Nano Energy (2015) **17**, 1–9

Available online at www.sciencedirect.com

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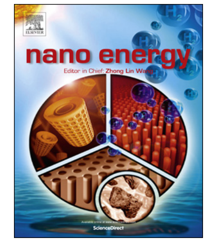

RAPID COMMUNICATION

Flexible self-healing nanocomposites for recoverable motion sensor

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Received 24 February 2015; received in revised form 6 July 2015; accepted 23 July 2015
Available online 31 July 2015

KEYWORDS
Self-healing;
High dielectric permittivity;
Percolation simulation;
Recoverable motion sensor;
Diels-Alder reaction

Abstract
The recoverable motion sensor with high sensitivity was made based on flexible self-healing nanocomposites. The preparation of these nanocomposites involved incorporating surface-modified $CaCu_3Ti_4O_{12}$ (S-CCTO) nanoparticles in self-healing polymer matrix based on dynamic Diels–Alder (DA) adducts. The dependences of electric and dielectric properties of the resultant composites on volume fractions of filler and frequency were investigated. It is found that composites present a high dielectric permittivity of 93 at 100 Hz with 17 vol% filler, approximately 36 times higher than that of pure film. These results agree well with the percolation theory. Furthermore, the hybrid film recovers its capacitance well following a cut and the self-healing process based on DA and retro-DA (r-DA) reaction. We herein show that a polymer matrix based on dynamic DA adducts can be used to make self-healing high-K polymer nanocomposites and recoverable motion sensors. This work may lead to new opportunities for the design and fabrication of various next-generation wearable sensor devices.

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http://dx.doi.org/10.1016/j.nanoen.2015.07.023
2211-2855/

Introduction

Flexible and sensitive motion sensors are now being heavily researched thanks to their potential applications such as rehabilitation/personal health monitoring, sport performance monitoring, and entertainment fields [1-8]. The ability to cover movable and arbitrarily shaped objects could be exploited in the development of wearable devices. These devices can be embedded into clothes and garments or even attached directly to the skin to monitor body motions, thus offering new opportunities for real-time health and wellness monitoring [9-15]. The main methods of fabricating flexible motion sensors rely on graphene sheets, carbon nanotubes, or silver nanowires on the flexible substrate, in which the sensors respond to the mechanical deformations by changes in resistance or capacitance [16-22]. In such devices, the functional materials themselves are directly exposed to strain and therefore stretched. Given this design, however, it is possible that these functional materials will become susceptible to structure fractures under bending, stretching, or any damage by accident. Such failure could not only severely limit the reliability and lifetime of the devices but also result in safety hazards [23]. Thus, the self-healing property for motion sensors, allowing them to repair themselves after damage, is important. Especially promising are sensors with the capability to restore configuration integrity and electrical properties after mechanical damage.

There are three main methods for creating self-healing polymeric materials: the storage of healing agents (hollow fibers, microcapsules), reversible covalent bond formation with external stimuli (Diels–Alder, or DA, reaction, disulfide groups, and thioles), and the construction of healing materials by noncovalent bonds [24-30]. As our report shows, the advantages of dynamic covalent bonds (DA adducts) under thermo-stimuli could provide high stability for self-healing materials. Polymer/ceramic nanoparticle-based high-*K* dielectric materials will enable the capacitance, and thus the sensitivity of the sensor. $CaCu_3Ti_4O_{12}$ (CCTO) has attracted considerable attention for its giant dielectric permittivity over a wide range of temperatures, from 100 K to 500 K, and has substantially contributed to the increment of composites' dielectric permittivity [31-34].

Here we introduce a new type of recoverable motion sensor that can retain the sensibility of self-healing polymer nanocomposites. The self-healing polymer matrix selected for the composite is a copolymer network based on two monomers (1, 1′- (methylene di-4, 1-phenylene) bismaleimide, or MDPB, and 2, 2′- (Thiodimethylene) difuran, or TDF), the chemical structures of which are shown in Figure 1. MDPB and TDF are cross-copolymerized through a reversible Diels–Alder cycloaddition reaction to form the healable network. With the maleimide groups coating on the surface-modified CCTO(S-CCTO), they not only can improve compatibility but also offer an excellent debonding and bonding process between polymer matrix and S-CCTO through DA and r-DA reaction upon thermo-stimuli (Figure 1). Because the DA reaction is reversible, furan and maleimide groups can couple again under heating to reform the broken bonds. We investigated the influence of S-CCTO on the dielectric properties of MT and its self-healing property. Adjustable dielectric properties were found and and they fit well with the percolation theory due to the microstructure change. With single-walled carbon nanotube (SWNT) sprayed on the surface as electrodes, a mechanically and electrically self-healing finger motion sensor was fabricated. This sensor can recover its sensitivity following a cut and self-healing process. This

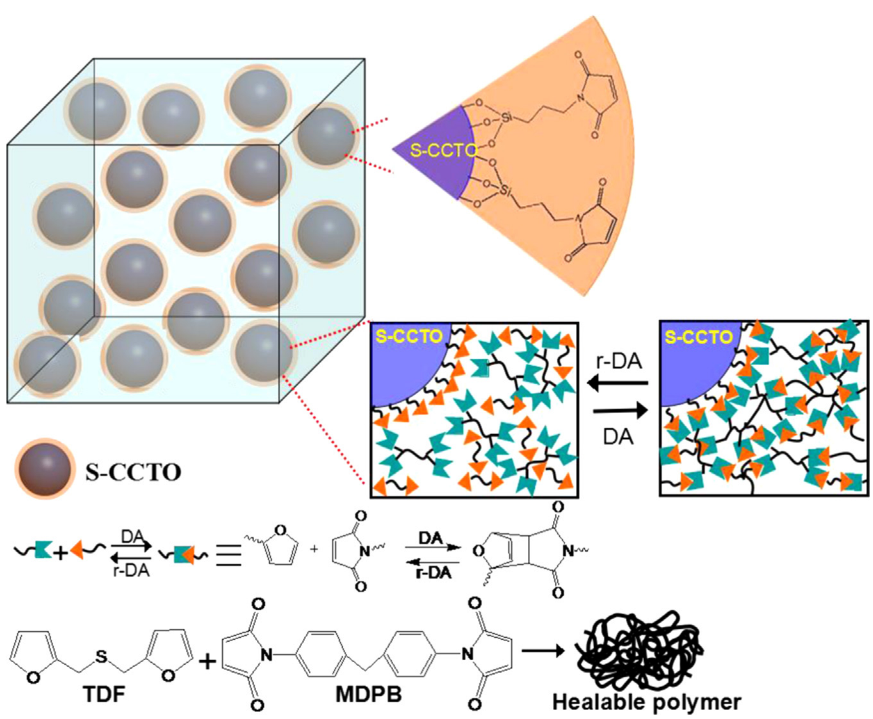

Figure 1 Schematic representation of the MT/S-CCTO hybrid film and the DA(65 °C), r-DA (105 °C) reaction process with the changes of temperature.