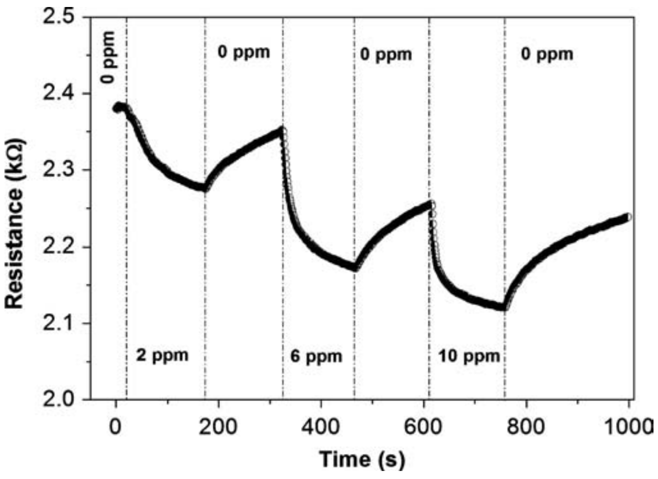

Fig. 7. Response of the film IDE/MWCNT/poly(1,5-DAN) formed with 10 polymerization cycles to different concentrations NO_2.

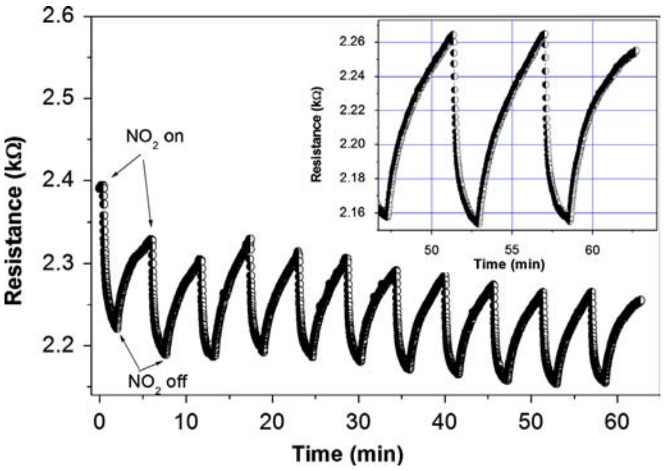

Fig. 8. Response–recovery cycles of the film IDE/MWCNT/poly(1,5-DAN) formed with 10 polymerization cycles to 5 ppm NO_2 and pure air; the inset: the last cycles.

Fig. 8 shows the response–recovery cycles of the film IDE/MWCNT/poly(1,5-DAN) with 10 cycles to 5 ppm NO_2 gas. The result indicates that the resistance of this film repeatedly changes according to exposure cycles to NO_2 and pure air. The good repeat performance of the film increases with increasing the testing-time (as seen the inset in Fig. 8 shows the last response–recovery cycles). After the synthesizing process, oxide/reducing unexpected-centers in the network MWCNT/poly(1,5-DAN) were created, wherein these centers could be irreversibly oxidized when exposed to NO_2. This effect can cause less repeated response of some first cycles in comparison to the last cycles when the film IDE/MWCNT/poly(1,5-DAN) is exposed to NO_2.

4. Conclusion

The carbon nanotube network made on interdigital electrode using polyelectrolyte as binder has been further used for electrosynthesis of electroactive poly(1,5-DAN) inside it. The characteristics on surface morphologies, electrochemical polymerizations and Raman spectra of the synthesized films showed that poly(1,5-DAN) was successfully deposited on multi-walled carbon nanotubes (MWCNT)/Pt electrode. This novel conducting polymer with free amino group system can be used as chemiresistor sensors for NO_2 gas at low concentration level. The thickness and porosity of the films IDE/MWCNT/poly(1,5-DAN) were found to have strong influence on their gas response–recovery times. Although the response–recovery times were long, the preliminary investigation on the film IDE/MWCNT/poly(1,5-DAN) has shown this to be a very-promising material for room temperature gas sensors. In future work, solutions to enhance the response–recovery times of these sensors for reality applications will be studied.

Acknowledgments

This work was financed by the grant-in-aid for scientific research from the National Foundation for Science and Technology Development of Viet Nam (NAFOSTED), code: 103.03.41.09.

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