Inspired by efficient cellulose-dissolving system: Facile one-pot synthesis of biomass-based hydrothermal magnetic carbonaceous materials

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ABSTRACT

The core-shell structure of carbon encapsulated magnetic nanoparticles (CEMNs) displays unique properties. Enhancing the magnetization of iron core, in parallel, improving the encapsulation of carbon shell are the two major challenges in the synthesis of CEMNs. Inspired by efficient cellulose-dissolving system, carbon encapsulated magnetic nano-Fe_3O_4 particles (Fe_3O_4@C) with ~10.0 nm Fe_3O_4 cores and 1.9–3.3 nm carbon shell, were successfully one-pot synthesized *via* a novel hydrothermal carbonization (HTC) process. The dissolving process in ionic liquids ([Emim]Ac and [Amim]Cl) completely cleaved the intra- and intermolecular H-bonds in cellulose, and favored the incorporation of Fe_3O_4 nanoparticles into the cellulose H-bonds systems during the regeneration process. Some stable linkages were formed in Fe_3O_4@C, taking Fe_3O_4 nanoparticles as a structure guiding agent. The morphology and properties of Fe_3O_4@C depended strongly on the type of carbon precursors and pyrolysis temperature. Well encapsulated nanostructure was obtained at HTC temperature 280 °C, when [Emim]Ac-treated holocellulose was used as the carbon source. Meanwhile, the thickness of the amorphous shell and magnetization increased with HTC temperature. More importantly, a novel elements for understanding the growth mechanism for the Fe_3O_4@C composite under HTC conditions was proposed.

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1. Introduction

The synthesis of carbon encapsulated magnetic nanoparticle (CEMNs) has been a hot topic, motivated by its potential applications in adsorbents, electrode, oxidative degradation, catalysis and biomedical applications (Figuerola, Di Corato, Manna, & Pellegrino, 2010; Gupta, Naregalkar, Vaidya, & Gupta, 2007; Qin et al., 2016; Tan, Jiang, Liu, Zhang, & Sun, 2016; Wang, Sun, Duan, Ang, Tade, & Wang, 2015; Yun, Lee, & Park, 2016; Zhang, Wu, Hu, Guo, & Wan, 2008). Carbon layer not only protects the magnetic nanoparticles from rapid environment degradation, also prevents their agglomeration by Van der Waals forces (Wang, Xiao, & He, 2006). Many synthesizing methods, such as arc-discharge method, radio frequency plasma, combustion waves, microwave heating, spray pysolysis, explosion, and chemical vapor condensation, have been extensively attempted (Aomoa et al., 2015; Duman, Tunc, Polat, & Bozoglan, 2016; Jacob, Genish, Klein, & Gedanken, 2006; Saraswati, Ogino, & Nagatsu, 2011; Shin, Yeol Lee, Yeo, & Choi, 2016; Wang, Zhang, Choi, & Kim, 2003; Wang, Zhang, Yu, & Zhao, 2007; Wu, Zhu, Liu, Xie, Zhang, & Hu, 2003; Zhang, Rao, Guo, & Qin, 2016). However, most of these approaches require high temperature and vacuum environment, which typically leads to operational complexity, high costs, and difficulty in the practical applications. Additionally, the unencapsulated nanocrystals and other carbon structures are usually generated, resulting in a very wide size distribution of the particles in a complex matrix. Furthermore, the prepared CEMNs are not applicable to the magnetic separation and adsorption in the biotechnology, since the absence of the available functional group limits the surface modification. Thereby, developing new synthesis methods and subsequently characterizing CEMNs are actively investigated.

Recently, much attentions have been attracted using carbohydrates as the carbon precursor to produce functional CEMNs with a narrow size distribution from the viewpoint of economic,

environmental and societal issues (Ghosh & Paria, 2012). Heating carbohydrates in water in a closed autoclave at the temperature around 180–280 °C for 4–24 h, which is higher than the normal glycosidation temperature and leads to aromatization and carbonization of carbohydrates yields such functional carbonaceous materials (Kruse, Funke, & Titirici, 2013; Titirici, Antonietti, & Baccile, 2008). This process refers to hydrothermal carbonization (HTC), which is a well-known process to prepare functional carbon spheres with superior characteristics that make it a promising route of wide potential application. Until now, glucose, especially, being one of the cheapest and most abundant carbohydrates, has been extensively employed as precursors to prepare CEMNs. It has been reported that the carbon coated Fe_3O_4 nanoparticles can be synthesized by two steps pyrolysis (hydrothermal and high-temperature carbonization) when glucose was used as the carbon precursor (Zhang, Niu, Hu, Cai, & Shi, 2010). Furthermore, the carbon-coated Fe_3O_4 with ~30 nm Fe_3O_4 as cores and 3–7 nm carbon as shells has been successfully fabricated through simple glucose hydrothermal reaction followed by heat treatment (Li, Li, Zhang, & Zhang, 2015). Recently, researchers prepared the CEMNs from a solution of iron chloride ($FeCl_2$) and wood derived sugars under HTC conditions. The obtained nanospheres were approximately 100–150 nm in diameter with an iron core diameter of 10–25 nm. These nanoparticles showed excellent catalytic performance when used as catalysts for the Fischer-Tropsch synthesis process (Yan, Street, & Yu, 2015).

The next challenging step in the preparation of CEMNs is the effective exploitation of lignocellulosic biomass as carbon precursor, which is definitely more complex than that of monosaccharides, oligosaccharides and polysaccharides due to a higher degree of structural complexity and the existence of lignin/hemicelluloses (Himmel et al., 2007). Meanwhile, highly efficient dissolution of biomass is another barrier for the preparation of CEMNs with homogeneous encapsulation and size distribution. Ionic liquids (ILs) were regarded as the most efficient solvents to deconstruct the hierarchy structure, dissolve lignocellulosic biomass, and have the advantage of chemical and thermal stability, nonflammability as well as immeasurably low vapor pressure (Clough et al., 2015; Kong & Chen, 2015). It is therefore the purpose of the present work is to employ the ILs system to dissolve rattan samples and one-pot synthesize the CEMNs in the presence of Fe_3O_4 nanoparticles (designated as $Fe_3O_4@C$) under the HTC condition. In order to avoid the interference of lignin, the hollocellulose was used as the carbon precursor to prepare CEMNs.

It is, to the best of our knowledge, the first time that hollocellulose was employed as a starting material to fabricate low-symmetrical carbonaceous materials by HTC. This method provides a facile, cheap, and general route toward the synthesis of carbonaceous materials with a variety of spheroidal morphologies, which will depend on the employed carbon precursors and temperature. Furthermore, the formation mechanism of the spheroidal CEMNs was explored by a series of experimental observations.

2. Methods

2.1. Materials

The rattan species of *Daemonorops margaritae (Hance)* Becc. was collected from Experimental Center of Tropical Forestry in Guangxi Zhuang Autonomous Region, China. Seven canes of wild rattan with an average length of 19.6 m and diameter of 31.5 mm were processed through a combination of chipping and milling. The rattan powder passing 40-mesh was employed as the starting material in this study. The main components of rattan were determined as: cellulose ~50%, hemicelluloses ~25%, and lignin ~20% (weight% of starting material). All other chemicals used in the

experiment were of analytical reagent grade and used without further purification. Ferric chloride ($FeCl_3 \cdot 4H_2O$) and ferrous chloride ($FeCl_2 \cdot 6H_2O$) were purchased from Beijing Chemicals Corporation (Beijing, China). Ultrapure water was prepared using Milli-Q water purification system (Bedford, MA, USA).

2.2. Isolation of hollocellulose

Delignification process was performed with acidified sodium chlorite following a modified method (Ishizawa et al., 2009). Briefly, 50 g extractive-free rattan sample was immersed with 1 L 7.5% $NaClO_2$ solution (w/v) and incubated at 80 °C for 2 h under acidic circumstance (pH = 3.8–4.0), adjusted with concentrated acetic acid. The process was repeated to ensure maximum lignin removal, and the solid residue was thoroughly washed with distilled water and then freeze-dried.

2.3. Preparation of Fe_3O_4 nanoparticles

The typical procedure for synthesis is described as follows: $FeCl_2 \cdot 4H_2O$ (2 g) and $FeCl_3 \cdot 6H_2O$ (5.2 g) were dissolved into 25 mL ultrapure water, and then acidified with 0.85 mL concentrated HCl. After being well mixed, the resulting solution was dropped into 250 mL of 1.5 M NaOH solution under vigorous stirring and N_2 protection at 80 °C. The obtained magnetic nanoparticles were separated from solution by a powerful magnet rinsed with ultrapure water and finally freeze-dried. The average size of the obtained Fe_3O_4 nanoparticles was around 10 nm, and the representative XRD pattern was indexed as face-centered cubic Fe_3O_4 (JCPDS #89-0688) (Fig. S1). The peaks $2\theta = 18.4°, 30.2°, 35.5°, 37.1°, 43.2°, 53.5°, 57.3°$, and $62.9°$ are corresponded to eight indexed planes (111), (200), (311), (222), (400), (422), (511), and (440), respectively.

Due to the excellent solubility property for cellulose, 30 g ionic liquid (IL) ([Emim]Ac or [Amim]Cl) was loaded into a 100 mL round-bottom flask and preheated to 110 °C to dissolve 3 g rattan holocellulose under nitrogen atmosphere. As the clear light-yellow holocellulose solution was momently obtained, 0.75 g prepared Fe_3O_4 nanoparticle was added and fully distributed with vigorous stirring. The regeneration process was proceed by slowly pouring the homogeneous solution into a large amount of ultrapure hot water (80 °C). In order to recovery ILs as completely as possible, violent agitation of the mixture and at least 3 baths of the regenerated materials were necessary. The solid products were separated by centrifuging and freeze-dried and the yields were determined to be 71% and 91%, respectively, corresponding to [Emim]Ac and [Amim]Cl. The lower yield of [Emim]Ac-treated sample was probably due to the obvious removal of hemicelluoses, which are abundant in holocellulose, under the alkaline conditions. By comparison, the same dosages of holocellulose and Fe_3O_4 nanoparticle were fully distributed in water for 12 h and the solid mixture was collected by filtration. Finally, these three samples were hydrocarbonized in the autoclave at 180 °C, 230 °C, and 280 °C, respectively, for 8 h. The black products were collected, washed with water and ethanol, and oven-dried at 105 °C for 12 h. The data of yields are listed in Table 1, and no significant variation is found among different samples hydrocarbonized at same temperature (for example: $Fe_3O_4@C$-Water$_{180}$, 58.3%; $Fe_3O_4@C$-EmimAc$_{180}$, 60.3%; $Fe_3O_4@C$-AmimCl$_{180}$, 63.4%). It suggests that hydrocarbonization process was not closely related to the dissolving treatment, although the crystal structure of cellulose was altered. On the other hand, the yields of obtained carbon-encapsulated nanoparticles gradually decreased with rising the hydrocarbonization temperature.