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ScienceDirect

Diamond & Related Materials 17 (2008) 462–466

DIAMOND AND RELATED MATERIALS

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Onion-like carbon for terahertz electromagnetic shielding

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Abstract

It is demonstrated that onion-like carbon (OLC) provides efficient attenuation of the electromagnetic spectrum over the wavelength range 12–230 THz as compared to detonation nanodiamonds (DND) at similar or higher concentrations. Some characteristics of OLC important for the processing of polymer composites such as surface functional groups, zeta-potentials and agglomerate sizes are reported.

Keywords: Diamond crystal; Nanoparticles; Onion-like carbon; UV protection; EM shielding

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1. Introduction

There is rapidly growing interest in the multilayered spherical carbon nanostructures [1–4]. Terminology for this class of nanocarbon materials is not well established and includes terms such as carbon onions, carbon nano-onions (CNO), multilayer fullerenes, onion-like fullerenes and onion-like carbon, to name but a few. Various physical methods have been utilized successfully for the production of multilayered spherical carbon nanostructures, including high-energy electron irradiation, arc-discharge (both in a gas atmosphere and in DI water), thermal treatment of carbonaceous materials, carbon ion implantation into a metal matrix, plasma-enhanced chemical vapor deposition and other methods. One of the potential methods for the large-scale production of multilayered caged carbon nanostructures is annealing of detonation nanodiamonds in an inert atmosphere or under vacuum conditions suggested in 1993 [5]. In order to distinguish this class of material from ideal carbon onions made up of layers of enclosed fullerene molecules of different sizes, the term *onion-like carbon* [5] was coined. Thus, onion-like carbon is a DND-derived subclass of carbon nano-onions. OLC *primary* particles are made up of concentric carbon shells that have a variety of defects in the carbon shells [1]. OLC shells can be rounded or elongated and since the starting DND material is agglomerated, corresponding OLC particles also form hierarchical agglomerates including structures where the whole agglomerate of primary OLC particles can be enclosed in larger graphite-like shells, depending on the annealing temperature [1]. A study of X-ray emission spectra of OLC combined with quantum-chemical simulations for the characterization of their electronic structure led to the conclusion that the onions produced by annealing of DND at an intermediate temperature (1400–1900 K) have holes in the internal shells (Fig. 1) [6]. The origin of such defects accompanying the OLC formation can be explained in terms of a deficit of diamond carbon atoms at the diamond/graphite interface to form perfect fullerene-like shells during DND annealing. The defects in the inner cores of OLC are well preserved by outer shells and can effectively interact with an electromagnetic field, contributing to the EM shielding properties of OLC. Also, since the average particle size of primary OLC is about 4–7 nm, OLC possesses higher reactivity as compared with carbon nano-onions produced, for example, by the arc-discharge in DI water method which results in an average size of primary particles 25–30 nm [7]. This property is important for the processing of polymer–OLC nanocomposites. Nanocomposites of polyimid, polyurethane, polymethyl methacrylate (PMMA) and polydimethyl siloxane (PDMS) with OLC had been successfully fabricated [8].

Recently it was reported that onion-like carbon obtained by annealing of detonation nanodiamonds is a new class of material that provides excellent EM shielding over the microwave

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doi:10.1016/j.diamond.2007.08.023

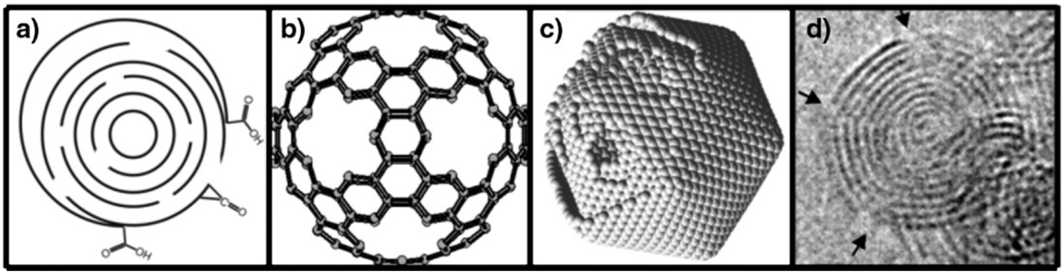

Fig. 1. Schematic representation of the structure of the OLC: enclosed graphite-like shells containing sparse surface groups on OLC surface and structural defects such as holes within sp^2 shells and surface steps of the curved nonclosed shells (a). Atomic models of the holes with zigzag arrangements of the carbon atoms at the edges (b) and surface steps of curved nonclosed shells (c) are also demonstrated. HRTEM picture (d) illustrates nonclosed shells with surface steps (indicated by arrows).

spectral band from 2 to 37 GHz [8–10]. Both OLC powders as well as polymer nanocomposites have been characterized as EM attenuating material [9]. It was found that both the DND annealing temperature and the OLC aggregate sizes influence EM shielding performance [9] and thus the performance needs to be optimized over a rather wide range of parameters. There is possibly a variety of mechanisms contributing to the broad band EM attenuation by OLC including electrical conductivity that can be tunable due to hierarchical assembly of the primary particles and the inner shells defects described above [1]. Thus, the dimensionality of the electrical conductivity of OLC and 'hybrids' of OLC containing DND cores varies between 0.5 and 1.5 (versus the 3-dimensional electrical conductivity for typical graphite materials) [11]. Temperature dependence of electrical resistivity of OLC is typical for systems with variable hopping-length hopping conductivity [11]. Based at the resistivity analysis [11], at least conducting elements at three structural levels can be identified: sp^2 patches between defect (holes) within a single graphitic nanoshell, aggregates of primary onions and conglomerates of the OLC aggregates. This distribution of the sizes of the conductive elements over a broad length scale would contribute to the wide band attenuation of the electromagnetic spectrum. Another group of authors [12] reported high dielectric loss in the 2–18 GHz frequency range for carbon nano-onions synthesized by DC arc-discharge in water method and carbon onions encapsulating Fe nanoparticles synthesized by chemical vapor deposition. Thus different classes of CNO are under study for EM shielding applications.

In the current paper based upon results of the characterization of OLC compositions with FTIR spectroscopy it is reported that certain OLC compositions could provide substantial EM attenuation over the 12–230 THz range. It is shown that OLC differs in this property from DNDs. Some of the OLC properties related to the processing of OLC-based polymer nanocomposites are also briefly discussed.

2. Experimental

The nanodiamonds used in this work were synthesized by the detonation of a mixture of TNT and RDX explosives. One type of ND was produced in a chamber containing a CO_2 atmosphere that served as a coolant (DND-1), oxidized in H_2SO_4:$HClO_4$, washed with water, and dried. Other types of ND were produced using an ice coating around the detonation charge, purified using ozone (Ch–O) or a mixture of sulfuric acid with chromic anhydride, washed with water, and dried (Ch–St). The average size of the primary particles for all samples was ~4 nm. Both types of DND are polydispersed powders; the primary particles form tightly and loosely formed aggregates with particle sizes ranging from tens to several hundreds of nanometers. For the purpose of fractionation, the Ch–St sample was additionally purified using ion-exchange resins, heat treated in air atmosphere and separated into several fractions.

OLC samples were obtained from DND-1 sample by heating in vacuum ($5 \cdot 10^{-4}$–$1 \cdot 10^{-4}$ Torr) at 1800 K (Dh-1 sample) and 1900 K (Dh-2 sample) and from 180 nm fraction of modified Ch–St sample by heating at 1400 K (Db-1 OLC sample). Sample Dice was obtained from Ch–O DND by heating at 2000 °K for 20 min. Particle sizes in suspensions were measured by photon correlation spectroscopy (PCS) using a Beckman–Coulter N5 submicron particle size analyzer and Nikomp 380 ZSL instrument. Zeta-potentials were measured with a Malvern Zetasizer Nano ZS instrument at 0.01 wt.% of OLC in suspensions.

Absorbance spectra were collected in the frequency range of 12–230 THz using a Varian 7000e FTIR spectrometer in transmission mode with averaging over 500 spectra. Absorbance was calculated over each KBr blank. Samples were prepared by mixing OLC or nanodiamond powders with SpectroGrade™ KBr powder (ICL, International Crystal Laboratories, Garfield, NJ 07026) in a Wig-L-Bug™ grinding mill (ICL) with agate vial and pestle (ICL) for 30 s. Pellets were pressed with a handheld Quick press (ICL). Spectra for Fig. 3 were collected for the samples of Dh-1 (0.2 mg/103 mg KBr) and Dh-2 OLC (1.5 mg/100 mg KBr). Spectra for Fig. 4 were collected for the samples of Dh-1 and Ch–St nanodiamond. DND was dehydrated at 400 °C for 1 h. Samples were prepared with controlled thickness of the KBr pellet (0.25 mm) and controlled concentration of the sample in the KBr powder. Samples were prepared at 2 levels of weight concentration for DNDs (1.06% and 2.26%) and 2 levels for the OLC (1.02% and 0.0218%).

3. Results and discussion

Since polydispersed nanodiamond powder is used for the production of OLC, the size distribution of OLC in suspensions is also polymodal, including particles with sizes up to several hundreds of nanometers (Fig. 2a). It is known that detonation nanodiamond primary particles have a narrow size distribution