Cellulosic Fiber-Derived Carbon Catalyzed by Iron Oxide Nanoparticles

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Cellulosic fiber-derived carbon catalyzed by iron oxide nanoparticles

By

Wen Che

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Forest Products
in the Department of Forest Products

Mississippi State, Mississippi
August 2012
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By

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Cellulosic fiber-derived carbon catalyzed by iron oxide nanoparticles

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The objective of this research was to study the catalytic graphitization of cellulose fibers coated with iron oxide nanoparticles. Bleached cellulose fibers and iron oxide nanoparticles coated cellulose fibers were pyrolyzed at five elevated temperatures. The crystallographic structures of carbon-encapsulated iron oxide nanoparticles were then investigated by the following techniques: Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Raman Spectroscopy, Transmission Electron Microscopy (TEM), and Selected-Area Electron Diffraction (SAED).

The graphitization of cellulosic fibers was enhanced by the presence of iron oxide nanoparticles. Moreover, iron oxide nanoparticles deposited on cellulosic fiber samples pyrolyzed above 800°C produced graphitic structures.

TEM and XRD were performed to identify and characterize the phase transitions of carbon-encapsulated iron oxide nanoparticles after pyrolysis treatment at four temperatures: 500°C, 800°C, 1000°C, and 1600°C. TEM of samples pyrolyzed at or above 800°C showed resulting units were core-shell structures consisting of dark grains and a light matrix with graphitic structure.

Key words: cellulosic carbon, iron oxide nanoparticles
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ................................................................................................ ii

LIST OF TABLES ............................................................................................................... v

LIST OF FIGURES ........................................................................................................... vi

CHAPTER

I. INTRODUCTION ............................................................................................................ 1
   Catalytic graphitization .............................................................................................. 1
   Core-Shell system of carbon materials .................................................................... 2
   Iron oxide nanoparticles ............................................................................................ 2
   Cementite/Cohentite .................................................................................................. 3
   Objectives .................................................................................................................. 4

II. EFFECT OF PYROLYSIS TEMPERATURE ON THE GRAPHITIC
    STRUCTURE OF CELLULOSIC FIBER-DERIVED
    CATALYZED BY IRON OXIDE NANOPARTICLES .............................................. 5
    Introduction .............................................................................................................. 5
    Experimental ............................................................................................................. 6
       Materials .................................................................................................................. 6
       Iron oxide nanoparticles solution preparation ..................................................... 7
       Iron oxide nanoparticles deposited cellulosic fibers .......................................... 7
       Pyrolysis treatment ............................................................................................... 8
       Raman spectroscopy ............................................................................................ 9
    Results and discussion ......................................................................................... 10
       SEM analysis ......................................................................................................... 10
       XRD analysis ....................................................................................................... 13
       Raman spectrum analysis .................................................................................... 18
    Conclusions ........................................................................................................... 22
    Literature Cited ....................................................................................................... 23

III. PHASE TRANSITIONS OF CARBON-ENCAPSULATED IRON
    OXIDE NANOPARTICLES BY CARBONIZATION OF
    CELLULOSIC FIBERS AT VARIOUS TEMPERATURES .............. 25
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>X-ray structural parameters of iron oxide coated cellulose fibers from (002) plane ................................................................. 18</td>
</tr>
<tr>
<td>2.2</td>
<td>Raman spectroscopic parameters of iron oxide nanoparticles coated cellulose fibers carbonized under 5 temperatures, obtained from Fig 2. 6 (b) ................................................................. 22</td>
</tr>
<tr>
<td>3.1</td>
<td>Scherrer mean crystallite dimensions of samples .................................................. 30</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Crystal lattice of graphite</td>
</tr>
<tr>
<td>2.2</td>
<td>Heat treatment process</td>
</tr>
<tr>
<td>2.3</td>
<td>SEM images showing the surface morphologies of (a) bleached cellulose fibers and (b) iron oxide nanoparticles coated cellulose fibers before heat treatment with scale bar of 100 nm.</td>
</tr>
<tr>
<td>2.4</td>
<td>SEM images showing the surface morphologies of (a) BF800, (b) FeF800 and (c) FeF1000 after heat treatment in nitrogen gas ambient at 800°C and at 1,000°C with scale bar of 100 nm.</td>
</tr>
<tr>
<td>2.5</td>
<td>XRD patterns of non-heated cellulose fibers, (a) BF800, BF1000, BF1200, BF1400 and BF1600 (b) XRD patterns of FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.</td>
</tr>
<tr>
<td>2.6</td>
<td>XRD patterns of non-heated cellulose fibers, (a) BF800, BF1000, BF1200, BF1400 and BF1600 (b) XRD patterns of FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.</td>
</tr>
<tr>
<td>2.7</td>
<td>The 002 line profile of FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.</td>
</tr>
<tr>
<td>2.8</td>
<td>Raman spectra of (a) BF800, BF1000, BF1200, BF1400 and BF1600 and (b) FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.</td>
</tr>
<tr>
<td>2.9</td>
<td>The relationship between the intensity ratio ($I_G/I_D$) and the heat treatment temperature of iron oxide nanoparticles coated cellulose fibers.</td>
</tr>
<tr>
<td>3.1</td>
<td>XRD pattern of iron oxide nanoparticles used for mixing the cellulosic fibers.</td>
</tr>
<tr>
<td>3.2</td>
<td>XRD patterns of Fe$_3$O$_4$ deposited cellulosic fibers at 500°C obtained under different ambient conditions: open to the air (combusted) and covered by distilled water.</td>
</tr>
</tbody>
</table>
3.3 TEM images of samples at 500°C obtained under different ambient conditions: (a) open to the air (combusted) and (b) covered by distilled water; the corresponding SAED patterns are displayed in the two insets......................................................................................31

3.4 XRD patterns of samples obtained at under different temperatures: 800°C and 1000°C .........................................................................................................................32

3.5 TEM images of samples at 800°C; the corresponding SAED pattern is given as the inset. .........................................................................................................................33

3.6 XRD patterns of samples obtained at 1600°C .........................................................................................................................34

3.7 TEM images of samples at 1600°C; the inset represents the corresponding SAED pattern. .........................................................................................................................34
CHAPTER I
INTRODUCTION

Carbon-based materials have recently drawn much attention, since they can possess remarkable mechanical and electrical properties. These unique properties can have a significant impact on the technological applications.

Catalytic graphitization

The carbonization of organic precursors, such as aromatic polyimide (Ko et al. 1996), coal (Saikia et al. 2009), and viscose rayon (Frushhour et al. 1998) is a popular method to fabricate carbon materials. However, most precursors for carbon have difficulty in developing a well-oriented graphitic structure even when processed at a temperature of 2000oC (Jekins et al. 1976). Catalysts, which are inorganic or organic compounds added to the precursors, have been proven effective in obtaining graphitic structure at lower temperature, and have brought certain desired properties into the resultant carbon (Dhakate et al. 1997).

The presence of the catalysts has been proven to promote carbonization. Many projects have investigated the influence of inorganic catalysts, such as iron oxide (Dhakate et al. 1997), iron (Park et al. 2005; Oka et al. 1999), nickel oxide (Katarzyna et al. 2011; Lee et al. 2005) and nickel (Tzeng et al. 2006), on the carbonization of various forms of carbon, such as cokes, amorphous carbon, polyimide, pitch, etc. The potential problem is that commercial organic precursors of carbonization are derived from non-renewable sources. Little research has been done on the influence of iron oxide particles
on carbonization of cellulose derived from wood and other biomass materials. Compared with other precursors of carbonization, cellulose, a major component of woody biomass, is a promising renewable resource. Moreover, iron oxide as the catalyst will not only enhance carbonization of cellulose at lower temperature, but also possibly form iron carbide which has important applications such as magnetic data storage, magnetic toner in ferrofluid, and biomedical applications (Scoot et al. 1998; Tartaj et al. 2003).

**Core-Shell system of carbon materials**

Carbon materials that contain nanoscale magnetic particles have received great interest due to their remarkable properties (Redl et al. 2003; Zhao et al. 2009; Subramoney et al. 1998; McHenry et al. 1994; Liu et al. 2004; Xiao et al. 1987). When bare magnetic nanoparticles are exposed to the air, they oxidize and become antiferromagnetic particles. Crystalline or amorphous carbon as the protective shell encapsulates the magnetic core and consequently improves the magnetic stability of the nano-sized particles. Recently, carbon-iron nanoparticles constituting magnetic core-shell systems show great potential for many applications: catalysts, environment, biology, optics, electronics, separation devices and mechanics (Hihara et al. 1994; Si et al. 2003; Zhao et al. 1996; Masuda et al. 2000; Sun et al. 1999; Dravid et al. 1995).

**Iron oxide nanoparticles**

Nanocrystal structures of core components need extensive investigation for exploiting their unique applications for materials, since the phases of magnetic nanoparticles in core-shell system are fragile and transferable among iron oxides, iron carbides and iron (Morjan et al. 2009). Iron oxides nanoparticles are of technological importance for promising applications, which result from multivalent oxidation states and
polymorphism such as hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄). The common iron oxide, magnetite (Fe₃O₄), has a spinel structure, where oxygen ions are closely packed to form the face centered cubic and Fe cations fill in the gaps of tetrahedral and octahedral sites (Cornelis et al. 1977). The wide applications of Fe₃O₄ nanoparticles in magnetic inks, magnetic fluids for drug delivery (Halbreich et al. 1998), and magnetic data storage (McHenry 2000) are attributed to their strong magnetic properties. Hematite (α-Fe₂O₃) is the most thermodynamical stable iron oxide and crystallizes in a rhombohedral structure. It has been used as a catalyst in chemical industry (Gong et al. 2002; Huo et al. 2000), as gas sensors to detect combustible gases (CH₄, C₃H₈) (Neri et al. 2002), and as a photoanode for photoelectrochemical cells (Lindgren et al. 2002). Maghemite (γ-Fe₂O₃), exhibiting acubic structure, is widely applied in magnetic materials and catalysts (Lai et al. 2003). Recent studies show that thermal decomposition of iron oxide nanoparticles occurs under appropriate conditions. For example, the oxidation of magnetite (Fe₃O₄) into maghemite (γ-Fe₂O₃) nanoparticles occurs satisfying under the condition with the temperature 250°C and oxygen for 2h (Sun et al. 2002). Maghemite (γ-Fe₂O₃), a metastable, low temperature phase of iron oxide, converted into hematite (α-Fe₂O₃) at temperatures above 300°C due to many factors including surface area, structural defects and crystallinity (Nasrazadani et al. 1993; Schimanke et al. 2000).

Cementite/Cohentite

Besides iron oxide nanoparticles, it is worth mentioning that an important core compound of Fe₃C (cementite/cohenite) also has attracted a great interest for exceptional applications in construction materials for carbon steel and iron alloys (Goodwin et al.)
and magnetic recording media (Morjan et al. 2009). However, most fabrications of Fe₃C need a complicated processing operation (Cheng et al. 2003) to acquire the single phase necessary for being integrated with steel. A relatively simple synthesis of iron carbide coated with carbon has been carried out from the carbonization of durene and ferrocene (Song et al. 2003).

**Objectives**

In order to provide enormous environmental and economic utilization of large biomass and generate multifunctional carbon materials, we propose to create finely ordered graphitic structure from the pyrolysis of cellulosic fibers using iron oxide nanoparticles as the catalyst. This study has two main objectives:

1. The effects of the pyrolysis temperature and iron oxide nanoparticles on the graphitization and crystallization will be evaluated by Scanning Electron Microscopy, X-ray Diffraction and Raman Spectroscopy. XRD and Raman analyses were adopted as complementary methods to estimate the crystallite parameters of graphitic structures.

2. Since the phases of core component (iron/iron oxide/ iron carbide nanoparticles) are alterable and each one has its own application, the morphology and crystal structures of the core should be intensely and thoroughly investigated. In this study, we show a facile method for the synthesis of carbon-magnetic nanoparticles system by applying four elevated pyrolysis treatment to the mixture including cellulosic fibers and iron oxide nanoparticles.
CHAPTER II
EFFECT OF PYROLYSIS TEMPERATURE ON THE GRAPHITIC STRUCTURE OF CELLULOSIC FIBER-DERIVED CATALYZED BY IRON OXIDE NANOPARTICLES

Introduction
Among the carbon materials, the ordered crystallite graphitic structures are evaluated in terms of various parameters including interlayer spacing, \( d \), crystallite height along c-axis, \( L_c \), crystallite width along a-axis, \( L_a \) and the average numbers of carbon layer \( (N) \) (Ko 1996) (Figure 2.1. Crystal lattice of graphite).

Currently, Raman Spectroscopy and X-ray Diffraction (XRD) are the most commonly used complementary methods to quantitatively characterize the graphitic
structures of carbon materials. The XRD spectra has been used to estimate interlayer spacing $d_{002}$ obtained from the (002) diffraction peak position by using Bragg’s equation, and derive the crystallite height $L_c$ along the c-axis, crystallite width $L_a$ along the a-axis calculated from the Scherrer formula (Saikia et al. 2009). Raman Spectroscopy is a powerful analytical technique used to evaluate the properties of carbon materials. In general, carbon materials with graphitic structures exhibit three distinct Raman bands, G band at about 1,580 cm$^{-1}$, D band at about 1,360 cm$^{-1}$ and D’ band at about 1,620 cm$^{-1}$. D and D’ bands are attributed to amorphous structures of carbon because of the defect-induced vibration in aromatic ring structure; G band is derived from the graphitic structures of carbon corresponding to the degenerate deformation vibration of aromatic molecules (Tai et al. 2009; Knight et al. 1989; Jawhari et al. 1995; Nistor et al. 1994).

To provide environmental and economic utilization of biomass and generate multifunctional carbon materials, we propose to create fine ordered graphitic structure from the pyrolysis of cellulosic fibers using iron oxide nanoparticles as the catalyst. SEM, XRD and Raman were used to investigate the effect of pyrolysis temperature on the graphitic structure of cellulosic fiber-derived carbon catalyzed by iron oxide nanoparticles. XRD and Raman analyses were adopted as complementary methods to estimate the values of interlayer spacing, $d_{002}$, crystallite height, $L_c$ and crystallite width, $L_a$.

**Experimental**

**Materials**

Commercial cellulose fibers, used as precursor fibers, were purchased from Weyerhaeuser NR Co. An average fiber length was measured around 2.5 mm. The
moisture content of the fiber was measured as 9.0% by moisture meter. Iron(III) chloride (MW: 162.21) and Iron(II) chloride (MW: 162.21) chemicals were obtained from Acros Organics. Ammonium hydroxide solution (14.5M) and hydrochloric acid (12M) were respectively obtained from Acros and Sigma-Aldrich.

**Iron oxide nanoparticles solution preparation**

The solution of iron oxide nanoparticles was synthesized based on the procedure described by Endo (1999). FeCl₂ and FeCl₃ were mixed at a molar ratio of 1:2 into aqueous solution with 2M HCl, then 0.7M NH₃ solution was added to the FeCl₂ and FeCl₃ mixture. The chemical reaction is:

$$2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_3 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl}$$

The reaction mixture was mechanically stirred at a constant speed for 30 minutes at ambient temperature. The chemical precipitation of iron oxide nanoparticles was decanted in the magnetic field and washed with distilled water until pH 7.

**Iron oxide nanoparticles deposited cellulosic fibers**

The aqueous solution of iron oxide nanoparticles was mixed with bleached cellulosic fibers with the mass weight ratio of 1:2 (iron oxide nanoparticles to dry bleached cellulosic fibers) using mechanical stirring (RW 16 BASIC, IKA-WERKE) for 30 minutes to ensure the uniform coating throughout the entire surface of the cellulose fibers. In order to receive a better combination of cellulose fibers and iron oxide nanoparticles, the mixture sat for 2 days, and was then rinsed with distilled water several times to remove unattached iron oxide nanoparticles. The iron oxide deposited-cellulose fibers were dried in an oven (POWERO-MATIC 60, Blue M Electric Company, U.S.A) at a temperature of 100°C until reaching constant weight.
**Pyrolysis treatment**

The dried iron oxide nanoparticles-deposited cellulosic fibers and control bleached cellulosic fibers were pyrolyzed using the procedure illustrated in Fig 2.2. The samples were first placed in a tube furnace (CF56822C, Blue M/Lindberg) under vacuum for two hours, and then purged with nitrogen at 50 ml/min. Samples were heated to the target temperature at a ramping rate of 5 °C/min, the temperature was then maintained for two hours for carbonization, and then cooled down to the room temperature in the nitrogen atmosphere. In this experiment, bleached cellulose fibers (BF) were carbonized at 5 temperatures, 800°C, 1000°C, 1200 °C, 1400 °C and 1600 °C (coded as BF800, BF1000, BF1200, BF1400 and BF1600). Iron oxide nanoparticles deposited cellulose fibers (FeF) were also carbonized at the above 5 temperatures (coded as FeF800, FeF1000, FeF1200, FeF1400 and FeF1600).

![Figure 2.2](Image)

**Figure 2.2**  Heat treatment process

**SEM and X-ray diffraction**

After the pyrolysis treatment, different analytical instruments including SEM, XRD, and Raman Spectroscopy were employed to characterize the morphology of the samples.
A scanning electron microscope (SEM, Zeiss Supra TM 40) was used to analyze the morphology of the microfibers with an accelerating voltage of 15 kV. The surface of the fiber sample was coated with a gold layer of 15 nm thick to provide electric conductivity.

With Cu-Kα radiation (λ= 0.15406nm), the X-ray diffractometer (Rigaku Ultima III) was used over 2θ range of 10˚ to 120˚ (40kV and 44mA). Using Bragg’s law (Eq.2.1), the interlayer spacing $d_{002}$ was calculated.

$$n\lambda = 2d \sin \theta$$

(2.1)

where: $n$ is an integer determined by the given order, and $\lambda$ is the wavelength.

Also, the Scherrer formula (Eq.2.2) was used to obtain crystallite height $Lc$:

$$L = \frac{K\lambda}{B_{2\theta}\cos\theta}$$

(2.2)

$\lambda$ is the wavelength of X-rays used (1.5418Å), $B_{2\theta}$ is the full widths at half maximum and $K$, a constant which was 0.91 for the 002 peak at 2θ=26˚ (Lo et al. 2007; Warren et al. 1965; Kercher et al. 2003).

The average numbers of layers in the direction perpendicular to the 002 plane per the lamella at Scherrer’s approach (Eq.2.3), $N_c$ was obtained from

$$N_c = \frac{L_c}{d}$$

(2.3)

where $L_c$ is the crystallite height and $d$ is interlayer spacing.

**Raman spectroscopy**

As a vibrational spectroscopic technique, Raman Spectroscopy has been used extensively for characterization of material including carbon-based material. In this work we used Raman to investigate the structural characteristics of the cellulosic fiber before
and after graphitization. All Raman spectra were acquired with a LabRam HR800 (Jobin Yvon Horiba) confocal Raman instruments using a 632.8 nm HeNe laser as the excitation source. The laser power is 1.3 mW. To facilitate the spectral acquisition, the heat-treated samples were first ground into small particles (~50 mesh), and a small amount of the resulting powders deposited onto a RamChip slide (Z&S Tech) for Raman spectral acquisition. One distinct advantage for using Ramchip slides as the sample holder is its negligible fluorescence and Raman background (Zhang et al. 2011; Zhang et al. 2010; Vangala et al. 2010). As a result, no substrate background subtraction is needed.

The first-order (1264-2298 cm\(^{-1}\)) Raman spectra were recorded. When the crystalline width, \(L_a\), from the 100 peak (2\(\theta\)=44°) was indefinite, it could be used in the Knight’s empirical formula by the Raman spectra (Gonzalez et al. 2002; Cuesta et al. 1998; Tuinstra et al. 1970):

\[
L_a = 4.35 (I_G/I_D)
\]  

(2.4)

where quantitative \(I_D/I_G\) ratio is the intensity ratio from Raman spectroscopy, \(I_G\) is the intensity of G-mode, and \(I_D\) is the intensity of D-mode. The quantitative \(I_G/I_D\) ratio also represents the degree of graphitization. This method was used as an alternative way to obtain \(L_a\), since the peak of (100) plane at 44° was indefinite in the XRD patterns of this study.

**Results and discussion**

**SEM analysis**

The surface changes of samples before and after the pyrolysis treatment are shown in Figs 2.3 and 2.4. As shown in Fig 2.3 (a) and (b), before the pyrolysis treatment no fine particles are observed on bleached cellulosic fibers. However, for iron
oxide nanoparticles-treated cellulosic fiber, the fine nanoparticles that acted as catalytic seeds of graphitic structure growth (Zickler et al. 2006), are clearly seen densely dispersed over the entire surface of cellulosic fibers in (b).

Figure 2.3  SEM images showing the surface morphologies of (a) bleached cellulose fibers and (b) iron oxide nanoparticles coated cellulose fibers before heat treatment with scale bar of 100 nm.
After pyrolysis treatment at 800˚C, no obvious surface change was observed for the bleached cellulosic fibers as shown in Fig 2.3 (a). On the other hand, the nanoparticles agglomerated on the substrate (Fig 2.3 (b)) contributing to catalytic graphitization at 800˚C. It was also noted that the particle sizes on the fiber specimen pyrolysis at 1,000˚C were larger (Fig 2.4 (c)) than that at 800˚C (Fig 2.4 (b)). The bigger size for the particles at the higher pyrolysis temperature may be due to the gradual stacked graphitic structure around iron oxide nanoparticles. The SEM observation indicated that catalytic graphitization reacted on the nanoparticle surface where the graphitic structure gradually stacked, especially at higher pyrolysis temperature. This result is consistent with the reaction mechanism of catalytic particles, such as iron oxide during the graphitization (Sheng et al. 2009).

Figure 2.4 SEM images showing the surface morphologies of (a) BF800, (b) FeF800 and (c) FeF1000 after heat treatment in nitrogen gas ambient at 800˚C and at 1,000˚C with scale bar of 100 nm.
XRD analysis

XRD patterns of the cellulosic fibers without and with iron oxide nanoparticles at five temperature levels are shown in Fig 2.5. The Bragg’s angle $2\theta$, interlayer spacing of the (002) plane, and numbers of layers in the direction perpendicular to c-axis of iron...
oxide nanoparticles coated cellulose fibers carbonized at 5-level temperatures. Numbers of layer $N_c$ from Scherrer’s equation were based on the assumption of homogeneous distribution of crystallites without irregularity.

In Fig 2.5 (a), two broad peaks near 2θ angles at 18° and 22° corresponding to the reflections of cellulose crystalline structures (Thygesen et al. 2005) occurred in the non-heated cellulose fibers. With increasing pyrolysis temperature these two peaks disappeared, which was caused by the decomposition of crystalline cellulose at the higher temperature. Meanwhile, two broad bands around degrees of 23° and 43° were detected in the XRD patterns of cellulosic fibers pyrolyzed at 800°C to 1,600°C, indicating that the amorphous structures rather than graphitic structures formed in the cellulose-based carbon.

As shown in Fig 2.5 (b), in addition to the 002 diffraction peak near the 2θ angles at 24° indicating the graphitic structure, many peaks were found during the graphitization of iron oxide nanoparticles deposited cellulose fibers. FeF800 and FeF1000 showed the diffraction peaks at 37.66°, 42.88°, 43.7°, 44.66°, 45.84°, 48.60°, 49.12°, and 61.18°, which can sequentially be indexed to the (210), (211), (102), (220), (112), (131), (221), and (222) planes of Fe₃C. On the XRD patterns of FeF samples carbonized at and above 1,200°C, extra peaks were detected at 44.66°, 65°, 82.32°, which can be assigned to the (110), (220) and (211) planes of Fe. These X-ray diffraction patterns revealed that Fe₃O₄ particles were converted to Fe₃C at 800°C and 1,000°C, and then Fe₃C was decomposed to iron at 1,200°C. It has been reported that under a reducing atmosphere (H₂), iron oxides were reduced to iron carbide that acted as the catalyst for the graphitization of cellulosic fibers. The iron carbide is in unstable state that would be further decomposed (Bonnet et al. 2003):
Fe$_3$C $\rightarrow$ 3Fe + C

Figure 2.5  XRD patterns of non-heated cellulose fibers, (a) BF800, BF1000, BF1200, BF1400 and BF1600 (b) XRD patterns of FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.

CO and H$_2$ were produced during the pyrolysis of cellulosic fibers according to the Broido-Shafizadeh Model (Shafizadeh et al. 1973). During the graphitization of cellulose-derived carbon with iron oxide nanoparticles, the reduction of iron oxide nanoparticles occurred in reduction atmosphere due to the hydrogen released by the pyrolysis of cellulose.
As pyrolysis temperature increased, the XRD peak near 2θ of 24° (Fig 2.6), corresponding to the (002) plane of the graphitic structure on FeF samples, became gradually narrower and higher, implying that the graphitization of FeF samples was enhanced as the pyrolysis treatment increased.

Figure 2.6 XRD patterns of non-heated cellulose fibers, (a) BF800, BF1000, BF1200, BF1400 and BF1600 (b) XRD patterns of FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.
As the heat temperature increased from 800°C to 1,600°C, and shown in Table 2.1, the $d_{002}$ spacing decreased from 3.3784 Å to 3.3659 Å, while the crystalline height, $L_c$, and layer numbers, $N_c$, increased from 64.177 Å to 284.476 Å and from 18.996 to 3.3659, respectively. The decrease in $d_{002}$, and the increase in $L_c$ and $N_c$ at the increased pyrolysis temperature, indicated the gradual growth of graphite crystal as the pyrolysis temperature increases. This confirms that the pyrolysis temperature influences the catalytic graphitization of FeF cellulosic fibers samples. Moreover, it was noted that the value of $L_c$ increased significantly when the pyrolysis temperature increased from 1,000°C to 1,200°C. The ramp rates of the increase in $L_c$ and $N_c$ between 1,200°C and 1,600°C was much lower than that between 800°C to 1,200°C, corresponding to a decreasing $d_{002}$,
indicating that the change in degree of graphitization on FeF samples happened between 800˚C to 1,200 ˚C.

Table 2.1  X-ray structural parameters of iron oxide coated cellulose fibers from (002) plane

<table>
<thead>
<tr>
<th>$d_{002}$ (Å)</th>
<th>$L_C$ (Å)</th>
<th>No. Of layers $N_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3784</td>
<td>64.177</td>
<td>18.996</td>
</tr>
<tr>
<td>3.3734</td>
<td>80.201</td>
<td>23.7742</td>
</tr>
<tr>
<td>3.3709</td>
<td>248.711</td>
<td>73.781</td>
</tr>
<tr>
<td>3.3684</td>
<td>251.267</td>
<td>74.595</td>
</tr>
<tr>
<td>3.3659</td>
<td>284.476</td>
<td>84.517</td>
</tr>
</tbody>
</table>

Besides $L_c$, $L_a$ derived from the 100 plane could also be calculated from the peak near 2θ angles at 44.6˚ in XRD patterns. However, as shown in Fig 2.7 (b), the identification of the peak at 44˚ was indefinite, because it was overlapped by Fe (110) at 44.67˚ and Fe₃C (220) at 44.57˚. In this case, the crystallite width, $L_a$, was alternatively obtained from $I_D/I_G$ in the Raman spectrum.

**Raman spectrum analysis**

Figs 2.8 (a) and (b) show the Raman spectra of cellulosic fibers with and without iron oxide nanoparticles after the 5-level pyrolysis treatment, respectively. As shown in Fig 2.8 (a), as the pyrolysis temperature increased cellulosic fibers samples had no discernable change in the intensity of the G band and so produced no graphitic structure of carbon. The shape of D band, derived from amorphous structure of carbon, became sharper which indicated that increasing pyrolysis temperature resulted in the stacked
amorphous structure of carbon without the significant accelerated formation of graphitic structure. In contrast, as the pyrolysis temperature increased, the shape of the G band for FeF samples became narrower and higher, and the D band gradually decreased in Fig 2.7 (b), implying that the amorphous structure of carbon is stacked on the crystalline region. These results further verified the catalytic influence of iron oxide nanoparticles on the graphitization, and the degree of graphitization enhanced by a higher pyrolysis temperature.
Figure 2.8  Raman spectra of (a) BF800, BF1000, BF1200, BF1400 and BF1600 and (b) FeF800, FeF1000, FeF1200, FeF1400 and FeF1600.

The Gaussian curve fitting for the separation of G/D bands of FeF samples is shown in Fig 2.7 (b). The curve fitting was performed to calculate the relative peak intensities ($I_G$ and $I_D$), and full width at half maximum (FWHM). Table 2.2 summarizes these peak intensity values and the crystalline width $L_a$, which were obtained by Knight’s empirical formula from FeF samples. The relationship between the $I_G/I_D$ and the heat-treatment temperature is shown in Fig 2.9.
As the pyrolysis temperature increased, the line widths of two bands gradually decreased and the $R$ and $L_a$ increased. These results indicated that a transformation occurred from disordered amorphous carbon into a higher oriented graphitic structure as the temperature increased. $L_a$ increased significantly from 45.88 Å to 64.5 Å when the pyrolysis temperature increased from 1,000°C up to 1,200°C (Table 2.2). The growth rate of $L_a$ between 1,200°C and 1,600°C was slower than that between 800°C and 1,000°C, as shown in Fig 2.8. These results implied that the graphitization of iron oxide deposited cellulose fibers was significantly accelerated below 1,200°C, and then the rate of growth on the graphitization slowed down after 1,200°C, which is consistent with the results from XRD.
Table 2.2  Raman spectroscopic parameters of iron oxide nanoparticles coated cellulose fibers carbonized under 5 temperatures, obtained from Fig 2. 6 (b)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Band width</th>
<th>Relative intensity</th>
<th>$I_G/I_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D (cm$^{-1}$)</td>
<td>G (cm$^{-1}$)</td>
<td>$R$</td>
</tr>
<tr>
<td>800˚C</td>
<td>151.900</td>
<td>74.628</td>
<td>0.793</td>
</tr>
<tr>
<td>1,000˚C</td>
<td>102.650</td>
<td>62.800</td>
<td>1.055</td>
</tr>
<tr>
<td>1,200˚C</td>
<td>78.727</td>
<td>44.135</td>
<td>1.48</td>
</tr>
<tr>
<td>1,400˚C</td>
<td>71.426</td>
<td>42.881</td>
<td>1.6</td>
</tr>
<tr>
<td>1,600˚C</td>
<td>57.759</td>
<td>39.543</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Conclusions

By the comparison of the cellulose fibers and iron oxide coated-cellulose fibers from X-ray Diffraction and Raman Spectroscopy after heat treatment, the pure cellulosic fibers without iron oxide nanoparticles did not generate a highly ordered graphitic structure even after heating at 1,600˚C. However, iron oxide deposited cellulosic fibers exhibited gradually enhanced graphitization pyrolysed from 800˚C to 1,600˚C, indicating the graphitization of cellulosic fibers was accelerated by iron oxide nanoparticles.

Furthermore, the pyrolysis temperature was primarily conducive to the degree of graphitization on iron oxide nanoparticles deposited cellulosic fibers. The graphitic structure showed a significant increase between 800˚C and 1,200˚C, then the effect of pyrolysis temperature on the graphitization of FeF samples was not significant above 1,200˚C.


CHAPTER III

PHASE TRANSITIONS OF CARBON-ENCAPSULATED IRON OXIDE NANOPARTICLES BY CARBONIZATION OF CELLULOSIC FIBERS AT VARIOUS TEMPERATURES

Introduction

The carbon-iron nanoparticles constituting magnetic core-shell system gained much attraction recently due to its potential in many applications: catalysts, environment, biology, optics, electronics, separation devices and mechanics (Hihara et al. 1994; Si et al. 2003; Zhao et al. 1996; Masuda et al. 2000; Sun et al. 1999; Sun et al. 1999). Employing either crystalline or amorphous carbon as the protective shell to encapsulate the magnetic core consequently improve the magnetic stability of the nanosized particles.

Nanocrystal structures of core components have been investigated for unique applications, since the phases of magnetic nanoparticles in core-shell system are fragile and transferable among iron oxides, iron carbides and iron (Morjan et al. 2009). Iron oxides nanoparticles are of technological importance for promising applications, which result from multivalent oxidation states and polymorphism such as hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄). The recent studies show that thermal decomposition of iron oxide nanoparticles occurs under appropriate conditions. For example, the oxidation of magnetite (Fe₃O₄) into maghemite (γ-Fe₂O₃) nanoparticles occurs at 250°C and an oxygen atmosphere for 2h (Sun et al. 2002). Maghemite (γ-Fe₂O₃), a metastable, low temperature phase of iron oxide, is converted into hematite (α-
Fe₂O₃) at temperature above 300°C due to factors such as surface area, structural defects and crystallinity (Nasrazadani et al. 1993; Schimanke et al. 2000).

Besides iron oxide nanoparticles, an important core compound of Fe₃C (cementite/cohenite) also has attracted interest for applications to construction materials for carbon steel and iron alloys (Goodwin et al. 1997) and magnetic recording media (Morjan et al. 2009).

Carbon-iron oxide nanoparticles system with tunable magnetic properties has the potential to produce low-cost, nontoxic and stable materials. Since the phases of the core component (iron/iron oxide/ iron carbide nanoparticles) are alterable and each one has its own application, the morphology and crystal structures of the core should be intensely and thoroughly investigated. In this research, we show a facile method for the synthesis of carbon-magnetic nanoparticle system by applying four elevated pyrolysis treatments to the mixture of cellulosic fibers and iron oxide nanoparticles. TEM was used to determine the iron/iron carbide nanoparticles encapsulated by graphitic layers. X-ray diffraction and selected-area electron diffraction patterns were performed to analyze the crystalline phase transitions of iron oxide nanoparticles at the various temperatures.

Experimental

Materials

Magnetite (Fe₃O₄) nanoparticles were prepared by the method described by Endo (1999). FeCl₂ and FeCl₃ (a molar ratio of 1:2) were dissolved in 2M HCl. The reaction mixture was mechanically stirred and a 0.7M NH₃ solution was slowly added with continuous stirring for 30 minutes.

\[ 2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_3 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} \]
The black precipitate of magnetite was decanted in the magnetic field, and the suspension washed with distilled water until a pH 7 was measured.

The Fe₃O₄ suspension was added to bleached cellulosic fibers (Weyerhaeuser NR Co.) with mass weight ratio of 1:2 (iron oxide nanoparticles to dry bleached cellulosic fibers) using the efficient mechanical stirring (RW 16 BASIC, IKA-WERKE) 30 minutes. In order to receive a better coating of Fe₃O₄ nanoparticles, the cellulosic fibers were left in the solution for 2 days, and then rinsed with the distilled water several times. The aqueous suspension was filtered to eliminate unattached iron oxide nanoparticles. The product was dried in an oven (POWERO-MATIC 60, Blue M Electric Company, U.S.A) at 100°C overnight.

Carbon encapsulated iron oxide nanoparticles were synthesized by pyrolyzing the combined precursor in tube furnace (CF56822C, Blue M/Lindberg) under which was vacuumed for two hours in a 50 ml/min nitrogen stream, and then were heated to the target temperature with the ramping rate of 5 °C/min for 2 hours for the carbonization. After pyrolysis samples were cooled down in a partial vacuum with nitrogen. In this experiment, the combined precursor - iron oxide nanoparticles-deposited cellulose fibers were pyrolyzed at four temperatures: 500 °C, 800 °C, 1000 °C, 1600 °C. After 500 °C, when the samples were removed from the vacuum, they were immediately immersed with distilled water, to prevent combusting upon exposure to air.

**Methods**

The crystal structures were characterized by X-ray diffraction (XRD) and selected area electron diffraction patterns (SAED). The morphology of the samples was examined by Transmission Electron Microscopy (TEM).
With Cu-Kα radiation (λ = 0.15406nm), the X-ray diffraction patterns were obtained by Rigaku Ultima III over 2θ range of 10° to 120° at 40kV and 44mA. Joint Committee on Powder Diffraction Standards (JCPDS) cards were used to determine chemical compositions and crystal structures of the samples. The Scherrer formula, Eq. 3.1, was used to obtain crystallite sizes \( L \), where \( \lambda \) is the wavelength of X-ray used, \( B \), and \( \theta \) are the full widths at half maximum of X-ray diffraction peaks and half diffraction angle, \( K \) is the constant 0.9 (Nidhin et al. 2008):

\[
L = \frac{K \lambda}{B \cos \theta}
\] (3.1)

TEM measurements were taken on JEOL JEM-100CX II using an accelerating voltage of 100 keV to compare crystallite sizes from XRD analysis. The samples were dispersed in ethanol matrix (100%) and dropped on a carbon-coated microscope grid until solvent evaporated. Selected area electron diffraction using parallel electron beam was taken to identify the crystal structures of samples during the TEM measurements.

**Results and discussion**

X-ray diffraction pattern of iron oxide nanoparticles showed that the chemical component was magnetite (Fe₃O₄), since the main reflections peaks (Fig 3.1) can be assigned to the planes of Fe₃O₄ (JCPD files no.98-0073). The estimation of mean crystallite sizes calculated by Scherrer equation was 9.87nm from the main diffraction peak (311) around 35.4° (Table 3.1). The sharp and strong peaks suggested that iron oxide nanoparticles of Fe₃O₄ have the fine crystal structures and high purity.
XRD analysis (Fig 3.2) of the samples after the pyrolysis treatment of 500°C (CFe500) exhibited two crystal phases under the different ambient conditions: the maghemite (γ-Fe₂O₃) phase (JCPD files no.99-2215), the hematite (α-Fe₂O₃) phase (JCPD files no.98-0060). When samples just removed from the vacuum furnace were exposed to air, they combusted and from the combusted product well-defined peaks can be assigned to hematite (α-Fe₂O₃). On the contrary, samples which were covered by distilled water immediately out of furnace displayed the narrow and strong peaks that can be indexed to maghemite (γ-Fe₂O₃).
Figure 3.2  XRD patterns of Fe$_3$O$_4$ deposited cellulosic fibers at 500°C obtained under different ambient conditions: open to the air (combusted) and covered by distilled water.

The crystal sizes were respectively calculated by the mean reflection peak (311) around 35.6° for γ-Fe$_2$O$_3$ and (104) around 33.16° for α-Fe$_2$O$_3$ (Table 3.1).

Table 3.1 Scherrer mean crystallite dimensions of samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fe$_3$O$_4$</th>
<th>γ-Fe$_2$O$_3$</th>
<th>α-Fe$_2$O$_3$</th>
<th>Fe$_3$C</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide nanoparticles</td>
<td>9.87</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CFe500(combusted)</td>
<td>-</td>
<td>-</td>
<td>44.76</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CFe500(distilled water)</td>
<td>-</td>
<td>13.41</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CFe800</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>57.15</td>
<td>41.16</td>
</tr>
<tr>
<td>CFe1000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>96.61</td>
<td>45.07</td>
</tr>
<tr>
<td>CFe1600</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>34.94</td>
</tr>
</tbody>
</table>

TEM observations (Fig. 3) of either combusted or covered by distilled water CFe500 showed that nanoparticles agglomerated, indicating a coalescent feature. The
SAED pattern of combusted CFe500 shown by the insets had bright spots, which point to the presence of $\alpha$-Fe$_2$O$_3$ (identified by 0.269, 0.229, 0.184, 0.135, 0.114, 0.107, 0.105, 0.961 and 0.908 nm reflections). The rings of CFe500 with distilled water were ascribed to $\gamma$-Fe$_2$O$_3$ (determined by 0.295, 0.252, 0.170, 0.209, 0.161 and 0.148 nm reflections).

![Figure 3.3](image.png)

Figure 3.3 TEM images of samples at 500ºC obtained under different ambient conditions: (a) open to the air (combusted) and (b) covered by distilled water; the corresponding SAED patterns are displayed in the two insets.

After the pyrolysis treatment at high temperatures 800˚C and 1000˚C, the diffraction peaks of samples in XRD patterns (Fig 3.4) displayed a mixture of alpha Fe (JCPD files no.98-0064) and iron carbide (JCPD files no.035-0772). The existence of Fe$_3$C iron carbide were identified by the carbide domain (Alexandrescu et al. 2010).
between 2θ=37˚-50˚, including (210), (002), (201), (211), (102), (220), (031), (112), (131) carbide reflections. The estimation of crystal sizes revealed that nanoparticles of CFe800 had smaller crystal sizes than that of CFe1000 (Table 3.1). The emerging peak (002) around 26˚ for graphitic structure was clearly found in the samples. TEM examination of CFe800 (Fig 3.5) showed that irregular darkish cores of nanoparticles were encased by lighter shell of graphitic structure. Consistent with the XRD, the SAED analysis (inset in Fig.5) exhibited the diffraction rings of Fe, Fe3C and graphitic carbon.

No trace of Fe3C in the samples after the pyrolysis treatment at 500˚C was found, because the shell of graphitic structures that provided the protection of magnetic core had not formed yet. Due to the presence of an oxidant, Fe3C oxidized into γ-Fe2O3 in the samples. The reason of the phase transition of CFe500 from γ-Fe2O3 to α-Fe2O3 after being exposed to the air was the different amount of oxidant the water and the air provided. In crystal structure hematite (α-Fe2O3) was more stable and gave less defects.

Figure 3.4 XRD patterns of samples obtained at under different temperatures: 800°C and 1000°C
Besides the peak of carbon around 26°, the diffraction peaks in the XRD pattern of samples at 1600°C can be indexed to alpha Fe, as shown in Fig 3.6. The crystal size of the core (Table 3.1) was smaller than that of CFe800 and CFe1000. In the TEM (Fig 3.7), the lighter shell seems much thicker and more compact than that of CF800. The SAED pattern displayed the typical rings which can be ascribed to (002), (004) crystal planes for C and (110), (211), (220) crystal planes for Fe.
Figure 3.6  XRD patterns of samples obtained at 1600°C

Figure 3.7  TEM images of samples at 1600°C; the inset represents the corresponding SAED pattern.
Iron oxides are converted into iron carbide at around 600˚C in carburizing and reducing atmospheres (H₂, CO, CO₂) (Bonnet et al. 2003). According to the Broido-Shafizadeh Model (Bonnet et al. 2003), cellulose decomposed and produced CO and CO₂ at lower temperatures of approximately 300˚C. After pyrolysis treatment at 800˚C, samples produced CO and H₂, which provided the reducing atmosphere to convert iron oxide nanoparticles into iron carbide. Fe was also found in the CFe800 and CFe1000; because iron carbide was in an unstable state, and decomposed to Fe and C (Shafizadeh et al. 1973). The crystal sizes of the Fe core seemed smaller than CFe800 and CFe1000 due to the decomposition of iron carbide.

It was reported that iron oxides or partially reduced iron catalyzed the carbonization of carbon materials (Shafizadeh et al. 1973). After 800˚C, the observations of the peak (002) at 26˚ for graphitic structures in XRD and the lighter shell embedded in darker core in TEM indicated that iron carbide/iron nanoparticles acted as nucleation sites for the growth of graphitic structures.

**Conclusions**

The Fe-C system derived from cellulosic fibers with Fe₃O₄ nanoparticles after the pyrolysis treatment was studied. XRD analysis and SAED patterns revealed three major phases: a maghemite (γ-Fe₂O₃) phase, a hematite (α-Fe₂O₃) phase, and iron carbide-iron (Fe₃C-Fe) and iron (Fe) phases. At a lower temperature (500˚C), the oxidation of Fe₃O₄ nanoparticles into γ-Fe₂O₃ occurred in the vacuum. Once in contact with air, samples spontaneously combusted and γ-Fe₂O₃ converted into α-Fe₂O₃. Above 800˚C, core-shell system was observed in TEM. The graphitic structures originated on the surface of iron carbide /iron nanoparticles. The iron carbide and iron formed in the reducing
environment of H₂ and CO produced by the decomposition of cellulose fibers at higher temperature. Iron carbide decomposed to iron above 1600°C, and the Fe-C system exhibited a thicker shell and smaller core than CFe800 and CFe1000.
Literature Cited


CHAPTER IV
CONCLUSIONS

Based on XRD and Raman Spectroscopy after heat treatment, pure cellulosic fibers without iron oxide nanoparticles did not generate a high ordered graphitic structure even after heating at 1,600°C. However, iron oxide deposited cellulosic fibers exhibited gradually enhancing graphitization when pyrolyzed from 800°C to 1,600°C, indicating the graphitization of cellulosic fibers was accelerated by iron oxide nanoparticles.

Furthermore, the pyrolysis temperature was the primary factor to accelerate the degree of graphitization on iron oxide nanoparticles deposited cellulosic fibers. The graphitic structure had a significant increase between 800°C and 1,200°C, and then the effect of pyrolysis temperature on the graphitization of FeF samples was minimal after 1,200°C.

XRD analysis and SAED patterns revealed the three major phases’ transformations of core structure during the different pyrolysis treatments: a maghemite (γ-Fe₂O₃) phase, a hematite (α-Fe₂O₃) phase, and iron carbide-iron (Fe₃C-Fe) and iron (Fe) phases. At lower temperature (500°C), once in contact with air samples spontaneously combusted and converted into α-Fe₂O₃. After pyrolysis at 800°C, samples showed a core-shell system in TEM. The graphitic structures originated on the surface of iron carbide /iron nanoparticles. The iron carbide and iron formed in the reducing force of H₂ and CO produced by the decomposition of cellulose fibers at higher temperature.
Iron carbide decomposed to the iron above 1600°C, and Fe-C system exhibited the thicker shell and smaller core than CFe800 and CFe1000.
REFERENCES


