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Sensitive conductive polymer composites based on polylactic acid filled with multiwalled carbon nanotubes for chemical vapor sensing

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ABSTRACT

The sensitive conductive polymer composites (SCPCs) have been attracting a great deal of research interest because of their unique response to external environmental stimuli. In this study, multiwalled carbon nanotubes/polylactic acid (MWCNTs/PLA) conductive composites were prepared by a physically blending method and fabricated into thin films. The dispersion behavior and morphological structure of the composites were characterized and confirmed by FTIR, SEM, TEM and UV–vis measurements. The influence of the mass fraction of MWCNTs and the molecular weight (MW) of PLA on conducting properties was investigated. The responses of the films against various organic vapors (polar and non-polar solvents) were measured by monitoring the change in resistance when exposed to the organic vapors. The experimental results revealed that the MWCNTs/PLA conductive composites had good film-forming properties, which showed a strong and selective response to polar chloroform vapor, with a low percolation threshold of about 2.9 wt%. The response intensities were enhanced with increasing the MW of PLA and decreasing the mass fraction of MWCNTs. The composite films exhibited fast response and favorable reversibility, reproducibility and stability, especially a detection limit as low as 50 ppm. Thus they could be used as gas sensors to detect the organic vapors in atmospheric environments.

1. Introduction

Sensitive conductive polymer composites (SCPCs) have received broad attention in the past two decades since they can respond to external and/or environmental stimuli including temperature, strain/damage and volatile organic compounds (VOCs) etc. [1–3]. They have extensively been used as self-controlled heating cables, overcurrent protectors (PolySwitch), and chemical vapor sensors [4–7]. In particular, with the development of modern civilization, the human is very concerned about their living environment and physical health, and hence the detection and elimination for various environmental pollutants in (indoor) air is increasingly significant. It is under such context that highly sensitive chemical gas/vapor sensors or electron noses emerge, which can be used to perform tasks such as a specific chemical or environmental gas monitoring, solvent leaking monitoring, ground mineral monitoring, and polymer crystal structure testing etc., exhibiting an attractive application prospect. The core of the sensors is the sensitive materials, which determines the sensor's selectivity, sensitivity, linearity, and stability, etc. Therefore, the choice and optimization of sensitive materials, and the development and applications of new functional materials have always been the hot spot of the sensor research [1–6].

Carbon nanotubes (CNTs) are a class of widely-used conductive fillers for preparing chemical gas sensing materials at present, and have unique structure and remarkable physical properties, such as a high specific area and aspect ratio, nanoscale size, low resistivity, hollow geometry and fine surface absorption properties [8–10]. However, the original pristine CNTs are prone to aggregation and entanglement owing to their high aspect ratios and strong van der Waals attraction, resulting in poor solubility and/or dispersity, which limit the formation of effective conducting networks and affect the reproducibility and stability of the sensor elements [11]. How to improve the distribution of conductive fillers becomes a key technology for preparing polymer/CNTs conductive composite sensing materials. Various methods are adopted to increase the chemical compatibility and dispersibility of the CNTs and therefore to improve the response properties of gas sensitive elements. Some encouraging results have been achieved, for example functionalization of the CNTs, surface modification, physical mixing, in situ polymerization, chemically-covalent graft polymerization etc. [11–16]. These researches are proven to be superior to traditional instrumental analysis methods due to their remarkable detection

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sensitivity, reproducibility, ease of miniaturization, portability, low cost, and ultralow power consumption [13]. Almost all the polymers can be employed as matrices of the SCPCs. Polylactic acid (PLA) has large stiffness, high tensile strength, good film-forming properties and gas permeability. Considering that the response of the sensors is influenced by the nature, molecular weights (MW) or chain length and molecular weight distribution, and even aggregate structure of polymer matrices [17,18], the participation of the PLA moieties with various MW is expected to be able to acquire some novel findings.

Chloroform is an organic compound with formula $CHCl_3$, and extensively used in pesticide formulations, fire extinguishers, anesthetic, rubber industry, and criminal use. In addition, it is a common reagent in experimental laboratories. Chloroform is a class of important environmental pollutants and is a source of danger to the environments. It would cause severe health effects such as irritation, headache, lung congestion, kidney and liver damage, and effects on the brain, convulsion and cancer [1]. Chloroform causes depression of the central nervous system (CNS), ultimately producing deep coma and respiratory center depression even deaths due to respiratory and cardiac arrhythmias and failure, and hence the anesthetic use of chloroform has been discontinued. To prevent and eliminate the effect of chloroform vapors on the human health, it is imperative to monitor the leakage and diffusion of chloroform vapor by exploiting novel gas/vapor sensing materials with good response properties for fabrication of sensors [19,20].

In this study, a facile solution mixing method was adopted to prepare MWCNTs/PLA conductive polymer nanocomposites followed by fabrication of vapor/gas sensing thin films. The dispersion and coverage of the MWCNTs were investigated, and the response against $CHCl_3$ vapor was assessed. By the aid of this simple and low-cost processing method the SCPCs consisting of MWCNTs and PLA are expected to be constructed with fast response and recovery properties. On the other hand, this simple technology can overcome some inconveniences brought about by complicated chemical reactions but at the same time maintain good dispersion and film-forming properties. More importantly, their responsivities are not lost upon exposing to $CHCl_3$ vapor. Finally, the MWCNTs/PLA SCPCs and their electronic nose devices with excellent vapor responsive performances have been developed for detecting $CHCl_3$ vapors in the in-door environments or air.

2. Experimental

2.1. Materials and reagents

MWCNTs (95 wt%, particle diameter 30–50 nm, and length 10–30 μm) were purchased from the Chengdu institute of Organic Chemistry, CAS, and were ground to powders in a mortar in advance, and then dried in an oven at 120 °C before use. Polylactic acid (PLA), with molecular weight of 3000, 6000, 20000, 50000 and 80000 g mol^{-1}, was provided by the Jinan Biological Engineering Company, China. Trichloromethane ($CHCl_3$, 98%) was obtained from the Sinopharm Chemical Reagent Company, China.

2.2. Experimental process

2.2.1. Preparation of MWCNTs/PLA conducting nanocomposites

The solution mixing method was used to prepare MWCNTs/PLA conducting nanocomposites. In brief, MWCNTs (including MWCNTs-COOH or MWCNTs-OH) with different mass fractions (0.5, 1, 2.5, 5, 10, 15, 20, 25, 30, and 35 wt% the total mass of the MWCNTs and PLA) were dispersed in 5–10 ml $CHCl_3$ in a round bottom flask, and then ultrasonicated for 1–2 h. After that, PLA with different molecular weights of 3000, 6000, 20000, 50000, and 80000 g mol^{-1} was dissolved in 3–5 ml $CHCl_3$. The two solutions were mixed together and stirred at 50 °C for 24 h, and then MWCNTs/PLA conducting nanocomposite dispersions were obtained. To acquire the solid sample, the dispersions were dried by a rotary evaporator and then by a drum wind dryer at 45 °C for 12 h.

2.2.2. Fabrication of the nanocomposite thin films

The above dispersions were uniformly spray-coated and deposited onto a spotless cylinder-like electrode element with two gold electrode leads at both ends and a ceramic substrate (A ceramic tube with inner diameter of 0.8 mm, outer diameter of 1.4 mm, and length of 4.0 mm) to fabricate the thin films. The coated thin film was allowed to volatilize at room temperature for 12 h, and then transferred to a vacuum oven for drying and annealing at 60 °C for about 24 h. The uniform and fine thin film samples were kept an almost identical coating thickness of approximate 1 μm ± 10% to eliminate effect of the film thickness on the sensitivity, and the thickness was recorded by the cross-section image of scanning electron microscopy (SEM).

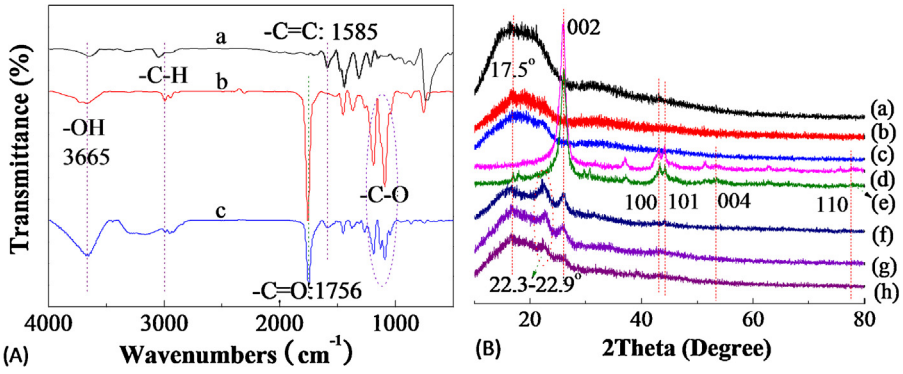

Fig. 1. (A) FTIR spectra of (a) the original pristine MWCNTs, (b) PLA with MW of 80000 and (c) MWCNTs/PLA conducting nanocomposite; and (B) XRD patterns of (a–c) PLA with MW: (a) 6000, (b) 50000 and (c) 80000; (d) the original pristine MWCNTs; and (e) MWCNTs/PLA_{6000}, (f) MWCNTs/PLA_{80000}, (g) MWCNTs-COOH/PLA_{80000} and (h) MWCNTs-OH/PLA_{80000} conductive nanocomposites.