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Graphene-size-tuned mechanical serration behaviors in nanocarbons

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ABSTRACT

Two vastly different types of load-displacement responses observed in graphitic nanostructures under nano-compression are compared in terms of serration behaviors. Different from commonly encountered linear/nonlinear elastic deformation, a periodic serration behavior related to plastic flow is observed in amorphous carbon nanospheres. The true stress-strain relation exhibits a sole feature of type C serration, and comprehensive statistical, dynamical and fractal analyses further demonstrate a chaotic characteristic of dynamics for those serration events. When entering a quasi-steady flow stage, the elastic stress in each serration event could maintain a relatively stable level near ~135 MPa, very close to the interlayer shear stress (ISS) of single crystalline graphite (~140 MPa). This finding indicates the dependence of shear deformation on weak van der Waals interaction (elastic constant C_{44}), instead of other structural factors associated with high elastic constants of graphite cells. Based on the experimental results, a microscale ISS-driven shearing mechanism is proposed. The local flexibility induced by small graphene lamellas may facilitate interfacial slip between neighboring domains with commensurate contact. Such slip mode may be responsible for the mechanical serration phenomenon in graphitic materials.

1. Introduction

Serration and noise phenomena are ubiquitous in mechanical responses of many structural and functional materials, for example, metals and alloys [1]. In many physical systems the term of serration refers to a sudden jerky response to an external force or field, exhibited as saw-like shapes of their corresponding curves. The serration behavior could be described by the Portevin-Le Chatelier (PLC) effect, which is related to avalanches of deformation processes, specifically inhomogeneous deformation [2]. In stress-strain curves, the serration characteristics appear as stress drops or strain jumps. While properties like strain rate sensitivity and critical strain mark the onset of the PLC effect, researchers have developed a nomenclature to describe the serrations. Rodriguez [3] summarized five types of serrations for the dynamic strain aging effect. Three common types of serrations are usually labelled as type A, B, and C in literature. Type A represents the intermittent behavior propagating with small stress drops, while type B shows the continuous "hopping" behavior with small serrations. Type C serrations, which are large, appear in the latter part of the plastic deformation. This response is identified with random nucleated static bands with large characteristic stress drops [4]. These three types are often dependent on strain rate, temperature, grain size, and so on [1]. Besides, type D and E are also reported by some authors [3,5]. Type D serrations appear as staircase steps, while type E exhibits random behavior.

As for graphitic materials from bulk to nanoscale, local deformation (indentation) [6,7] and global deformation (compression) [8–10] are both powerful approaches to investigate the mechanical properties such as Young's modulus, ultimate strength, and stress-strain relations. Regardless of load types, there are usually similar load-displacement responses for most graphitic materials, that is, linear [11] or nonlinear elastic deformation [6,8,9,12,13], as well as hysteresis loops that occur during loading (elastic) and unloading (anelastic) cycles. In addition, pop-in events are sometimes observed during loading cycles, together with pop-out events for unloading cycles [8–10]. In contrast, purely plastic deformation has been rarely seen due to the intrinsic brittleness of graphitic materials. In this work, a comparative investigation of the mechanical response of three arc-synthesized nanocarbon structures subjected

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to uniaxial compression has been performed, including polyhedral graphite (PG), carbon nanohorn (CNH) aggregates, as well as a newly discovered amorphous carbon (AC) nanospheres with oversized shapes of several hundreds of nanometers, far greater than conventional AC in arc soot (several to tens of nanometers). Generally, there are two remarkable types of compressive responses observed in tested samples. The first type shows common features of nonlinear elastic deformation for PG and CNHs like many other graphitic materials, while the second exhibits an unexpected serration behavior in both load-displacement and stress-strain data for those AC nanospheres. Unfortunately, the present understanding on such mechanical serration behavior for graphitic materials is poor. To this end, comprehensive analyses are performed to elucidate the underlying physical process, and some related parameters describing such phenomenon have been established. On the basis of experimental results, a possible shearing mechanism is proposed dependent on the tunable influence of graphene size.

2. Experimental

Three nanocarbon samples were fabricated by direct-current (DC) arc plasma evaporation of pure graphite under atmospheric conditions. The respective buffer gases for mass production of PG, CNHs, and AC nanospheres are helium/hydrogen (50 kPa, volume ratio 5:1), argon (0.15–0.2 MPa) and argon (0.3–0.35 MPa). The positive pressure in the arc discharge process is found to be essential for the oversizing growth of nanocarbons compared with their conventional counterparts [14,15]. The details of the arc discharge device, sample collection and post-treatment are available in Supplementary Material. In addition, a combination of sample characterization including high-resolution transmission electron microscope (HRTEM, JEM-2100), selected-area electron diffraction (SAED), X-ray diffraction (XRD, D8 Advance, Bruker) and Raman spectroscopy (HR-800, Horiba) were carried out for detecting sample morphology and crystal structure. HRTEM was performed using the acceleration voltage of 200 kV with a resolution of 0.23 Å. XRD measurement was done under radiation with a source of non-monochromatic Cu Kα X-ray. Raman spectroscopy was recorded with a HR-800 laser confocal micro-Raman spectrometer using laser excitation wavelength of 532 nm. The spectra were collected from a wavenumber range of 1000–3500 cm^{-1}. According to HRTEM observation, the typical morphology and SAED pattern of each sample is shown in Fig. 1 of main text, while the histogram of size distribution is given in Fig. S1 of Supplementary Material. In addition, the XRD patterns and Raman spectra are presented in Fig. S2. *In situ* compression measurements were performed in a focused ion beam workstation combined with a field-emission scanning electron microscope (FIB/FESEM, Helios 600 Nanolab). The uniaxial compression was carried out by a 1 μm-diameter flat-end diamond indenter serving as the compression anvil (PI 85 SEM Picoindenter, Hysitron Inc.) The core part of such mechanical testing system is the load-displacement transducer, which could provide high sensitivity, a large dynamic range with a maximum force up to 10 mN and a linear displacement output up to 5 μm. The capacitive transducer working in conjunction with an extremely fast 78 kHz control system ensured that the Picoindenter provides superior stability at the nanoscale. The resolution of original data depends on a low force/displacement noise level (<0.4 μN, <1 nm). The Picoindenter was regularly calibrated by a push-to-pull device provided by Hysitron Inc. for the accuracy of data collection (see Figs. S3–S4 in Supplementary Material). Before testing, a comparison of set and actual displacement of the indenter was carefully performed under loading for further calibration. The nano-compression experiments were undertaken with the following parameters: displacement mode with a rate of 10 nm/s, magnification 50,000 ×, and tilt angle 0°. The dynamic compression process was recorded using an affiliated charge-coupled device (CCD) camera. It allows real-time correlation between the microstructural and geometry evolution and mechanical responses. The qualified individual sample was selected randomly in the field of view of SEM. For each sample, more than 6 nano-compression tests were performed with good reproducibility, showing distinct mechanical responses for different microstructures. Due to the prior calibration of testing system, no more correction is needed for the analysis of original load-displacement data.

3. Results

3.1. Materials characterization

Fig. 1 presents an overview of the morphologies and microstructures of the samples characterized by HRTEM. In Fig. 1a–c, the mass production of PG, CNHs and AC nanospheres are successfully achieved by arc evaporation of graphite under optimal conditions. The histograms of size distribution for these samples are given in Fig. S1 of Supplementary Material. By analyzing over 100 particles for each sample, the mean sizes are 222.1, 231.9, and 361.1 nm for PG, CNHs and AC nanospheres, respectively. The PG has a closed framework of concentrical graphite layers within the polyhedron, where the facets observed at the surface have side lengths of several tens of nanometers. (see Fig. 1d). Unlike graphite, the distortion of these facets of PG could lead to the appearance of Moiré patterns [16] (see some black stripes in Fig. 1a and d). The PG are always solid polyhedra due to the outward growth of a polyhedral nucleus. As shown in Fig. 1b and e, the CNHs is a nanocarbon aggregate made up of a large amount of horn-like carbon nanotubes at the periphery, and an interior solid core constructed by disordered graphenes [17–19]. For AC samples, the particle is approximately spherical, obviously different from those of PG and CNHs samples. The microstructural detail in Fig. 1f shows unambiguously that the AC nanospheres compose of small graphene lamellas in an arbitrary arrangement. The characteristic size of such graphene lamellas fall within a range of several nanometers. According to the results of SAED, the diffraction patterns of PG, CNHs and AC reveal a structural transition from crystalline to amorphous, as shown in Fig. 1g–i. Furthermore, the XRD and Raman spectra of the samples are also given in Fig. S2 of Supplementary Material, providing consistent evidence of microstructures for each sample with varying graphitization. In XRD results, the peaks at $2\theta = \sim 26^{\circ}$ indicative of graphitic (002) reflection are gradually weaken and broaden from the reference data of bulk graphite to CNHs. For the AC samples, there are few strong reflections, indicating the amorphization. The Raman spectra confirms the structural variation of PG, CNHs and AC according to the intrinsic vibration of E_{2g} mode (G band) and defective A_{1g} mode (D band). The sharp G peak for the PG indicates a similar graphitic microstructure compared to bulk graphite, while the broaden G band reveals a turbostratic nature of CNHs. The higher D relative to G and the broader G band show a highly disordered structure and very low graphitization of AC nanospheres. Generally, the XRD and Raman results are consistent with the observation of HRTEM and SAED. In addition, the intensity ratio of D/G bands, I_D/I_G, is widely used for quantitatively determining the nano-graphite size, L_a, in graphitic systems, based on an empirical relation, $L_a = 4.4\,(I_D/I_G)^{-1}$ [20,21]. Thus the L_a values of PG, CNHs and AC nanospheres are 18.6, 5.5, and 2.9 nm, respectively, giving a satisfactory agreement with the characteristic graphene sizes of three nanocarbons as shown in Fig. 1d–f (see red lines).