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Probing the mechanical properties of carbon nanohorns subjected to uniaxial compression and hydrostatic pressure

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ABSTRACT

Carbon nanohorns (CNHs) as an important carbon nanostructure have been studied in many fields and shows huge potential for applications. Previous studies exhibit that CNHs consist of single-walled carbon nanohorns in the periphery and a graphene-based core in the center. However, the knowledge of their mechanical properties is still lacking. Here, the mechanical behaviors of CNHs subjected to uniaxial compression and hydrostatic pressure have been probed. Under uniaxial compression, two opposite dynamic responses were found to demonstrate different natures of flexible nanohorns and hard cores. The former shows good elastic recoverability but a hardening effect during multiple cycle loading, while the latter possess good load-bearing ability reflected by high compressive strength (max. Value of 18.8 ± 4.5 GPa) and high stiffness (max. Young' modulus of 84.6 ± 27.8 GPa). In hydrostatic state, the mechanical response is monitored by simultaneous Raman measurements through the shift of either G or 2D phonons of CNHs. The results show that two anomalies at pressures of ~3 and ~7.5 GPa have occurred, resulting from the nanohorns' cross-sectional shapes from circular-to-oval and oval-to-peanut-like structural phase transitions, respectively. Analysis based on Grüneisen parameter demonstrates the similarity of hydrostatic behaviors of CNHs and single-walled nanotubes, indicating high structural stability under high pressure.

1. Introduction

Carbon nanohorns (CNHs) [1–3] reveal quite intriguing potential for applications in nano-engineering (adsorbents [4], biorecognition and biosensing [5], catalyst support [6], drug delivery [7], nano-reinforcement [8], etc), electrochemical device and energy storage (supercapacitors [9], hydrogen storage [10], electrode material [11], etc). The configuration of such carbon nanostructure is more complex than graphene or carbon nanotubes (CNTs), featuring thousands of protruding single-walled carbon nanohorns with a diameter of 1–5 nm and a length of tens of nanometers in their periphery. On the other hand, the interior structures of CNHs comprise randomly oriented single-layer graphene sheets instead of nanohorns in their cores [12]. Laser or arc evaporation of graphite could massively yield this material with sizes in a range of 80–100 nm, and two types were usually found as dahlia- and bud-like CNHs according to their edge appearance [13]. Such unique structure leads to distinct properties compared with other nanocarbons, for instance, a pressure-tuned electrical behavior was found by compressing a single CNHs via conductive AFM technique [14], reflecting different natures of surface nanohorns and the cores. With respect to mechanical behavior, theoretical studies basically focused on various types of single nanohorn, because of easy modeling. The predictions show general characteristics for this conical carbon, such as conical-angle-dependent tensile strength [15,16], buckling behavior under compression [17] and nonlinear mechanical response [18]. Unfortunately, the experimental reports on the mechanical behavior of CNHs are very limited, probably due to the fact that very small size of conventional CNHs (80–100 nm).

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Bhushan et al. [19] reported their attempt to probe the mechanical response of conventional CNHs under uniaxial compression, finding the pop-in events happened as a characteristic for nanohorns' buckling during deformation. For some aspects of application [8,20], the precise determination and monitoring of mechanical response, and stress/strain are key requirements. However, until now, experimental studies for their mechanical behaviors are still lacking and the deformation mechanism has not yet been well-established either qualitatively or quantitatively, though it is of fundamental importance. Recently, a positive pressure-assisted arc discharge method [21] that effectively enhancing the size of CNHs is arguably an experimental advance that has been made toward overcoming the challenge of performing compressive tests on CNHs.

In this work, a large number of bud-like CNHs within a broad size range of 150–500 nm has been successfully prepared, allowing us to put the wheels in motion to directly measure them via current techniques. The mechanical measurements under uniaxial compression and hydrostatic pressure have been performed using *in situ* nano-compression and diamond anvil cell (DAC) techniques, respectively. *In situ* transmission/scanning electron microscopies (TEM/SEM) nanomechanics characterization of nano-objects has attracted widespread attention for its unprecedented, amazing performance of mechanical behavior [22,23]. Such state-of-the-art nanomechanical systems provide opportunity to have access to real-time dynamic response of materials subjected to uniaxial compression. It is generally recognized that bulk graphite is very fragile and easily slide along the direction perpendicular to *c*-axis. However, it was found that graphite-like nanoparticles [22] exhibit a nonlinear elastic behavior under uniaxially compressive load, and possess high breaking strength and high stiffness. For another thing, to assess the degree of stress transfer of a material under triaxial stress state, probing the shift of phonon frequencies is an effective way. DAC coupled with *in situ* Raman spectroscopy has been proven very successful in monitoring phonons of a whole range of graphitic materials under hydrostatic pressure, including graphite [24,25], CNTs [26–30], graphene [31], and graphite-like nanoparticles [32–34]. Here, the original mechanical responses of CNHs have been explored by the abovementioned techniques. Our results show that CNHs has distinct mechanical behaviors under uniaxial and hydrostatic stress states. The whole CNH being uniaxially compressed exhibits two evident characteristics: i) near linear elastic deformation of surface nanohorns featuring with pop-in events, showing low strength but good recoverability, ii) while the core of CNHs exhibits a nonlinear compressive property with excellent load-bearing ability reflected by high breaking strength and high stiffness. Under high pressure, the hydrostatic behavior of CNHs is similar to that of CNTs, specifically, a multistage structural transition resulting from the variation of tubular shape that actually changing the band structures. The similarity also demonstrates the high restorability and structural stability of CNHs [29,30]. This work expands the knowledge base of the overall mechanical properties of CNHs, which are essential for both fundamental research and application focusing on the nanomechanics of such complex nanocarbon.

2. Experimental

2.1. The preparation and characterization of CNHs

The bud-like CNH aggregates used in this work were produced by a positive-pressure-assisted direct current (DC) arc discharge method in Ar gas as described in previous publication [21]. Commercial pure graphite (99.99%) rods of 6 and 15 mm in diameter were set as anode and cathode, respectively. The electrodes were installed horizontally in a high-vacuum closed stainless steel chamber filled with argon (~3 atm). The DC current was maintained at ~110 A and the discharge voltage was kept at 30 V by controlling the gap distance between the two electrodes. Raw CNH samples were collected from the inner wall of vacuum chamber.

The bright-field imaging of the samples was acquired by employing a HRTEM (JEM-2010F, JEOL). SEM images were obtained by using a field emission scanning electron microscope (SU6600, Hitachi). Raman spectra were recorded from 1000 to 3500 cm^{-1} using laser excitation wavelength of 532 nm (HR-800 laser confocal micro-Raman spectrometer, Horiba Jobin Yvon).

2.2. In situ uniaxial compression

In situ quantitative nano-compression tests were carried out in a combined system of focused ion beam (FIB)/scanning electron microscope (SEM) (FEI Helios 600 Nanolab), equipped with a flat-end diamond indenter serving as the compression anvil (PI 87 SEM Picoindenter, Hysitron Inc). The core part of such nanomechanical testing system is the force-displacement transducer, which provides high sensitivity, large dynamic range, and a linear displacement output. The loading rate was controlled by displacement mode with 10 nm s^{-1} throughout the whole experiments. The real-time deformation process was recorded using an affiliated charge-coupled device (CCD) camera. To make sure CNHs are evenly rested on the substrate, a droplet of the ethanol solution containing the sample was placed on a chemically cleaned Si wafer and then the ethanol was allowed to evaporate. The qualified individual CNH was selected randomly in the field of view of SEM.

2.3. Hydrostatic experiments

A DAC device with a diamond culet size of 500 μm was used for generating pressures up to ~10 GPa. The sample was contained in a 200 μm diameter hole in a T301 gasket which was preindented to a thickness of about 100 μm and clamped between two diamond anvils. Two type I_a diamonds with low fluorescence were used for Raman measurements. Pressures were calculated from the shift of the ruby R_1 fluorescence line. A mixture of methanol-ethanol (4:1) was used as the pressure transmitting medium (PTM) for the true hydrostatic state. Raman experiments were carried out using a Renishaw inVia Raman microscope (Renishaw, UK) with 532 nm wavelength excitation. Raman spectra were collected in a backscattering geometry with a 2400 grooves mm^{-1} grating, and the slit width was selected as 65 μm corresponding to a resolution of ~0.5 cm^{-1}. All the Raman measurements were conducted as the sample was compressed in steps at ambient temperature. The samples were held under each pressure for about 10 min until the equilibrium was established. In recording the data, pressure was increased at intervals of about 30 min, including duration times. Before testing, the raw CNH samples were further purified by heat treatment (annealing temperature ~450 °C, heating rate ~2 °C min^{-1}, holding time ~10 min, air atmosphere) to eliminate the byproducts like amorphous carbon generated during arc discharge. After purification, the purity of CNHs could reach above ~95%.

3. Results and discussion

Fig. 1a exhibits the overall morphology of as-prepared CNH aggregates. The periphery of CNH aggregates consists of a large number of carbon nanohorns, whose detailed structure is shown in Fig. 1b. The basic structures of surface nanohorns are exhibited to be single-walled, conical tubulets with a variety of shapes, and the cone shaped cap usually has an angle of ~20° (See Fig. S1 in supplementary information). According to the TEM observation,