Materials Letters 203 (2017) 42–45

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Temperature effects on formation of carbon-based nanomaterials from kraft lignin

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ARTICLE INFO

Article history:
Received 4 March 2017
Received in revised form 9 May 2017
Accepted 28 May 2017
Available online 29 May 2017

Keywords:
Kraft lignin
Multi-layer graphene
Formation mechanism
Iron oxides nanoparticles
α-Fe nanoparticles

ABSTRACT

The formation of carbon-based nanomaterials was investigated through heating iron nitrate promoted kraft lignin at different temperatures up to 600 °C under argon gas at atmospheric pressure. High-resolution transmission electron microscopy and electron diffraction images showed that multi-layer turbostratic-structured graphene presented in samples heated at 600 °C. X-ray diffraction results indicated that iron oxides nanoparticles started their formation as an amorphous carbon matrix at 300 °C, and turned into α-Fe nanoparticles at 600 °C. It is believed that the formation of observed multi-layer graphene materials is based on the dissolution and precipitation mechanism of carbonaceous gases from lignin decomposition acting as carbon sources and α-Fe working as the catalyst.

1. Introduction

Lignin is the most abundant aromatic biopolymer on earth [1]. Each year, there are 70 million tons of lignin as a byproduct from the pulping industry worldwide [2]. However, most of the lignin, especially kraft lignin (80% of the world's chemical pulping lignin production [3]), is simply burned onsite for energy and cooking chemical recovery. Lignin contains more than 60% carbon and can be an alternative carbon source for carbon-based nanomaterials production. Carbon-based nanomaterials such as carbon nanotubes, graphene-encapsulated metal nanoparticles, and multi-layer graphene materials, etc. draw much attention from worldwide research groups because of their unique electric, magnetic, and mechanical properties. Recent research activities of using various solid carbon materials such as synthetic polymers [4], saccharides [5], and woody biomass [6–10] as carbon sources to synthesize carbon-based nanomaterials under metal catalysts of various forms such as metallic particles/films and metal salts. Scientists tend to use the dissolution and precipitation theory for interpretation of the formation of graphene materials from solid carbon materials when the metals having a high dissolution capacity of carbon such as iron and nickel are used as the catalyst [10–13]. But limited literature was found in investigating how solid carbon materials participate the formation of graphene materials, i.e., in the gas or solid forms during thermal decomposition of a biopolymer as the carbon source at the wider range of heating temperatures from 200 to 1000 °C when a metal salt is used as the catalyst source, and also the transformation process of the metal salt to metallic catalyst. In our recent study, the mixture of kraft lignin and iron nitrate nonahydrate was thermally treated at different temperature levels up to 1000 °C. The temperature effect on formation of carbon-based nanomaterials was investigated. This paper reported observations and findings from experiments performed at temperatures up to 600 °C.

2. Experimental

2.1. Materials

Kraft lignin supplied by Domtar Corp. (North Carolina) was used as a carbon source, which contained 97.1% lignin, 0.53% ash, and 1.7% sugar, and had a pH value of 6.2. Iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98% purity), from Sigma-Aldrich, Inc., was used as the metal catalyst for the thermal treatment.

2.2. Precursor preparation

40 grams of kraft lignin were impregnated with 200 mL of iron nitrate solution (0.27 mol/L) to prepare the lignin-iron nitrate suspension. The weight ratio of iron to oven-dry lignin was 7.5%.

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http://dx.doi.org/10.1016/j.matlet.2017.05.125
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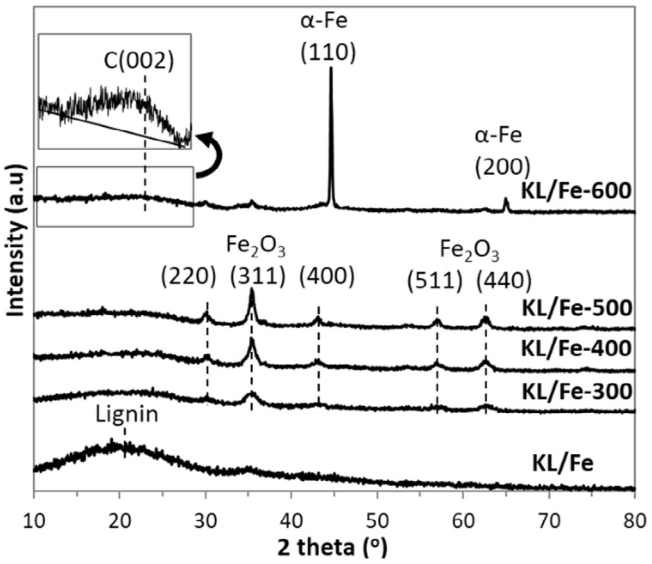

Fig. 1. XRD patterns of KL/Fe and KL/Fe-X samples.

The suspension was stirred in a 120 °C oil-bath for 0.5 h to evaporate water and obtain a sticky mixture, followed by drying the mixture for 2 h at 80 °C and then 48 h at 105 °C to obtain the dried precursor (KL/Fe).

2.3. Thermal treatment

The thermal treatment of KL/Fe samples was carried out in a split-hinge two-inch quartz tube electric furnace (Lindberg/BlueM1200) equipped with a temperature controller (Lindberg/BlueUTC150) under atmospheric pressure with an argon gas at a flow rate of 1.8 L/min. Four targeted temperature levels (300, 400, 500, 600 °C) were evaluated. For each run, four grams of KL/Fe samples were loaded into two porcelain boats (each holds 2 g) and inserted into the middle of the quartz tube. The thermal treatment started with argon gas (99.99%) flowing through the quartz tube for 15 min to remove oxygen from the system, followed by raising the temperature to a targeted level at a ramping rate of 20 °C/min. After holding each evaluated temperature for 1 h, the furnace was turned off. The sample was allowed to cool down naturally to room temperature, then removed out from the quartz tube, ground and labeled as KL/Fe-X, where X represents the evaluated temperature level, for instance, KL/Fe-300 represents the sample heated at 300 °C. In addition to the thermal treatment of KL/Fe samples using the described furnace system, the temperature-programmed decomposition-mass spectroscopy (TPD-MS) analysis of KL/Fe samples (5 g) was performed with the temperature raised from room temperature up to 600 °C at a ramping rate of 10 °C/min in a flowing nitrogen (99.99%, 150 mL/min) atmosphere at room pressure.

2.4. Characterization

X-ray diffraction (XRD) was performed on KL/Fe and KL/Fe-X samples with an Ultima3 diffractometer (CuKα radiation with λ = 1.5406 Å). The grain size of iron compounds in KL/Fe-X samples was calculated using Scherrer equation [14]:

$$L = \frac{0.9\lambda}{\sqrt{\left(B_M^2 - B_S^2\right)} \times \cos\theta}$$

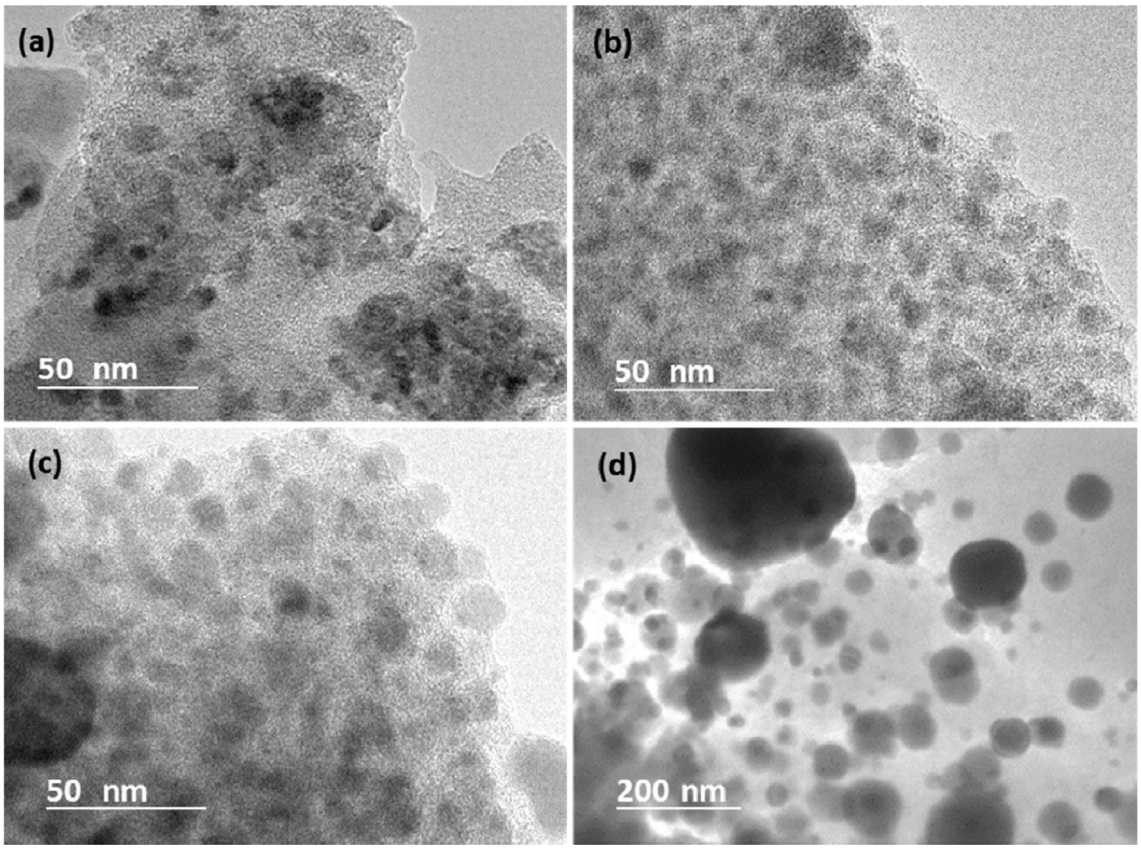

Fig. 2. Bright-field HRTEM images showing particles sizes of (a) KL/Fe-300, (b) KL/Fe-400, (c) KL/Fe-500, and (d) KL/Fe-600 samples, respectively.