

Effect of reduction on graphitization behavior of mesophase pitch-derived
carbon fibers

Y. A. Kim*, H. Muramatsu, M. Kojima, T. Hayashi, M. Endo,

Faculty of Engineering, Shinshu University, Wakasato 4-17-1, Nagano 380-8553, Japan

C. Kim

Faculty of Applied Chemical Engineerig, Chonnam National University, 300 Yong-bond
dong, Buk-gu, Gwangju 500-757, Korea.

M. S. Dresselhaus

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307, USA

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ABSTRACT

Chemically reduced solid-state mesophase pitch carbon fibers below 1000°C in a flow of hydrogen gas was heat treated up to 3000°C in an argon atmosphere in order to evaluate the effect of hydrogen on the graphitization behavior. Major phenomena observed during the reduction process are chemical transformation from an ether to a hydroxyl group (corresponding to the rupture of the C-O-C bond) and their subsequent evolution as gases. Finally, oversupplied hydrogen might be utilized to satisfy the dangling bond. For sample heat treated at 3000°C, the low crystallinity indicates that hydrogen atoms covalently bonded to the end planes of graphitic layers act as an effective barrier to crystallite growth.

Keywords: A. Carbon Fibers; B. Hydrogen effect; C. ESR; D. Crystallite size

*Corresponding author. E-mail: yak@endomoribu.shinshu-u.ac.jp

1. INTRODUCTION

It is well known that the graphitization process is one of the most basic and important processes in carbon science because this technique is a very powerful tool for modifying the structure of carbon materials [1-3]. Graphitization itself is very simple transition process from a disordered to ordered structure, accompanying the removal of foreign atoms and defects. Therefore, the graphitization behavior strongly depends on the microstructure and composition of the initial carbons. In this sense, one of the most important factors affecting the graphitization behavior and surface properties of carbon materials is how to remove hetero-atoms effectively, especially those situated at edge sites.

Up to now, there are few reports of the effect of the reduction process on carbon materials because of the slow reaction rate of hydrogen with carbon materials, even under high hydrogen pressures [4, 5]. However, it is assumed that the reaction of hydrogen with other atoms, such as oxygen, nitrogen and sulfur, will proceed easily at atmospheric pressure. Also, hydrogen will satisfy the dangling carbon bonds situated at the end planes of graphitic layers. Therefore, it is expected that the reduction process will be interesting for modifying the surface properties and graphitization behavior of carbon materials.

In this study, the reduction of as-received mesophase pitch-based carbon fibers were performed in a flow of hydrogen gas at relatively low temperature from 570 to 1150°C, and then the chemically reduced sample at 1000°C was graphitized at 3000°C in order to evaluate the effect of hydrogen on both their surface properties and graphitization behavior.

2. EXPERIMENTAL

The carbon fibers used in this study were prepared using a melt-blown method from a petroleum mesophase pitch, and oxidized in air at around 300°C, and then milled to be in lengths in the range of several tens of micrometers [6, 7]. The reduction of carbon fibers was carried out using a conventional resistance furnace with 30 sccm of flowing hydrogen gas at a specific temperature for 1 hour. For comparison, the same samples were heat treated at the same temperature in an argon atmosphere. The chemically reduced sample at 1000°C was heat treated up to 3000°C in a high purity argon atmosphere for 10 minutes using a graphite resistance furnace.

In order to study changes in the carbon fibers caused by the reduction process, X-ray diffraction (XRD), Raman scattering, electron spin resonance (ESR), atomic analysis, field emission scanning electron microscope (FE-SEM) and scanning tunneling microscope (STM) analysis of the samples were carried out. An X-ray diffractometer (Rigaku RINT2000, 40 kV, 30 mA) with a $\text{CuK}\alpha$ ($\lambda=0.154056\text{nm}$) X-ray source was used to measure the Bragg reflections from all the samples, and the crystallite size L_c and L_a in the c and a direction of the samples were obtained from the widths of the (002) and (110) XRD lines, respectively. The FE-SEM observation was performed using an acceleration voltage as low as 5kV, and using a Hitachi S-4100 instrument, in order to get sufficient resolution to study the morphology of the samples. Raman spectra were taken at room temperature under ambient conditions using a Renishaw Raman Image Microscope System 1000 equipped with a CCD multichannel detector and using a laser excitation source for 514.5 nm Ar-ion laser. The optical power focused at the samples was maintained at 5mW to avoid annealing effects. Curve fitting of the Raman features with a Lorentzian lineshape function was performed to obtain the pertinent Raman parameters. ESR measurements were performed in the X-band at a frequency $\nu \approx 9.09$ GHz, using DPPH to calibrate both the g-factor and the ESR peak-to-peak linewidth. For all samples, the sample mass in the ESR cell was on the order of 2~3 mg. The ESR spectra were obtained using 1.0 mW of microwave power in a 20 torr He atmosphere.

3. RESULT AND DISCUSSIONS

[Figure 1](#) shows FE-SEM photographs of carbon fibers heat-treated at 1000°C (a), (b) in an argon atmosphere, and (c), (d) in a hydrogen atmosphere at different resolutions. Very small particles attached to the surface of the carbon fibers are observed for samples (a), (b), which are basically by-products of the cutting process. These particles might contain a high portion of oxygen-containing functional groups, and those particles also exhibit disordered structures as compared with that of carbon fibers, because they are structurally second-aggregated contaminated carbons. Through the reduction process, the amount of these small particles decreases drastically ([Fig. 1 \(c\) and \(d\)](#)), maybe due to gasification. From the above images, it is assumed that the reduction and gasification of the small particles occur strongly because of their high reactivity.

X-ray diffraction profiles for these samples are shown in [Fig. 2](#), and from these

measurement, crystallographic parameters such as crystallite sizes $L_{c(002)}$, $L_{a(110)}$, are obtained using Bragg and Scherrer formulas as summarized in Table 1. All samples show very broad 002 diffraction peaks, indicating that these are typical low-temperature carbon materials. Even though no big difference is found among the diffraction profiles for the various samples, the reduced samples show a somewhat decreased interlayer spacing and an increased crystallite size, especially for samples heat treated at 1000°C. This is due to the removal of contaminated carbons (less ordered structures) because the X-ray technique gives us information about an average of bulk carbons.

Basically, the hydrogen reaction with carbon materials will occur on the near surface of the host materials, based on the diffusion depth of hydrogen into carbon materials. Therefore, Raman spectroscopy is expected to be more sensitive to the variation of the microstructure caused by the reduction process. The first-order Raman spectra for these samples is shown in Fig. 3. The half width at half maximum (HWHM) intensity of the G peaks at around 1590 cm^{-1} and the D peaks at around 1355 cm^{-1} for both samples show a small decrease with increasing temperature. No large difference is observed as a result of the reduction process. To identify the Raman spectroscopic parameters, such as the Raman frequency, and the HWHM, curve fitting is performed using the Lorentzian lineshape function. As shown in Table 2, the G peaks and the intensity ratio, R (I_D/I_G) values of the H₂-MPCF series are quite similar as compared with those of the Ar-MPCF series. The most interesting information obtained from the Raman spectra is that the HWHM of the D peaks for the H₂-MPCF series have lower values as compared with those of Ar-MPCF for the HTT range from 850 to 1150°C. Recently, there have been many reports for the interpretation of the nature of the D peak in carbon materials [8-10]. This is general agreement that this peak is due to a breakdown in the $k=0$ selection rule of large crystals. The pristine sample used in this study contains a large amount of oxygen containing functional groups derived from both the stabilization and milling processes. These oxygen-containing functional groups might preferentially situate themselves at the edge sites of crystallites. Hydrogen atoms might react with the carbonyl group or ether group, resulting in an increased portion of hydroxyl, carboxyl and hydrogen in grain boundaries below 850°C and in the evolution of gases, such as water, above 850°C. Therefore, it is possible to say that homogeneous boundary conditions (edge carbons) are strongly related to the sharp HWHM of the D peak for hydrogen reduced samples above

850°C.

The ESR technique has been used to characterize the microstructure of various carbon materials, especially giving us information on the chemical processes occurring on carbon surfaces [11-13]. Figure 4 shows the room temperature ESR spectra for Ar-MPCF and H₂-MPCF heat treated at 700°C and 1000°C, respectively. Even though small deviations from Lorentzian behavior are observed, we assume that the lineshape is Lorentzian in our lineshape analysis, and obtain ESR parameters, such as peak-to-peak linewidth, and g-factor from the ESR spectra. Ar-MPCF heat treated at 700°C shows very broad lineshape (see Fig. 4 (c)), whereas H₂-MPCF at 700°C shows a much sharper lineshape (see Fig. 4 (a)). Oxygen containing functional groups such as ether and carbonyl groups introduced during the stabilization process are reduced to hydroxyl and carboxyl groups by hydrogen. Also, no large difference is found between the two samples heat-treated at 1000°C, regarding their g-factor, indicating that chemically reduced oxygen-containing compounds are evolved as water at this temperature. This observation is closely consistent with the Raman data, especially regarding the HWHM of the D-band.

To clarify the reduction process, graphitization at 3000°C was carried out for Ar-MPCF and H₂-MPCF samples heat treated at 1000°C. No large change in the macro-morphology of the graphitized Ar-MPCF1000 (see Fig. 5 (a) and (b)) was observed. On the other hand, we can observe very interesting macro-morphology, which is seen in the forms of the contracted cross-sectional morphology of the graphitized H₂-MPCF1000 material at the tips for both low and high magnification images (see Fig. 5 (c) and (d)). From this phenomenon, it is suggested that at least a small portion of hydrogen atoms diffuse into the crystallites, especially for the cross section of the carbon fibers, after hydrogen completes into reaction with the edge carbon atoms in the grain boundaries and also with the defective parts within the crystallites. It is further suggested that abrupt evolution of gases, such as water or methane occurs below 1500°C, resulting in the formation of this peculiar morphology of the carbon fibers. Figure 6 (a) and (b) show XRD patterns of graphitized Ar-MPCF1000 and H₂-MPCF1000, respectively. Graphitized Ar-MPCF1000, as compared with graphitized H₂-MPCF1000, exhibits larger interlayer spacing and a smaller crystallite size. Also, the higher intensity of the D peak, the clearly developed D' peaks and the less developed G' peak, as well as the higher R (I_D/I_G) values from Raman spectra (Fig. 7) indicate that abrupt volume change caused by the drastic

evolution of hydrogen in grain boundaries below 1500°C prohibit the structural development and also rearrangement of the basic structural units, resulting in a lower crystallinity and distorted cross-sectional morphology. How to remove the hydrogen atoms especially bound to the edge carbons kinetically will be a very important factor to control the crystallinity of carbon materials.

4. CONCLUSIONS

The reduction of mesophase pitch carbon fibers was carried out in a flow of hydrogen gas around 1000°C. It is suggested from the ESR study that main chemical transformation from ether and carbonyl to hydroxyl and carboxyl occurs by hydrogen atoms at lower reaction temperature (e.g., 700°C). With increasing reduction temperature, hydroxyl will be removed as carbon dioxide and oversupplied hydrogen will satisfy (or stabilize) the dangling carbons. Therefore, the surface properties of carbon materials, especially activated carbons, can be controlled by the reduction process because this process makes it possible to control the fraction and type of oxygen-containing functional groups and also to remove the contaminated carbons effectively.

It is expected that the growth of the crystallite will start after the evolution of hydrogen atoms. Therefore, it is very interesting to follow the state of the carbon situated on the grain boundary (the edge carbons) after the bond breakage of C-H bond in the range from 900 to 1500°C. In order to make the edge carbons stable energetically, large graphene sheets have to be stacked regularly. Otherwise, the edge carbons will transform into loops on adjacent graphene sheets by chemical bonding [14]. When the reduced sample is graphitized at 3000°C, the relatively lowered crystallinity is ascribed to a large fraction of hydrogen bonds while morphological changes at the tips (appearing as a contracted cross sectional morphology) is mainly due to the abrupt evolution of gases (volume changes) and partly to the rupture of C-O-C bond.

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Captions of figures

1. FE-SEM photographs of carbon fibers heat treated at 1000°C (a), (b) in an argon atmosphere and (c), (d) in a hydrogen atmosphere at different resolutions, respectively.
2. X-ray diffraction profiles of carbon fibers heat treated at 700°C and 1000°C in (a) argon and (b) hydrogen atmospheres, respectively.
3. First-order Raman spectra of carbon fibers heat treated (a) in an argon atmosphere and (b) in a hydrogen atmosphere, respectively.
4. The room temperature ESR spectra for carbon fibers (a) at 700°C, (b) at 1000°C in a hydrogen atmosphere, and (c) at 700°C, (d) at 1000°C in an argon atmosphere, respectively.
5. FE-SEM images of (a), (b) graphitized Ar-mMPCFs and (c), (d) graphitized H₂-mMPCFs, respectively.
6. X-ray diffraction profiles of (a) graphitized Ar-mMPCFs and (b) graphitized H₂-mMPCFs, respectively.
7. Raman spectra of (a) graphitized Ar-mMPCFs and (b) graphitized H₂-mMPCFs, respectively.

Table 1 Crystallographic parameters based on X-ray diffraction.

I.D.		Interlayer spacing (d_{002}) (nm)	L_c (nm) ^{a)}	L_a (nm) ^{b)}
Atmosphere	HTT (°C)			
Ar	700	0.3597	1.47	1.90
	1000	0.3567	1.65	2.70
H ₂	700	0.3577	1.56	1.90
	1000	0.3537	1.77	3.91

^{a)} $L_c = (0.91\lambda)/(\beta\cos\theta)$ for (002) line using the Scherrer equations

^{b)} $L_a = (1.84\lambda)/(\beta\cos\theta)$ for (100)/(101) line using the Scherrer equations

Table 2 Fitting parameters of the Raman spectra.

I.D.		G-band (cm ⁻¹)		D-band (cm ⁻¹)		I_D/I_G ^{c)}
Atmos.	HTT (°C)	ν ^{a)}	WHM ^{b)}	ν ^{a)}	WHM ^{b)}	
Ar	570	1592.2	88.9	1356.8	236.3	0.7483
	700	1592.0	88.0	1354.5	239.0	0.8100
	850	1601.2	82.1	1354.2	235.3	0.8968
	1000	1597.8	83.9	1358.2	240.0	0.9089
H ₂	570	1591.4	87.3	1361.2	234.7	0.7738
	700	1588.0	88.6	1357.9	237.0	0.7968
	850	1591.5	82.5	1354.9	214.5	0.8489
	1000	1593.1	82.9	1354.9	183.7	0.8905

a) ν indicate the Raman frequency of G- and D-band

b) WHM is half width at half maximum

c) I_D/I_G is the intensity of D band over the intensity of G band

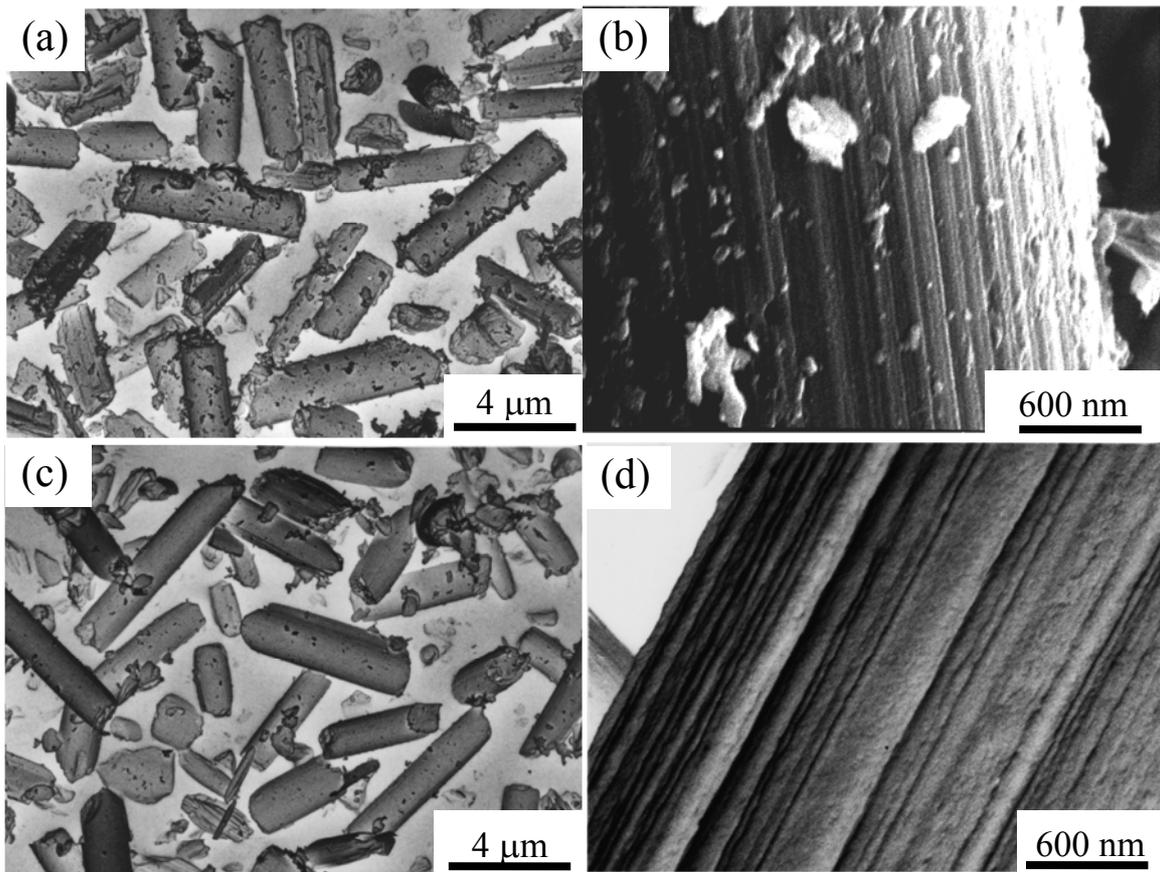


Figure 1

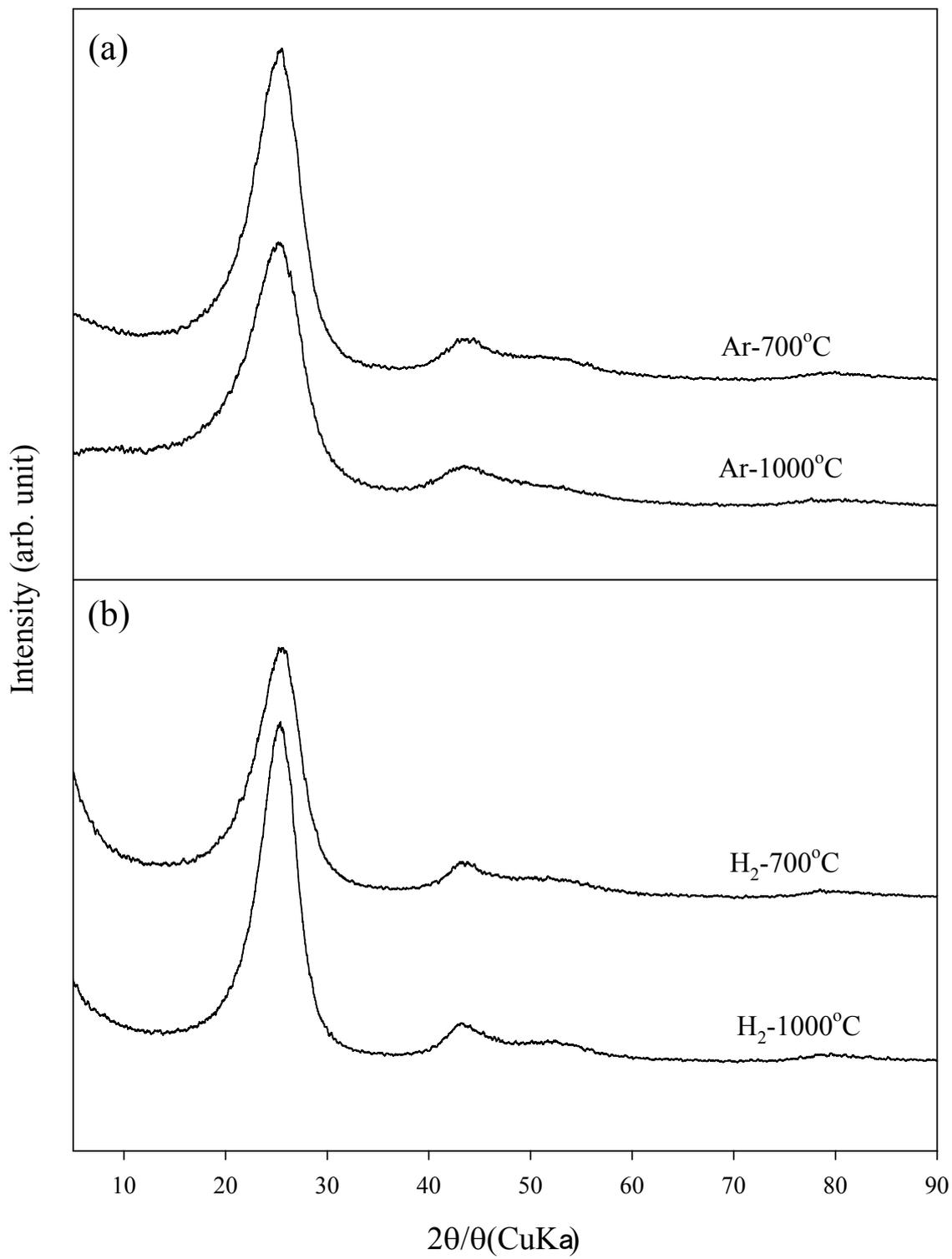


Figure 2

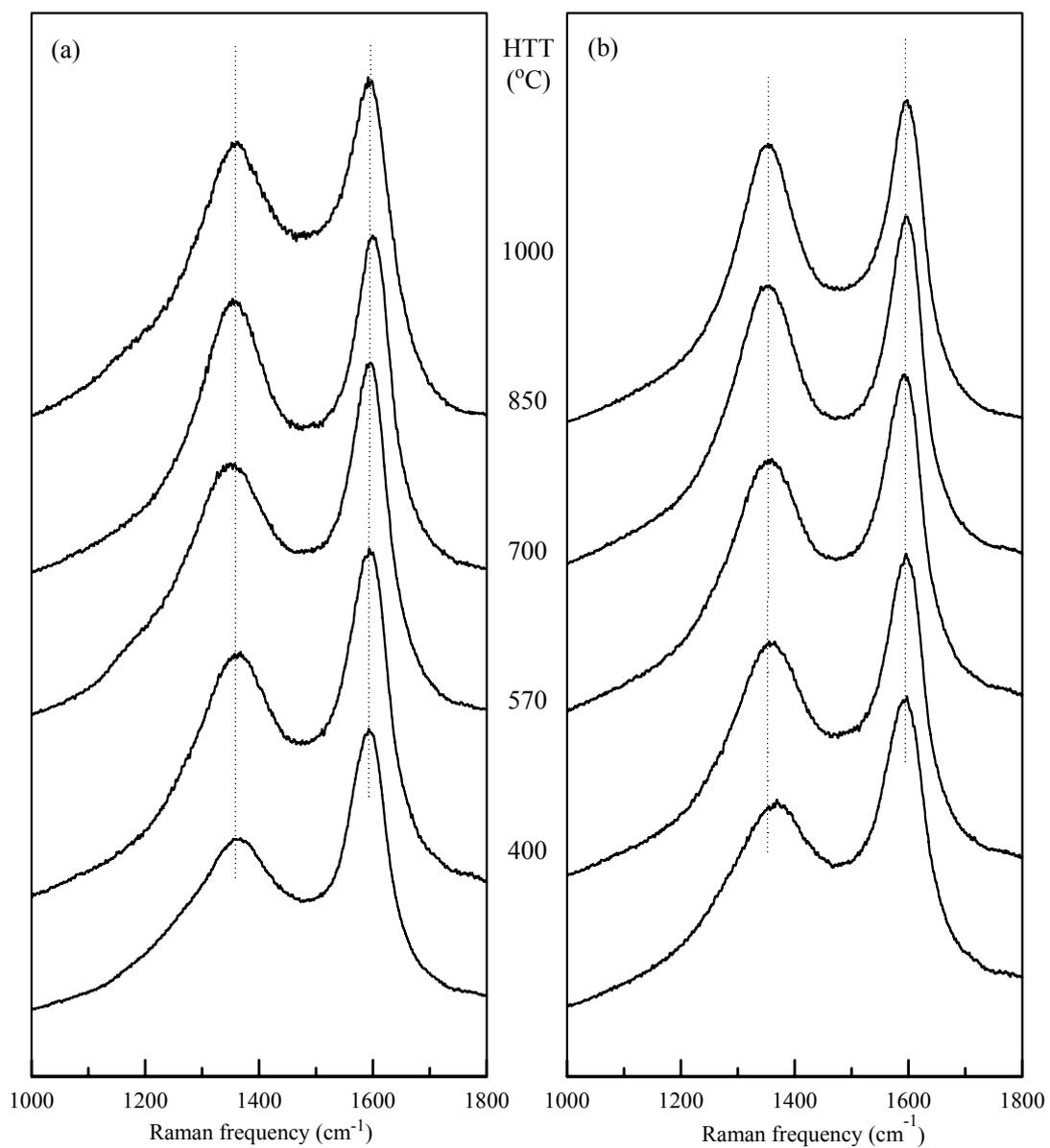


Fig. 3

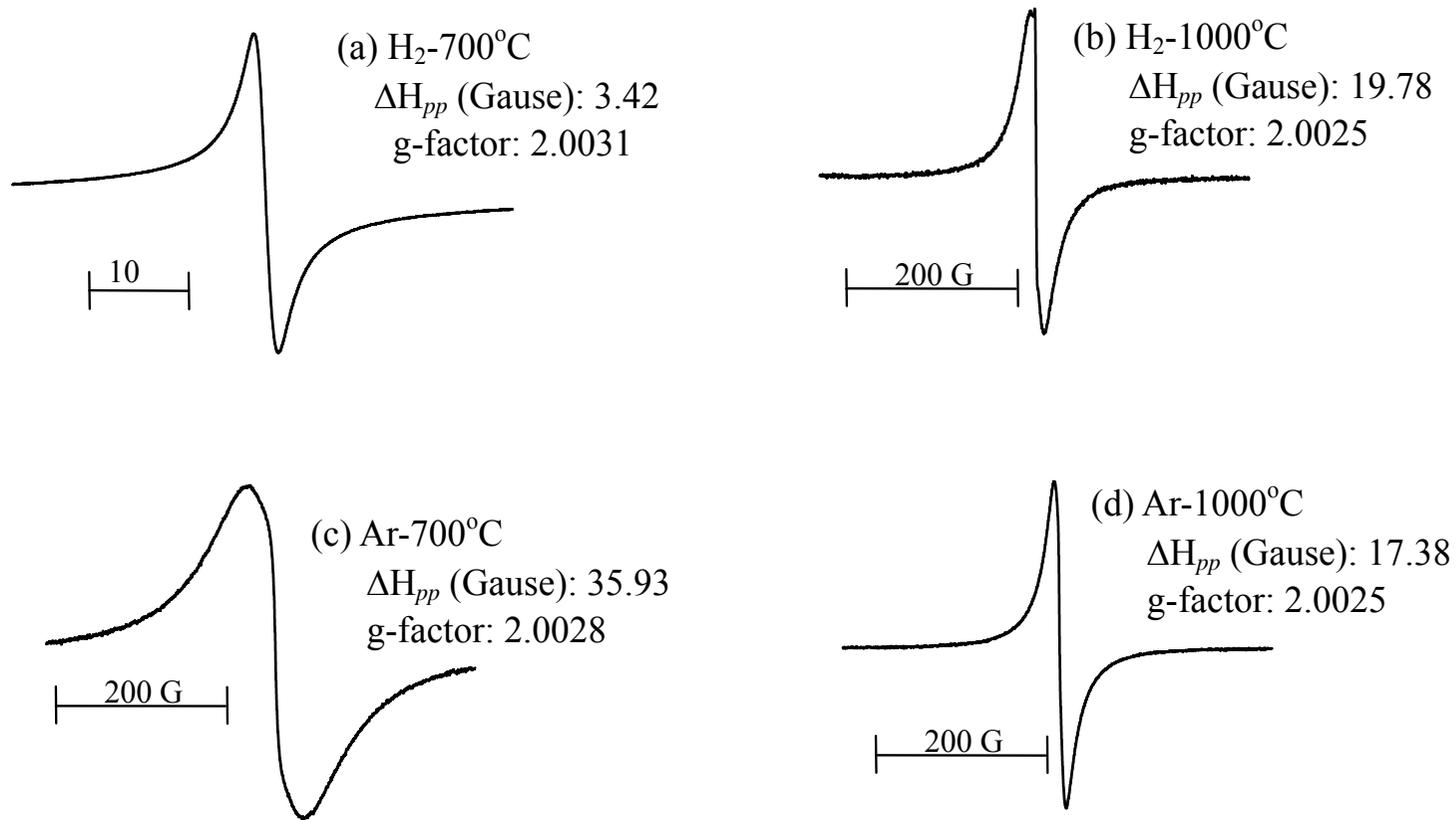


Figure 4

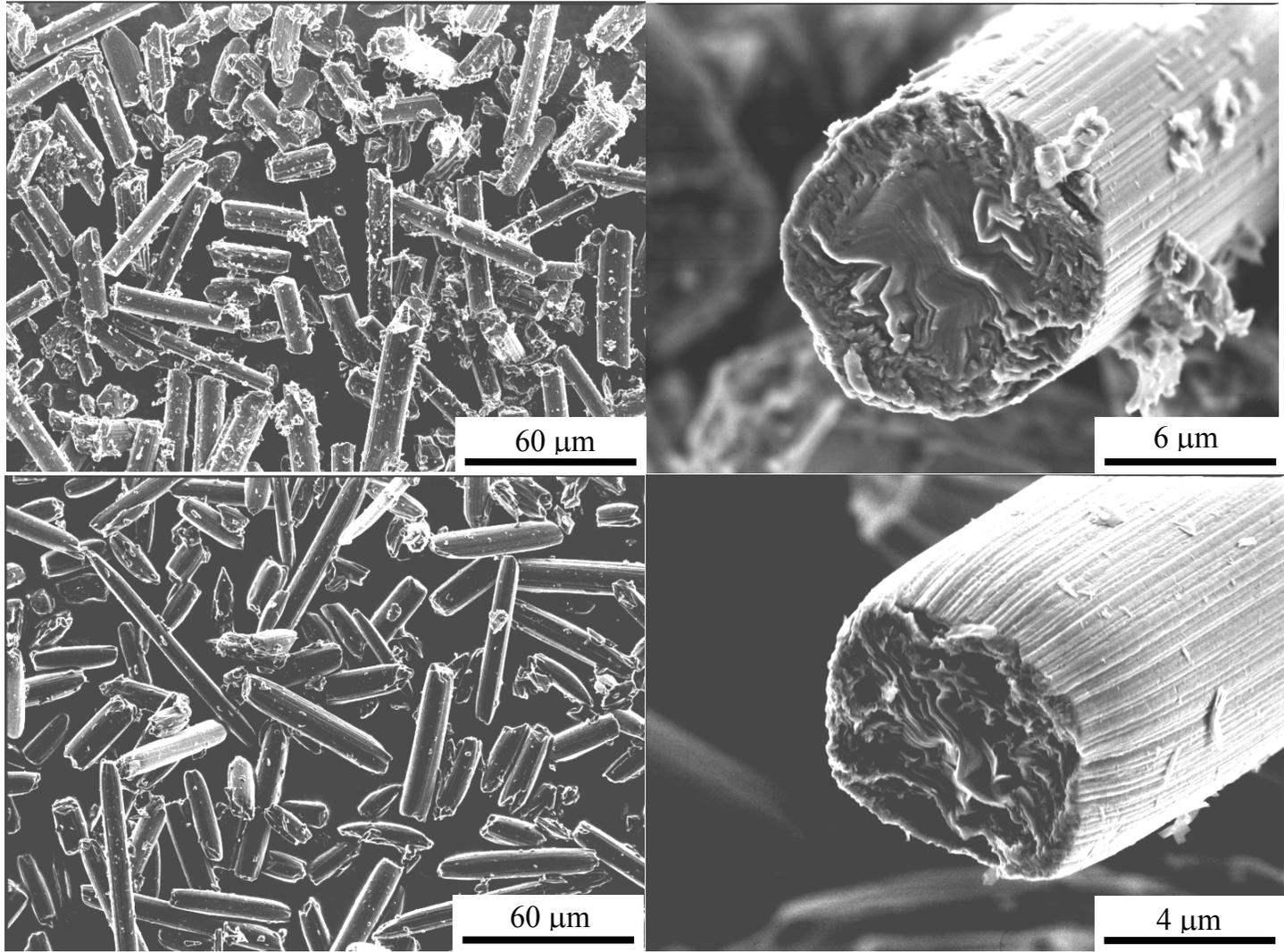


Fig. 5

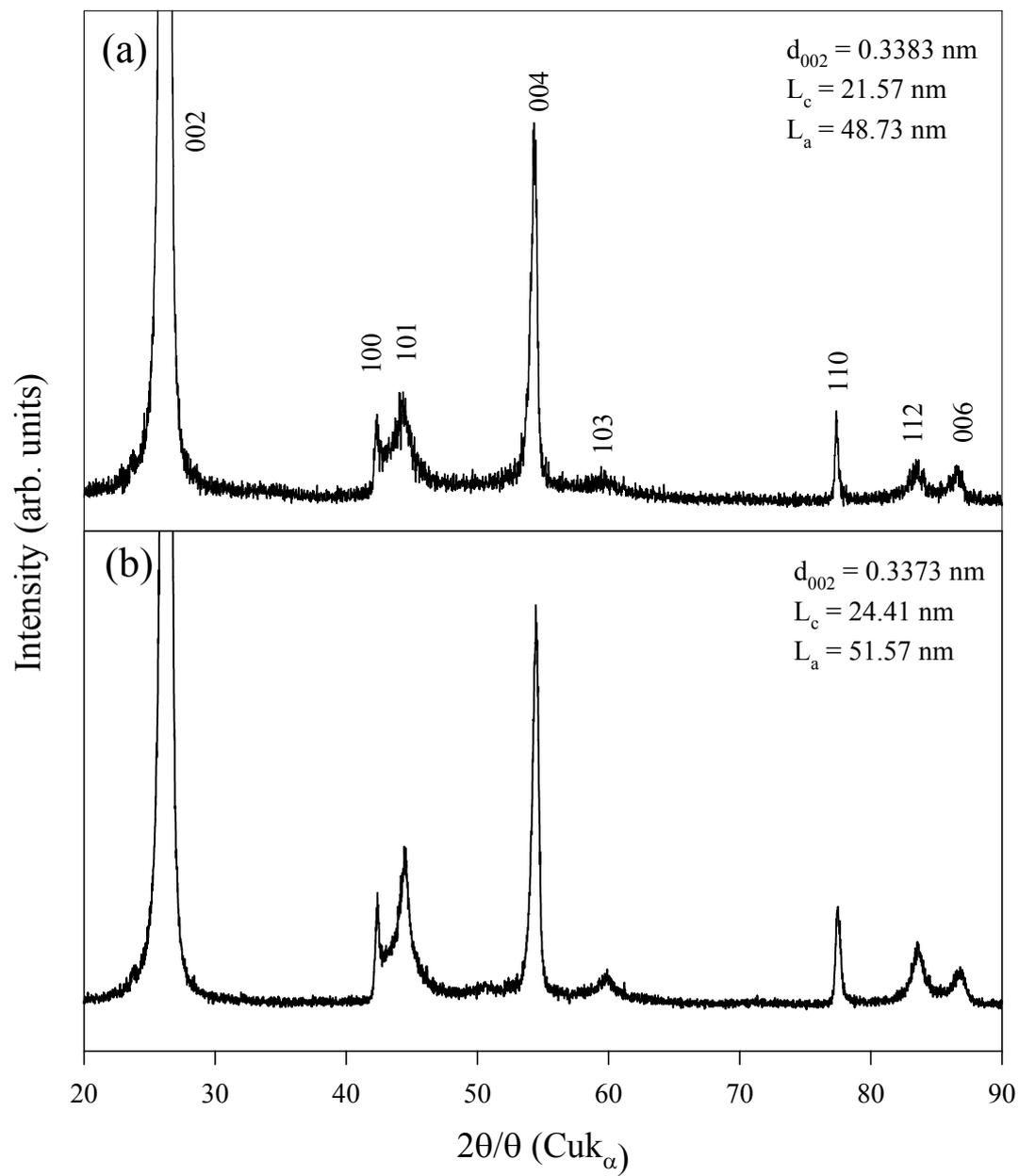


Fig. 6

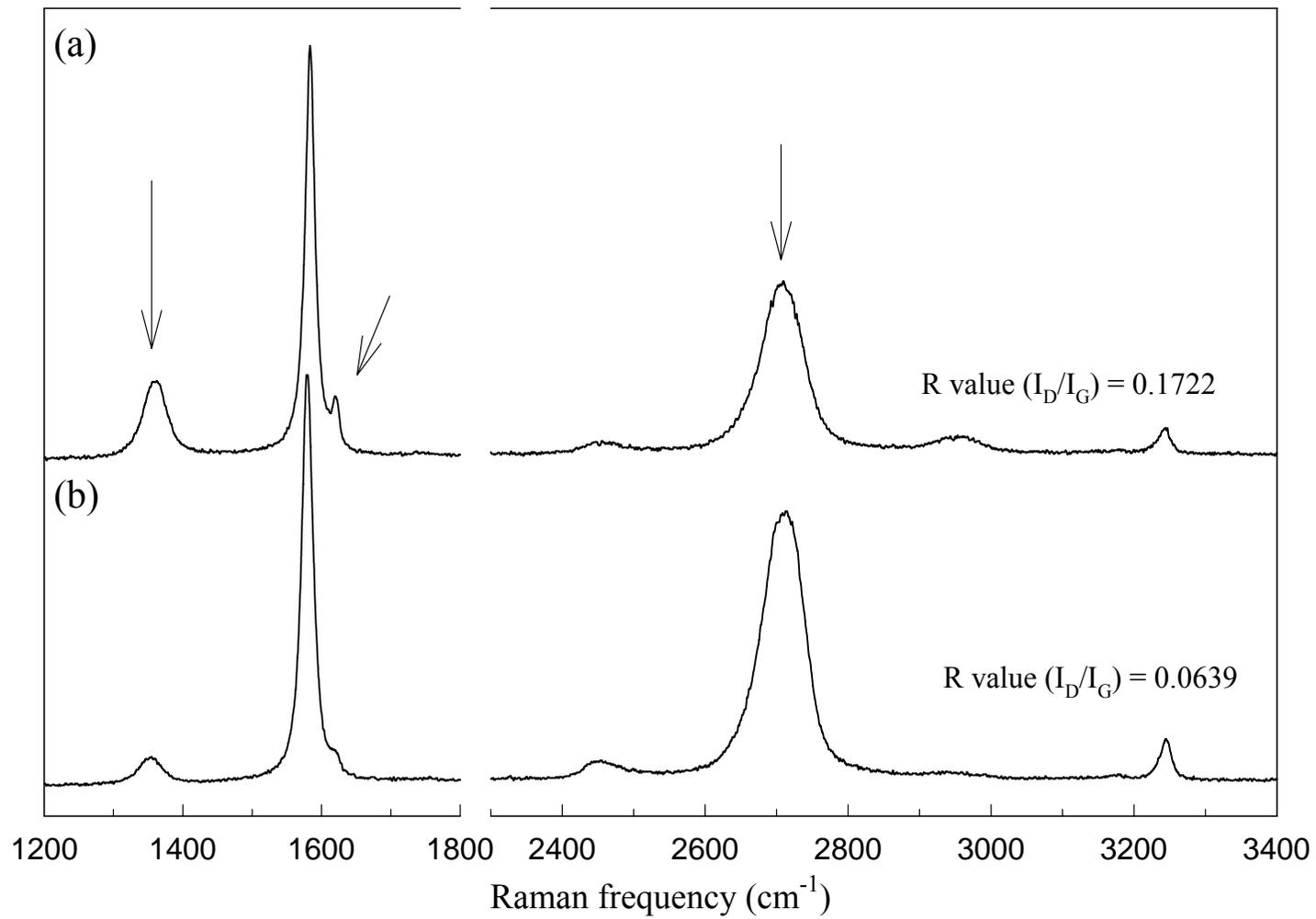


Fig. 7