Structural transition of carbon nanoparticles caused by energetic collisions

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A broad general interest in the process of affecting the energetic deposition of flying nanoparticles has prompted a new opportunity to consider the medium-energy region in which the nanoparticles maintain their integrity and must respond to the energetic shock caused by collisions. We herein report our experimental results on the structural transition of the carbon nanoparticles induced by such energetic collisions. The beam energy was varied from 0 keV to 30 keV for a nanoparticle with over 5000 carbon atoms. Electron energy loss spectroscopy, X-ray photoemission spectroscopy, and Raman spectroscopy were carried out on the samples using a series of beam energies. These tests revealed that some graphitic sheets were formed at the higher beam energy while the sp^3 ratio was unexpectedly higher for a medium beam energy.

Keywords: Carbon nanoparticles; structural transition; electron energy loss spectroscopy; energetic collisions.

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1. Introduction

The process of collision of flying nanoparticles at a solid surface is of broad physical interest.^{1–4} The kind of change that takes place in these nanoparticles when they collide with a solid surface energetically has been considered in different cases, as specified by the average kinetic energy per atom in the nanoparticles.^{1–4} The average kinetic energies (E_k) are comparable with the average atomistic binding energies because the inner bonding is the critical difference between a nanoparticle and a loosely-packed group of the same atoms.^{5,6} The nanoparticles land softly with no obvious structural change when their kinetic energy is much lower than the binding energies ($E_k < 0.1$ eV/atom). Molecular dynamical simulations indicate that the nanoparticles are crushed completely when their kinetic energies are much greater than the binding energies ($E_k > 10$ eV/atom).¹ A study of this type also provides a good opportunity to prepare atomically smooth films, as demonstrated experimentally.^{1–11} There is still no clear consensus on how nanoparticles behave when they collide at a medium kinetic energy comparable to the binding energy ($E_k \sim 1$ eV/atom), although some theoretical approaches have been proposed.^{12–14} It is reasonable to assume that the nanoparticles will not be crushed by the energetic collision, but instead be pressed against the interatomic potential inside the deposited nanoparticles. This may allow reconstruction within the nanoparticles at the atomic level, providing an opportunity to generate the structural transition of the nanoparticles by energetic collision with a medium kinetic energy. We report here on the experimental evidence of the occurrence of such structural transitions.

2. Experimental Procedure

Carbon nanoparticles were selected in this experiment in view of their significance in the graphite–diamond transformation, in the synthesis of nanosized diamonds, and in the establishment of the size-related phase diagram of nanocarbon.^{15–18} The experiments were carried out using a home-made instrument with a gas-aggregation nanoparticle source and a group of planar electrostatic electrodes. The nanoparticles were generated by the source, and carbon nanoparticles with a diameter of 2–3 nm were selected to form a particle beam. The nanoparticles were then accelerated causing collision with substrates (Formvar and silicon) at kinetic energies from a few eV up to 30 keV, corresponding to a directional flight velocity of 10^2 – 10^4 m/s. The sp^3 -hybridized atom ratio (the sp^3 ratio) in the carbon nanoparticles is usually used to describe their structures and determine their physical performance, i.e. how diamond-like they are.¹⁸ This sp^3 ratio was characterized by means of electron energy-loss spectroscopy (EELS) attached in a transmission electron microscopy (TEM). The change in the sp^3 ratio with respect to the change in the kinetic energy of the incident nanoparticles was therefore analyzed by considering three categories, i.e. no obvious change, becoming more diamond-like, and becoming more graphite-like, respectively.

3. Results and Discussion

A transition towards more graphite-like structures is clear in our results. Figure 1(a) shows the typical EELS curves from samples with beam kinetic energies of 0, 10, 15, 20, and 30 keV. The nanoparticles contain around 5000 atoms as determined by the detailed analysis of scanning TEM results. The EELS spectra show that the diamond-like bonding dominates in the nanoparticles with kinetic energies in the range of 0–15 keV ($\sim < 3$ eV/atom).¹⁹ A sharp π peak located in the energy range of 280–290 eV is apparent, indicating that the dominance of π bonding after the nanoparticles has collided with the surface at a kinetic energy of 20 keV (> 4 eV/atom).

The detailed analysis shows the results in terms of the kinetic energy-dependent structures of the nanoparticles, as shown in Fig. 1(b), in which the sp^3 ratio is plotted against the kinetic energy of the flying nanoparticles.¹⁹ These data were obtained by fitting the EELS peaks using the standard spectra of graphite and diamond. The estimated velocity is shown in the upper x -axis. The sp^3 ratio of soft-landing nanoparticles is 53% and the ratio at a kinetic energy of 5 keV is 56%. This implies no obvious change in structure. The sp^3 ratio decreases to 20% when the kinetic energy increases to 20 keV and then decreases to 17% at 25 keV and 8% at 30 keV. The nanoparticles are in fact almost totally graphitized, confirming the structural transition towards graphite. It is interesting to note that the sp^3 ratio increases steadily to 85% as the kinetic energy increases from 5 keV to 15 keV, which indicates the transition of the structures in a more diamond-like direction.

Fig. 1. EELS analysis of the deposited carbon nanoparticles on Formvar films with various energies. (a) EELS data for the core loss of the carbon edge for the low-coverage isolated nano-islands formed by nanoparticles colliding with a range of kinetic energies. The kinetic energies increase from the bottom of the figure upwards. The appearance of the sharp peak in the 280–290 eV energy window marks the formation of graphite-like bonding within the nanoparticles (π bond). The inset is a typical TEM image of a sample with the lower beam energy. (b) The ratio of the sp^3 -hybridized atoms plotted against the kinetic energy. The results were obtained from the EELS data using the method used in Ref. 19. The structural transition at a kinetic energy of 20 keV is clearly shown. The upper x -axis is the estimated value of the velocity of the nanoparticles.

There is evidence that the atoms inside the nanoparticles are reconstructed during the impacts, forming more four-coordinated tetragonal bonds. Notably, a transition towards both more diamond-like and more graphite-like structures is observed.

As stated above, the sp^3 ratio of the deposited carbon nanoparticles varies with the change in their kinetic energy, which implies the occurrence of the structural transition. Our TEM observation shows that the nanoparticles remain separate after the structural transition (Fig. 1(a)), which implies that each nanoparticle undergoes the transition individually. The carbon nanoparticles are also made to collide energetically with silicon substrates. This is just to exclude the possibility that the structural changes in the nanoparticles occur as a result of a chemical reaction with the substrate materials. The experiments using silicon substrates are carried out simultaneously with the same experiments carried out on Formvar surfaces. The silicon substrates with the deposited nanoparticles are then removed for X-ray Photon-activated electron spectra (XPS) analysis. The XPS results for the C_{1s} peak are shown in Fig. 2(a). The center of the C_{1s} peak can be seen to shift slightly towards a higher energy while the beam energy increases from 0 keV to 15 keV before dropping back later on. The spectra are further analyzed according to the previous method.²⁰ The relative value of the sp^3 ratio is plotted against the kinetic energy, as shown in Fig. 2(b). We observe both the transition in a diamond-like direction at a kinetic energy of 5–10 keV, and transition in a graphite-like direction at a kinetic energy greater than 15 keV. As the incident energy increases, the sp^3 ratio rises in the lower energy range and falls at the greater incident energy. The trend of the curve is the same as that seen in the experiments with the Formvar surfaces although the point of transition between the rise and fall is different.

The two experiments on Silicon and Formvar show the same results in terms of the kinetic energy-dependent structural transitions of nanoparticles during the energetic collisions on solid surfaces, and reveal the lack of influence of both the

Fig. 2. XPS analysis of the deposited carbon nanoparticles on silicon surfaces for various energies. (a) The XPS peak of the samples, where the deposition energies are indicated. This is a zoom-in of the C_{1s} peak, where the shift of the peak is apparent. (b) The ratio of the sp^3 -hybridized atoms plotted against the kinetic energy obtained by fitting the XPS peak as shown in the inset.

chemical composition of the solid surface and the coalescence of nanoparticles. The observed structural transition must be the result of energetic collisions. In fact, the energy-dependent curves of the structures (Figs. 1(b) and 2(b)) form lines in the size-kinetic energy-structure phase diagram of nanocarbons. The structural changes in the deposited nanoparticles demonstrate that the energy loss effectively influences the carbon nanoparticles. The process is clearly not the same as that when an atomic ion of carbon collides with the surface with the same E_k during which most of the impact energy is transferred to the solid surface and penetration is considered to be the dominant effect. The sp^3 ratio reduces to a very low value at a higher E_k and remains low even at the higher energies in both experiments. The same phenomena occur even when E_k reaches the high energy region. Therefore, it is reasonable to assume that this loss of sp^3 may be attributed to the higher energy, essentially in the crushing of the nanoparticles and the resulting loss of the $3d$ sp^3 bonding. We highlight the special effect of the increase in the sp^3 ratio in the medium-energy region before the nanoparticles are crushed. In this region, the particle structures are found to be sensitive to the change of E_k as shown in our experiments. It might be expected that the loss of kinetic energy is effectively transferred to the nanoparticles themselves. This deposition of energy affects the interatomic potential in the nanoparticles, favoring the reconstruction of the atoms, and resulting in an energy-dependent structural change.

In Fig. 3, we show the high-resolution TEM images of a sample for a beam energy of 20 keV. We note that the nanoparticles maintain their shapes when the beam energy is 15 keV, as shown in the inset of Fig. 1(a). However, in Fig. 3(a), the nanoparticles show the obvious coalescence, forming the graphitic sheets. The lattice

Fig. 3. Compositional analysis of the samples at the higher beam energy. (a) High resolution TEM image of the samples deposited at 20 keV, where some crystalline sheets are formed with the graphite-like wrinkles, as shown in the inset. (b) Raman spectrum of the sample.

with a spacing of 0.34 nm can clearly be seen, as shown in the inset. Figure 3(b) shows the Raman spectrum which has two phonon peaks, commonly termed *D* mode (1350.73 cm^{-1}) and *G* mode (1591.05 cm^{-1}), respectively, confirming the formation of the disordered graphitic sheets.

4. Conclusion

In conclusion, the energetic collision of carbon nanoparticles with a medium average kinetic energy at solid surfaces successfully induces the structural transition of the particles. Transitions in both the diamond- and graphite-like directions then ensue. The increase in the sp^3 ratio is discovered as a particular effect in the medium-energy region. These findings may offer a new means of studying phase stability and phase diagrams at the nanoscale.

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