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An investigation into carbon structures in iron-loaded charcoal based on the Raman shift and line-shape of the G'-band

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Abstract

Charcoal samples prepared from wood impregnated with Fe³⁺ were characterized using Raman spectroscopy to investigate ordered structures consisting of sp²-carbon atoms. The iron-loaded charcoal samples were synthesized at relatively low temperatures (600–850 °C). Most of the Raman peak-tops of G'-bands observed in the charcoal were positioned in the narrow range of 2700–2690 cm⁻¹; however, the G'-band positions of the charcoal synthesized in a carbonization-temperature (CT) range (650–750 °C) varied widely with measurement points and some of them displayed wavenumber values lower than 2690 cm⁻¹. The G'-band positions were also affected by holding time at CT. None of the G'-bands observed in the iron-loaded charcoal exhibited positive asymmetrical line-shapes, unlike graphite. We proposed the ordered structures of sp²-carbon atoms in the iron-loaded charcoal based on the Raman spectral features of the G'-bands.

Keywords Iron-loaded charcoal, G'-band, Raman spectroscopy, Graphene, Graphite

Introduction

Carbon materials have attracted much attention of many researchers because of diversities in the chemical bonds of carbon atoms, and their application fields are expected to be broadened widely. Woody biomass has been promised to be a sustainable resource for carbon materials. T. Suzuki and K. Suzuki reported that partly crystallized charcoal with high electrical conductivity can be synthesized from wood impregnated with iron or nickel salts and confirmed that the charcoal has nanoshell-structure [1, 2]. The name “graphite nanoshell chains” was proposed for the nanoshells because the shells linked to one another like chains [2].

The most noticeable characteristic of metal-loaded charcoal is the occurrence of carbon crystallization at low temperatures (≤ 1000 °C). We have examined iron-loaded charcoal prepared under various conditions using ⁵⁷Fe Mössbauer and Raman spectroscopy, and showed the correlation between the reduction to Fe⁰ and crystallization of carbon in the charcoal [3, 4]. However, a deeper understanding of carbon structures in iron-loaded charcoal is required to expand the application of the charcoal to functional carbon materials.

Several characteristic Raman bands are observed in carbon materials, and their spectral parameters provide insights into the electronic states and structures of carbon atoms. Among the Raman bands, so-called D- and G-bands, which are due to chemical bonds involving sp²-carbon, have frequently been used for studying coal, charcoal, and carbide. In addition to these two bands, G'(2D)-bands have recently attracted the interest of carbon-material researchers, because their Raman shifts and intensities are a useful tool for predicting the properties of functional carbon. In the

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last two decades, there have been numerous theoretical or experimental studies concerning new carbon materials, such as graphene and carbon nanotubes in terms of the G'-band.

The D- and G'-bands are not ordinary Raman bands, and their Raman shifts are dependent on excitation wavelength. Moreover, the G'-band is due to an overtone of the D-band; nevertheless, the intensity of the G'-band is not proportional to that of the D-band. The G'-band is activated from a double-resonance Raman scattering mechanism and its Raman parameters are sensitive to the structures consisting of sp²-carbon atoms [5–7]. Although the Raman D- and G-bands are detectable in nearly all carbon structures, no G'-band observed in carbon with amorphous or disordered structures has been reported, to our knowledge.

We confirmed that the G'-band occurrence corresponds to the crystallization of carbon using X-ray diffraction analysis in iron-loaded charcoal [8], and revealed from the Mössbauer data that the G'-band occurs with the production of Fe⁰ species that can act as a catalyst for carbon crystallization [3, 4]. Therefore, the G'-band has been used as an indicator of crystalline carbon in the previous works [3, 4, 9].

In recent years, several studies reported that the Raman shift and line-shape of the G'-band are dependent on the number of graphene layers [10–13]. Thus, the Raman G'-bands have the potential to contain further information on the carbon structures in iron-loaded charcoal; however, we focused only on the occurrence and intensity of the G'-bands and have not sufficiently explored their Raman shifts and line-shapes in the previous works [3, 4, 9].

The aim of this short article is to investigate the ordered structures of sp²-carbon atoms in iron-loaded charcoal by analyzing the G'-bands in their Raman spectra. We discuss the ordered carbon-structures and their development in iron-loaded charcoal, based on the Raman shift and line-shape of the G'-band.

Materials and methods

Graphite and graphene samples

Synthetic graphite powders were purchased from Sigma-Aldrich Co. LLC (USA), Thermo Fisher Scientific Corp. (USA), and FUJIFILM Wako Pure Chemical Corp. (Japan). The samples of single-layer and multi-layer graphene deposited on a metal plate were obtained from Graphene Platform Corp. (Japan). The graphite powders were submitted to Raman measurement without further grinding.

Preparation of iron-impregnated wood powder and its carbonization

Previously synthesized iron-loaded charcoal samples were used in this study. The details of the impregnation with Fe³⁺ and carbonization procedure were described in the previous work [4]. Each charcoal sample was kept in a sample tube with an airtight cap at room temperature in the dark until additional measurements. The period for storing the charcoal samples was approximately 6 months.

The charcoal samples are abbreviated as FeX-Y-Z, where the letters X, Y, and Z denote the Fe³⁺ content in raw wood, carbonization temperature (CT), and holding time (HT) at CT, respectively. For example, the charcoal sample synthesized from wood powder containing Fe³⁺ of 3 w/w% at 700 °C using 0.5 h HT is denoted as Fe3-700-0.5.

Raman spectroscopy

As for iron-loaded charcoal samples, we analyzed the G'-bands in the Raman spectra reported previously [4] and obtained from additional measurements in the present study.

The additional measurements were carried out more than 15 times an iron-loaded charcoal sample; therefore, the Raman measurements were totally repeated at more than 45 different points a charcoal sample. The conditions of the Raman measurements for the iron-loaded charcoal were described in detail previously [4]. The same conditions were applied to the Raman counting of graphite samples. The Raman measurements for graphite were repeated more than 15 times at different points a sample.

The Raman spectra of graphene samples were recorded with laser power of 0.15 mW and 5-times accumulations of counting Raman signals. The Raman scattering measurements of graphene were repeated at more than 10 different points a sample. Other conditions were set at the same as those of iron-loaded charcoal.

Results and discussion

Figure 1 depicts the Raman spectra in the G'-band range of graphite and graphene samples purchased from chemical manufactures. Fig. 1a, c and e shows a typical Raman spectrum of a graphite powder obtained from Sigma-Aldrich Co. LLC (USA), Thermo Fisher Scientific Corp. (USA), and FUJIFILM Wako Pure Chemical Corp. (Japan), respectively. The G'-bands of the three spectra are obviously asymmetrical and appear to comprise two components: a peak at ~2720 cm⁻¹ and a shoulder at ~2680 cm⁻¹. For each graphite sample, a few G'-bands exhibited a different line-shape from that of the typical

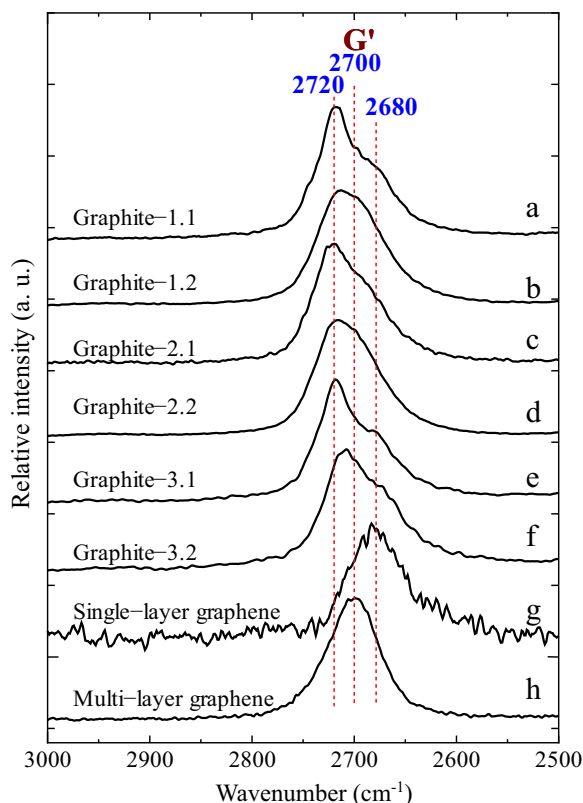


Fig. 1 Raman shifts and spectral line-shapes of G'-bands of graphene and graphite samples: **a**, graphite-1.1; **b**, graphite-1.2; **c**, graphite-2.1; **d**, graphite-2.2; **e**, graphite-3.1; **f**, graphite-3.2; **g**, single-layer graphene; **h**, multi-layer grapheme. Graphite-1, -2, and -3 were purchased from Sigma-Aldrich Co. LLC (USA), Thermo Fisher Scientific Corp. (USA), and FUJIFILM Wako Pure Chemical Corp. (Japan), respectively. Single-layer and multi-layer graphene samples deposited on a metal plate were obtained from Graphene Platform Corp. (Japan)

spectrum, as shown in Fig. 1b, d and f. The peak-tops of these G'-bands were observed at wavenumbers lower than 2720 cm^{-1} but higher than 2700 cm^{-1} .

None of the Raman G'-bands due to two graphene samples showed significant spectral changes with measurement points. The peak-top of the G'-band due to the single-layer graphene (Fig. 1g) was positioned at a wavenumber lower than that due to the multi-layer graphene (Fig. 1h). This result agrees with the preceding Raman studies regarding graphene [10–13]. Many studies, theoretically and experimentally, have shown that a G'-band due to multi-layer graphene is composed of multiple components and the whole spectral line-shape of the band is not symmetrical [10, 11, 14]. However, in this study, distinct asymmetry could not be recognized in the G'-bands due to the multi-layer graphene sample, as shown in Fig. 1h.

Figure 2A and B depicts the typical Raman spectra of Fe3-Y-1 charcoal in the G'-band (A: 3000–2500 cm^{-1}) and G- and D-band (B: 1700–1200 cm^{-1}) ranges, respectively. After the 6-month storage, no significant changes were observed in the Raman spectra for all the iron-loaded charcoal samples.

As shown in Fig. 2A, the Raman spectra of Fe3-600-1 and Fe3-650-1 charcoal had no positive G'-band; however, a faint G'-band was observed in a few spectra of Fe3-650-1 charcoal. The typical Raman spectra of iron-loaded charcoal synthesized at ≥ 700 °C present a G'-band at ~ 2690 cm^{-1} , and the intensity relative to the G-band tends to increase with CT. None of the G'-bands observed in the iron-loaded charcoal samples presented a positive asymmetrical line-shape. Interestingly, the G'-bands at wavenumbers lower than 2690 cm^{-1} were confirmed in some Raman spectra of charcoal samples synthesized at the CTs of 650, 700, and 750 °C as described later.

As seen in Fig. 2B, the D- and G-bands are observed in all the iron-loaded charcoal samples and their line-shapes markedly vary with CT. Nevertheless, we do not discuss the carbon structures in terms of the D- and G-bands, because these two bands are also detectable for non-crystalline carbon. It was presumed that carbon in the iron-loaded charcoal synthesized even at 900 °C was partly in non-crystallized states [3]; therefore, the spectral components due to non-crystalline carbon in the D- and G-bands will not be negligible for the charcoal samples used in this study.

The Raman spectra of Fe3-700-1 charcoal at four different measurement points are shown in Fig. 3. Most of the G'-bands due to Fe3-700-1 charcoal were detected at ~ 2690 cm^{-1} , as shown in Fig. 3b and c, and some G'-peaks occurred at slightly higher wavenumbers, as shown in Fig. 3d. It should be noted that a few G'-bands were positioned at wavenumbers lower than 2690 cm^{-1} (Fig. 3a), and their relative intensities were weak. Furthermore, all the line-shapes of the G'-bands appeared to be symmetrical, unlike those due to the graphite powders shown in Fig. 1. Additionally, similar results were obtained from the G'-bands observed in Fe5-700-1 charcoal.

Figure 4 depicts the Raman spectra with a lower-wavenumber G'-band of Fe3-650-1 and Fe3-750-1. Although nearly all of the Raman spectra of Fe3-650-1 charcoal presented no G'-band, a very weak G'-band was detected in a few spectra. All the G'-bands observed were positioned at ~ 2675 cm^{-1} for Fe3-650-1. On the other hand, almost all the Raman spectra of Fe3-750-1 showed a positive G'-band in the range of 2700–2690 cm^{-1} ; however, the lower-wavenumber G'-band was observed at only a few measurement points.

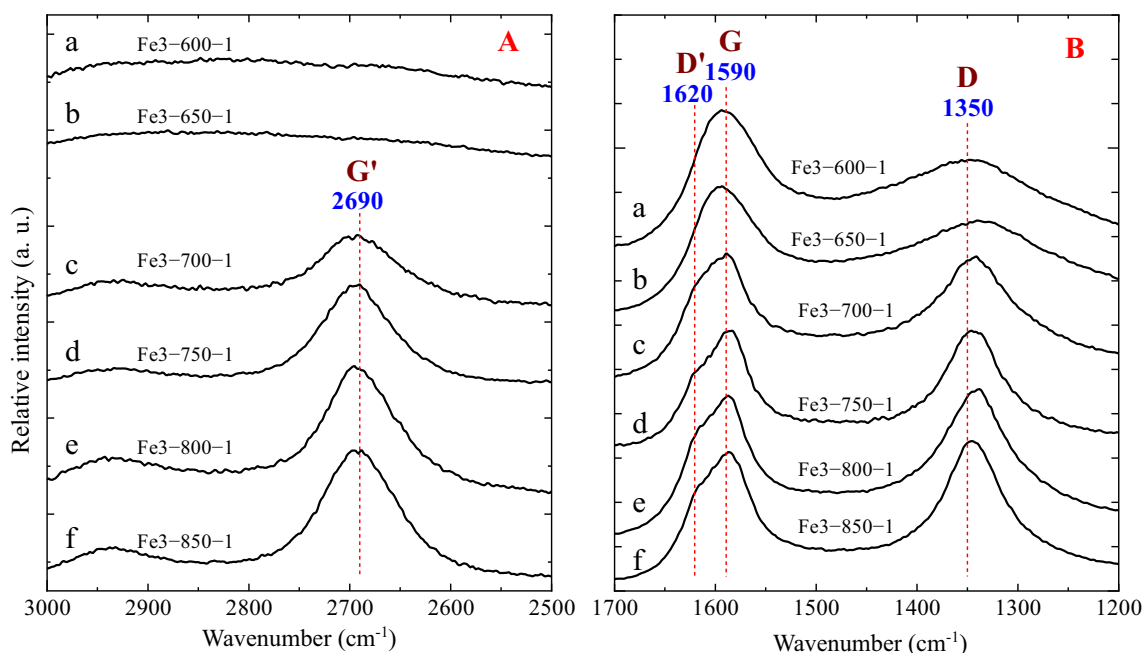


Fig. 2 Raman spectra in two regions, **A** (3000–2500 cm⁻¹) and **B** (1700–1200 cm⁻¹), of Fe3-Y-1: **a**, Fe3-600-1; **b**, Fe3-650-1; **c**, Fe3-700-1; **d**, Fe3-750-1; **e**, Fe3-800-1; **f**, Fe3-850-1

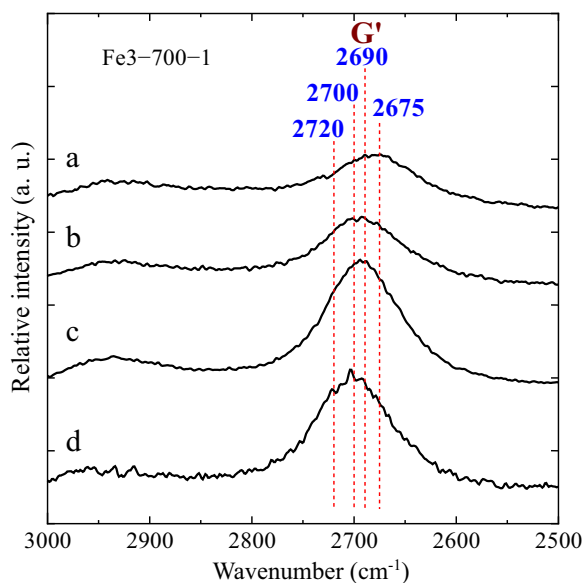


Fig. 3 Measurement-point dependence of Raman shifts and spectral line-shapes of G'-bands observed from Fe3-700-1: **a, b, c, d**, Fe3-700-1

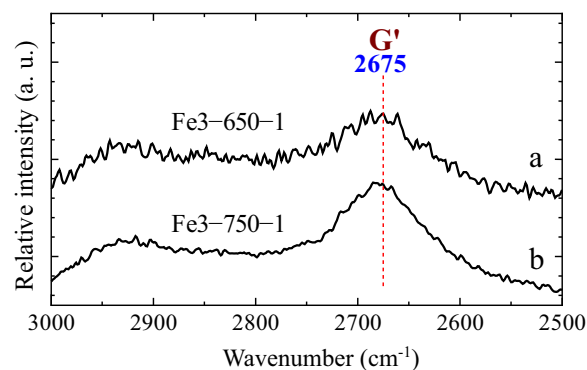


Fig. 4 Raman spectra with a lower-wavenumber G'-band of Fe3-650-1 and Fe3-750-1 charcoal samples: **a**, Fe3-650-1; **b**, Fe3-750-1

Figure. 5 shows the Raman spectra of Fe3-700-0.5 charcoal at four different points. Fe3-700-0.5 charcoal was synthesized with a shorter HT, and some of their Raman spectra exhibited a G'-band positioned at approximately 2660 cm⁻¹, as demonstrated in Fig. 5a and b. In contrast, all the Raman G'-bands due to

Fe3-700-3 charcoal were observed in the wavenumber range of 2700–2690 cm⁻¹. These results reveal that HT is a factor affecting the growth of ordered carbon-structures. However, as we discuss later, the effect of HT will be restrictive.

As described above, the observation of the lower-wavenumber G'-bands was restricted to the Raman spectra of the charcoal samples synthesized in the CT range of 650–750 °C. This range is roughly equal to the critical CT range (650–700 °C), in which the reduction to Fe⁰ and crystallization of carbon progressed rapidly [4]. Thus, it can be presumed that a G'-band observed

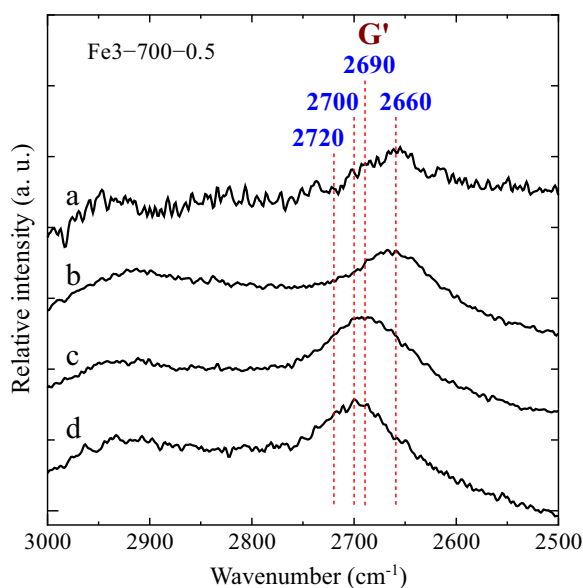


Fig. 5 Measurement-point dependence of Raman shifts and spectral line-shapes of G'-bands observed from Fe3-700-0.5: **a, b, c, d**, Fe3-700-0.5

in iron-loaded charcoal is shifted to higher wavenumbers with the growth of ordered carbon-structures.

It is generally accepted that the G'-band of graphene is shifted to higher wavenumbers with an increase in the number of layers [10–13]. Most of the published G'-band positions due to single-layer graphene range from 2664 to 2680 cm^{-1} when a 532-nm laser was used as an excitation light source [15–18]. Assuming that the correlation between the G'-band shift and graphene-layer number are applicable to the ordered carbon-structures in iron-loaded charcoal, the G'-band shifts observed in this study may suggest that structures analogous to single- or few-layer graphene occur in the iron-loaded charcoal synthesized in the critical CT range and then grow with increasing CT and/or HT. Two points worth noting obtained from the Raman shift and line-shape of the G'-band are as follows.

First, CT and HT are effective factors controlling the formation and growth of ordered structures consisting of sp^2 -carbon atoms because the observation of lower-wavenumber G'-bands was limited to the Raman spectra of Fe3-650-1, Fe3-700-1, Fe3-750-1, Fe5-700-1, and Fe3-700-0.5 charcoal samples. The lowest-wavenumber G'-bands were observed at $\sim 2660 \text{ cm}^{-1}$ only in Fe3-700-0.5 charcoal, and they may suggest that the ordered structures of carbon at the first stage are similar to those of single- or few-layer graphene.

Second, the G'-bands observed in the iron-loaded charcoal samples maintain symmetrical line-shapes, even after being shifted to higher wavenumbers; in other

words, no G'-bands exhibiting positive asymmetrical line-shapes were observed in the iron-loaded charcoal samples used in this study.

A number of Raman studies mentioned that the line-shapes of G'-band due to graphene theoretically exhibit asymmetry except for single-layer graphene. Some of them asserted that G'-bands due to multi-layer graphene are analogous to graphite in spectral line-shape when the layers sufficiently increase in number [10, 12]. However, others showed that the G'-bands due to multi-layer graphene did not necessarily exhibit remarkable asymmetry [15, 19, 20]. Hence, the symmetrical line-shapes of the G'-bands positioned in the range of 2700–2690 cm^{-1} suggest the development from the structures like few-layer graphene to those like multi-layer graphene. Moreover, the layer of graphene-like structures in iron-loaded charcoal probably increases with CT and/or HT. However, the layer numbers of the developed carbon-structures are likely much smaller than those of bulk graphite.

The growth mechanism of the ordered carbon-structures deduced from Raman data will be supported by the transmission electron microscope images of cobalt- and nickel-loaded charcoal prepared at 900 °C [1, 2]. According to the formation mechanism of nanoshell-structure proposed by K. Suzuki [1, 2], nano-size metallic iron particles, which are produced by the reduction of Fe^{3+} and act as a catalyst for carbon crystallization, split and/or fuse repeatedly; therefore, they cannot keep in the same place for long periods. In other words, the formation mechanism suggests that the layer number reaches an upper limit in relatively short HT and it is not so large. Thus, it can be presumed that the G'-band did not show the same line-shape as bulk graphite because of the insufficient increase in the layer number of crystallized carbon.

Conclusion

In this study, we revealed that the Raman G'-bands of iron-loaded charcoal have a tendency to shift to higher wavenumbers with increasing CT and/or HT in the CT and HT ranges of 650–800 °C and 0.50–3.0 h, respectively. The G'-band shifts suggest the growth of ordered carbon-structures. There were no significant changes in symmetry of the G'-band shapes with CT or HT. The obtained results may provide a clue to clarify the growth mechanism of ordered carbon-structures in iron-loaded charcoal.

Abbreviations

CT	Carbonization temperature
HT	Holding time
FeX-Y-Z	The letters of X, Y, and Z are the content (w/w%) of Fe^{3+} in wood, CT, and HT, respectively

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Author contributions

TY and SY designed this study, and wrote the initial draft of the manuscript. SS prepared iron-loaded charcoal samples. TY and SY performed measurements and analyses of Raman spectra. All authors have contributed to data collection and interpretation, and critically reviewed the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

Not applicable.

Declarations

Competing interests

The authors declare that they have no competing interests.

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