Influence of bond defects on coiling of graphite

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Abstract

The effect of annealing at 1400 °C in argon on the bond structure of graphite ball milled for 100h at 400rpm in polar (water) and in non-polar (n-dodecane) liquids was investigated primarily by near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and transmission electron microscopy (TEM). Carbon K-edge NEXAFS allows the distortion of bonds in the hexagonal lattice to be investigated. It is shown that in-plane sp² bonds are strained and distorted after ball milling because sp³ bonds are introduced. Not surprisingly, annealing of the milled product restores sp² bonds but at the same time, coiling and formation of tube-like structures takes place. It is well established that graphite is not formed on annealing, and hence the results shown here demonstrate that the loss of sp³ carbons on annealing must proceed via a different mechanism by which they are formed by milling.

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1. Introduction

Graphite consists of stacks of parallel two-dimensional graphene sheets with carbon atoms being arranged in hexagonal rings through localized in-plane hybridised 2s, 2pₓ, and 2pᵧ (sp²) orbitals. The individual sheets are weakly bonded by delocalized out-of-plane 2pᵧ orbitals, which overlap at 90° to the graphene plane to give a delocalized π-electron system. Under suitable conditions, i.e. high-temperature treatment, graphite can be transformed into new ordered structures, sometimes with curvature e.g. carbon nanotubes. However, as the π orbitals of the carbon atoms overlap most effectively when they are parallel, the graphene sheet has lowest energy when it is completely flat. Therefore, the coiling up of a graphene sheet is an energetically unfavourable process.

Chen et al. [1,2] reported that ball milling of graphite develops reactive nanoporous carbons with high surface areas, which upon annealing produce multiwalled carbon nanotubes. They proposed a phenomenological model in which milling at ambient temperature provides enough energy to nucleate new structures. The subsequent annealing at 1400 °C facilitates growth process, resulting in nanotubes.

In this work, we show that these processes are related to the formation and loss of sp³ carbons during milling and annealing. We employ near edge X-ray absorption fine structure (NEXAFS) spectroscopy, which is sensitive to the short-range, atomic-scale order [3] and, therefore, gives information on bond strain and bond type. In this technique, the core level electrons are excited into various unoccupied states (e.g. π* and σ*) by the absorption of X-ray photon generated by a synchrotron. A subsequent electronic de-excitation primarily causes emission of Auger electrons and fluorescence photons resulting in the NEXAFS spectra. The longrange nano-structure modification of graphite is also monitored using transmission electron microscopy.

2. Experimental

This work builds upon previous work performed by our research group and others examining the change of the level of disorder of graphite during ball milling, and the effect of disorder on the formation of carbon nanotubes upon annealing [4–6]. Here, we employ milling of graphite in polar (water) and non-polar (n-dodecane) liquids.
2.1. Sample preparation

High-purity (>99.9% purity) polycrystalline graphite powder (Fluka) was ball milled in a Pulverizette 6 (Fritsch) planetary mill. Two-gram samples were loaded in a stainless-steel container with volume of 80 ml containing 25 ml n-dodecane or 25 ml water. Then, 300 stainless steel balls with diameter of 5 mm were added. The ball to powder weight ratio was 75. The milling was carried out for 100 h at 400 rpm. The milled powders were dried at 125 °C for 12 h under reduced air pressure (~10³ Pa) and then the powders were annealed in an alumina tube furnace at 1400 °C for 4 h in argon (99.999% purity) flowing at 15–20 ml/min.

2.2. Characterization

The C K-edge NEXAFS spectra were acquired at the wide range, bending magnet beam line 24A at the National Synchrotron Radiation Research Centre (NSRRC) in Hsinchu, Taiwan. The soft X-ray energy of the beam line ranges from approximately 10–1500 eV. Before the measurements, samples were heated in the ultra-high vacuum analysis chamber at ~200 °C for 24 h in order to minimize the adventitious surface contaminants. All spectra were acquired via relatively bulk sensitive fluorescence yield mode and were normalized to the reference beam intensity measured on a gold grid monitor. The incident X-ray energy was calibrated using the reference π* peak of precursor graphite recorded at 285.4 eV. For quantitative comparison, all spectra were background and baseline corrected from the carbon pre-edge and post-edge regions, respectively. The normalization procedures were carried out using an algorithm developed by Newville et al. [7] and implemented in software IFEFFIT.¹

Coiled and tube-like structures formed during the annealing of the milled graphite samples were examined by a Philips Biofilter-120 transmission electron microscope (TEM) operating at 120 kV. Samples for TEM observation were prepared by mixing sample powder with acetone and dispersing the sample aggregates by ultrasound treatment. A drop of the suspension was transferred onto lacy carbon foils supported on copper grids for examination.

3. Results and discussion

3.1. Comparison of unmilled, milled and annealed graphite by TEM

TEM micrographs of milled under protective atmosphere and unmilled graphite particles were reported elsewhere [4–6] but it is necessary here to report results on materials prepared in polar (water) and non-polar (n-dodecane) liquids. TEM micrographs of these products show minor morphological differences between graphite samples milled in either liquid (Fig. 1a and b). The graphite flat plate-like particle morphology is generally preserved, though the sharpness of the particle edges compared to the precursor graphite (not shown) is decreased. Thus, extended ball milling in liquid does not have any apparent effect on the long-range order. However, annealing at 1400 °C in a flow of argon gas changes sheet morphology. Micrographs of graphite milled in water show groups of twisted tube-like structures with quite irregular shapes along with a number of bent and coiled ribbons (Fig. 1c). It can be seen that the tubular structures coexist with flat spirals, which suggests a link between the nanotubes and lamellar structures. Similarly, annealing of graphite particles milled in n-dodecane resulted in the formation of buckled and twisted sheets, creating regions of thicker and distorted graphite particles coexisting with larger flat stack of sheets in the same structure (Fig. 1d).

3.2. Comparison of milled and unmilled graphite by C K-edge NEXAFS

Fig. 2A shows the fluorescence yield, C K-edge NEXAFS spectrum of the precursor graphite. Four main peaks of the graphite spectra are observed at approximately 285.4, 287.7, 288.8 and 291.9 eV. The presence of the peak at 285.4 eV is attributed to electronic transitions from the C 1s level to unoccupied π* states of sp² carbon. In principle, if sp² carbons are present, they would also contribute to the same transition [3,8] but this is unlikely since they were never reported for graphite using any other technique. Rather, this spectral feature corresponds physically to excitations of the out-of-plane π-bonds along the c-crystallographic axis [8]. The major spectral feature with an onset at about 291 eV is primarily attributed to C 1s→σ* excitations and corresponds physically to the in-plane carbon–carbon bonds within the hexagonal graphene rings. The spectral position and intensity of σ* excitation is sensitive to the in-plane structural changes [9,10]. At the energy region higher than 292 eV, the overlapping between different sp² and sp³ neighbour shells transform the spectra into broad oscillations.

Upon milling in water and in n-dodecane, there is a distinctive broadening of the π* features at 285.4 eV, suggesting the presence of distorted sp² sites and defects. Milling also changes the spectral position and intensity of the σ* states at about 292 eV (Fig. 2B and C). In particular, graphite milled in n-dodecane shows intense σ* excitation, which is stronger than the respective excitation of the precursor graphite or graphite milled in water. The observed shift of approximately 0.4 eV towards lower energy of the σ* transitions for both milled samples suggests a distortion and strain of the in-plane carbon–carbon bonds [3,11,12]. The extent of the bond distortion appears similar for either liquid, though the different intensity of the σ* features

¹http://cars9.uchicago.edu/~ravel/software/exafs/
for products prepared in different liquids suggests that the number of distorted bonds depends on the type of liquid.

There are a series of other peaks in the spectra but they are less useful for analysis. For example, the literature assignment of the peak at 287.7 eV is ambiguous. Such excitations in the energy range of 286–288 eV were attributed to the presence of unsaturated bonds between carbon and heteroatoms such as oxygen [13,14] but also may be due to the presence of transition metals [15]. Likewise, the peak at 288.8 eV is generally ascribed to $\sigma^*$ C–H transition [3] due to the saturation of surface carbon dangling bonds with hydrogen or for incorporation of hydrocarbon species. However, a more recent report associated the C–H bond electronic excitation in the energy range of 290–292 eV [8].

3.3. Annealing of milled graphite

Fig. 3 shows the normalized C K-edge NEXAFS spectrum of the milled graphite, annealed at 1400°C in ultra-pure argon and the precursor polycrystalline graphite (for comparison). In general, the C K-edge NEXAFS spectra of the annealed graphite are well defined. The $\pi^*$ resonance at 285.4 eV for either samples became narrower, with bandwidth being similar to that of the spectrum of the precursor graphite. Significant changes are found at the $\sigma^*$
bonds in the sample. The NEXAFS spectrum is proportional to the number of



3.4. $\pi^*/\sigma^*$ ratio semi-quantitative analysis

It is possible to quantify the changes in number of carbons with sp$^3$ bonds compared to sp$^2$ bonds upon milling and annealing. The analysis is based on the assumption that the intensity of the $\sigma^*$ bands decreases and is even lower than that of the precursor graphite. Therefore, the NEXAFS spectroscopy suggests that the fraction of sp$^2$ bonds to sp$^3$ bonds increases during the annealing of milled graphite.

The most striking difference between the NEXAFS spectra of annealed and milled samples is the intensity variation of the peaks in the range of 287–289 eV. While it is difficult to make discrete assignments, these are not due to impurities containing heteroatoms because these excitations are stronger in the adsorption spectra of the precursor graphite than in the milled samples. Rather that these modifications are also due to bond changes during milling and annealing.



3.5. Coiling mechanism

As noted above, NEXAFS spectroscopy reveals milling significantly changes the sp$^2$ bonded hexagonal network. The carbon–carbon bonds exhibit more sp$^2$ character disrupting the delocalisation of the $\pi$ electrons. The localization of the $\pi$ electrons must be reflected in a slight increase carbon–carbon bond distances of the neighbouring carbon atoms, which become sp$^3$ bonded. This means that the milled graphite bond structure consists of atomic size regions in which carbons are predominantly sp$^2$ bonded and others where carbons with predominantly sp$^3$ bonds exist. Thus, the overall free energy of the system increases. During annealing, the system is driven to minimize its free energy by restoration of the sp$^2$ bond character and delocalization of the $\pi$-electrons over the entire hexagonal network. The stress accumulated during milling is partially liberated by relief of the bond distortion and the formation of more ordered bond structures. So, the annealing facilitates $\pi$-electron rearrangements and formation of $\pi$-conjugated hexagonal rings since they have the lowest bond angle distortion. The results shown here do demonstrate that the loss of sp$^3$ carbons on annealing must proceed via a different mechanism by which they are formed by milling. Besides, the increased free energy during milling is recovered, at least in part, by energy savings from coiling of the graphene sheets.

It is worth noting that the level of bond modification and defect formation should not be excessive. Elsewhere, it is shown that if the hexagonal network is completely destroyed, the annealing at 1400 °C cannot provide sufficient energy to move enough atoms around and, therefore, the system will remain amorphous [5,6]. Restoration of such heavily distorted system would require much higher temperatures where the formation of flat graphene structure containing only hexagonal structures is a kinetically and thermodynamically favourable process. Thus, there should be an optimal defect/temperature ratio, which is beneficial for coiling of the defective graphene sheets.

4. Summary and conclusions

For the first time, spectroscopic evidence for permanent modification of carbon–carbon sp$^2$ bond character to form sp$^3$ bonds during the milling of graphite for 100 h at 400 rpm in liquid is reported. The principal chemical change occurring when the milled graphite is annealed at 1400 °C for 4 h in argon consists of restoration of the sp$^2$ in-plane bond character of the hexagonal graphene sheets with removal of sp$^3$ bonds. Annealing facilitates conjugation of the double in-plane bonds and at the same time
makes the graphene sheets to coil. However, this process is not reversible to form graphite, but rather the removal of sp³ structures results in coiling. It is clear that there is more than one competing energy-minimizing processes by which the two-dimensional sheets coil.

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