



Magnetic separation of carbon-encapsulated Fe nanoparticles from thermally-treated wood char

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ARTICLE INFO

Article history:

Received 27 July 2012

Accepted 1 January 2013

Available online 11 January 2013

Keywords:

Wood char

Fe nanoparticles

Carbon-encapsulated Fe nanoparticles

Magnetic separation

X-ray diffraction

High-resolution transmission electron microscopy

ABSTRACT

Wood char, a by-product from the fast-pyrolysis process of southern yellow pine wood for bio-oil production, was carbonized with Fe nanoparticles (FeNPs) as a catalyst to prepare carbon-encapsulated Fe nanoparticles. A magnetic separation method was tested to isolate carbon-encapsulated Fe nanoparticles from the carbonized char. X-ray diffraction pattern clearly shows that Fe-containing materials were completely separated from the carbonized wood char mixture using a magnet. The amorphous carbon in the material which adhered to the magnetic bar was significantly decreased in comparison with the non-adhered material. Carbon graphitic layers encapsulated FeNPs were observed in the adhered material through high-resolution transmission electron microscopy. In addition, many long and tangled-multi-layered graphitic carbon structures grew from the surface of carbon-encapsulated Fe nanoparticles.

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1. Introduction

Previously, we reported that well-aligned graphitic carbon structures and Fe nanoparticles encapsulated in carbon matrix can be formed through thermal treatment of pine wood char with Fe nanoparticles (FeNPs) as catalyst at 1000 °C. To remove FeNPs from the carbonized char, 25% of nitric acid was used, but some FeNPs were still detected after the acid treatment [1]. Many researchers have reported that transition metals used as catalysts for the preparation of carbon nanomaterials are not easily removed thoroughly because those metallic catalysts are encapsulated by graphitic layers or surrounded by amorphous carbons [2,3]. Thus, it was thought that FeNPs used as catalyst are well protected by certain kinds of carbon structures.

On the other hand, carbon-encapsulated metal nanoparticles have attracted much attention for their unique physical and chemical properties, especially in the fields of catalyst and information technologies such as magnetic data storage, xerography, electronics, and biomedicines [3–7]. Based on our previous study, we expected that Fe-contained carbon nanomaterials could be simply separated by using a magnet from the carbonized wood char mixture. The objectives of this study were to explore the possibility of using magnetic separation of Fe-contained carbon nanomaterials from the Fe-carbonized wood char mixture and to

characterize both materials adhered and non-adhered on a magnet using high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and Raman spectroscopy.

2. Experimental

The pine wood char powder (averaged 20 μm in length) was thermally treated in the presence of FeNPs (averaged 25 nm in diameter, Sun Innovations Inc. Fremont, CA, USA) as a catalyst under the same experimental condition as we previously reported [1]. Thus, the mixture of 50 mg of FeNPs (1 part by weight) and 200 mg of char powder (4 parts by weight) was loaded into a porcelain boat and then heated to 1000 °C at a ramping rate of 20 °C/min under an argon stream with a flow rate of 1 L/min in an electric furnace (Mellen SC12R—0.75 × 3) equipped with a temperature controller (Mellen PS 305-120-15-S1). Approximately 1 g of thermally treated wood char powder mixture was placed on a letter-size copy paper and then subjected to magnetic separation using a telescope magnetic bar (KOBALT, USA) with the assumption that Fe-containing carbon materials will stick on the magnetic bar. The magnetic bar was put into the sample and slowly stirred to attract Fe-containing materials. The separation process was repeated until no particles adhered to the magnet. The carbon materials that adhered on the magnet were collected and weighed to calculate their yield. The remaining non-adhered materials were calculated by subtracting the adhered materials from the sample weight taken initially. After their separation,

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both magnetically adhered and non-adhered samples were characterized using HRTEM, XRD, and Raman spectroscopy. For the HRTEM, samples were prepared by grinding them using an agate mortar and ethanol was added to further reduce their size and then a drop of these suspensions was dripped onto a 300 mesh copper grid with a perforated support film. HRTEM analysis was performed on a JEM 2100F (JEOL, Japan) equipped with an EDAX (Ametek). XRD was performed with a Rigaku SmartLab X-ray diffractometer using Cu K α radiation ($\lambda=1.5418$ Å). Raman spectra were recorded at the room temperature using Jobin Yvon LabRam HR spectrometer (Horiba, NJ, USA) with a 514.56 nm Ar laser.

Table 1

Carbonization yield of wood char after thermal treatment, and the yields of magnetically adhered and non-adhered materials.

Component weight (mg)		Carbonization yield (%)		Magnetic treatment (%)	
Pine wood char	FeNPs	With FeNPs	Without FeNPs	Adhered	Non-adhered
200	50	62.5	53.1	56.3	43.7

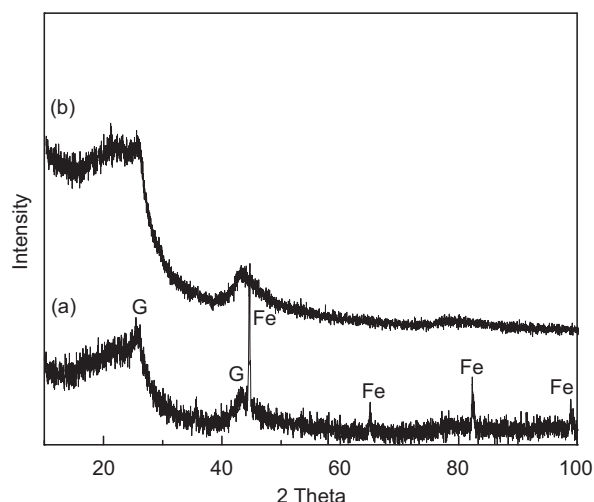


Fig. 1. Powder X-ray diffraction patterns of magnetically adhered (a) and non-adhered materials (b). G: graphite, Fe: iron.

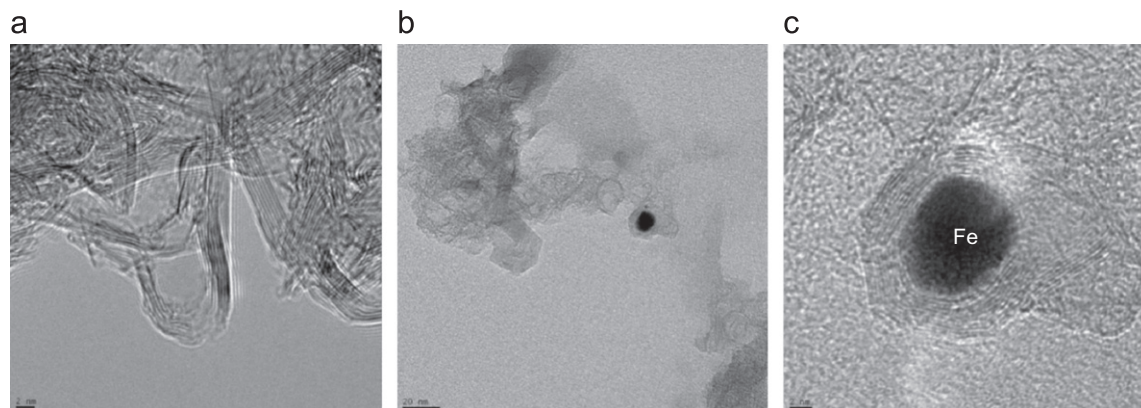


Fig. 2. HRTEM images of magnetically adhered materials: (a) typical graphitic carbon structures, (b) carbon-encapsulated Fe nanoparticle and tangled graphitic structures, and (c) enlarged image of Fe nanoparticle in (b).

3. Results and discussion

Table 1 shows the carbonization yield of wood char powder after thermal treatment. The average yield of 10 replicates (2000 mg wood char powder and 500 mg FeNPs) was 62.5%, i.e., the yield percentage number was calculated based on the equation, (weight of pine char and FeNP mixture after thermal treatment/weight of pine char before thermal treatment) $\times$ 100. The carbonization yield after weight correction of FeNPs in the wood char powder was 53.1%, i.e., the yield percentage number without FeNPs was calculated using the equation, [(weight of pine char and FeNP mixture after thermal treatment – weight of FeNPs used)/weight of pine char before thermal treatment] $\times$ 100. After the magnetic separation of the thermally-treated sample, the weight percentages of the magnetically adhered and non-adhered materials were 56.3% and 43.7%, respectively. If the adhered material contained all the FeNPs added into wood char powder as the catalyst for thermal treatment, the weight percentage of carbon in the adhered material was 35.7%.

Fig. 1 shows XRD patterns of magnetically adhered and non-adhered materials. The adhered material shows the typical iron's lattices on the XRD spectrum. The non-adhered material reveals broad bands in the range of 10–25° on XRD spectrum. This range mostly originated from amorphous carbons. In the case of the adhered materials, the amorphous region was significantly reduced. Graphite (002), (100) and (101) planes, which appear at 26°, 42.9° and 43.7°, respectively, were not clear on the spectrum. This phenomenon may occur due to the strong intensity of the iron peaks on the XRD spectrum. The XRD results also indicate that the magnetic separation technique used in this study is an effective way to separate Fe-carbon structure-contained materials from amorphous carbon.

Fig. 2 shows typical HRTEM images of the adhered material. FeNPs were encapsulated by well-aligned and multi-layered graphitic shells (Fig. 2c). In addition, long and tangled graphitic carbon structures were also observed (Fig. 2a). These graphitic carbon structures were likely to grow from the surface of FeNPs (Fig. 2b). Some research has reported that at elevated temperatures the amorphous carbon in wood char decomposed into free carbon atoms and these carbon atoms deposited onto Fe particle surface in the form of graphene layers and settled in the lowest energy [7–9]. In our study, this reaction may also occur. But due to the larger size of the FeNPs used in this experiment as catalyst compared to Fe ions which yielded a majority of multi-layered graphitic shelled Fe [8], the growth of long graphitic carbon structures seems to be the prevailing reaction during the carbonization in this study.

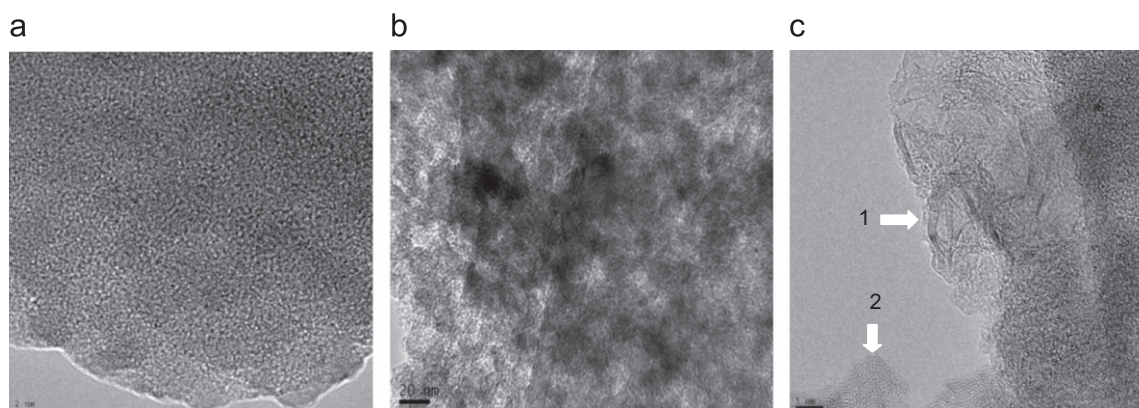


Fig. 3. HRTEM images of magnetically non-adhered materials: (a) amorphous carbon structure, (b) overlapped graphene sheets, and (c) graphitic carbon structures (1) and onion-like structure (2).

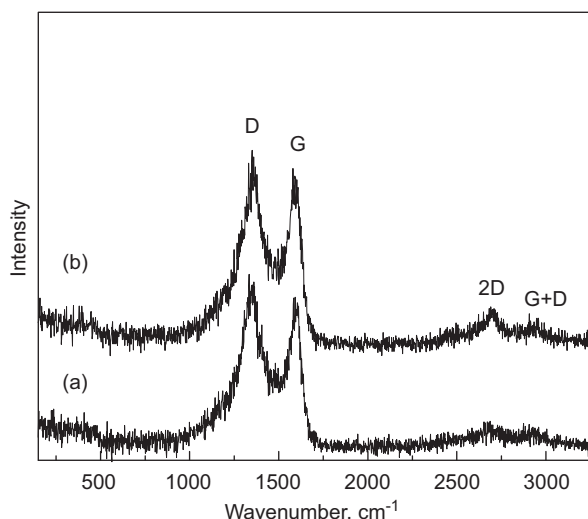


Fig. 4. Raman spectra of magnetically adhered (a) and non-adhered materials (b).

On the other hand, in the case of the non-adhered portion, most of the carbon structures are made up of amorphous carbon structures (Fig. 3a), but some had graphene (Fig. 3b), onion-like and graphitic carbon structures (Fig. 3c). Occurrence of graphene in the non-adhered materials was confirmed by the HRTEM, and also Raman analysis as shown in Fig. 4 indicated its possibility.

Raman spectroscopy can be used to characterize carbon structures of carbonaceous materials such as graphite and diamond-like carbon and provides information on the molecular structure and chemical bonding of carbon atoms in carbonized materials [10]. The Raman spectra of magnetically adhered and non-adhered materials shown in Fig. 4 consisted of two distinct peaks, the G and D bands that appeared around 1580 and 1350 cm^{-1} , respectively. The height and width of these bands were similar to each other. The existence of these bands indicates the vibration of sp^2 -hybridized carbon bonded with structural imperfections and the in-plane vibration of sp^2 -bonded crystalline carbon [11]. On the other hand, the non-adhered material had a quite clear 2D band other than D and G bands on the spectrum. The 2D peak (also called G' in the literature) is the second order of the D peak [12]. The 2D peak ranged from 2650 to 2750 cm^{-1} , which corresponded to the turbostratic graphite [12]. The stacking of its graphene layers is rotationally-random with respect to one another along the C axis [13]. Thus, graphene may occur in the non-adhered materials, but it mostly exists in the form of overlapped graphenes with turbostratic structure.

4. Conclusions

A magnetic separation technique was investigated to separate carbon-encapsulated Fe nanoparticles from the wood char powder thermally treated in the presence of FeNPs as a catalyst. Fe-containing carbon materials were well separated using a magnet. The materials adhered on the magnet showed a significant decrease in amorphous carbon compared to the non-adhered materials. Carbon graphitic layers encapsulated FeNPs were observed in the adhered material and also long- and tangled-multi-layered graphitic carbon structures were observed around these FeNPs. In conclusion, the magnetic separation is an effective method to isolate Fe-ECNMs and to reduce amorphous carbons from the carbonized wood char powder.

Acknowledgments

This work was supported by the USDA Forest Service through Grant no. 11JV111112409711121332. The authors would like to acknowledge Dr. Fumiya Watanabe (Nanotechnology Center, the University of Arkansas at Little Rock) in taking the high resolution TEM images and Dr. Shane C. Street (University of Alabama) for allowing us to use FT-Raman spectrophotometer. This manuscript was approved for publication as Journal Article no. 659 FP of the Forest and Wildlife Research Center, Mississippi State University.

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