A new family of carbon materials with exceptional mechanical properties

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Abstract

A new family of carbon materials with ultrahigh-strength and nano-onion grains has been successfully produced from nano-diamond particles by spark plasma sintering. It is believed that the spark plasma and applied pressure help overcome the difficulties in densification. Also diamond has a much greater density than that of graphite, leading to the volume expansion when nano-diamond particles transform to graphite onions during heating, facilitating the consolidation. The as-prepared bulk graphite with a density of 1.84 g/cm^3 has ultrahigh bending strength, modulus and microhardness, 150 MPa, 31.3 GPa and 2.6 GPa, respectively, due to the unique microstructure of nano-graphite onions.

1 Introduction

Carbon materials are extensively used as electrodes, refractories, nuclear reactor parts, etc. because of their low electrical resistivity and resistance to harsh environments [1, 2]. Especially, with the development of high-temperature nuclear reactors, the need for advanced carbon materials is growing faster than ever [3]. The preparation of high-strength carbon materials becomes quite important in modern technologies.

Graphite is the most important carbon material. Graphite, however, has a fatal weakness that the weak interlayer bonding brings about easy cleavages between graphene layers, directly leading to the low mechanical properties. The current bulk graphite is manufactured by an arduous process of bonding coke fillers with coal-tar pitch by carbonizing and graphitizing the artifact [4, 5]. This process involves many cycles of baking and impregnation, and the final graphitization at very high temperatures. Moreover, repeated baking and impregnation lead to serious density dis-uniformity to as-prepared graphite bulks. People have long been searching for a way to producing high-strength bulk graphite by directly sintering graphite powders, which proves, however, unachievable because of the high stability of graphite. Strong covalent bonds between graphite atoms result in slow self-diffusion of carbon atoms, making graphite powder sintering extremely difficult even at a temperature of 2000 °C and under a pressure of tens of MPa. We once produced graphite bulk materials by spark plasma sintering (SPS) carbon nanotubes [6, 7], but the produced material inherits the anisotropy of carbon tubes that may cause distortion or mismatch to graphite components [4]. Other approaches have to be investigated.

Transformation of nano-diamond (ND) particles to graphite onions was observed decades ago [8–12]. Since the success of the low-cost preparation of ND particles [13, 14], especially the use of ceramic precursor to mass produce ND powders [15], using these "onions" to produce high-performance bulk graphite has become significant. Our earlier research shows the consolidation of ND particles needs specially designed sintering processing. Here we report the dense, isotropic ultrahigh-strength bulk carbon (UHSBC) materials prepared by sintering ND particles. This material has a microstructure of nano-graphite onion grains that consist of curved graphene layers. Such a microstructure is completely different with that of current graphite. To our knowledge, no such material has been reported so far.

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2 Experimental procedure

2.1 Preparation of samples

Three types of single crystal ND particles (average size 100, 50, 10 nm and percentages of 50, 40 and 10 wt%, respectively) were used as raw materials, which are all purchased from Henan Yuxing Huajing Weizhuan Co. Ltd., China. All the powders were produced by mechanical pulverization method.

ND powders were ground in a mortar for 10 min before being mixed with 50 ml absolute ethanol in a beaker under ultrasonic of 120 W for 20 min. Then the dispersed suspension was heated to evaporate the solvent under stirring. The resulting product was placed in an oven of 70 °C for 10 h and sieved with a 100 mesh stainless steel sieve to get the mixture. Sintering was carried out on a SPS apparatus (Dr. Sinter 2040, Sumitomo Coal Co. Ltd., Japan). The pellets were heated to 1600 °C at a heating rate of 150 °C/min with a pressure of 80 MPa and a soaking time of 5 min.

2.2 Sample characterization

Raman spectra of the original ND powders and the polished samples were collected at room temperature on a laser Raman co-focal microspectrometry (Renishaw in Via Reflex, UK, 100 mW laser power, 20× objective lens) with laser excitation wavelength of 514 nm. The samples were also analyzed using X-ray diffraction (XRD, Bruker D8 Advance, Germany) with Cu-Kα radiation. The step width was 0.01° with a scanning range of 15°–85°. Microstructure of isotropic graphite bulk materials was characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800), and high-resolution transmission electron microscopy (HRTEM, JEOL 200CX) at an operation voltage of 200 kV.

Archimedes method was employed to determine the sample density. Nanoindentation test was carried out on a nanoindentation device of Bruker UMT TriboLab equipped with Berkovich pyramidal indenter. Three-point bending tests were performed on the universal testing machine (UTM, AGS-10KNG). The crosshead speed was 0.1 mm/min.

3 Results and discussion

3.1 Microstructure of the UHSBC material

XRD data (Fig. 1a) of the ND particles soaked at 1600 °C for 5 min clearly show the transformation to graphite onions, and no ND remained in the final graphite onion sample. The four distinct peaks on XRD of the graphite onions correspond, respectively, to the (002), (100), (004) and (110) planes in the hexagonally packed structure of graphite [16], and the diffraction peaks for ND centered at 44° and 75° disappear completely, confirming the absence of ND within the sintered sample.

The grain size of UHSBC can be calculated by the Scherrer equation:

$$D = \frac{K\lambda}{\beta\cos\theta}, \tag{1}$$

where D is the mean size of the crystal grains, K is a constant related to crystallite, λ is the X-ray wavelength, β is the full width at half maximum, θ is the Bragg angle. According to XRD patterns, the average grain size of UHSBC is estimated to be 113 nm. This is not a convincing value as the
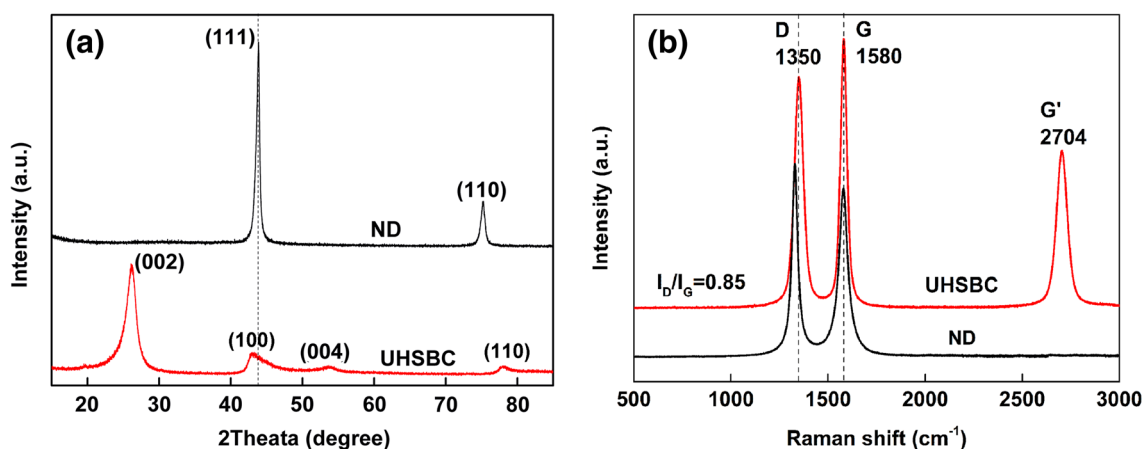

Fig. 1 **a** XRD patterns of ND and UHSBC, and Raman spectra of ND and UHSBC (**b**)

Scherrer equation is assumed to work well only when the size of tested grains is much smaller than 100 nm.

The Raman spectrum for ND sample reveals the peak at 1332 cm^{-1} of the sp^3 bonding of carbon atoms of diamond (Fig. 1b) [17]. Another broad peak at 1580 cm^{-1} can be assigned to sp^2 bond stretching vibrations of C=C groups due to a trace of other carbon phase in NDs. The Raman spectrum of the sintered sample shows that the graphitic (G) band becomes narrower and the diamond peak disappears while the disorder-induced defect (D) band signal emerges at 1350 cm^{-1}, demonstrating the change of ND to graphite onions. At the same time, the G′ band emerges at 2704 cm^{-1}. For graphitic materials the intensity of the G band (I_G), due to the in-plane stretching motion between pairs of sp^2 carbon atoms, is very much greater than that of the D band (I_D), believed to be due to a double-resonance, and is enhanced by edge effects and dangling bonds of the sp^2 carbon sites [18, 19]. If I_D is smaller than I_G the number of defect sites is significantly lower than that of graphitic sites. The I_D/I_G value for the carbon onions in this work was found to be 0.85, indicating some defects present within the carbon onion structure, in good agreement with other Raman spectra on carbon onions [20–22].

The representative images of different regions of the UHSBC samples consolidated at 1600 °C are presented in Fig. 2. TEM data demonstrate that ND particles transform to graphite onions, and most of these "onions" have a size of tens of nanometers except a few bigger ones from the bigger ND particles (Fig. 2a). The outer graphene layers of neighboring "onions" seem to be tangled together (Fig. 2b, c), implying that bonding happens between vicinity "onions". With the applied pressure, while the phase transformation

proceeds and volume expansion of particles takes place, the particles push against each other and the outer layers of "onions" are squeezed and tangled together to form strong bonds among graphite onions in the UHSBC. The averaged interlayer distance between the graphene shells is 0.36 nm for the majority of the UHSBC nanoparticles (Fig. 2d). According to the TEM data the theoretical density of graphite onions is estimated to be 2.1 g/cm^3 while the density of the compacted UHSBC sample is 1.84 g/cm^3. From the viewpoint of powder sintering, the UHSBC is highly densified.

Selected area electron diffraction (SAED) pattern is shown in Fig. 2c. The fuzzy and divergent ring diffraction patterns manifest the polycrystalline feature of UHSBC. The ring diffraction patterns correspond to the (002), (100) and (110) planes of graphite, respectively.

3.2 Sintering mechanism

During SPS, the continuous discharge between the particles instantaneously creates a huge local temperature increase, causing the phase transition from NDs to carbon onions. This transformation associated with the volume expansion contributes to the consolidation of the UHSBC (Fig. 3). With the applied pressure and temperature increase, especially with the phase transformation where carbon atoms are activated and at higher energy levels, carbon atoms migrate towards neighboring onions and voids among "onions" [23, 24]. Under the action of pressure, the outer graphene layers of the "onions" are distorted and squeezed to stack densely. Some outer graphene layers are even stripped off carbon

Fig. 2 TEM (**a**) and HRTEM (**b**–**d**) images of graphite onions derived from NDs after the phase transformation in SPS. Curved graphene layers form graphite onions, and the outer graphene layers are tangled together and bind the graphite onion grains to form UHSBC (**b, c**). SAED pattern (**c**). Interlayer distance between the carbon shells (**d**)
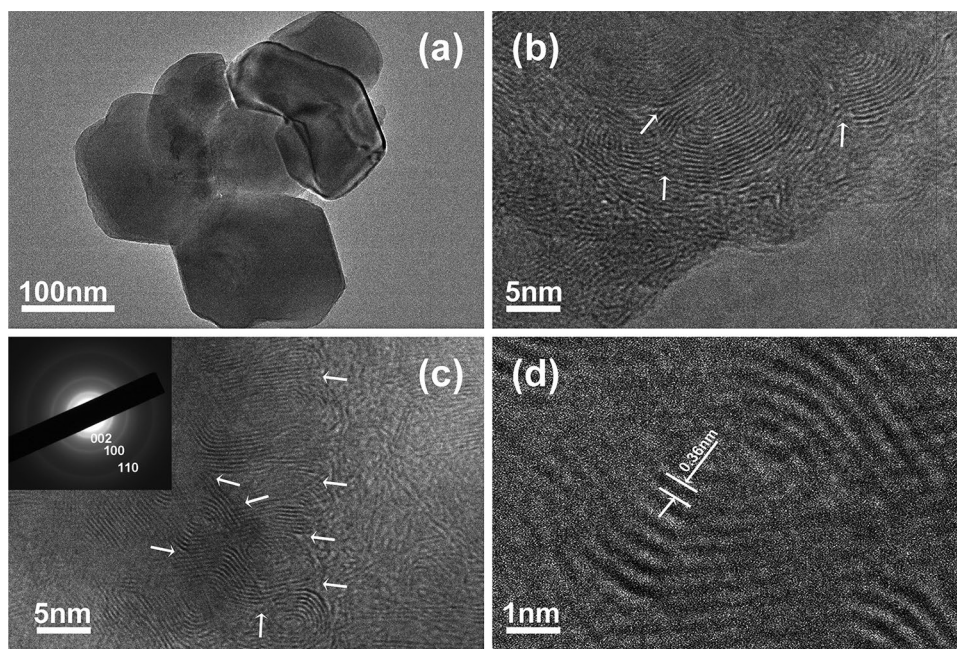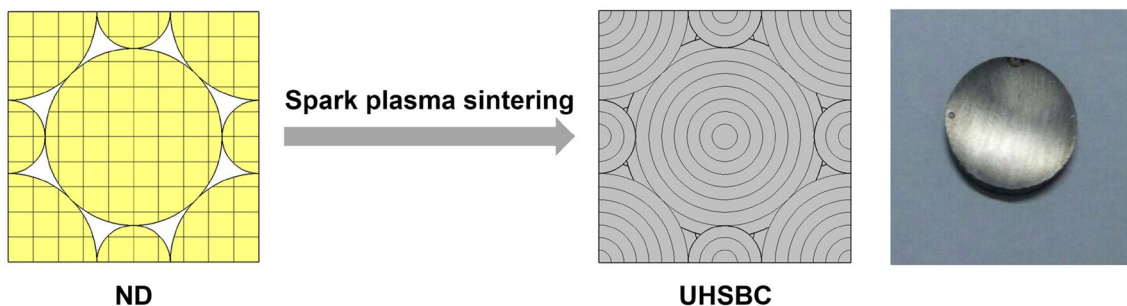
Fig. 3 Schematic illustration for the consolidation

onion and pushed to fill into the voids among "onions", as confirmed by HRTEM (Fig. 2).

3.3 Mechanical properties of the UHSBC material

To understand the mechanical properties of the as-produced material, carbon die (average grain size 1 μm, Carbone Lorraine Co., Ltd., China) was used as a control sample. The topography of carbon die and UHSBC before and after polish is shown in Fig. 4. The carbon die inherits the anisotropy of ordinary graphite grains and big pores while the UHSBC has a uniform and dense structure.

Nanoindentation and bending tests were performed on the polished samples. The test results are shown in Table 1. The UHSBC samples (sample code 1, 2, 3) with the same preparation method show ultrahigh mechanical properties

compared to common graphite materials and our carbon die chosen as a control sample (sample code 4, 5, 6) in the experiment.

Figure 5 shows FESEM micrographs at different magnifications of the fracture surfaces after bending test. Compared to the graphite die, the fracture surface of as-prepared UHSBC has a much fine structure of nanosized grains.

As we know, for brittle materials, the Griffiths' formula depicts the relationship between the strength (σ_c) and crack size c:

$$\sigma_c = \sqrt{\frac{2E\gamma}{\pi c}}, \tag{2}$$

where E is the elastic modulus, γ is the surface energy per unit area and c is the length of crack.

Fig. 4 FESEM micrographs of carbon die before (**a**) and after (**c**) polish, UHSBC before (**b**) and after (**d**) polish
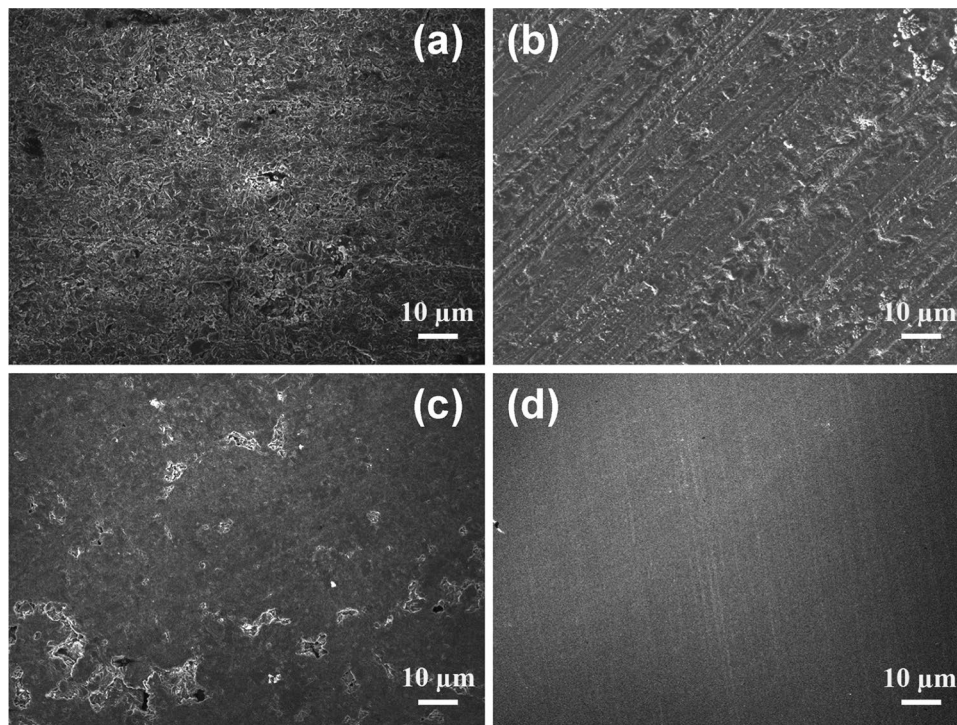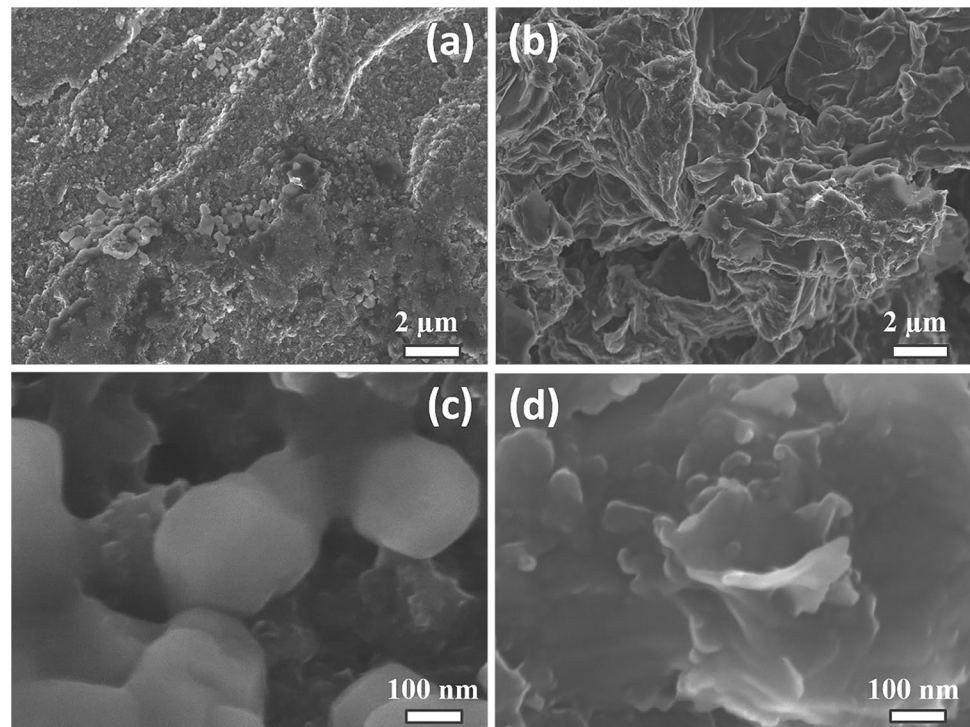
Table 1 Mechanical properties of different samples

Sample	Bulk density (g/cm^3)	Young's modulus (GPa)	Microhardness (GPa)	Bending strength (MPa)
UHSBC	1.84	31.3	2.6	150
Carbon die	1.80	7.7	0.5	67
Common graphite	1.70–1.80	6–15	–	20–40
IG-15	1.90	11.8	–	54

Fig. 5 FESEM micrographs of fracture surfaces of UHSBC material (**a, c**) and carbon die graphite (**b, d**) at different magnifications

In the current research, the fine structure of UHSBC mainly contributes to the ultrahigh strength. The tiny size of graphite onions means that pre-existing cracks in UHSBC are much smaller than in normal graphite materials. Although the density of UHSBC is slightly greater than that of graphite die used in our work, this minute difference does not make such significant strength difference. One more factor may be that graphite onions are much stronger than layered graphite grains. For a layered graphite grain, the bond strength between two layers is 40 MPa while the in-plane strength is 130 GPa. The interlayer weak binding brings about easy cleavages between graphene layers, directly leading to the low strength of the current graphite bulk material. Such easy cleavages would not happen in graphite onions, indicating the produced UHSBC is intrinsically a strong material. A bulk graphite material of such nano-onion microstructure has never been produced.

Figure 6 shows the load–displacement curves from the indentation tests. The hysteresis curves suggest unrecovered structural changes within the indented materials. For UHSBC, hysteresis curves at different places tend to overlap with each other, indicating the uniformity of the structure. Young's modulus and microhardness of the UHSBC are determined to be 31.3 and 2.6 GPa, respectively. The Young's modulus and microhardness of carbon die graphite chosen as a control sample are 7.7 and 0.5 GPa, respectively, in agreement with the reported values for common graphite materials (6–15 GPa for Young's modulus and 0.5–1.0 GPa for hardness) [25, 26]. These results demonstrate the as-prepared UHSBC is much stiffer and harder than the current graphite materials. Understandably, the graphene layers forming the graphite onions possess extremely high tensile strength to counteract high-level tension stresses acting on the graphite onions, making the graphite onions unyielding. Such a performance helps boost the Young's modulus of the as-prepared UHSBC.

There are two factors responsible for the hardness improvement. First, as seen in Fig. 6c, the indenter needs
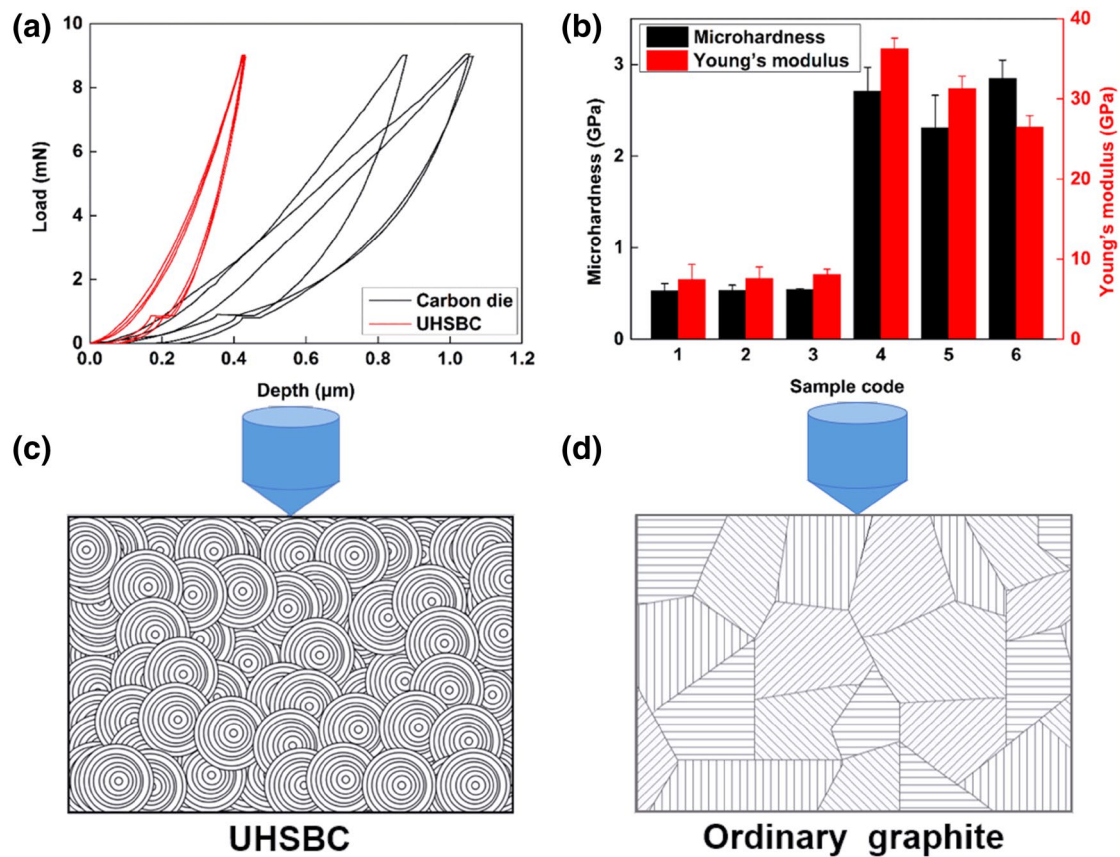
Fig. 6 Load–displacement curves of UHSBC carbon die (**a**). Microhardness and Young's modulus of UHSBC and carbon die (**b**). Schematic illustration for the indentation on the UHSBC material (**c**) and ordinary graphite (**d**)

much more efforts to fracture the strong graphene layers of the graphite onions. By contrast, for the ordinary graphite grains, the binding strength between (002) planes is weak and only small efforts are needed to trigger sliding and cleavages of (002) planes (Fig. 6d). Second, the as-prepared UHSBC has a fine structure with an onion-grain size of tens of nanometers, about ten times smaller than that of common graphites. With decreasing grain size, the yield stress increases and plasticity typically decreases, demonstrated by the well-known Hall–Petch formula:

$$\sigma_{y} = \sigma_{0} + kd^{-1/2}, \tag{3}$$

where σ_{y} is the yield stress and σ_{0} is a material constant for the starting stress for dislocation movement. The k is the strengthening coefficient and d is the average grain diameter.

4 Conclusions

In summary, dense ultrahigh-strength bulk carbon (UHSBC) material has been fabricated by spark plasma sintering from nano-diamond powders. In view of the unique microstructure of graphite onion grains, the UHSBC is a new family of carbon material. This study makes use of the advantages of high density of diamond and phase transition sintering to produce dense UHSBC materials at a moderate sintering temperature and under a moderate pressure.

UHSBC with a density of 1.84 g/cm^3 produced in this work processes ultra-strong bending strength, 150 MPa, and ultrahigh Young's modulus and microhardness, 31.3, 2.6 GPa, respectively, demonstrating the high stability of graphite onions when subject to stresses. This bulk carbon material is expected to play critical roles in harsh environments under intensive stress where the conventional graphite cannot survive.

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