Structural Dislocations in Anthracite

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ABSTRACT: Anthracite is composed primarily of polycyclic aromatic hydrocarbons that exist as curved layers of graphenic sheets of various sizes. The bright field high-resolution transmission electron microscopy (HRTEM) image of raw anthracite reveals four kinds of edge dislocations, suggesting that radical-induced dislocation networks are formed during the geologic evolution of bituminous coal into anthracite and that they play an important role in the chemistry of this carbon-rich material. The dislocations result in graphenic layers merging into a massive interconnected network and can explain why samples reductively alkylated by solubilizing dodecyl groups fail to exhibit the high solubility in organic solvents of other similarly functionalized nanomaterials.

SECTION: Nanoparticles and Nanostructures

Carbon nanomaterials promise to find many applications in areas that include electronics, photonics, energy, and sensing. Graphene occupies an important position in this emerging area. In view of our interest in the synthesis of soluble carbon nanomaterials,1–7 and graphene,8,9 we have investigated routes to other soluble materials that have a high carbon content. Anthracite is of interest in this regard, as it is composed primarily of polycyclic aromatic hydrocarbons that exist as curved layers of graphenic sheets of various sizes.10 The carbon content can be as high as 98%. Surprisingly, however, a low level of solubility was achieved when the same protocol (reductive alkylation) that was used to solubilize graphite/graphene was applied to anthracite.11

The functionalization reaction was carried out as illustrated in Scheme 1. The resulting dodecylated anthracite exhibited low solubility in organic solvents, indicating a low level of reductive alkylation. A detailed investigation using NMR spectroscopy showed that the dodecyl groups were attached to the edges of the anthracite.11 This mode of addition is not unexpected since it has been shown that graphite experiences edge functionalization exclusively under the same conditions.9,12

A study was then undertaken to identify the structural features of anthracite that inhibit exfoliation and thus solubility.13 Scanning electron microscopy (SEM) can be used to produce images that contain information about the sample’s surface topography. The SEM of a sample of raw anthracite reveals clearly why exfoliation has proven to be difficult. The image presented as Figure 1 reveals a structure in which graphenic layers appear to merge.

The “crosslinking” that is evident from the SEM image suggests that some sp3 hybridized carbon has survived during the geologic process that leads to coalification of the bituminous coal precursor. Indeed, a solid state 13C NMR spectrum of anthracite revealed the presence of a very small amount of aliphatic carbon.11 Raman spectroscopy provides a sensitive technique that can be used to correlate chemical composition with optically discernible morphology of carbonaceous material. The Raman spectrum of a solid sample of the anthracite collected using a Renishaw 1000 microraman system equipped with a 785 nm laser source exhibits a strong broad disorder D band at 1301.3 cm−1 with a shoulder at 1188 cm−1.14 A much weaker G (graphitic) band at 1597 cm−1 reflects the aromatic ring system (Figure 2).

The observation of dislocations in graphite,15,19 and other nanomaterials20 suggested that dislocations might play an important role in altering the physical and chemical properties of anthracite. Indeed, the bright field high-resolution transmission electron microscopy (HRTEM) image of the raw anthracite (Figure 3) provides the direct evidence for the reluctance (at least in part) of anthracite to undergo exfoliation and thus solubilization during the functionalization reactions. The HRTEM image in Figure 3 reveals four kinds of dislocations, suggesting that the formation of these previously unrecognized radical-induced dislocation networks plays an important role in the processes that occur during the geologic evolution of bituminous coal into anthracite.

The two main types of dislocations are edge dislocations and screw dislocations (dislocations found in many materials are...
The extra plane in a $a'$ is positioned to react by radical addition to the aromatic rings of a parallel graphenic layer. This gives the Y-type dislocation $b'$ as further depicted in $b''$. This process forms $sp^3$-hybridized centers identified by the blue atoms in $b''$. The chemistry finds ample precedent in recent studies that demonstrate that the addition of carbon-centered radicals to the aromatic rings of graphene is a facile process.11

A helical structure formed from a left-hand screw dislocation of the graphene layers is illustrated in $c'$ and $c''$. The colored bonds between $sp^2$-hybridized carbons in the spiral highlight the dislocation line. Such structures are likely to form as a natural growth path.13 This may also result from a process involving a cascade of radical additions in which each graphene layer adds to an adjacent parallel layer. A common dislocation loop consists of two screw dislocations running in opposite directions (green bonds in Figure 3d) and connected by the edge-segments (red, in accord with Figure 3a).

The quarternary aliphatic carbons in Figure 3b$''$ are the only type of aliphatic carbon directly involved in the dislocations. Solid state $^{13}$C NMR also indicated the presence of very small amounts of proton-bearing aliphatic carbons,12 which could easily result from the occasional presence of a CH$_3$ group on an aromatic ring or the occasional presence of a CH$_2$ group or perhaps even a CH(CH$_3$)$_2$ group bridging two aromatic rings. Such bridging would, of course, make exfoliation and solubilization even more difficult.

**EXPERIMENTAL METHODS**

The anthracite that was used for this study was provided by Dr. John Crelling (Southern Illinois University) and came from the Mammoth seam that is located in Schuylkill county Pennsylvania. The composition of the sample was determined by XPS to be 92% carbon and 6.4% oxygen. Nitrogen, silicon and sulfur were each present in <1%.

HRTEM images are recorded using a JEOL 2100 field emission transmission electron microscope (JEM 2100F TEM) and operated at an accelerating voltage of 200 kV. Raman spectra were collected using a Renishaw 1000 micro-Raman system equipped with a 785 nm laser source. SEM image was recorded
Figure 3. Bright-field HRTEM image of raw anthracite showing four dislocation structures. A radical-rich form of the edge dislocation (a), with simulated TEM (a’), obtained from a fully relaxed sandwich atomic structure (a’). Edge-radical sites bind to the adjacent layers resulting into a Y-form (b), containing sp³-carbon atoms, marked blue in (b”), and a corresponding TEM simulation (b’). A staggered series of graphene-planes (c) are signatures of screw dislocation helical organization (c’), as its simulated TEM (c’) shows. Nearby screw dislocation segments (d) likely belong to the same dislocation loops, completed by the edge segments marked by red edge-atoms (d”), and as its corresponding simulated TEM (d”) shows.

using an FEI Quanta 400 scanning electron microscope at an electron beam voltage of 30 kV.

ASSOCIATED CONTENT

Supporting Information. Detailed descriptions of the XPS of anthracite. This material is available free of charge via the Internet at http://pubs.acs.org.

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