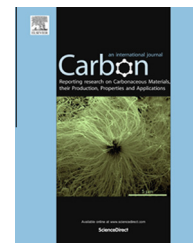


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Annealing-induced structural changes of carbon onions: High-resolution transmission electron microscopy and Raman studies

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ABSTRACT

The first- and second-order Raman spectra of carbon nano-onions (CNOs), produced via annealing of detonation nanodiamonds with a mean grain size of ~5 nm in the argon ambience at the maximal temperature of annealing process (T_{MAX}) varying from 1500 to 2150 °C, are analyzed together with the high-resolution transmission electron microscopy (HRTEM) images. The combined analysis provides a deep insight into the annealing-induced atomic-scale structural modifications of the CNO nanoparticles. The Raman and HRTEM data unambiguously demonstrate the reduction in the number of defects in the CNO structure, as well as indicate the conversion from the diamond sp^3 -bonded carbon phase to the sp^2 -bonded carbon phase with increasing T_{MAX} and its almost full completion for $T_{MAX} = 1600$ °C.

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1. Introduction

Multilayered quasi-spherical carbon nanoparticles, or carbon nano-onions (CNOs), currently attract much attention because of their unique structural and physical properties, which are different from the properties of the other nano-sized carbon materials—including nanodiamonds, graphene, fullerenes, and carbon nanotubes [1–11]. The structure of this material is still under discussion and usually described as a

few enclosed fullerene-like layers or concentric graphitic shells, with a hollow inside, nanodiamond core or perfect fullerene in the centre [1]. CNOs have been considered as potentially interesting material for a number of applications. As a solid lubricant, CNOs can provide better lubrication than the commonly used graphitic materials [2]. Perfect shielding capabilities of CNOs at microwave, infrared and terahertz frequencies have also been demonstrated recently [3–5]. Besides being used as an electrode material for Li-ion batteries, CNOs

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were used as electrode materials for supercapacitors due to their large external surface area, which is easily accessible for alkali ion adsorption [6]. CNOs also find applications in fuel cells [7], heterogeneous catalysis [8], gas and energy storage [9] and electro-optics [10]. Finally, hollow CNOs are promising biocompatible nanocapsules for drug delivery systems [11].

Among various methods used for the production of CNOs, the annealing of 4–5-nm detonation nanodiamonds in the inert atmosphere is one of the most common [12]. The primary CNO particles obtained with this method consist of very defective concentric carbon sp^2 shells enclosed one into another. However, the number and types of defects can be essentially reduced via ordering the CNO structure by increasing the maximal annealing temperature T_{MAX} [1,13,14]. Since the atomic-scale structure of CNOs is a key parameter determining their mechanical, electronic and electromagnetic properties, the possibility to control the annealing-induced structural transformation is critically important for the fabrication of the CNO-based materials with desired functional properties.

A first comprehensive study of the annealing-induced structural transformation in CNOs has been done using the X-ray diffraction (XRD) technique about one decade ago [15]. Unfortunately, the XRD did not allow getting a reliable data on the CNO structural changes with increasing T_{MAX} above 1700 °C. For example, the changes in the coherent scattering sizes of graphitic nanocrystals did not exceed ~8% in the T_{MAX} range of 1700–2000 °C. Therefore, other independent precise methods are needed to detect the fine changes in the structure of CNOs during their transformation with annealing procedure.

The Raman scattering, which is one of the most powerful methods of studying graphitic materials, is a quite adequate technique for this purpose. This method provides a contactless and rapid way of getting information on chemical composition, structural properties and morphology of different carbon allotropes—including nanostructures like graphene, nanodiamonds, fullerenes and nanotubes [13,16–24]. The Raman spectroscopy has already been used for studying the CNO structures and, particularly, the annealing-induced structural transformation in CNOs synthesized from detonation nanodiamonds [1,14,24–26]. However, important aspects of the temperature-induced CNO structural changes are still not clear enough due to the difficulties in getting their Raman spectra of good quality.

In this work, we apply a new Raman technique (Stream-Line™ Plus, Renishaw), which allows measuring the excellent quality Raman spectra of highly absorbing CNO samples (without damaging the samples) by using high laser power with reduced laser power density. We analyze the first- and second-order Raman spectra of CNOs, produced by annealing of detonation nanodiamonds with grain size of ~5 nm in the argon atmosphere at T_{MAX} varying from 1500 to 2150 °C, to understand the annealing-induced atomic-scale structural modifications of the CNO nanoparticles. The Raman data evidences a reduction in the number of defects in the CNO structure, points to its conversion from sp^3 to sp^2 phase, and

shows the transformation of the CNO shape from quasi-spherical to polyhedral, probably faceted, with increasing T_{MAX} .

2. Materials and methods

CNOs were prepared via annealing of the well-purified nanodiamond powder (grain size ~5 nm, ash content <0.03 wt.%) in a large-scale, high-temperature commercial furnace SCC-U-80/150 (manufactured by Kurata Giken Co. Ltd., Aichi, Japan) in the dry argon atmosphere, along with the heating process with T_{MAX} of up to 1500–2150 °C, similar to the method described in Ref. [27]. Here we used the chemically superpurified detonation nanodiamonds, which were practically free (<14 ppm for each item) from the 3d-transition metal impurities like Fe and Ni, in order to exclude their parasitic catalytic impact on the possible particle growth and enlargement during the heat treatment process. The argon gas, filling the closed internal volume of the electrical furnace after its preliminary evacuation up to the technical vacuum, was under the pressure of ~50 kPa at 300 K. The gas pressure was kept fixed inside the furnace during the annealing, until the furnace was cooled down to the room temperature.

The annealing procedure was performed as follows: the nanodiamond powder in a graphite crucible was heated from the initial temperature of 950 °C up to the desired maximal temperature T_{MAX} in the range of 1500–2150 °C, with a heating rate of about 15 °C per minute, kept at this temperature for 20 min, and then cooled down to the room temperature, with a cooling rate of about 0.7–1.0 °C per second during the first 300 °C interval of cooling. The temperature of the crucible with the sample inside was controlled by optical pyrometer (Chino Corporation AL3000/AH3000) with accuracy of about 1% in the range 1500–2100 °C. Seven CNO samples were thus prepared for the study, with T_{MAX} of 1500, 1550, 1600, 1650, 1750, 1950, and 2150 °C.

The high resolution transmission electron microscope (HRTEM) JEOL JEM 2010FEF, 200 kV was used for the observation of the annealing-induced modification of the samples' structure. A relatively low acceleration voltage of about 120 kV was intentionally chosen to prevent a destruction of the internal and external structure of the nanoparticles and graphene sheets during their prolonged exposure to the focused electron beam. The actual lateral resolution was high enough to resolve the internal structure of the isolated CNO nanoparticles.

The Raman spectra of the CNO samples were measured using “inVia” Renishaw micro-Raman spectrometer with the 457.9- and 514.5-nm lines of the Ar^+ laser and the 633-nm line of the He–Ne laser as the excitation sources. The spectra were collected in the backscattering geometry using the 50× Leica objective (NA = 0.78), and normalized on a spectral sensitivity of the “inVia” Renishaw measured with a black-body radiation unit. The laser power of 20 W/cm² on the sample surface was used, preventing the sample heating. The samples for the Raman measurements were prepared by depositing and drying a drop of the aqueous colloid dispersion of the CNO powder on a copper substrate.

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