Synthetic Metals 209 (2015) 583–587

Contents lists available at ScienceDirect

Synthetic Metals

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

Short communication

Combined high permittivity and high electrical conductivity of carbon nano-onion/polyaniline composites

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ARTICLE INFO

Article history:
Received 13 June 2015
Received in revised form 10 August 2015
Accepted 19 August 2015

PACS indexes:
81.05.ub
77.84.Lf
72.80.Le
77.22.Gm

Keywords:
Carbon nano-onions
Polyaniline
Composites
Dielectric permittivity
Dielectric relaxation

ABSTRACT

We report high dielectric permittivity values for electrically conducting carbon nano-onion/polyaniline (CNO/PANI) composites. Broadband Dielectric Spectroscopy (BDS) measurements conducted under isothermal conditions from 16 K to room temperature in the frequency range between 1 mHz and 1 MHz, revealed a Cole–Cole relaxation mechanism. The intensity of the relaxation is comparable with the observed huge static dielectric constant values, and indicates a correlation between the intense capacitance effects and the relaxation. The relaxation dynamics involve single or two phonon assisted tunneling of the relaxing electric charge carriers (protons and electrons) at low temperatures, which transition to multi-phonon assisted tunneling relaxation above 100 K. Within the Mott–Davis model describing phonon-assisted tunneling relaxation in disordered media, the typical spatial scale relaxation occurs and is found to correlate with the size of the CNOs. The capacitance correlates with the large effective CNO surface areas.

The spherical and concentric graphene layers that constitute the carbon nano-onions, CNOs, provide high effective surface areas, when compared with other allotropes of carbons, such as carbon nanotubes, graphene, graphite etc. [1,2]. In principle, percolation of electric charge competes with trapping. CNO and conducting polymer (CP) composites are highly conducting due to the conjugated bond structures of the CPs and the intrinsic electronic properties of the CNOs. Nevertheless, the structural and electrical heterogeneity of the CNO/CP composites are expected to yield high static dielectric constant values, i.e., static dielectric permittivity. The present work addresses the capacitive nature of a good conductor at a microscopic level. The dual nature of composites is important for their further applications, such as for electrode materials for energy storage supercapacitors and for biocompatible electrodes. For technological applications, high capacitance results in significant charge storage, while a conductivity percolation network provides effective charge transfer. Alternatively, water-dispersed composites may form materials with hydrophilic hydrogels, yielding soft biocompatible electrodes that are compatible with tissues or organs in order to emit or collect electric signals (charge flow) stemming from biological processes.

The procedures for the functionalization of CNOs with phenyleneamine-terminated groups have been already reported in previous studies [3,4]. To introduce functional groups onto the CNO surfaces, the carbon nanostructures were treated with 4-aminobenzoic acid (4-ABAc). The reaction led to a pronounced increase of the dispersibility of the carbon nanostructures in protic solvents, and induced further polymerization of aniline to obtain CNOs/PANI [3]. The carbon nano-onion structures with very homogeneous layers of polyaniline can be clearly seen using TEM at high magnification (Fig. 1a). The diameters of the CNO/PANI particles are between 8 and 20 nm. The results of the SEM studies of CNOs and of the polyaniline composites on a gold foil are shown in Fig. 1b–d. The morphology of each modification step of the CNO surfaces differs from that of the films formed by non-functionalized nanostructures (Fig. 1b). The non-modified CNO particles formed spherical aggregates with diameter sizes between 5 and 20 μm. Oxidation of the CNO particles with 4-ABAc (Fig. 1c) formed

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http://dx.doi.org/10.1016/j.synthmet.2015.08.020
0379-6779/

more uniform and homogenous structures (aggregates approximately 1–3 μm in size). Further modification of the oxidized CNOs resulted in surface films (Fig. 1d), indicating that the composites exhibit a more porous structure, which should enable a more efficient accumulation of charge.

The scope of the present work was to investigate the interplay between high capacitance and high electrical conductivity of the CNO/PANI composites and prove the hypothesis that the large static dielectric permittivity value is related to the polarization (and charge storage) linked to the CNOs. The dynamics of electric charge flow from 16 K to room temperature provides information of the dynamics of electric charge carriers at a microscopic scale. Broadband Dielectric Spectroscopy (BDS) can simultaneously probe the dc and ac conductivity originating from the localized motion of electric charges and charge trapping (capacitance effects). Making measurements over a broad frequency range, different time and over spatial scales can provide long scale charge transfer properties along the volume of the specimen down to the nano-scale. Therefore, the spatiotemporal nature of BDS can probe the conduction percolation network of a material, as well as charge localization or immobilization due to its structural and electrical heterogeneity [6,7]. BDS measurements of onion-like structure/non-conductive polymer composites have already been published [8].

The CNO/PANI composites were compressed using an IR press to form disk shaped pellets of 4 mm diameter and 0.4 mm thickness. The small dimensions of the sample avoid having to silver-paste the two parallel surfaces in order to obtain Ohmic contacts. Instead, two thin indium foils were mechanically attached and squeezed on the parallel surfaces (comparative BDS scans at room temperature were done with various electrode materials such as bronze, gold, platinum etc. to test electrode effects); indium, being a soft metal, can make good contact with the specimens surfaces. The indium–specimen–indium 'sandwich' was placed in a capacitor type sample holder of a high-vacuum liquid helium cryostat (ROK, Leybold–Hereaeus) operating from 15 K to room temperature. A LTC 60 temperature controller was used to stabilize the temperature with an accuracy of 0.01 K. Complex permittivity measurements were performed in the frequency range between 1 mHz and 1 MHz with a Solartron SI 1260 Gain-Phase Frequency Response Analyzer, and a Broadband Dielectric Converter (Novocontrol). The data acquisition system was monitored by the WinDeta (Novocontrol) software.

The films were imaged by secondary electron SEM with the use of an S-3000N scanning electron microscope from FEI (Tokyo, Japan). The accelerating voltage of the electron beam was 20 keV. Transmission electron microscopic (TEM) images were recorded using the FEI Tecnai^{TM} G2 20 X-TWIN instrument. The accelerating voltage of the electron beam was 200 keV, the TEM point resolution was 0.25 nm, the TEM line resolution was 0.144 nm, the maximum diffraction angle was ±12°, and the working distance was 10 mm.

The real and imaginary components of the complex dielectric permittivity ε^* are related to the reversibly stored energy (capacitance effects) and the dissipated energy, respectively, during one cycle of the externally applied harmonic field of frequency f. Isotherms of Im(ε^*) and $Re(\varepsilon^*)$ vs. f are presented in Fig. 2. The low frequency region of $Re(\varepsilon^*)$ provides an estimate for the value of the relative static dielectric constant ε_s using the

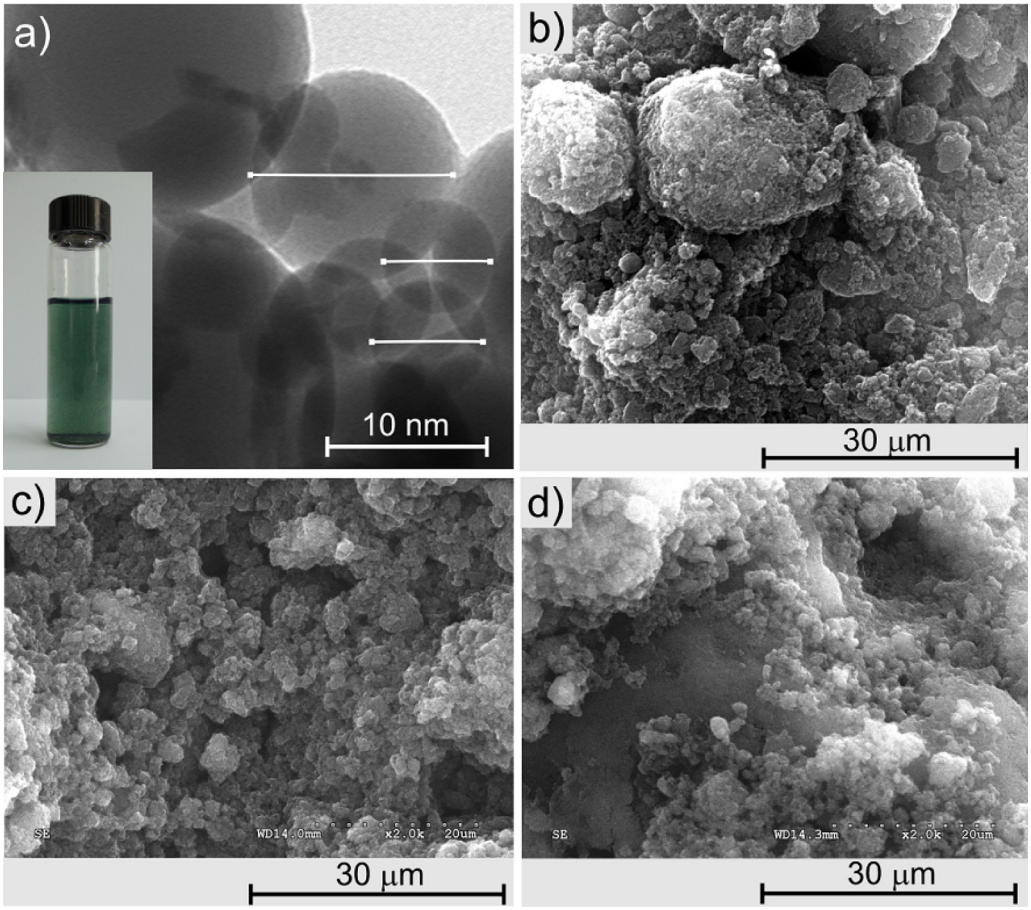

Fig. 1. (a) TEM images of CNOs/PANI, insert: the samples in 0.1 M HCl; (b–d) SEM images of the gold foil covered with (b) pristine CNOs, (c) oxidized-CNOs, and (d) CNOs/PANI.