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Low temperature synthesis of graphene-encapsulated copper nanoparticles from kraft lignin

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ABSTRACT

The formation of graphene-encapsulated copper nanoparticles was investigated through carbonizing a mixture of kraft lignin and copper sulfate pentahydrate at the temperature up to 500 °C. The abrupt conversion of copper ions into its atoms occurred at 300 °C. The formation of graphene layers surrounding copper nanoparticles started as early as the heating temperature reached 400 °C. Most copper nanoparticles were covered with less than five graphene layers when the temperature reached 500 °C. The average diameter of graphene-encapsulated copper nanoparticles was 12.75 and 11.62 nm for temperature at 400 and 500 °C, respectively. The heating temperature had no significant effect on the size of graphene-encapsulated copper nanoparticles in the evaluated temperature range. It is believed that the formation of graphene-layered shell surrounding copper nanoparticles is based on the mechanism of self-limiting theory with solid carbon as the carbon source.

1. Introduction

Graphene-encapsulated metal nanoparticles (GEMNs) have been extensively studied by scientists in the last decades due to their noble properties, and potential applications ranging from composites to biomedical materials. The unique core-shell structure of GEMNs also enables its application in harsh environment because of the protection from graphene shells [1]. GEMNs have been successfully synthesized by various processes including chemical vapor deposition (CVD) [2], carbon implantation into catalyst substrate [3], thermal treatment [4], etc. However, these methods involve high temperatures up to 2800 °C [5,6] and natural gas is used as the carbon source. Little attention has been paid to the low temperature synthesis process (<600 °C) and the onset of the growth of GEMNs.

The evolution of both carbon and metal catalyst sources before and after the growth of the graphene structure surrounding the metal catalyst is important for understanding the formation mechanism of GEMNs. Understanding the fundamental forming process of GEMNs is also critical to broaden ways to improve the product yield and quality. However, the formation mechanism of GEMNs has not been fully understood experimentally. There are multiple formation mechanisms proposed by scientists based on their experimental results. Recently, scientists are inclined to the dissolution-precipitation theory for metals that have a high dissolution capacity of carbon, such as iron, nickel; and to the self-limiting theory for those have a poor dissolution capacity of carbon, such as copper [7].

Lignin is a renewable carbon source and the second most abundant biopolymer next to cellulose on earth. In general, lignin contains about 60% carbon, 5–6% hydrogen, 0.5–1% ash, and 30% oxygen. The estimated amount of lignin production in the existing pulping industry worldwide is more than 70 million tons per year [8]. The production of value-added products from lignin is difficult due to its complex chemical structure. Lignin is mainly burned onsite to provide steam for power production. However, lignin has many potential usages as a carbon source for the manufacture of value-added carbon-based nanomaterials. In this paper, the mixture of kraft lignin and copper sulfate pentahydrate was carbonized, and the process of forming graphene-encapsulated copper nanoparticles (GECNs) at a low temperature range (<600 °C) was investigated.

2. Experimental

2.1. Materials

Deionized water purified BioChoice Lignin (BCL-DI, Domtar Corp., North Carolina) was used as the carbon source. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) used as the metal catalyst and nitric acid (HNO_3) used for purification were procured from Sigma

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Aldrich. A mixture by weight of 3.9 parts of $CuSO_4$ $5H_2O$ and 4 parts of BCL-DI were dissolved into 10 parts of distilled water. The mixture was heated at 80 °C and kept stirring on a hot plate stirrer for 12 h, followed by 24 h oven dry at 103 °C. The Cu-lignin mixture was ground well in an agate mortar before thermal treatment.

2.2. Thermal treatment

Three replicates at four temperature levels (200, 300, 400, 500 °C) were evaluated. The thermal treatment of a Cu-lignin mixture was carried out in a split-hinge 50 mm-quartz tube electric furnace (Lindberg/Blue M 1200) equipped with a temperature controller (Lindberg/Blue UTC 150). For each experimental run, two porcelain boats, each holding around 1.5 g of Cu-lignin mixture, were placed in the middle of the quartz tube. Before heating, air in the system was excluded by flowing Argon gas for 15 min at a flow rate of 1200 sccm. Then temperature was raised to the evaluation temperature level at a ramping rate of 20 °C/min, and was held at that temperature for 30 min. The furnace was then turned off. The sample cooled down naturally to ambient temperature under an argon atmosphere, and was then transferred to a desiccant.

2.3. Purification

GECNs (0.5 g) was dissolved into 30 ml of 20% HNO_3 solution in a 125 ml conical flask. The suspension was then heated up to the boiling point and kept boiling and stirring for 30 min. The suspension was filtered by a membrane (pore size: 0.45 μm) (VWR, Radnor, PA) and was rinsed with 550 ml deionized water. The residue was dried in the oven at 60 °C for 6 h and then 103 °C overnight.

2.4. Characterization

X-ray diffraction (XRD) Powder was performed with a Rigaku SmartLab X-ray diffractometer (Rigaku) using Cu Ka radiation (λ = 1.5418 Å). Fourier Transform Infa-red Spectroscopy (FTIR) analysis was conducted using a Nicolet™ iS™50 FT-IR Spectrometer (Thermo Scientific™). Each spectrum was obtained in 3 s and the scanning range was from 4000 to 400 cm^{-1}. High-resolution Transmission Electron Microscopy (HRTEM) samples were dissolved in acetone by sonication and then a drop of this suspension was dripped onto a 300 mesh copper grid with a holey support film. HRTEM analysis was performed on a JEM 2100 F (JEOL). The vent gas was analyzed with a Dycor-Dycor Dymaxion Residual Gas Analyzer (RGA) (AMETEK Process Instruments). The size distribution of nanoparticles was analyzed with the ImageJ software (http://imagej.nih.gov/ij/index.html).

3. Results and discussion

3.1. GECN morphology and formation

Fig. 1 shows the TEM images of Cu-lignin mixture heated at 300, 400, and 500 °C, respectively. The copper nanoparticles observed in the mixture heated at 300 °C were not shelled (Fig. 1a); while particles were shelled with graphene layers (Fig. 1b) at 400 and 500 °C. After purification almost all copper atoms in GECNs synthesized at 400 °C were washed out (Fig. 1c), while many GECNs at 500 °C stayed intact. This leaching could be due to the defects of incomplete graphene shells formed around particles. Graphene layers formed at 400 °C could be considered as a premature phase, i.e., the copper particles have not been completely covered with graphene layers yet. As the temperature continued to rise to 500 °C, many copper nanoparticles were completely

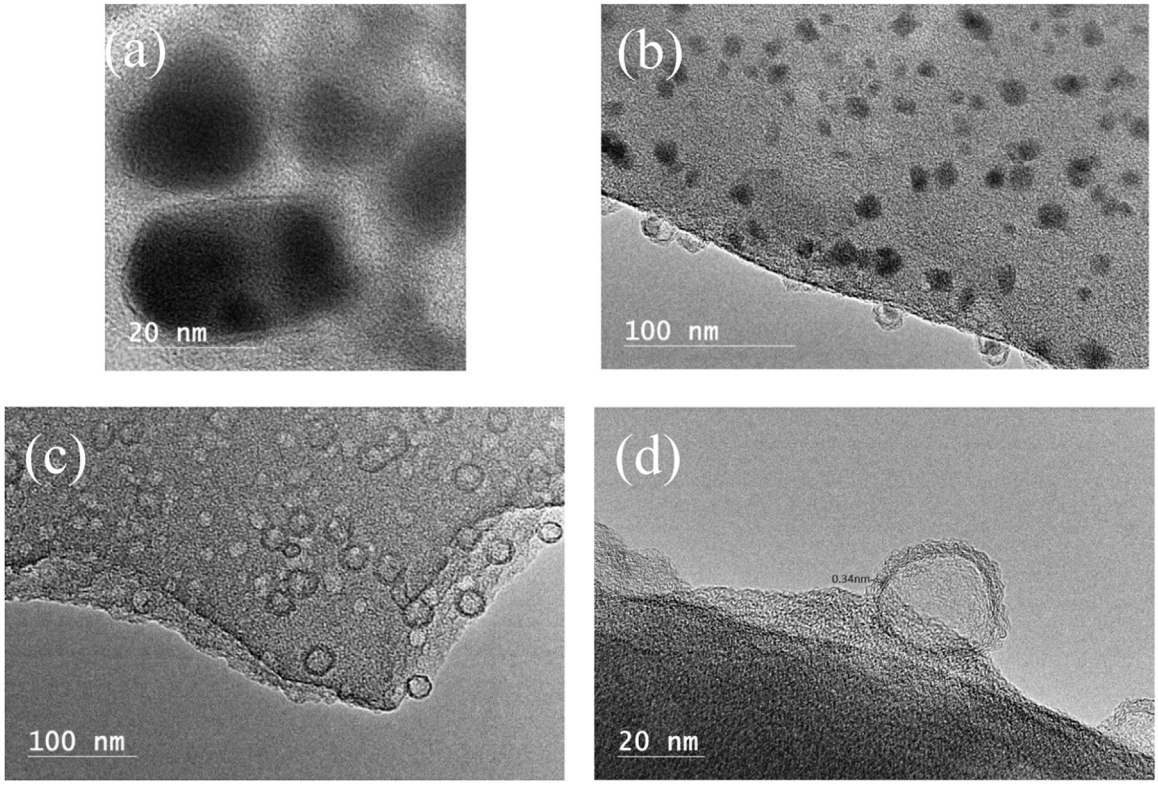

Fig. 1. HRTEM images of Cu-lignin mixture treated at (a) 300 °C, (b) 400 °C w/o HNO_3 treatment; (c) 400 °C with HNO_3 treatment; and (d) emptied graphene-layer shell nanoparticle.

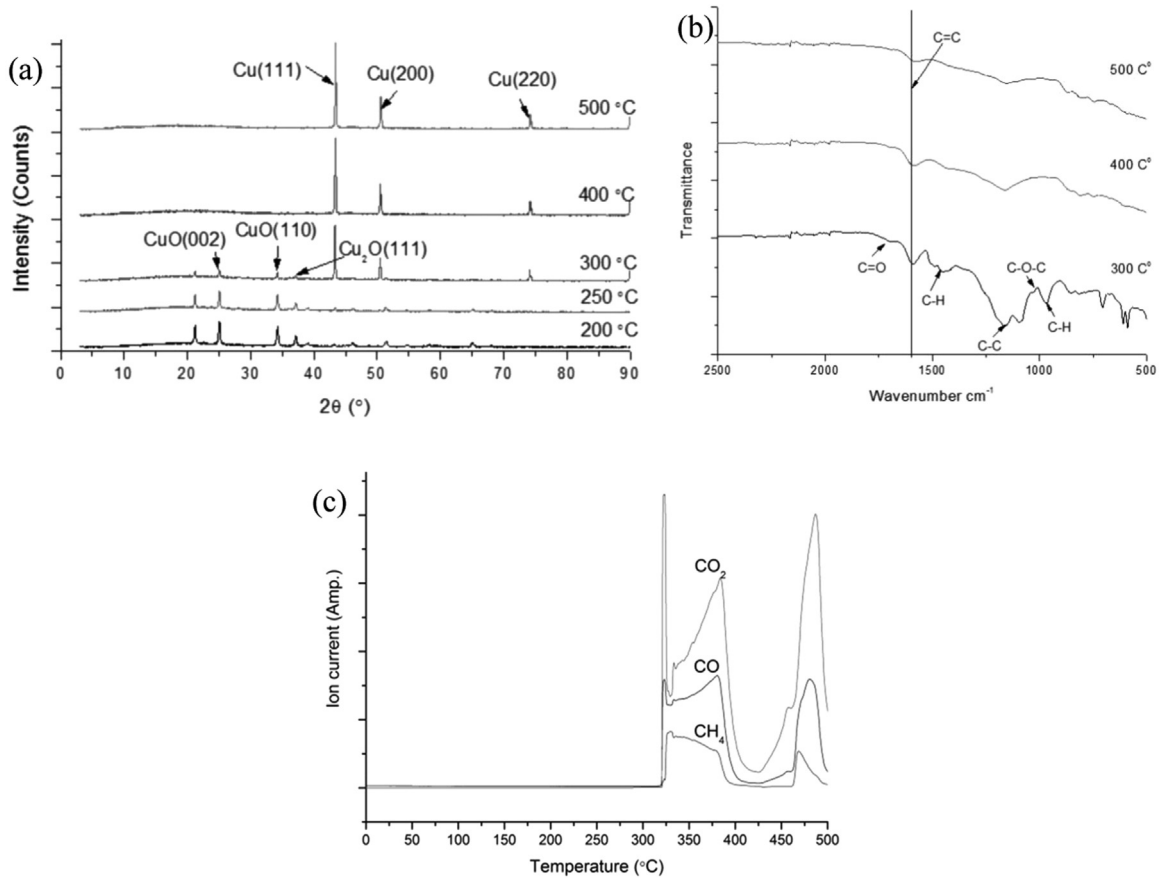

Fig. 2. (a) XRD and (b) FTIR spectra of Cu-lignin mixture treated at various temperatures; and (c) RGA results of gases released from Cu-lignin mixture heated to 500 °C.

covered with graphene layers. Fig. 1d shows a graphene shell with the D-spacing between the graphene layers being 0.34 nm. The number of graphene layers was less than five. The average diameter of graphene-encapsulated copper nanoparticles was 12.75 (with its coefficient of variation of 30%) and 11.62 nm (with its coefficient of variation of 45%) for temperature 400 and 500 °C, respectively. Statistical mean comparison analyses indicated that there was no significant difference between two particle sizes at the 5% significance level. This indicates that temperature has no significant influence on the size of graphene-encapsulated copper nanoparticles in the evaluated temperature range [9].

Fig. 2(a) is the XRD spectra of the Cu-lignin mixture heated from 200 to 500 °C. The spectra shows that copper element existed mainly as Cu^{2+} and Cu^{1+} at 200 and 250 °C, and only few were in the form of copper atoms. This indicates that the copper ions start their conversion to Cu atoms at 200 °C. Large amounts of copper ions were converted into Cu atoms as the temperature increased to 300 °C. As the temperature increased to 400 °C, all copper ions were converted into copper atoms. The valence change of Cu element as the temperature increased from 200 to 500 °C was also accompanied by the decomposition of lignin. The FTIR spectra (Fig. 2b) shows that the intensity of the aromatic C=O bond at 1700 cm^{-1} decreased with increasing temperature from 300 to 500 °C, which indicates the breakdown of C=O bond leading to the release of CO and CO_2 gases [10]. Fig. 2(c) confirmed that large amounts of CO and CO_2 gases were generated at 330, 380, and 480 °C, respectively. The intensity of aromatic C=C bond at 1600 cm^{-1} did not decrease much, because the bond was stable at the low temperature range. The C-H absorbance at 1450 cm^{-1} and below 1000 cm^{-1} decreased as the temperature continuously went up from 300 to 500 °C. The C–O–C bond at around 1050 cm^{-1} vanished at 400 °C. All these results indicate that the structure of lignin changed abruptly above 300 °C, and the carbon source in the form of gas or solid phase for the formation of graphene shells surrounding Cu particles was from the breakdown of C=O, C–H, and C–O–C bonds, rather than the C=C bond.

3.2. GECNs synthesis mechanism

The graphene layers around copper particles may form directly from the gas and melt phase of carbon. As heating temperature researched above 300 °C, copper ions were converted into copper atoms, and formed nanoparticles. Meanwhile, as heating temperature increased to 350 °C an amorphous carbon shell formed around copper nanoparticles [11,12]. As heating temperature continued to rise to 400 °C, the amorphous carbon shell were converted into graphene layers by the catalytic effect of copper. Limited number of graphene layers could be synthesized due to the isolation effect [13]. Many defects would exist on the graphene layers of particles formed at 400 °C, because large amount of oxygen and hydrogen containing functional groups were still in the system. The graphene-layer formation on copper nanoparticles observed in this experiment also would be from a gas phase carbon source, i.e., CH_4. This is because in general lignin starts to release CH_4 at 400 °C [10]. CH_4 is widely used as the gas carbon source to synthesize graphene at a wide range of temperature. CH_4 would be deposited on available surface of copper nanoparticles and grow into graphene layers at a right temperature. The possible explanation of graphene-layers formation at 400 °C is the copper nanoparticle sizes. It was believed that GECNs were mainly formed through solid phase carbon source. This is because gas phase carbon source tends to form a single-layer graphene on the surface of copper due to the low solubility of carbon atoms on copper, which effectively passivates the surface of copper and strongly

obstructs the growth of multilayer graphene [14].

4. Conclusions

The forming process of graphene-layers encapsulated copper-core nanoparticles using kraft lignin as the carbon source was investigated. Abrupt conversion of copper ions into its atom form was observed at 300 °C. The formation of graphene layers could starts at 400 °C, and most copper nanoparticles were covered with less than five graphene layers as heating temperature reached 500 °C. The average diameter of GECNs was 12.75 and 11.62 nm for temperature 400 and 500 °C, respectively. The heating temperature has no significant effect on the size of graphene-encapsulated copper nanoparticles in the evaluated temperature range. It was proposed that the formation of graphene-layers surrounding copper nanoparticles was based on the self-limiting mechanism which used a solid carbon as the carbon source.

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