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Structural evolution and Raman study of nanocarbons from diamond nanoparticles

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Abstract

Nanocarbons with a variety of morphologies were found after diamond nanoparticles (ND) were annealed at a low temperature. The conversion of ND to nanocarbons is a process of structural evolution that causes increase of sp^2 bonding structure and decrease of sp^3 bonding structure in nanostructure. While being annealed, ND are converted to carbon onions and undergo phase transition in a series of ND → bucky diamond → carbon onions → graphitic ribbons. The structural evolution of nanocarbons reflects the higher stability of planar graphitic ribbons over carbon onions.

1. Introduction

It is well known that diamond with sp^3 hybridization and graphite with sp^2 hybridization are traditional forms of crystalline carbon. Since the discovery of carbon onions, much interest has been concentrated on the structure and morphology of the family of nanosized carbons including diamond nanoparticles (ND), fullerenes and nanographites [1–3]. As a new kind of carbon allotrope, fullerenic nanocarbons (fullerenes, carbon onions and related structures) are characteristically constructed by curved graphene, whereas nanographites by planar graphene.

For nanosized carbon system, structural evolution and relative stability between carbon allotropes are of great importance due to their unusual properties and wide potential applications in the field of engineering. The conversion of ND to carbon onions has been experimentally observed and this has promoted a lot of studies in the investigation of the structure of nanocarbons [4–6]. Kuznetsov et al. have reported the formation of ribbon-like graphite from ND at a high temperature in a closed chamber and explained it as a result of carbon redistribution process via carbon transport reactions [7].

In our recent experiments, various nanocarbons including bucky diamond, carbon onions and graphitic ribbons were found after ND were annealed at a low temperature. To elucidate the structural evolution, we carried out systematic experiments on ND annealed at 1400 °C. These experiments provide us with much information that can deepen the understanding on the structural evolution of nanocarbon allotropes.

2. Experimental

The average diameter of ND is about 5 nm. Annealing of ND was carried out in a tube furnace under flowing argon atmosphere (99.99%) at 1400 °C for 20 min, 60 min and 120 min. Details of annealing process have been previously described [8]. The HRTEM images were obtained using a PHILIPS TECNAI G^2F20 electron microscope operating at 200 kV. Raman spectra were determined by Renishaw In via spectroscopy system. The laser was argon ion laser with 514.5 nm excitation source with power output of 20 mW.

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3. Results and discussion

3.1. Raman spectroscopy analyses

Fig. 1 shows Raman spectra of ND annealed at 1400 °C for 20 min, 60 min and 120 min, respectively. It is known that the C–C stretching mode of vibration can be detected at 1332 cm^{-1} for sp^3 bonded materials of diamond. As shown in Fig. 1a, a peak of ND Raman spectra at 1332 cm^{-1} is observed indicating sp^3 bonding structure. Another broad peak at 1620 cm^{-1} can be assigned to sp^2 bond stretching vibrations of C=C groups [9–15]. The existence of the Raman peak at 1620 cm^{-1} is in agreement with HRTEM observation of the original ND covered with a small number of amorphous carbon fragments.

As seen in Fig. 1b–d, Raman spectra of annealed ND display two broaden bands at ~1585 cm^{-1} and ~1350 cm^{-1} corresponding to the G-band and D-band of carbon onions, respectively. The G-band indicates that graphite structure develops, while the D-band points out many structural disorders in the nanocarbons [16]. In Fig. 1b and c, the Raman peak in the region 1332–1350 cm^{-1} is attributed to the overlap of sp^3-bonded ND and disordered sp^2-bonded carbon, which indicates the existence of the sp^3:sp^2 mixed-phase systems-bucky diamond. After the annealing of ND at 1400 °C for 120 min, the peak of sp^3-bonded ND is absent and the D peak corresponding to disordered carbon centers at 1350 cm^{-1} exactly (shown in Fig. 1d). The relative intensity of I_D/I_G gradually decreases with the increase of annealing time. This means that the phase transition of nanocarbons from ND is a gradual graphitization process, which leads to an increase of sp^2 bonding and decrease of sp^3 bonding in nanostructure. In the course of conversion there exist many disordered graphite fragments (as seen in Fig. 2d and Fig. 3); therefore weak shoulder of 1620 cm^{-1} at G peak is still present in Fig. 1c and d.

3.2. HRTEM observation

Fig. 2 presents the HRTEM images of ND annealed at 1400 °C for 20 min, 60 min and 120 min, respectively. Fig. 2a shows an HRTEM image of original ND with the characteristic diamond (111) *d* spacing of 0.206 nm. The original ND are covered with a small number of amorphous graphite fragments. As seen in Fig. 2c, ND annealed at 1400 °C for 60 min are mostly transformed into carbon onions with a variety of morphologies and a single-wall carbon nanohorn is also found (marked by arrow in Fig. 2c). It can be seen that the carbon onions are irregular and less than 10 nm. The phase transition of ND to carbon onions is ascribed to the elimination of dangling bonds and the closure of graphite sheets [8]. Between ND and carbon onions, there exists an intermediary phase–bucky diamond with a diamond core encased in fullerene-like shells (shown in Fig. 2b).

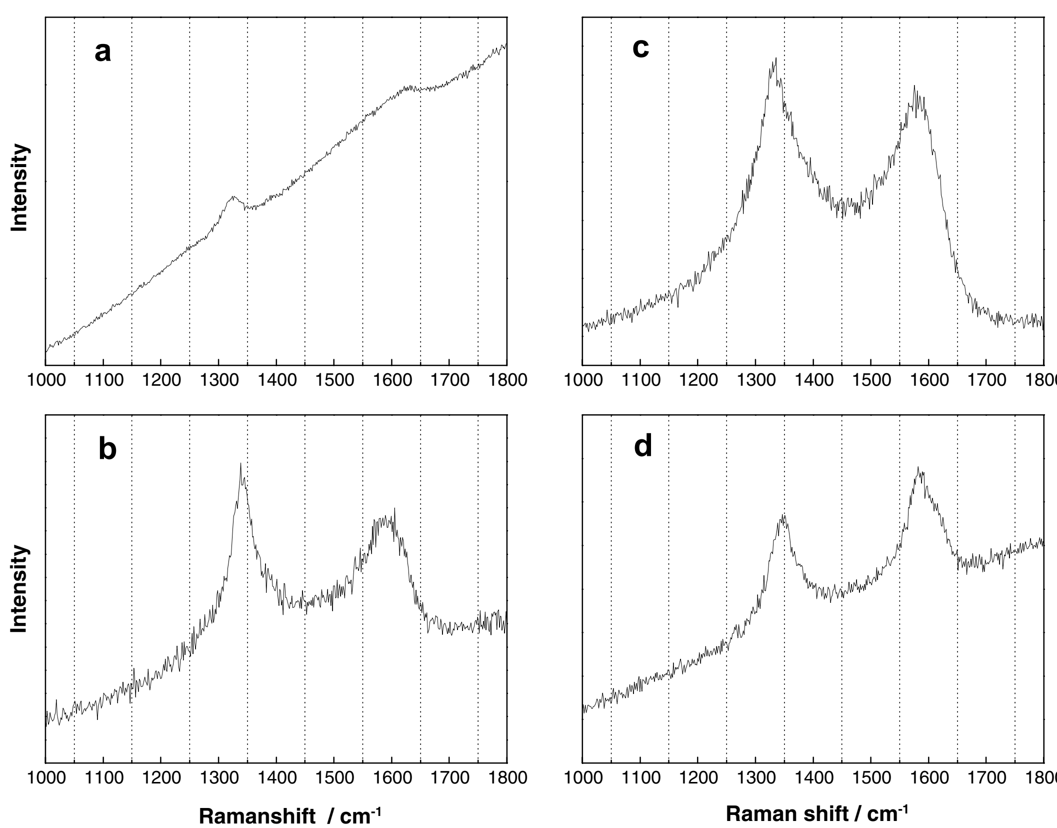

Fig. 1. Raman spectra of (a) original ND; ND annealed at 1400 °C for (b) 20 min, (c) 60 min and (d) 120 min.

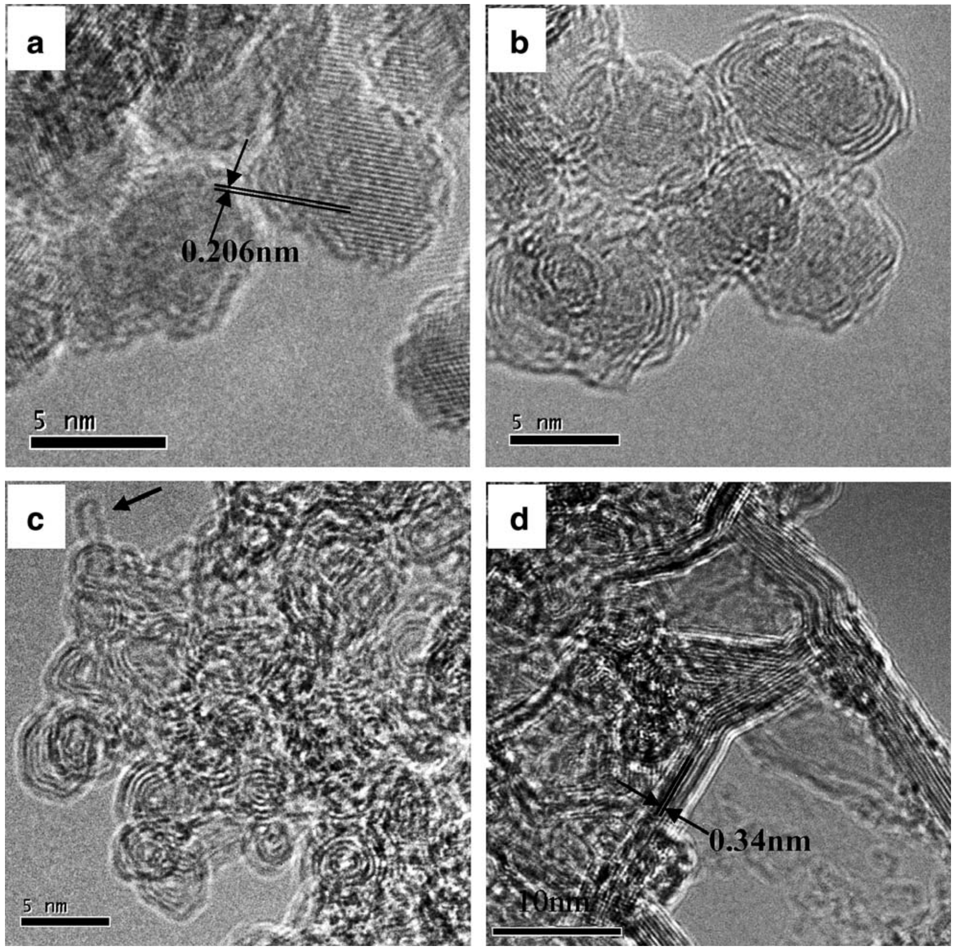

Fig. 2. HRTEM images of (a) original ND; ND annealed at 1400 °C for (b) 20 min, (c) 60 min and (d) 120 min.

Besides carbon onions, lots of graphitic ribbons can be observed in the HRTEM image of ND annealed at 1400 °C for 120 min, as shown in Fig. 2d. The graphitic ribbons are composed of planar graphitic layers with the length varying from 10 to 20 nm, and have interlayer spacings of about 0.34 nm.While being annealed, the outer layers of assembled nanoparticles tend to link up to form ribbon-like graphite. Fig. 3 is the HRTEM image of the ribbon-like graphite on the surface of assembled onions. Enoki et al. and Kuznetsov et al. have demonstrated that impurities (oxygen and hydrogen containing gases) of flowing argon atmosphere in annealing process lead to carbon redistribution in nanocarbons with lower surface energy [7,15,17–19]. The oxygen and hydrogen containing gases participate in the carbon redistribution processes via carbon transport reactions to accelerate the ND graphitization process and decrease the temperature of graphitization onset. The intersection of two onions forms the ignition point and the ribbons are formed via a tangential relaxation to relieve the strain induced by the onion curvature. When the annealing time is increased, all the curved layers of assembled onions are changed into planar graphitic ribbons. It is reasonable that the conversion of planar graphite from curved layers results in the drop of the surface tension induced by the onion curvature, which is the driving force to form the graphitic ribbons. The surface tension induced by the onion curvature makes carbon onions metastable; therefore carbon onions incline to become a more stable phase-graphitic ribbon. This change shows the higher stability of graphitic ribbons with the length of 10–20 nm over carbon onions. It can be deduced that the

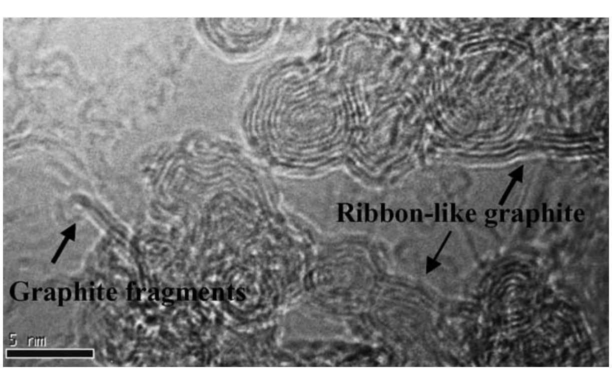

Fig. 3. HRTEM image of ribbon-like graphite by the linkup of assembled nanoparticles.

graphitization of ND to nanocarbons is a process of structural evolution that causes an increase of sp^2 bonding and decrease of sp^3 bonding.

4. Conclusion

Diverse nanocarbons including bucky diamond, carbon onions, single-wall carbon nanohorn and graphitic ribbons were found after ND were annealed at a low temperature. The phase transition of nanocarbons from ND is a process of structural evolution that causes increase of sp^2 and decrease of sp^3 bonding structure. ND are transformed into carbon onions and the curved graphitic layers of assembled nanoparticles tend to link and form the graphitic ribbons. The surface tension induced by the onion curvature makes carbon onions metastable and a more stable phase (graphitic ribbons) comes into being. ND undergo phase transition in a series of ND-bucky diamond-onions-ribbons and the structural evolution of nanocarbons reflects the higher stability of graphitic ribbons with the length of 10–20 nm over carbon onions.

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