J Mater Sci (2009) 44:4200–4204
DOI 10.1007/s10853-009-3560-2

LETTER

Nanoscopic observation of mesoporous carbons prepared by catalytic carbonization of Fe- and Ni-containing phenol formaldehyde resins

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Received: 27 January 2009 / Accepted: 9 May 2009 / Published online: 21 May 2009

The importance of carbons possessing mesopore is widely recognized in some application fields [1, 2]. It is also pointed out that the existence of turbostratic (Ts) nanotextures in carbon enhances its H_2S decomposition capability [3]. These studies may suggest that the carbon possessing both mesopore and Ts nanotexture is an attractive material. Recent studies show that 'catalytic carbonization (graphitization)' is expected to be a method to form simultaneously mesopore and Ts nanotexture in carbons without following successive gaseous activation [4, 5]. Ts nanotexture is composed of partially graphitized carbon crystals that are distorted; therefore, the space among Ts nanotextures has been believed to be mesopore, according to the model proposed by Huttepain and Oberlin [6]. However, the location of mesopores present in carbons is still based on mere supposition. Indeed, even a correlation between mesopore and Ts nanotexture has not been studied yet. The final goal of our study is to establish a preparation technique for carbons possessing both mesopores and Ts nanotextures. This goal is accomplished by pursuing the possibility of controlling the amounts and sizes of mesopores by changing the characteristics of Ts nanotexture in carbons. In this letter, Fe- and Ni-catalyzed carbons are prepared under a certain carbonizing condition, then mesopore and nanoscopic morphology of carbon nanotextures are characterized by three different techniques: N_2 adsorption/desorption, X-ray diffraction (XRD), and nanoscopic observations of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We also show in this letter that the nanoscaled SEM and TEM observations are useful to consider the nanoscopic morphology and nanotexture of carbons.

Designated amounts of ferrocene and nickel nitrate hexahydrate (Kanto Chemical Co., Inc.) are dissolved separately in methanol and added into resol-type phenol formaldehyde resin (Gun-Ei Chemical Industry Co., Ltd.). These resins are then thermoset at 80 °C, and the resin blocks thus hardened are heat-treated in flowing Ar at 5 °C/min up to 1,000 °C. The temperature is finally held at

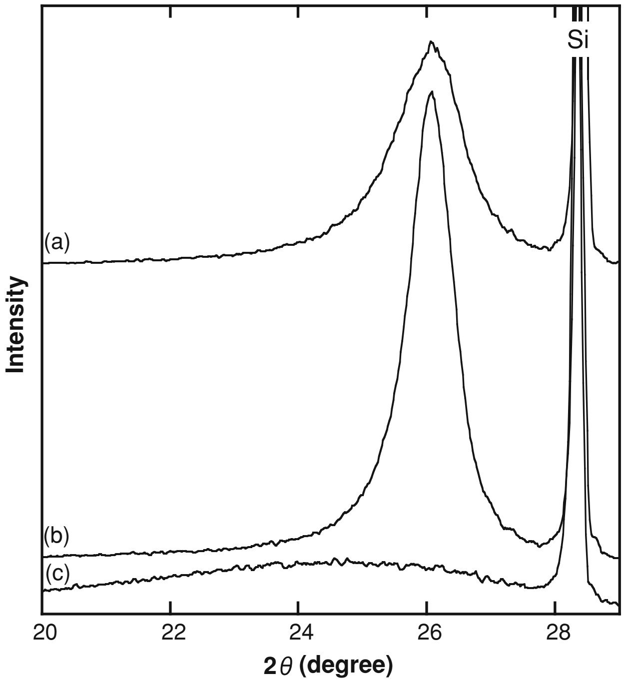

Fig. 1 XRD patterns around 002 line of phenol resin carbons heat-treated at 1,000 °C for 1 h: (a) Fe-containing carbon (FePF); (b) Ni-containing carbon (NiPF); and (c) carbon without catalysts (PF). High purity silicon is used as an internal standard substance

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Fig. 2 N_2 adsorption/desorption isotherms of carbons (45–60 mesh) at 77 K: **a** Fe-catalyzed carbon (FePF); **b** Ni-catalyzed carbon (NiPF); and **c** phenol resin carbon without catalysts (PF). Closed symbols: adsorption, open symbols: desorption. A_{BET}: specific surface area calculated by BET plot, A_{meso}: mesopore surface area calculated from DH method of adsorption branch

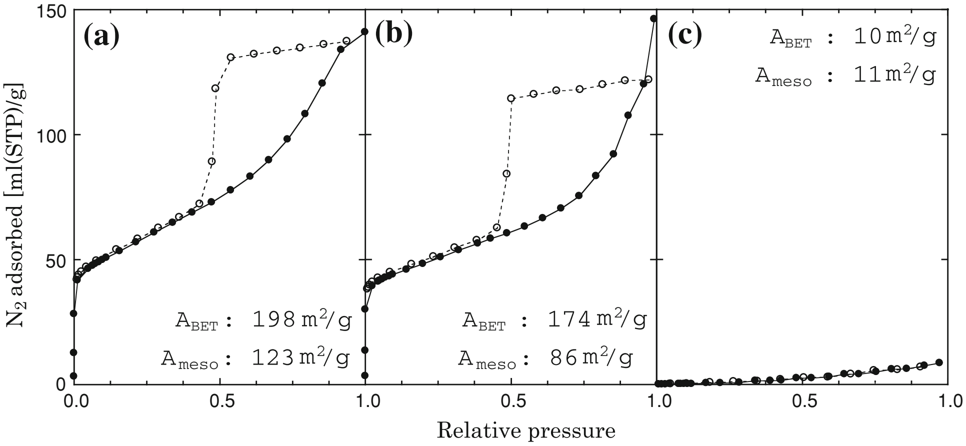
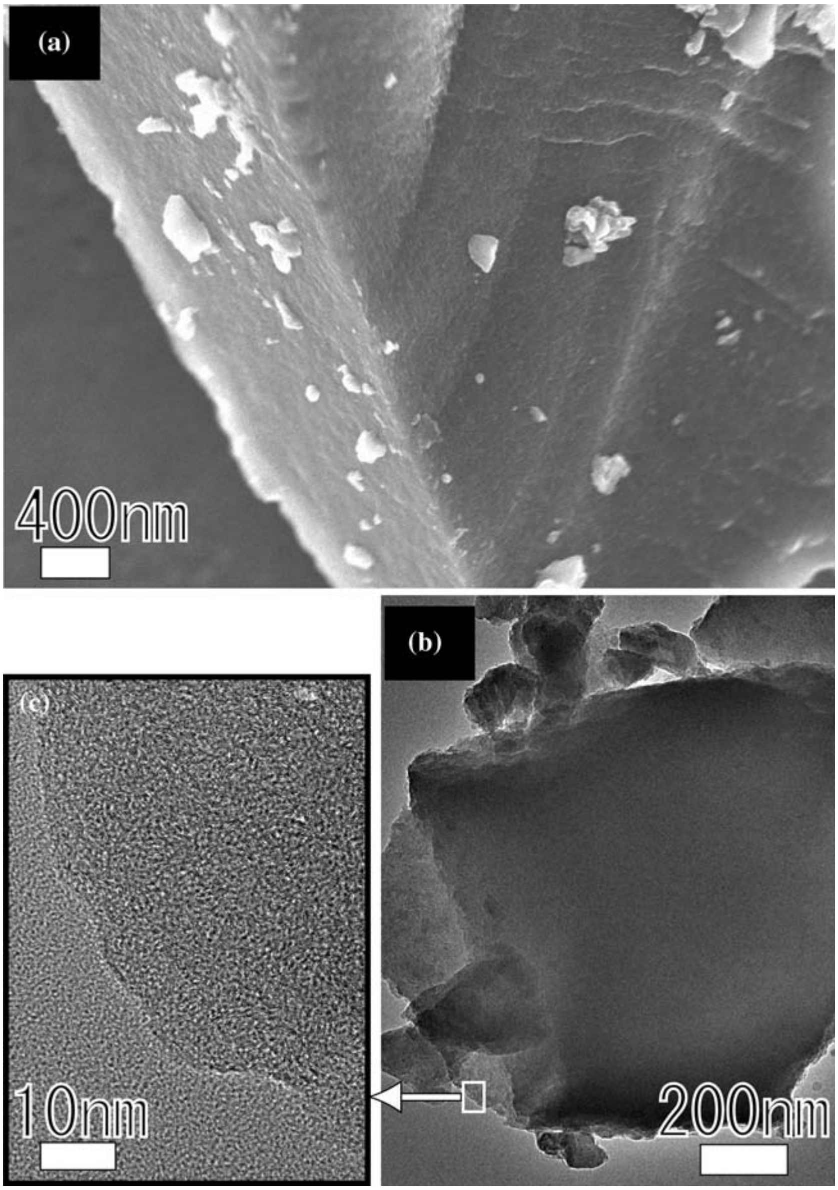


Fig. 3 Cross-sectional morphology and amorphous nanotextures of carbon without catalyst (PF) carbonized at 1,000 °C for 1 h: **a** SEM image; **b** TEM image; and **c** high magnified TEM image



1,000 °C for 1 h in order to prepare Fe- and Ni-containing carbons (FePF and NiPF). Each carbon sample contains about 1.0 mmol of Fe or Ni in one gram of 1,000 °C heat-treated carbons. The carbon sample including no metal, represented as PF, is also prepared at 1,000 °C as a reference sample. After the carbonization of the three types of carbons (0.5–1.5 cm in size), they are crashed, sieved into a certain range of fine particle sizes, and then subjected to subsequent measurements.

XRD 002 profiles for the three types of carbons are presented in Fig. 1. The broad 002 profile for PF indicates that PF has amorphous nanotextures. Rather sharp peaks appear in the 002 diffraction profiles for FePF and NiPF. Roughly calculated interlayer spacing (d_{002}) and average crystalline size in *c*-direction (Lc) for both of FePF and NiPF samples are 0.34 nm and 10 nm, indicating that Ts nanotextures emerge in FePF and NiPF.

N_2 adsorption/desorption isotherms for the three types of carbons are obtained at 77 K by Belsorp18 plus (BEL Japan Inc.). The isotherms show that FePF and NiPF adsorb a considerable amount of N_2, compared to PF (Fig. 2). Hysteresis loops appear on the isotherms for FePF and NiPF, implying the existence of mesopores in these carbons. The values of specific surface area and mesopore surface area are also presented in Fig. 2.

SEM (Hitachi S-5200) and TEM (JEOL JEM-2100F) are used, respectively, to observe the nanoscopic morphology and nanotexture of the three types of carbon specimens. These observations reveal cross-sectional morphology and nanotexture inside the carbons since the

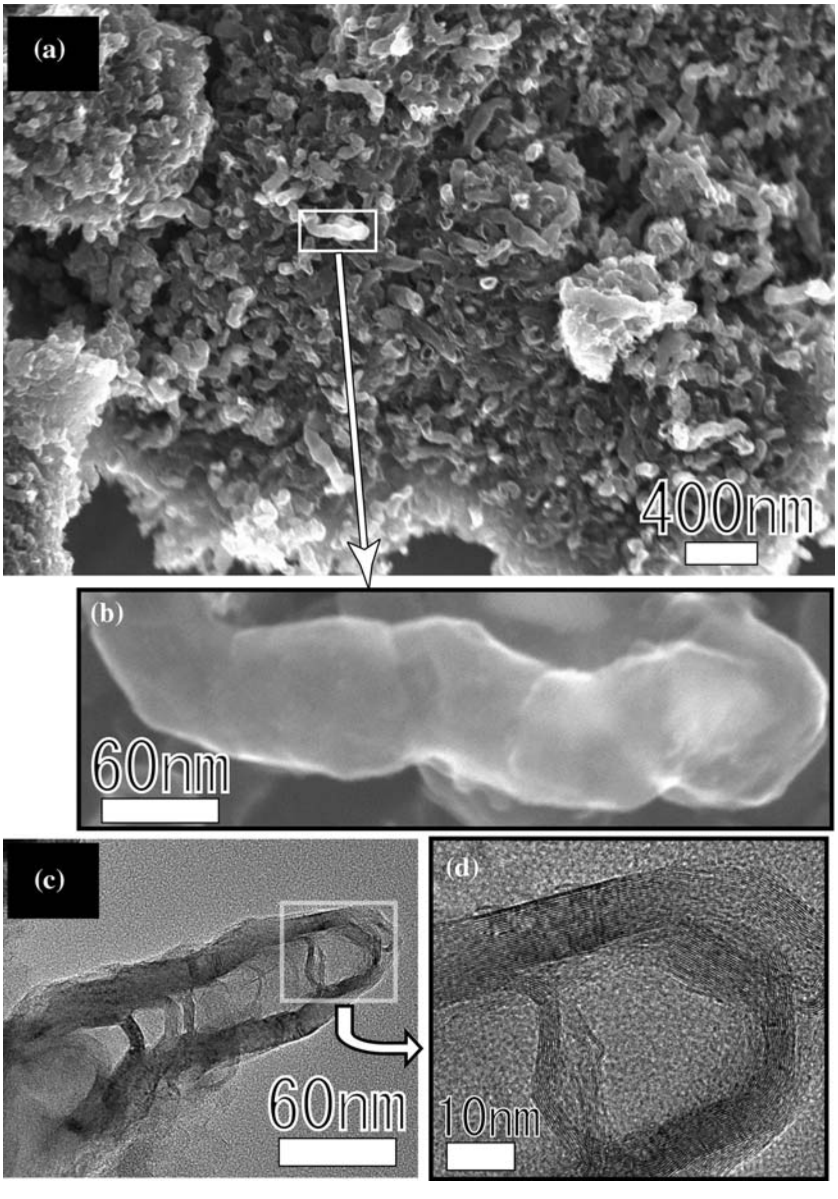


Fig. 4 Nanoscaled SEM and TEM observations of Fe-containing carbon (FePF) carbonized at 1,000 °C for 1 h: **a** cross-sectional morphology; **b**, **c** carbon whiskers observed for the same magnification by SEM and TEM; and **d** hemisphere or cup-like structured Ts nanotextures

carbon specimens are prepared by grinding 1,000 °C heat-treated PF, FePF, and NiPF. A smooth cross-sectional surface for PF is seen in the SEM image (Fig. 3a). Fine particles on the smooth surface would be carbon fragments attached during the grinding. The TEM image displays typical amorphous nanotextures (Fig. 3b, c).

The nanoscopic morphology and Ts nanotexture, observed by SEM and TEM, are different between FePF and PF. The SEM images indicate that a surface of FePF is covered entirely by whiskers with a relatively uniform diameter of ca. 60–70 nm (Fig. 4a, b). The TEM images offer further information with regard to the whiskers observed by SEM. A whisker is composed of Ts nanotextures and the inner part of a whisker is void as seen in Fig. 4c. The close observation in Fig. 4d indicates that the hemisphere or cup-like structure of Ts nanotextures is stacked together to form carbon nanotube in FePF.

The morphology of NiPF, based on SEM observations, differs from that of FePF. NiPF is composed of 'block-like' structure, widely ranging from 100 nm to 300 nm in size (Fig. 5a, b). Ts nanotextures inside 'blocks' for NiPF are somewhat linear with a size of more than 100 nm in the *a*-crystalline direction (Fig. 5c, d). It seems that Ts nanotextures are poorly stacked to form block-like structure.

It is presented in this letter that Ts nanotextures are catalytically induced and assembled to form characteristic shapes of carbon: carbon nanotube in FePF and carbon block in NiPF. We here define this assembly of Ts

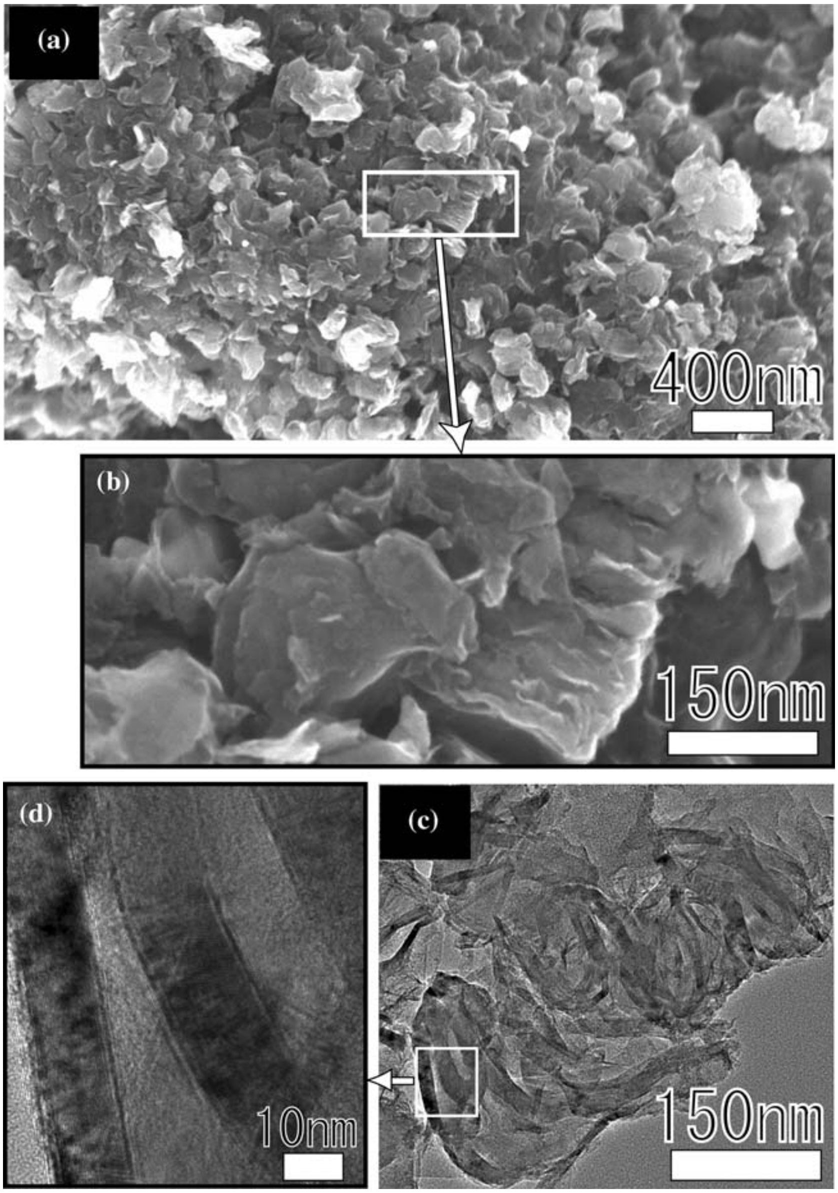


Fig. 5 Nanoscaled SEM and TEM observations of Ni-containing carbon (NiPF) carbonized at 1,000 °C for 1 h: **a** cross-sectional morphology; **b**, **c** carbon blocks observed for the same magnification by SEM and TEM; and **d** linear Ts nanotextures

nanotextures as ‘nano cluster’ (NC). Fe- and Ni-catalyzed carbons composed of NCs possess high porosity, especially with mesopores, as shown previously in Fig. 2. Mesopores possibly exist as space surrounded by NCs, although the possibility for mesopores to exist among Ts nanotextures as described by Oberlin’s model [6] cannot be excluded. Whatever the origin of mesopores is, our results imply that catalytic carbonization is an attractive method to control the extent and possibly the structure of mesopores by altering the types and amounts of catalytic additives.

One should remember that Fe- and Ni-catalyzed carbons consist of different types of NCs, although they show relatively similar carbon crystalline parameters of d_{002} and Lc characterized by XRD. In many studies [3, 5, 7, 8], carbon crystalline structure or Ts nanotexture has been determined on the basis of XRD parameters, which do not provide any information about NCs. Our results suggest that nanoscale observations by both SEM and TEM are important to understand the carbon nanostructures from the viewpoint of NC of carbon.

A further report will appear soon with respect to the relationship between the carbon nanotextures and the amounts of mesopore present in catalyzed carbons.

Acknowledgements The authors would like to express their thanks to Prof. Hideyuki Yoshimura (Meiji Univ.) for his technical assistance in electron microscopy and Prof. Toshihiro Nakamura (Meiji Univ.) for his technical assistance in XRD.

References

1. Nagano S, Tamon H, Adzumi T et al (2000) Carbon 38:915
2. Shiraishi S, Kurihara H, Oya A (2001) Electrochem Commun 69(6):440
3. Ozaki J, Yoshimoto Y, Oya A et al (2001) Carbon 39:1605
4. Hatori H, Kobayashi T, Hishiki S et al (2002) Synth Met 125:183
5. Sakata Y, Tanihara M, Muto A et al (1999) Bamboo J 16:41 (in Japanese)
6. Huttepain M, Oberlin A (1990) Carbon 28(1):103
7. Bin Y, Chen Q, Nakamura Y et al (2007) Carbon 45:1330
8. Oya A, Marsh H (1982) J Mater Sci 17:309. doi:10.1007/BF00591464