A Novel Polycaprolactone-*Grafted*-Carbon Black Nanocomposite-Based Sensor for Detecting Solvent Vapors

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ABSTRACT: A novel vapor sensor is fabricated with polycaprolactone-*grafted*-carbon black (CB-*g*-PCL) as sensing materials. The influence of PCL with different grafting contents and solvents with various solubility and concentrations including benzene, deionized water, epoxy chloropropane (ECP), ethanol, toluene, and tetrahydrofuran on the response of electric resistance was investigated. When compared with mixture of PCL and carbon black, the CB-*g*-PCL-based sensor shows high sensitivity and good reproducibility. Sensor with moderate content of grafting PCL showed high sensitivity to vapors. The electric resistance of sensor drastically increased in ECP, ethanol, and deionized water with similar solubility with PCL and showed slight increase in benzene, toluene, and tetrahydrofuran with different solubility. The study on the response of electric resistance of CB-*g*-PCL to different vapors confirmed the swelling-induced sensing mechanism of sensor based on polymer-grafted-conductive nanomaterials.
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Key words: polycaprolactone; carbon black; graft; vapor sensor

INTRODUCTION

Polymer composites containing conductive carbon black (CB) as gas sensing materials have attracted much attention, in respect that polymer composites can produce obvious changes in resistance, when exposed to certain gasses or organic solvents.[1–4] Various CB-containing polymer composites have been designed and prepared to meet different requirements. Li et al.[5] prepared CB-filled polystyrene composites by in situ polymerization and found these materials responded sensitively to the nonpolar solvents but did not show obvious response to the polar solvent. Sisk and Lewis[6] found that insulating organic polymer doped with low loading of CB (1–12 vol %) exhibited higher signal to noise ratio. For these gas sensing systems prepared by simply blending of polymer with CB, repeatability and stability are their bottlenecks, because the conductive particles tend to aggregate and cannot disperse in the polymer matrixes due to the weak interaction between particles and polymers. Polymer grafting onto CB is an efficient method to solve the problems above, in which the polymer is linked to the surface of CB by covalent bond.[3–5] Additionally, polymer-*grafted*-CB possesses better processibility, because they can disperse homogenously in common solvent and the composite films can be easily fabricated by drop coating, spin coating, or dip coating.[4]

On the other hand, the nature of the polymer, such as polarity or crystallinity, is one of important factors determining the gas sensing properties of sensor containing polymer modified composites.[7–11] Doleman et al.[7] have found that, compared with amorphous polymers, semi-crystalline polymer exhibited larger response in resistance to vapors, due to the increasing distance caused by solvation of crystalline phase. Polycaprolactone (PCL) is a kind of semi-crystalline polyesters, with nontoxic, low melting point, ease of processibility, biodegradability, intermediate character between polarity and nonpolarity, and good compatibility with other polymers, which is expected to be an excellent sensing polymer.[12,13] Tsubokawa et al.[8,9] have investigated the solvent sensing properties of PCL-*g*-CB through a "graft to" method; however, the "graft to" approach generally brings about lower grafting polymer density and content than those from the "graft from" approach, which is important for the vapor sensing properties of polymeric nanocomposites.[3,4,12,14] Previously, we[3,4] have prepared polycaprolactone-*grafted*-carbon black (CB-*g*-PCL)

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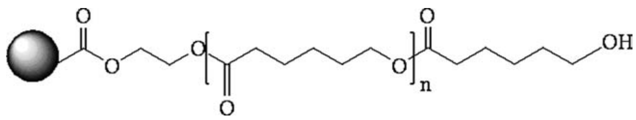

Scheme 1 The structure of CB-*g*-PCL.

through surface initiated polymerization, in which the grafting polymer content reached up to 51.9 wt %, and we also found these materials showed obvious temperature-sensitive resistance effect, as a result of changes in crystal structure of PCL. These composites are expected to be served as vapor sensing materials, as the solvation of crystalline polymer would also produce the similar change in crystal structure. Herein, we investigated systematically the influence of PCL with different grafting content and solvents with various solubility and concentrations including benzene, deionized water, ECP, ethanol, toluene, and tetrahydrofuran on the response of electric resistance of the CB-*g*-PCL-based vapor sensor. The sensors containing CB-*g*-PCL could respond to the concentration of solvents and exhibited desirable stability and reproducibility.

EXPERIMENTAL

Materials and reagents

Primary CB particles (VXC 605) with an average diameter of 30 nm and a specific surface area of 254 m^2/g were obtained from Cabot. CB-*g*-PCL was prepared according to the literature method[12] and the structure was shown in Scheme 1. All solvents were purchased from commercial sources and were of analytical pure grades.

Preparation of electrodes

A typical method to prepare a electrode was as follow: first, eight insulated cooper strings (D = 0.12 mm) were inserted into a cube made from polyester (D = 8.0 mm), encapsulated by epoxy resin; then one end of the electrode was linked with electric wires, and the other end was finished, washed with dilute sodium hydroxide aqueous and hydrochloric acid, plated with silver, and rewashed with sodium hydroxide aqueous, dilute hydrochloric acid, and double-redistilled water in succession [Fig. 1(A)]. The electrode has many output modes, and various initial resistances can be achieved by choosing different output modes to increase the sensitivity.

Preparation of CB-*g*-PCL modified electrodes

A typical CB-*g*-PCL vapor sensor electrode was prepared in the following way: 0.25 g CB-*g*-PCL was added into 2-mL tetrahydrofuran (THF), which was dispersed with ultrasound wave about 10 min, and evaporated to 1 mL; then ca. 50 μL solution was dripped onto the surface of the prepared electrode (S = 0.5024 cm^2); after 20 min, the electrode was dried at 40°C under vacuum for 2 h [Fig. 1(A)].

Measurement of vapor sensing performance of CB-*g*-PCL modified electrode

The measurement system consists of the vapor sensors, sample injector, vapor chamber, and the electronic data acquisition system (Fig. 2). Among them, the injection device is used to transport liquid solvents into gas chamber, and the gas inlet and vent were used to pass background gas (nitrogen). Gas chamber is made from the hard glass (volume is about 1452 mL). The chamber is fixed on a magnetic stirrer and sealed with vacuum silicone grease, the temperature of which is balanced through the magnetic stirrer. Gas sensors are then placed in the middle of chamber for real-time measurement. The data recorder is constructed with a DT-9932FC digital multimeter and special data acquisition software. Multimeter was connected to the computer, from which the resistance change of sensor can be

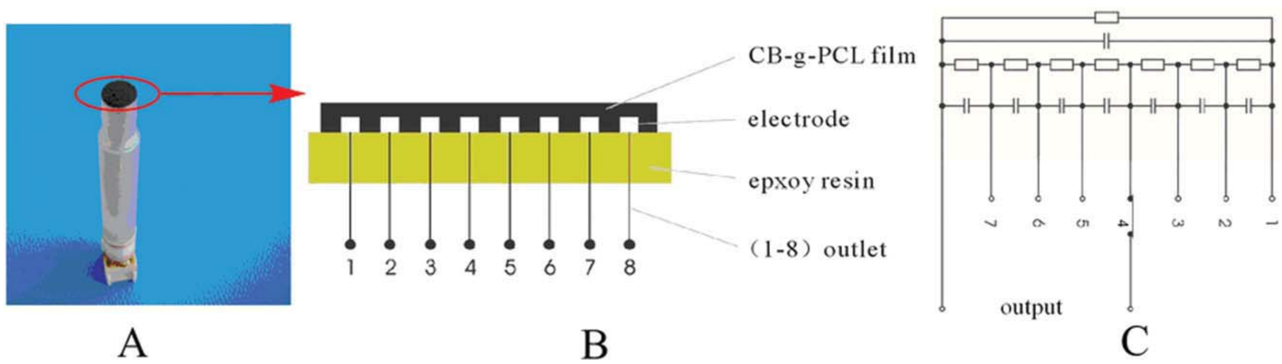

Figure 1 Photo (A), representation model (B), and equivalent circuit (C) of the vapor sensor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

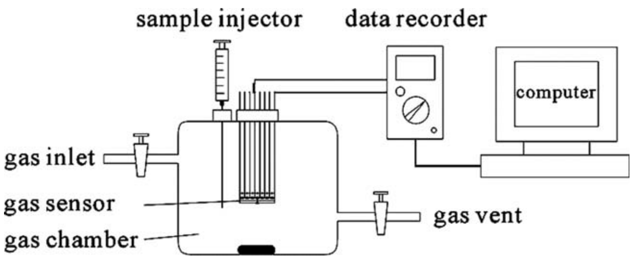

Figure 2 Representative model of measurement system for sensing organic vapors.

observed in real-time and the data can be stored for processing and analysis.

To test the sensitivity of the sensor, highly pure nitrogen (99.99%) is first charged into the chamber for 5 min to get rid of the air. On exposure to the target vapor, the resistance of the sensor suddenly increases and then remains constant. After replacing the vapor with highly pure nitrogen, the resistance decreases quickly and then keeps stable. All tests are carried out at the same condition. To estimate the performance of the sensors based on CB-*g*-PCL, the sensitivity and selectivity are necessary to be studied. The sensitivity of the sensor is defined by $\Delta R/R$, where R is the initial resistance, and ΔR is the resistance of the CB-*g*-PCL film when exposed for 5 min minus the initial resistance. The selectivity is determined by the pattern recognition analysis of the sensor arrays.

Determination of the concentration of the sample vapor

The concentration of vapor can be expressed as

$$C = \frac{\upsilon \times (273 + T_B) \times 22.4 \times d \times p}{273 \times V \times 10^{-9} \times m}$$

where υ is the volume of solvent injected into the chamber (mL), V is the volume of the chamber (V = 1452 mL), C is the concentration of solvent vapor (ppm or mL/m^3), T_B is the room temperature (T_B = 24°C), m is the molecular weight of solvent (g/mol), d is the liquid density of solvent (g/cm^3), and p is the the purity degree of the liquid (assuming full conversion of 1 mol of liquid to 22.4 L of gas).

RESULTS AND DISCUSSION

Influences of the film composite on the sensitivity of sensor

To select a sensing system with higher sensitivity, we first study the influence of content of grafted PCL on the sensitivity of sensor containing CB-*g*-PCL. The tested sample (A, B, C, and D) was listed in Table I and anhydrous ethanol was used as the test vapor. Under the same conditions, 25 μL of anhydrous ethanol were gradually injected into the sealed chamber (10 min), their resistance responses to anhydrous ethanol were shown in Figure 3. It is found that the content of PCL and method to prepare the composites play an important role in the sensitivity of sensor. The sensitivity of sensor first increases when the content of PCL decreases from 46.5 to 40.6%, but high content of CB in CB-*g*-PCL reduces the sensitivity of vapor sensor because of its high electric conductivity. The result indicated a moderate content of grafting PCL was favor of improving the sensitivity of sensor based on CB-*g*-PCL. Additionally, when compared with the sensor containing CB/PCL blends (Sample D), grafted polymer enhances the resistance response to ethanol vapor (Sample B). This difference may be caused by the poor dispersing of CB in matrix for Sample D, which results in unconspicuous distance change between CB and thus low resistance response. These results indicated the polymer grafted on CB is in favor of improving the sensitivity of sensor.

TABLE I
The Content of PCL and Method of Preparation for Sensing Materials

Sample	Film materials	Content of CB (%)	Content of PCL (%)	Method of preparation
A	CB-*g*-PCL	80.4	19.6	Graft
B	CB-*g*-PCL	59.4	40.6	Graft
C	CB-*g*-PCL	53.5	46.5	Graft
D	CB/PCL	59.1	40.9	Blend

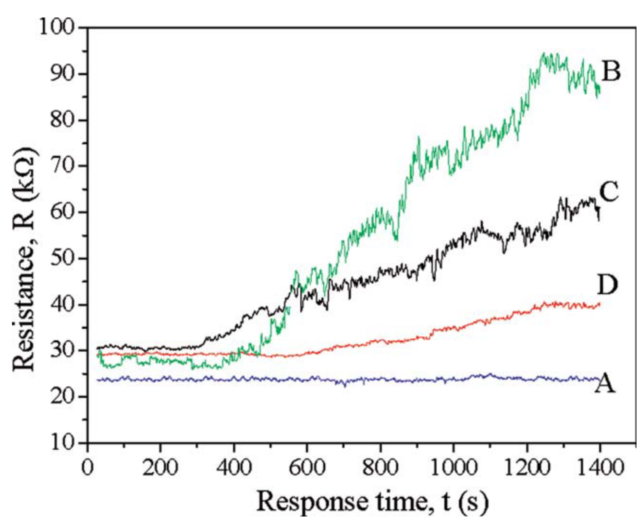

Figure 3 Dependence of resistance on time for sensors containing CB-*g*-PCL and CB/PCL when injecting 25 μL of ethanol: (A) CB-*g*-PCL (19.6% PCL), (B) CB-*g*-PCL (40.6% PCL), (C) CB-*g*-PCL (46.5% PCL), and (D) mixture of CB and PCL (40.9%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

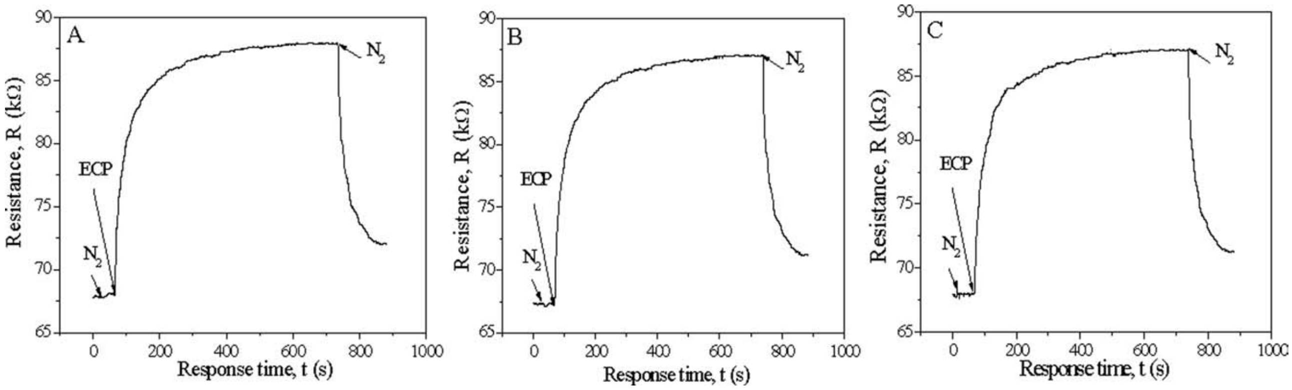

Figure 4 The typical resistance response of sensor containing CB-*g*-PCL to 25 μL (4902 ppm) epoxy chloropropane (ECP) with time: (A) the first time, (B) the second time, and (C) the third time. Baseline resistance of the sensor is about 67.1 kΩ.

Therefore, a proper sensor system is important for their sensing performance and herein, we choose the sensing materials of CB-*g*-PCL with 40.6% PCL for subsequent vapor sensing test.

Reproducibility of vapor sensor containing CB-*g*-PCL

The reproducibility is another important factor influencing the performance of vapor sensor, so we took epoxy chloropropane (ECP) as an example to test the stability of prepared sensor. Figure 4 shows the typical resistance response of sensor with time to 4902 ppm of ECP. It is evident that the both processes of adsorption and desorption show very sharp response, about 20 s is enough for the resistance to arrive the peak and the total response time from the start point to a steady line is about 100 s. Figure 4 also shows that the repeated response of resistance change to ECP are almost the same, even though tested repeatedly for over eight times, which indicates this sensor system can be reused for many times.

The response of sensor to different vapors

The study on the sensitivity and reproducibility showed that sensor containing CB-*g*-PCL with 40.6% PCL could respond sensitively and stably to vapors. We investigated systematically the sensing performance of CB-*g*-PCL sensor to different vapors. Six solvents with different polarity and solubility parameter were chosen, including benzene, deionized water, ECP, ethanol, toluene, and tetrahydrofuran, and resistance response to different vapors were shown in Table II and Figure 5. Figure 5 shows that CB-*g*-PCL-based sensor is more sensitive to polar solvents with similar solubility with PCL, such as deionized water, ECP, and ethanol, than weak polar solvents, such as benzene and toluene, and shows largest resistance response to ECP. The exception of tetrahydrofuran with larger polarity possibly results from the relatively larger difference between solubility parameters of tetrahydrofuran and PCL.

We also tested the response of sensor to the concentration of vapors. Figure 6 shows the dependence of the resistance of sensor on the concentration of various vapors. The concentration was regulated by varying the volume of added solvents: 0, 5, 15, and 20 μL. It was found the sensor containing CB-*g*-PCL responses sensitively to the concentration of vapors and the change of resistance increases with the increasingly concentration of vapors. When comparing with other vapors sensing results of sensor based on mixture of CB and PCL, the sensor based on CB-*g*-PCL exhibits excellent sensitivity. For example, Xie

TABLE II
The Data of Some Physical Parameters of Solvents and Resistance Response of Sensor Containing CB-*g*-PCL (40.6% PCL) to Different Vapors at 24°C[a]

Solvent	Polarity[15] (*D*)	Solubility parameter[16]	Concentration (*C*, ppm)	$(R_{max} - R_0)/R_0$	$\text{Log}\{10^5 \times [(R_{max} - R_0)/R_0]/C\}$
Benzene	0.00	9.15	4.7×10^3	0.074	0.197
Deionized water	1.84	23.4	2.3×10^4	0.560	0.386
Epoxy chloropropane	1.80	11.2	5.4×10^3	0.242	0.651
Ethanol	1.69	14.3	7.2×10^3	0.214	0.473
Toluene	0.45	8.91	4.0×10^3	0.068	0.230
Tetrahydrofuran	1.75	9.09	5.2×10^3	0.077	0.170

[a] The solubility parameter of PCL is 12.85.[17]

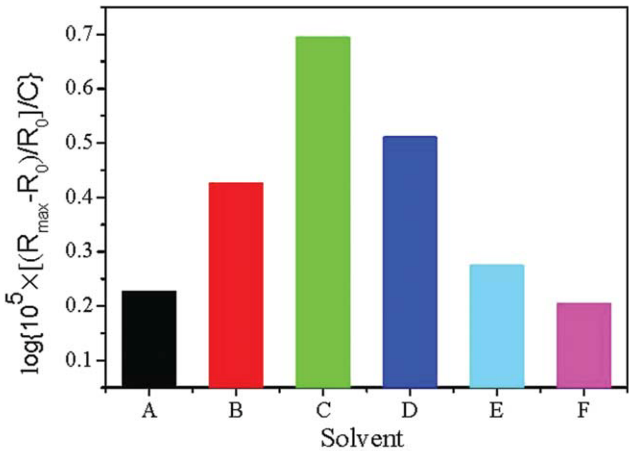

Figure 5 The resistance change of sensor to different vapors: (A) Benzene, (B) water, (C) epoxy chloropropane, (D) ethanol, (E) toluene, and (F) tetrahydrofuran. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

et al.[18] have reported that sensor based on mixture of CB and PCL showed a sensitivity ($(R_{max} - R_0)/R_0$) of 0.004 to ethanol at 1000 ppm, which was much smaller than that of sensor made from CB-*g*-PCL ($(R_{max} - R_0)/R_0 = 0.027$).

Taking ethanol as an example, we got the main characteristic parameters of the sensor as follows: the initial resistance $R_0 = 67.1$ kΩ; impedance in response to the value of $[(R_{max} - R_0)/R_0C] = 2.82 \times 10^{-5}$; response time $t_1 = 45$ s. These results show that sensor based on CB-*g*-PCL nanocomposites could be an excellent vapor sensor.

Responsive mechanism of sensor with CB-*g*-PCL

Based on previous research on conductive properties of polymer-*g*-CB[19,20] and gas sensing properties of polymer-grafted-carbon nanomaterials,[9,21] we proposed the response of resistance to vapor possibly resulted from the gradual phase transfer of the polymer crystal induced by vapor swelling. The vapor sensing mechanism of sensor containing CB-*g*-PCL was presented as follow. With vapor entering into the polymer network, the crystalline PCL would swell and the polymer chain changed into a disordered state, so as to increase the distance between CB particles and thus change the resistance of composites. As a result, the resistance change of sensor to vapor depends on the swelling degree of polymer due to interaction with vapor, which is determined by two physical parameters: polarity and solubility parameter.

As PCL is a kind of intermediate polar polymer, the sensor can response strongly to intermediate polar solvents, such as ECP and ethanol, but show small resistance change to weak polar solvents, such as benzene and toluene, except tetrahydrofuran and water. As for tetrahydrofuran, even though it has strong polarity and can dissolve PCL easily, larger difference between the solubility parameters of tetrahydrofuran (9.09) and PCL (12.85) caused that CB-*g*-PCL-based sensor only shows small resistance

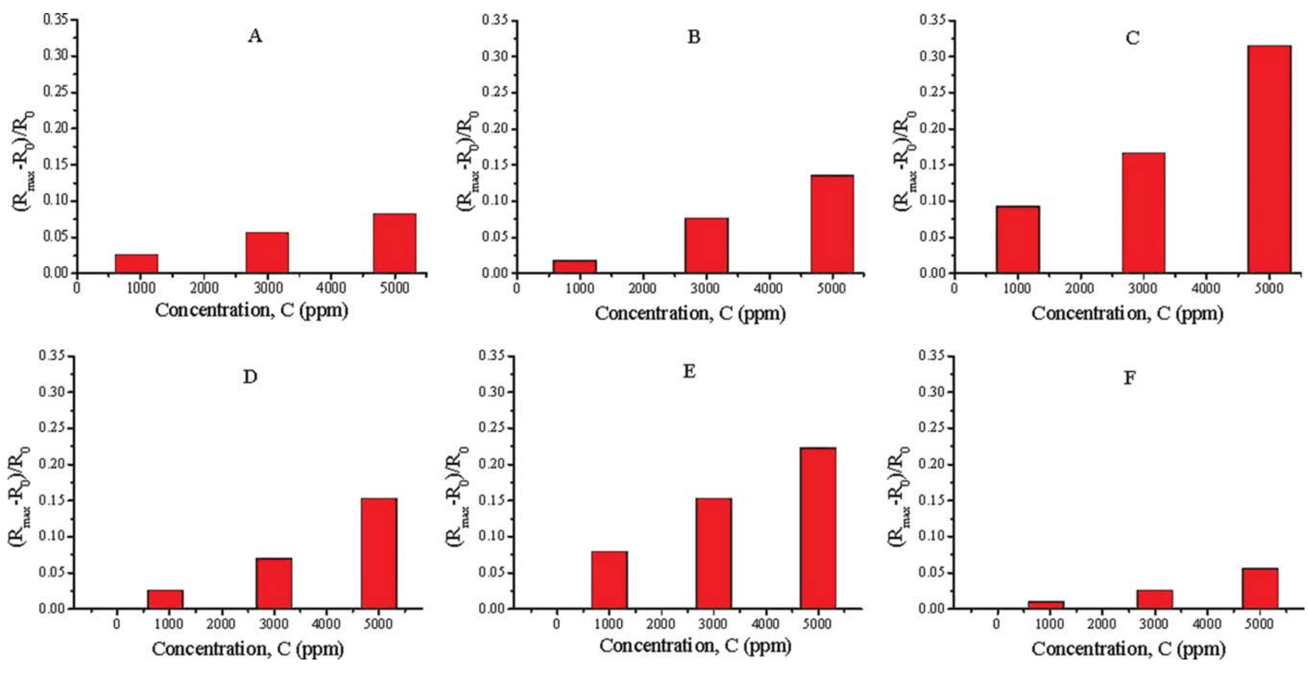

Figure 6 Dependence of resistance of sensor on concentration of vapor: (A) Benzene, (B) water, (C) epoxy chloropropane, (D) ethanol, (E) toluene, and (F) tetrohydrofuran. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

change when exposing to tetrahydrofuran. It is complicated for water, which has larger difference of solubility parameter between water (23.4) and PCL but relatively strong resistance response. Li et al.[22] have studied the gas sensing properties of mixture of poly(methyl methacrylate) and carbon nanotubes functionalized with carboxylic acid. They found that strong hydrogen bonding interactions between carboxylic acid and vapor would enhance resistance response. Actually, the prepared CB-g-PCL was firstly functionalized with carboxylic acid[12] and it is impossible to completely functionalize all of carboxylic acid with PCL, so the unreacted carboxylic acid might interact with water to increase the resistance change of sensor. As ECP has proper polarity and similar solubility parameter with that of PCL, the CB-*g*-PCL-based sensor responses sensitively to this kind of solvents. The study on the properties of resistance response to different vapors confirmed the swelling-induced sensing mechanism of sensor containing CB-*g*-PCL.

CONCLUSIONS

A novel sensor is fabricated with CB-*g*-PCL. It was found that sensor with moderate content of grafting PCL showed high sensitivity to vapors. When compared with sensor composed of mixture of CB and PCL, sensor with CB-*g*-PCL exhibited excellent vapor sensing performance with higher sensitivity and reproducibility. The study on the sensing properties of sensor to different vapors with different concentration confirmed the swelling-induced mechanism was responsible for the resistance change of sensor to solvents. As a result, a sensitive and selective sensor can be prepared by careful selection of the polymer grafted on the surface of conductive particles. The results also showed that CB-*g*-PCL nanocomposite can serve as a sensitive and stable sensing material to toxic ECP.

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