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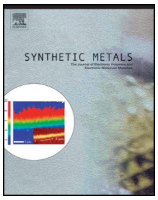

Reduced graphene oxide filled cellulose films for flexible temperature sensor application

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ABSTRACT

Graphene based polymer nanocomposites are widely used in flexible electronics and in sensing technology. However, ecofriendly materials with utmost performances are still under investigation. Here we report a simple, flexible, partially transparent and efficient temperature sensor fabricated from composite film of reduced graphene oxide (rGO) and cellulose. The rGO nanosheets are obtained by partial reduction of graphene oxide through low-temperature multi-step annealing. The relative capacitance of the sensor changes as a function of temperature for all thermally reduced rGO filled composites. Upon temperature stimulation, charges form at the rGO–cellulose interface. This mechanism allows the composite films to act as high performance capacitive sensors capable of detecting temperature variations. The functional properties of the reusable, ecofriendly and inexpensive rGO–cellulose device, allow for potential temperature sensor application, which is one among the best ever reported.

1. Introduction

Cellulose, the most abundant natural polymer on earth, is an inexhaustible source of raw material for scores of ecofriendly and biocompatible products [1]. Cellulose and its derivatives have been proposed for a variety of applications including coatings, laminates, optical films, pharmaceuticals, food and textiles [2–8]. It is also considered as a promising base material for flexible sensors due to the advantage of its low cost, light-weight, relatively high thermal stability, high sorption capacity, alterable optical appearance and biocompatibility [9,10].

Among sensors that detect several environmental parameters such as strain, pressure, temperature as well as the presence of foreign particles, the temperature detection has much significance in most of the physical, electronic, chemical, mechanical and biological systems [11–14]. The sensing property of temperature sensors is marked by a sudden increase/decrease in resistivity or capacitance with temperature indicated by a positive/negative temperature coefficient [15]. The foremost characteristics a temperature sensor system should possess are high sensitivity, wide-operating temperature range, long-term stability against other ambient influences such as humidity. In order to optimize these parameters, control systems that keep temperature within specified limits are often used [1]. The main criteria of selecting a material for a perfect temperature sensor are its accuracy, faster response, medium independent nature and easily conditioned output. Polymeric sensor devices have an additional advantage that the heating/sensing element can be principally in any shape based on the nature of polymer [1,11,13]. Designing temperature sensors with small hysteresis, good linearity, low temperature coefficient and short response time is a great challenge, and nowadays advanced nanoparticles especially conducting carbon are employed for it [1,15–17]. For example, two dimensional graphene nanosheets and their derivatives have been studied for various sensor devices due to its ultra-high specific surface area ($\sim$2630 m^2/g) and excellent electronic properties [18,19].

Owing to the difficulties in developing sensing materials, the current main strategy is to fabricate innovative structural behaviors from naturally available materials like cellulose. The presence of large number of hydroxyl groups along its skeleton causes the formation of comprehensive networks of intra- and inter-molecular hydrogen bonds in cellulose and makes two structural regions – crystalline and amorphous – in the same polymer [8]. This is helpful in obtaining flexible biomaterials in which polar fillers are uniformly bonded with the neat matrix. The polarity is induced by the presence of functional groups in filler particles. For instance, graphene oxide (GO) [20–22] contains a large number of functional groups such as hydroxyl, epoxides,

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carboxyls and carbonyls on its surface. Such polar graphitic derivatives filled cellulose composites with very high mechanical, thermal and gas permeability properties are reported [2–7,22–24]. However the low conductivity of GOs does not allow the fabrication of electronic devices and reduced GOs are largely used for those purposes.

Here we introduce a new type of temperature sensor device where cellulose forms the base matrix and the thermally reduced GO (rGO) as the filler. Though rGOs are synthesized by various means, [23–27] thermal reduction [13,25–26] provides enhanced electrical conductivity, higher specific surface area, less agglomeration and higher dispersion rates [28–35]. In this way we realized a new temperature sensitive material where the polymer chains exfoliate into the interlayers [31] of thermally reduced rGOs. The reduction temperature of GO is tuned to institute enough conjugated and non-conjugated filler networks within the matrix so as to derive the best composite material. The morphology and structural property relationship of the cellulose/rGO composite is determined with the help of Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectral analyses. A mechanism involving tunneling of charge carriers is proposed between the cellulose and thermally reduced rGOs (reduced at 50, 100, 200 and 400 °C) for temperature stimulation. The sensing is correlated with the dielectric behavior as well as the molecular level interactions based on the reduction temperature of GO. Hence a flexible and optically translucent temperature sensor capable to store energy and to regulate the device temperature by detecting high-temperature conditions is realized out of the cellulose/rGO composite film.

2. Experimental details

2.1. Materials

Cotton pulp of 98% purity and degree of polymerization 4500 was obtained from Junsei Chemicals, South Korea. Natural flake graphite, and other reagents such as dimethyl acetamide (DMAc), LiCl, H_2SO_4, HNO_3, HCl, $KMnO_4$ and 30% H_2O_2 solution were procured from Sigma-Aldrich. The 99.5% isopropyl alcohol was purchased from Daejung, South Korea.

2.2. Sample preparation

First, a cellulose solution was prepared by dissolving cotton pulp with LiCl/DMAc solvent according to the previously reported method [1]. 2/8/90 mixture of cotton pulp (heated with LiCl to remove adsorbed water molecules), LiCl and anhydrous DMAc (99%; Aldrich) were heated at 155 °C with mechanical stirring for 4 h in order to obtain a solution. This cellulose solution was centrifuged at 11,000 rpm to eliminate the undissolved cellulose fibers

Second, thermal reduction of GO (obtained by improved GO synthesis [36]) to rGO was carried out prior to composite preparation. For thermal reduction, nitrogen gas was passed through GO for 30 min in a sealed container to create an inert atmosphere on its surface and the resulting product was placed in a pre-heated muffle furnace at different temperatures 50, 100, 200 and 400 °C for 60 min.

Third, rGOs (reduced at different temperatures) were dispersed in DMAc by 3 h of mechanical stirring with stirring speed 500 rpm, followed by mixing with the cellulose solution. This composite solution was casted on a glass plate using doctor blade and cured using a deionized (DI) water and isopropyl alcohol mixture with the ratio of 4:6 for 3 h. This slow curing process prevents aggregation of rGOs and eliminate remnant LiCl and DMAc [37]. Finally the cured composite was rinsed in DI water bath twice and dried in a vacuum oven at 60 °C. Table 1 shows the various composite samples used in this study.

2.3. Composite characterization

Optical transmittance of the samples was studied using UV–visible spectrophotometer. For this the spectra of the films in the range of 200–800 nm wavelength were recorded with a Hewlett Packard (8452A) diode array. Cold FE-SEM images of the composite films were taken with a cold field emission scanning electron microscope (JEOL JSM-6400F) to study the sample morphology. The AFM and TEM images of the synthesized GO are given in Supplementary information (Fig. S1), from which the thickness and flake size of the platelets were determined.

FTIR spectrometer (Bruker Optics, Billerica, MA) was used to characterize the chemical composition of the samples under vacuum. The FTIR spectra obtained were in the range of 500–4000 cm^{-1} by averaging 16 scans at 1 min intervals to minimize the effects of dynamic scanning. The resolution was 4 cm^{-1}. Raman spectra were checked using a Raman spectrometer (Bruker, RFS 100/S) where A YAG laser with a wavelength of 1064 nm was used as excitation source, with a laser power of 130 mW. Here also the effect of dynamic scanning was minimized by averaging 20 scans at 1 min intervals and the spectra in the range of 100–3500 cm^{-1} were recorded. XRD patterns were checked with a thin film X-ray diffractometer using CuKα target radiation at 40 kV and 50 mA, at a scanning rate of 0.015°/min. The diffraction angle was varied from 5 to 40°.

2.4. Dielectric and sensing characterization

The temperature responses of the composite films were also recorded as the capacitance responses using the LCR meter at different temperature levels. The measurement frequency was maintained to be 500 Hz and the oscillation level 1 V. Each sample was analyzed and 5–10 measurements were taken at each temperature. The sample dimension was maintained as 3cm × 3 cm × 0.25 μm. Sensor data is plotted as normalized capacitance change versus time curves. This relative capacitance (A_c) measurement of the sensor is expressed by Eq. (1).

$$A_C = \frac{C - C_o}{C_o}, \tag{1}$$

where C is the film capacitance in the presence of temperature and C_0 the initial capacitance. Finally the electrical properties of the

Table 1
Samples prepared for the analysis.

Sl. no.	Notation	Cellulose (wt%)	rGO 50 (wt%)	rGO 100 (wt%)	rGO 200 (wt%)	rGO 400 (wt%)
1	Cellulose	100	–	–	–	–
2	CrGO50	99	1	–	–	–
3	CrGO100	99	–	1	–	–
4	CrGO200	99	–	–	1	–
5	CrGO400	99	–	–	–	1