Low-Temperature Production of Genuinely Amorphous Carbon from Highly Reactive Nanoacetylide Precursors

Ken Judai, Naoyuki Iguchi, and Yoshikiyo Hatakeyama

College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

Correspondence should be addressed to Ken Judai; judai@chs.nihon-u.ac.jp

Received 7 September 2015; Accepted 14 March 2016

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Copper acetylide is a well-known explosive compound. However, when the size of it crystals is reduced to the nanoscale, its explosive nature is lost, owing to a much lower thermal conductance that inhibits explosive chain reactions. This less explosive character can be exploited for the production of new carbon materials. Generally, amorphous carbon is prepared by carbonization of organic compounds exposed to high temperature, which can induce partial crystallization in graphite. In this work, we present a new method in which the carbonization reaction can proceed at a lower annealing temperature (under 150°C) owing to the highly reactive nature of copper acetylide, thus avoiding crystallization processes and enabling the production of genuinely amorphous carbon materials.

1. Introduction

Amorphous carbon has been known for a long time under various denominations such as coal, soot, and carbide-derived carbon. This form of carbon consists of free, reactive carbon, without any crystalline structure. However, most carbon materials can be categorized into diamond-like carbon, graphite-based carbon, and carbyne, which represent the main crystalline forms of carbon, involving sp³, sp², and sp carbon hybridization, respectively [1–5]. On the other hand, no apparent progress has been made in the production of genuinely amorphous carbon.

Research on the carbyne carbon form has been limited because of its instability, whereas diamond-like carbon has been studied extensively only in the last decade. Amorphous carbon is usually associated with graphite-based materials [1]. It is generally prepared by carbonization of organic compounds exposed to a high temperature, which can induce partial crystallization in graphite [6]. For the production of commercial carbon materials, graphite-based carbon is activated in order to increase its surface area. The activated carbon can no longer be considered as amorphous.

We have previously investigated the nanostructure of metal acetylide molecules and their application to gas sensors [7], catalysis [8], and so on [9, 10]. The explosive nature of compounds like copper acetylide has limited investigations on their use [11]. However, reducing the size of the crystals to the nanoscale eliminates their explosive nature, due to the much lower thermal conductance that inhibits explosive chain reactions. The less explosive character of the nanosized compounds can be exploited for the production of new noble carbon materials.

Herein, we report a new method for preparing genuinely amorphous carbon materials. Self-assembled copper acetylide nanowires were used as precursors for amorphous carbon [9]. As the high reactivity of copper acetylide allows the carbonization reaction to proceed at a lower annealing temperature, unwanted crystallization processes are avoided and genuinely amorphous carbon materials can be prepared. Although thin amorphous carbon films can be prepared by physical vapor deposition at low temperature [12–14], this work approach can produce amorphous carbon in bulk amounts, not in only film amounts.

In addition to the amorphous character, the new carbon material exhibited a high surface area associated with a meso- and microporous structure. Mesoporous carbon materials have recently attracted interest as viable and inexpensive materials for use in numerous applications, such as super...
capacitors [10], absorbents, electrodes [2], and catalytic supports [8, 15]. The unique amorphous character combined with the high surface area of the materials introduced in this work will significantly enhance its applicability in the above applications.

2. Materials and Methods

A schematic procedure for the preparation of amorphous carbon is illustrated in Figure 1. Copper (I) chloride (1 g) was dissolved in 5% aqueous ammonia solution (100 mL), and acetylene gas was introduced into the solution flask at a flow rate of 0.05 mL/min for 3 h, after which a dark brown precipitate of copper acetylide (C$_2$Cu$_2$) was obtained; the chemical reaction is shown as follows:

$$2\text{CuCl} + \text{C}_2\text{H}_2 + 2\text{NH}_3 \rightarrow \text{C}_2\text{Cu}_2 \downarrow + 2\text{NH}_4\text{Cl} \quad (1)$$

The extremely slow flow rate is the key to generate self-assembled C$_2$Cu$_2$ nanowires [9]. The product was separated by suction filtration and annealed under vacuum. To avoid explosive reactions, the sample was slowly heated up (1°C/min) to 150°C. Carbonization of C$_2$Cu$_2$ was achieved by maintaining the sample at 150°C for 24 h for the separation reaction resulting in copper and carbon. Copper was then eliminated by dipping the sample in concentrated sulfuric acid for 30 min. This process allowed us to obtain genuinely amorphous carbon at a temperature as low as 150°C.

The amorphous carbon prepared as described above was analyzed by powder X-ray diffraction (XRD) measurements using Cu Kα emissions (Rigaku, RINT-2000) and Raman spectroscopy with a 532 nm laser (Elforlight, G4 60). The Raman spectra were analyzed by powder X-ray diffraction (XRD) measurements. Figure 2 shows powder XRD patterns for the three carbon materials examined. A strong peak was observed for graphite, denoting perfect crystallinity. Even though the measurements were taken with the same sample amounts and for the same duration, the peak intensity of the activated carbon was two orders of magnitude lower than that of graphite. This difference is due to the lower crystal quality of the carbon sample: in other words, the amorphousness of the activated carbon resulted in a lower intensity of the XRD signal. The XRD peak signal for the amorphous carbon in this work was buried in noise even for the same measuring conditions, which highlights its superior amorphousness compared to that of the activated carbon. No structural information could be obtained from the XRD measurements for the carbon material prepared in this work, owing to its highly amorphous character.

A Raman spectroscopic analysis was performed to compare in detail the three carbon materials. Figure 3 illustrates the Raman spectra of the samples excited by a 532 nm laser. The vertical scales of the Raman spectra were normalized in order to compare the intensities of the different samples.

The Raman spectrum for graphite (Figure 3(a)) shows the sharp G band peak at 1585 cm$^{-1}$, which is the most prominent vibration of the graphite lattice. The other prominent mode is the D band around 1400 cm$^{-1}$, which is associated with the occurrence of defects or of a large number of edges in the graphite carbon sample [1]. A large number of edges denote a small domain size in graphite. Even though no D band peak could be observed, a 2D band at double vibrational energy

3. Results and Discussion

We have succeeded in producing carbon materials by only employing processes performed under 150°C. The annealing temperature is one of the most important parameters to design and control the chemical properties of carbon materials. The main advantage of low-temperature carbonization is the high degree of amorphousness produced. Typical carbon materials are exposed to over 800°C for the carbonization, which induces crystallization of carbon to graphite [6]. In order to assess this, we have compared the spectroscopic properties of three samples: the carbon prepared in this work, graphite as an example of perfect crystalline structure, and commercial activated carbon.

The crystallinity or amorphousness can be checked by X-ray diffraction measurements. Figure 2 shows powder XRD patterns for the three carbon materials examined. A strong peak was observed for graphite, denoting perfect crystallinity. Even though the measurements were taken with the same sample amounts and for the same duration, the peak intensity of the activated carbon was two orders of magnitude lower than that of graphite. This difference is due to the lower crystal quality of the carbon sample: in other words, the amorphousness of the activated carbon resulted in a lower intensity of the XRD signal. The XRD peak signal for the amorphous carbon in this work was buried in noise even for the same measuring conditions, which highlights its superior amorphousness compared to that of the activated carbon. No structural information could be obtained from the XRD measurements for the carbon material prepared in this work, owing to its highly amorphous character.

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could be detected. The D band corresponds to an optically forbidden Raman transition, which can only occur at defect carbons or edges in graphite. However, the 2D band transition can be optically allowed even in the perfect graphite lattice. In the Raman spectrum of activated carbon (Figure 3(b)), the D band can be clearly observed at 1357 cm\(^{-1}\), indicating that the activated carbon sample contains a large amount of defects. A comparison of the Raman spectra of graphite and commercial activated carbon (Figure 3(b)) shows a significant difference in the intensity of the D band, suggesting a higher concentration of defects in the activated carbon sample.

**Figure 2:** Powder X-ray diffraction patterns for graphite (a), commercial activated carbon (b), and amorphous carbon prepared in this work (c).

**Figure 3:** Raman spectra for graphite (a), commercial activated carbon (b), and amorphous carbon prepared in this work (c). The samples were excited by a 532 nm laser light with 30 mW power.
activated carbon shows that the peak widths of the G band
are also different. The chemical environments of graphitic
carbon differ from those found in amorphous carbon, which
manifests itself as a broad peak in the Raman spectrum.
The peak width in these spectra thus represents a suitable
parameter for estimating the amorphousness of a sample.

The Raman spectrum for the amorphous carbon in
this work (Figure 3(c)) exhibits broader G and D band
peaks than those of the activated carbon. This means that
the low-temperature carbonization process can generate a
carbon material of lower crystallinity and more genuinely
amorphous than commercial activated carbon. The peak
position of the G band is 1603 cm$^{-1}$, and the ratio of the D
band intensity to that of the G band, $I_D/I_G$, is 0.95. The Raman
spectrum in this work closely resembles that of an amorphous
carbon film fabricated by physical vapor deposition [1, 4, 12–
14]. However, this process can produce genuinely amorphous
carbon in bulk amounts and not just in amounts required
for film formation. Low-temperature carbonization is the key
point to producing amorphous carbon.

It should be pointed out that the signals in the present
Raman spectra can be assigned to the graphitic G and D bands. The copper acetylide precursor of the present
amorphous carbon contains a carbon-carbon triple bond.
Although there are some techniques that can produce carbon
materials with triply bonded carbons, the carbon triple
bond of polycarbyne shows an intense Raman peak around
2000 cm$^{-1}$ [16, 17]; no such polycarbyne peak can be observed
in Figure 3(c). Therefore, despite using acetylide precursors,
which contain carbon triple bonds, the resulting materials
are based on the graphite structure. Preliminary $^{13}$C NMR
measurements also identified the chemical shift signals of sp$^2$
carbon (graphite), but not of sp (carbyne) or sp$^3$ (diamond)
carbon. Whereas the Raman spectrum mainly provides
information on the carbon hybridization, basically showing the
predominance of a graphite-like carbon environment, the
broadness of the G band and the intensity of the D band
indicate the genuinely amorphous character of the sample.

Thermogravimetric analysis was performed for the amorphous carbon prepared in this work, as shown in Figure 4.
The sample was heated up at a ramp rate of 10°C/min
under atmospheric (20%) oxygen gas concentration. Around
10% weight loss can be observed below 100°C; this was
owing to the desorption of water molecules from the carbon
porous surface. The combustion of carbon starts at 150°C.
This relatively low combustion temperature denotes chemical
instability of carbon. It should be pointed out that the burning
temperatures of the sample spanned a wide range, from 150
to 550°C. A wide range of different chemical environments
must then be present in the amorphous carbon, and a
respective wide range of combustion temperatures is also expected. The wide range of the temperature regions
in the thermogravimetric spectrum confirms the genuinely
amorphous character of the carbon prepared in this work.
The total weight loss over 600°C reaches up to 97%. The
contamination of metal ash was less than 3%. Considering
the method used for the preparation of the samples, most
of this contamination should be represented by elemental
copper.

Nitrogen adsorption-desorption experiments were also
carried out for the amorphous carbon prepared in this work.
The specific surface area determined from these measurements
represents one of the most important properties of
carbon materials. Figure 5 shows the nitrogen adsorption and
desorption isothermal equilibrium curves of the amorphous
carbon. Two distinct regions are visible in the curves, a
microporous region for relative pressures below 0.1, and
a mesoporous region at a relative pressure between 0.4
and 1.0. The amorphous carbon produced in this work
contained substantial amounts of both microporous and
mesoporous surfaces. Even though the generation method
did not involve carbon activation, the microporous specific
surface area, obtained using BET analysis, reached values of about 540 m²/g (Figure 6).

The adsorption and desorption curve exhibits hysteresis in the mesoporous region (a mesopore is defined as a pore with diameter between 2 and 50 nm); this was caused by condensation of nitrogen in the mesopores. The amorphous carbon was produced through carbonization of \( \text{C}_2\text{Cu}_3 \) followed by acid treatment to remove elemental copper. Carbonization results in the segregation of carbon and copper elements, which leads to the formation of pure copper nanoparticles of diameter between 5 and 30 nm, as measured in a previous transmission electron microscopy study [8]. These copper nanoparticles are removed in the acid treatment, generating a porous space of the same size. The size of the copper nanoparticles and thus that of the mesopores can be controlled by the acetylide substituent. Mesoporous carbon materials have large potential for catalytic support applications, in which metal catalysis can be supported in the carbon mesopores. In fact, the catalytic application of copper nanoparticles supported in amorphous carbon has been previously investigated [8].

### 4. Conclusion

We have succeeded in preparing genuinely amorphous carbon materials. The high reactivity of copper acetylide allows the carbonization reaction to proceed at a lower annealing temperature (under 150°C), and carbon materials with superior amorphpousness can be prepared. In addition to the amorphic character, the new carbon material exhibited a high surface area associated with a meso- and microporous structure even though the material was produced without any activation process. The unique amorphic character combined with the high surface area will significantly enhance its applicability.

### Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

### Acknowledgments

This work was partially supported by the N. Research Project at Nihon University. The authors acknowledge Professor Hashimoto and Dr. Niwa for technical support in the X-ray diffraction and thermogravimetric and nitrogen absorption-desorption measurements.

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