TEMPERATURE-EFFECT OF RAMAN SPECTRA IN CARBON ONION

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Abstract

The temperature dependence frequency shift of Raman spectra of carbon onion is investigated in the range of 98K to 873K. The frequency decreases with increasing temperature for all peaks, and the shifts in Raman frequencies are linear in temperature of the sample. The relatively strong temperature dependence in carbon onion may be due to the pure temperature effect and a size.downshift in the C-C stretching frequency induced by the thermal expansion. Moreover, the pure temperature effect$(d\omega/dT)_V$ without anharmonic contribution is achieved and plays an important role in the frequency shifts with temperature in carbon onion.

Keywords: Temperature dependence, Carbon Onion, Raman spectra

Introduction

After the discovery and mass synthesis of carbon onion[1], several experimental and theoretical works have appeared suggesting intersting physical properities for indicated that the micro-structure and band gap[2-3]. Besides, the preparation can lead to various shape: single nucleus, twinnucleus,and encapsulating metal. It could be interesting to be able to indentify them.

The Raman scattering of carbon materials is sensitive to structural disorder of the material[4]. As a result, Raman spectroscopy provides a useful non-destructive technique for structural characterization of carbon materials surfaces; and by using laser microprobe techniques, this capability can be applied to microstructural features only a few microns in size. The temperature dependence of first-order Raman scattering provides valuable information about anharmonic terms in the lattice potential energy. There are some studies thus far on the temperature dependence of Raman spectra in detail for carbon nanotube, graphite and the possibility of identifying the presence of carbon materials[5-7]. From all there results, a few reports have made mention of carbon onion.

In this paper, we present Raman microapectrocsopic study covering frequency ranges from 40 to 2000cm^{-1} showing the temperature effect on spectra and structure of carbon onion. Distinct spectral characteristics will be given carbon onion. A reversible structural transformation will also be shown.

Experimental

The carbon onion were prepared by the arc-discharge in water method. The discharge apparatus comprised, simply, graphite electrodes, an open vessel (2L), and a DC power supply. The graphite cathode (20 mm in diameter) and anode (6 mm in diameter) were submerged in liquid and aligned horizontally. The whole procedure took place at the depth of 3 cm below the liquid surface. The optimized discharge voltage was 22–26 V and the current was 40 A. The arc discharge in water was found stable and could run for 20 s by adjusting the cathode–anode gap to be approximately 1 mm.

Products of arc discharge were characterized with field emission scanning electron microscope (SEM: JEOL 6700F) and high-resolution transmission electron microscopic investigations (HRTEM: JEOL 2010). All Raman spectra were measured by a micro-Raman spectrometer with a 514.5 nm Ar ion laser. The carbon onion samples were sealed in a heating/cooling stage where liquid nitrogen was used as a cryogenic source and a resistance heater for heating. The sample temperatures were measured using a Pt-based thermal couple with an accuracy of ±0.1K.

Results and Discussion

A bulky deposits bridged between the electrodes and fine powders dispersed in liquid were observed. The floating samples obtained using pure graphite electrodes were examined by SEM and TEM, shown in Fig.1. Aggregates of carbon structures with globular morphology were observed . The samples were nearly spherical which the size range of 10–40 nm, and the average particle size is about 25 nm. The concentric graphitic layers of carbon onions are resolved clearly in Fig.1b.

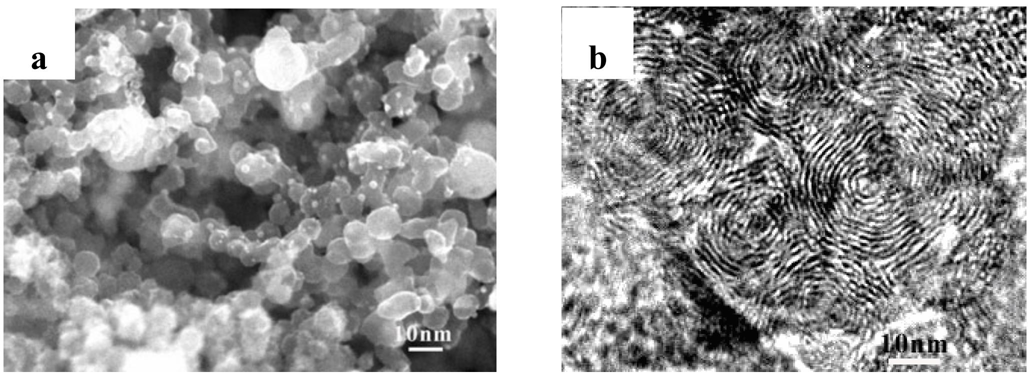

Fig.1 Images of carbon onions synthesized by arc-discharge in water. a)SEM, b)HRTEM.

Smoothed tracings of the spectra obtained from 83K to 873K are shown in Fig.2a. The primary features of the spectra are shown by the solid lines. Two main peaks can be distinguished in Fig.2a, all in the C-C stretching vibration range 1300-1600cm^{-1}. At the first sight, all examined carbon onion present a strong band at 1573cm^{-1} and 1350cm^{-1}, similar to those of graphite[6]. The origins of these peaks are discussed in term of the phonon density of states and phonon dispersion curves of graphite. Raman microspectroscopic technique allows to focus only on the pure microcrystal of the carbon onion, thus, no band corresponding to other materilas is present[8]. It is shown the change of the Raman spectra of the carbon onion at different temperatures dues to laser illumination. With increasing temperatures the wave numbers of the Raman peaks downshift simultaneously. The result indicates that the strong temperature effect is a common property of carbon onion.

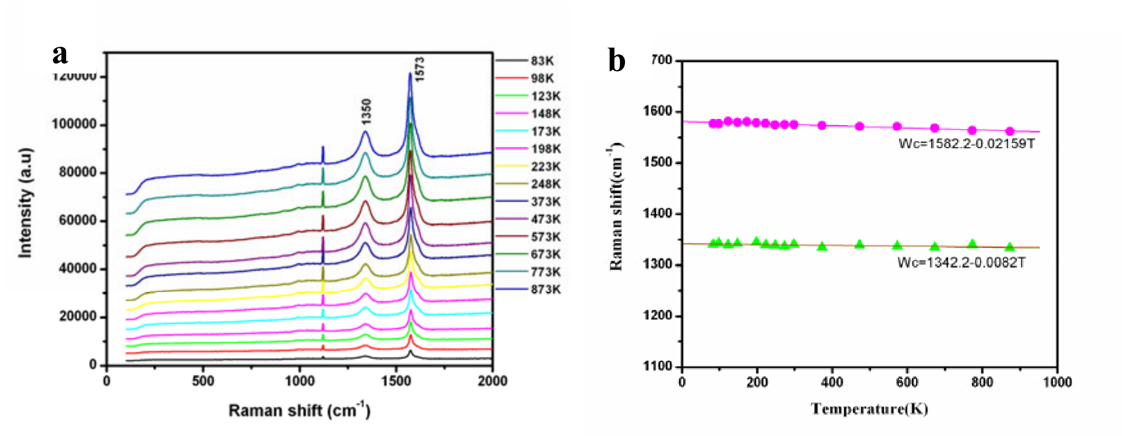

Fig.2 a)Raman spectra and b) the peak ferquencies of D and G bands on temperature for carbon onions synthesized by arc-discharge in water.

The temperature-dependent frequencies of these G and D peaks are displayed in Fig.2b. It is easy to see that the temperature variations of each G frequency can be fitted by a straight line, that is ,thay have simple linear relationship. Howerer, their slopes (i.e., dw/dT, temperature coefficient of Raman frequency shift) are different. The slope data indicate that G peak relative to carbon onion with the higher temperature has the larger frequency downshift. In a word, G frequencies also exhibit simple linear decrease with increasing temperature, which is associated with the lengthening of the C-C bond[4,7]. According to the temperature coefficients of GM frequencies, the value of carbon onion is significantly smaller than MWCNT. C-C bond length results from the thermal expansion of the material upon the temperature increase. The thermal expansion induces a longer C-C distance and a downshift in the C-C stretching frequency.

Conclusions

In summary, carbon onion are thus characterized by their Raman spectra. A temperature induced frequency shift is observed for G and D peaks in the Raman spectra of carbon onion. The frequencies of two peaks shift down linearly with increasing temperature. It is because of thermal expansion caused by the lengthening of the C-C bond and a downshift in the C-C stretching frequency.

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