Article

Green Synthesis of Carbon-Encapsulated Magnetic Fe₃O₄ Nanoparticles Using Hydrothermal Carbonization from Rattan Holocelluloses

Linxin Dai ¹, Zhi Jin ², Xinge Liu ¹, Long Feng ¹, Jianfeng Ma ^{1,*} and Zhe Ling ^{3,*}

¹ Key Laboratory of Bamboo and Rattan Science & Technology, International Center for Bamboo and Rattan, Beijing 100102, China; dailinxin21@163.com (L.D.); liuxinge@icbr.ac.cn (X.L.); fenglong@icbr.ac.cn (L.F.)

² Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, China; 13661011605@163.com

³ Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

* Correspondence: Majf@icbr.ac.cn (J.M.); jiling19@njfu.edu.cn (Z.L.)

Abstract: How to design a simple and scalable procedure for manufacturing multifunctional carbon-based nanoparticles using lignocellulosic biomass directly is a challenging task. Based on the green chemistry concept, we developed a novel one-pot solution-phase reaction to prepare carbon-encapsulated magnetic nano-Fe₃O₄ particles (Fe₃O₄@C) with a tunable structure and composition through the hydrothermal carbonization (HTC) of Fe²⁺/Fe³⁺ loaded rattan holocelluloses pretreated with ionic liquids (EmimAc and AmimCl). The detailed characterization results indicated that the Fe₃O₄@C synthesized from the holocelluloses pretreated with ionic liquids (ILs) under alkaline conditions tends to have a higher saturation magnetization, probably due to the increased iron ions loading. Moreover, increasing the HTC temperature led to an increased abundance of hydroxyl groups on the surface of the synthesized particles and an elevated saturation magnetization. When EmimAc-treated holocelluloses were used as the carbon precursors, well-encapsulated Fe₃O₄@C nanoparticles were obtained with a maximum saturation magnetization of 42.6 emu/g. This synthetic strategy, coupled with the structure of the iron carbide-based composite and the proposed mechanism, may open a new avenue for the development of carbon-encapsulated iron oxide-based magnetic nanoparticles.

Keywords: rattan holocelluloses; ionic liquids pretreatment; Fe²⁺/Fe³⁺ loading; carbon-encapsulated magnetic nanoparticles

Citation: Dai, L.; Jin, Z.; Liu, X.; Feng, L.; Ma, J.; Ling, Z. Green Synthesis of Carbon-Encapsulated Magnetic Fe₃O₄ Nanoparticles Using Hydrothermal Carbonization from Rattan Holocelluloses. *Coatings* **2021**, *11*, 1397. <https://doi.org/10.3390/coatings11111397>

Academic Editor: Alessio Lamperti

Received: 22 October 2021

Accepted: 10 November 2021

Published: 17 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Carbon-encapsulated magnetic nanoparticles (CEMNs) have distinctive structures and chemistry that make them have a high potential as absorbents [1,2] and electrodes [3,4] and in microwave adsorption [5], oxidative degradation [6], catalysis [7], and biomedical functions [8]. Unlike traditional activated carbon materials [9,10], abundant surface functional groups [11] are easily modified carbon shell and nano-size effect endowed CEMNs with excellent properties in the environmental, energy, and medicine fields. Until now, several approaches have been adopted in preparing carbon-coated nanosized metal particles, but these methods involve high energy consumption, require sophisticated procedures, and have difficulty producing high-purity materials in large quantities [12,13]. Therefore, exploring environmentally friendly and efficient strategies is urgently required in order to overcome these limitations.

Recently, glucose, sucrose, starch, etc., were used as carbon precursors to prepare CEMNs in a water reaction medium under self-generated pressure and moderate temperatures (180–280 °C). By a one-step hydrothermal carbonization (HTC) process of glucose and Fe(NO₃)₃·9H₂O followed by annealing under Ar, uniform and small Fe₃O₄ nanocrystals

(about 9 nm) encapsulated in interconnected carbon nanospheres (about 60 nm) have been fabricated to produce high-rate Li-ion battery anodes [14]. Similarly, a one-pot simple procedure for the preparation of graphite carbon-coated magnetic Fe_3O_4 through a glucose hydrothermal reaction followed by high temperature pyrolysis have been developed [15]. Using a modified hydrothermal method, more complex magnetic carbon composites ($\text{Fe}^0/\text{Fe}_3\text{C@CS}$) have also been synthesized [16]. More recently, lignin-based oligomer precursors were also used to prepare CEMNs. Novel Co@C core-shell nanoparticles were prepared by using a straightforward low-temperature carbonization process [17]. For these carbon precursors being homogeneously dispersed or dissolved in water, the prepared CEMNs achieved a complete core-shell structure and excellent application performance.

However, the next challenging step in the preparation of CEMNs is to directly exploit lignocellulosic biomass as a carbon precursor and find a novel synthesis route to prepare magnetic nanoparticles at a low temperature with higher yields and purities. Although considerable efforts have been directed toward the synthesis of carbon microspheres with insolubilized biomass in water using HTC [18–21], there are few reports concerning the use of lignocellulosic biomass as a carbon precursor in the fabrication of CEMNs. Its use as a carbon precursor is definitely more complex than that of simple sugars due to a higher degree of structural complexity and its insolubility in water. It is, therefore, the purpose of the present study to contribute towards extending HTC from complex biomass to the convenient synthesis of CEMNs. Inspired by a highly efficient biomass dissolving system, in this work, we designed a novel method for fabricating $\text{Fe}_3\text{O}_4\text{@C}$ composites with complete core-shell structures and high saturation magnetization through a green wet chemical route under hydrothermal conditions. In this study, Fe_3O_4 cores were formed via the reaction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ under an alkaline condition. At the same time, the carbon shells that were carbonized from rattan holocelluloses protected the Fe_3O_4 cores. The synthesized products may have promising applications in clinical diagnostics, therapeutics, molecular biology, bioengineering, catalysis, and magnetic storage devices.

2. Materials and Methods

2.1. Materials

The rattan cane (*Daemonorops margaritae* (Hance) Becc.) chips were ground to pass a 40-mesh sieve (aperture of 450 μm) to prepare rattan holocelluloses. The typical procedure is described as follows: rattan powder delignification in aqueous sodium chlorite/acetic acid reagent. The solid-to-liquid ratio was 1:26 (w/v), and the acetic acid and sodium chlorite loads were 0.1 mL/g and 0.3 g/g, respectively. The mixture was heated to 80 $^\circ\text{C}$ and maintained for 1.0 h. After delignification, the samples were carefully washed with deionized water until water pH became neutral. The analytic grade ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from Alfa Aesar Inc. (China). All chemical solutions were prepared using deionized (DI) water with a resistivity of 18.2 $\text{M}\Omega \text{ cm}^{-1}$, which was also used to rinse and clean the samples.

2.2. One-Pot Synthesis of $\text{Fe}_3\text{O}_4\text{@C}$ Nanoparticles

Due to the excellent solubility properties of cellulose, 60 g of ionic liquids (ILs) (EmimAc or AmimCl, Dalian Institute of Chemical Physics, Chinese Academy of Science) was loaded into a 100 mL round-bottom flask and preheated to 110 $^\circ\text{C}$ to dissolve 3 g rattan holocelluloses under nitrogen atmosphere. As a clear light-yellow holocelluloses solution was obtained, a 3 mL solution with 1:1 M ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ was dropped at the same time followed by vigorous stirring. The simultaneous iron ions deposition and cellulose regeneration process was proceeded by slowly pouring the homogeneous solution into a large amount of ultrapure water (80 $^\circ\text{C}$) or alkaline solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$), labelled as ACI/EAC_{H2O} and ACI/EAC_{NH3}, respectively. The precursors were filtered off. After drying in oven at 105 $^\circ\text{C}$ for 12 h, 3 g regenerated holocelluloses precursor was dispersed in 30 mL deionized water. The solution was then sealed in a 50 mL Teflon inlet and heated in an oven at 180 $^\circ\text{C}$, 230 $^\circ\text{C}$, and 280 $^\circ\text{C}$ for 8 h. Then, the obtained nanoparticles were washed

with ultrapure water and ethanol several times, and then freeze-dried. By comparison, the mixtures of 3 g rattan holocelluloses and 3 mL solution with 1:1 M ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ underwent the same treatment to produce the magnetic nanoparticles, denoted as $W_{\text{H}_2\text{O}}$ and W_{NH_3} , respectively. The yields of synthesized nanoparticles were calculated by the following equation:

$$\text{Yield (\%)} = \frac{\text{Weight (CEMNs, g)}}{\text{Weight (Iron ions loaded holocelluloses precursor, g)}} * 100\% \quad (1)$$

2.3. Characterizations

Crystal structure and internal microstructure of CEMNs were identified using an X-ray diffractometer (Philips X'Pert PRO, PANalytical, Almelo, the Netherlands) with a scattering angle ranging from 10° to 80° 2θ and at a scanning speed of $2^\circ/\text{min}$. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Escalab 250 (Thermo Scientific, Waltham, MA, USA) with $\text{Al-K}\alpha$ X-ray to investigate the chemical states of elements. A Shirley background was first subtracted followed by component fitting using Lorentzian-Gaussian functions with a 30% Lorentzian component. 633 nm-Raman spectroscopy (Horiba Jobin Yvon, Kyoto, Japan) was used to investigate the graphitic degree. A 30 s integration time was chosen to achieve spectra with good counting rates, while the laser power of the incident beam was kept at 5 mW to prevent irreversible thermal damage to the specimen surfaces. Surface morphology of the Fe-C products was observed using scanning electron microscopy (Carl Zeiss Merlin, Oberkochen, Germany) at 20 kV. Microstructural characteristics of the samples were characterized by HRTEM at 200 kV (JEOL-2010F, JEOL, Tokyo, Japan). Magnetization measurements of magnetic (Fe-C) nano-composition were performed at room temperature using vibration sample magnetometer (SQUID-VSM, Quantum Design, San Diego, CA, USA). Before all the measurements, the samples were vacuum dried. The thermal stability and degradation behavior for the synthesized materials were characterized by thermogravimetric analysis using a TA analyzer (Discovery TGA 55, TA, New Castle, DE, USA) at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

3. Results and Discussion

3.1. XRD

The XRD patterns of the Fe-C products prepared at 180 – 280°C are shown in Figure 1. The broad peaks centered at 18° for the nanoparticles synthesized at 230°C and 280°C correspond to the amorphous structure of polymer-like carbons [22], indicating that these corresponding feedstocks have been carbonized as carbon. The typical XRD patterns of magnetite ($2\theta = 18.4^\circ, 30.2^\circ, 35.5^\circ, 37.1^\circ, 43.2^\circ, 53.5^\circ, 57.3^\circ$, and 62.9° corresponding to eight indexed planes (111), (200), (311), (222), (400), (422), (511), and (440)) were detected within the series of W_{NH_3} (Figure 1A), EAC_{NH_3} (Figure 1B), Acl_{NH_3} (Figure 1C), and $\text{EAC}_{\text{H}_2\text{O}}$ (Figure S1A) samples. Clearly, the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles were finally obtained after the regeneration of EmimAc-dissolving holocelluloses and were stable under different hydrocarbonization temperatures. However, the typical XRD patterns of magnetite are completely unable to be observed for AmimCl (Figure S1B). The phenomena could potentially be ascribed to the acidity or basicity of the ILs themselves. The EmimAc exhibited a certain alkalinity in favor of forming Fe_3O_4 nanoparticles in the dissolving process, which could have been simultaneously adsorbed on the fibers. Thereby, it is not surprising to observe the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles in this manner after they have been regenerated in hot water. On the contrary, the AmimCl creates an acidic condition, which could be unable to form Fe_3O_4 nanoparticles within the dissolution system, least of all the regeneration in hot water. The data of yields are listed in Table 1, and it can be seen that the yields of the obtained carbon-encapsulated nanoparticles gradually decreased with the rising hydrocarbonization temperature. Moreover, the EAC_{NH_3} procedure was in favor of manufacturing samples with high yields, and, when hydrocarbonized at 280°C , the EAC_{NH_3} -280 nanoparticles displayed the highest yields of 37.9%.

Figure 1. XRD patterns of the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles derived from holocelluloses (A), EmimAc (B) and AmimCl (C) dissolved holocelluloses and regenerated in $\text{NH}_3 \cdot \text{H}_2\text{O}$.

Table 1. Yields, graphite degree, and magnetic parameters of the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles.

Samples	Yield (%) ^a	Raman ^b	Magnetic Parameters		
		I_G/I_D	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
W_{NH_3} -180	53.1	0.53	8.9	0.4	13.6
W_{NH_3} -230	43.1	0.65	11.5	1.0	15.9
W_{NH_3} -280	34.2	0.73	15.2	1.5	20.2
EAC_{NH_3} -180	85.9	0.62	13.1	0.2	3.1
EAC_{NH_3} -230	37.8	0.85	33.6	0.4	2.7
EAC_{NH_3} -280	37.9	0.83	42.6	0.6	4.1
$\text{EAC}_{\text{H}_2\text{O}}$ -180	78.4	0.60	10.4	0.3	2.5
$\text{EAC}_{\text{H}_2\text{O}}$ -230	33.8	0.65	13.8	0.4	1.9
$\text{EAC}_{\text{H}_2\text{O}}$ -280	31.5	0.80	15.1	0.3	2.1
ACI_{NH_3} -180	65.5	0.74	14.2	0.1	1.5
ACI_{NH_3} -230	31.6	0.84	28.2	0.3	1.5
ACI_{NH_3} -280	23.6	0.89	33.0	0.6	0.9
$\text{ACI}_{\text{H}_2\text{O}}$ -180	65.5	0.64	-	-	-
$\text{ACI}_{\text{H}_2\text{O}}$ -230	32.8	0.72	-	-	-
$\text{ACI}_{\text{H}_2\text{O}}$ -280	31.1	0.82	-	-	-

^a Weight% based on the starting material. ^b I_G : Integration of the G band; I_D : Integration of the D band.

3.2. Raman and XPS

Further information about the microstructural evolution of the carbon shell as a function of the HTC temperature was studied using Raman spectroscopy (Figure 2A,B). The typical Raman spectra of the $\text{Fe}_3\text{O}_4@\text{C}$ core-shell structure showed characteristic wide D and G bands around 1340 cm^{-1} and 1585 cm^{-1} , respectively, typical for disordered graphite and graphitic lattice vibration [23,24]. An increase in the I_G/I_D ratios for the series of $\text{Fe}_3\text{O}_4@\text{C}$ demonstrates an enhancement of the degree of graphitization (Table 1). In comparison, the corresponding values for the typical amorphous carbon and highly ordered pyrolytic graphite are approximately 0.3 and 4.0, respectively [25]. This proves that the carbon shells in the $\text{Fe}_3\text{O}_4@\text{C}$ consisted of a low degree of graphite carbon layers.

Figure 2. Raman spectra of the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles W_{NH_3} (A) and EAcNH_3 (B) hydrocarbonized at different temperatures.

XPS has often been used for the surface characterization of various materials, and unambiguous results are readily obtained when the various surface components each contain unique elemental markers [26]. Here, in order to further analyze the carbon shell in the core/shell products, XPS was performed on the nanoparticles obtained by the EAcNH_3 process (Figure 3A and supporting materials Figure S2A,E). The high-resolution XPS C 1s spectra of nanoparticles, shown in Figure 3B and the supporting materials Figure S2B,F, were resolved into five individual component peaks that represent C=C (284.2 eV), C-C (284.8 eV), C-OH (285.3 eV), C-O-C (286.3 eV), O-C=O (288.4 eV), respectively [27]. Meanwhile, it can be observed that, at 180°C , the $\text{Fe}_3\text{O}_4@\text{C}$ is rich in oxygen-containing functional groups (carboxyl and carbonyl groups) (Table 2). Increasing the HTC temperature leads to the increase of C-C (11.9–34.3%) and C-O (21.4–32.3%), which is largely due to intramolecular condensation, dehydration, and decarboxylation reactions. The slight loss of C-C bonds at 280°C is most probably due to the less thermally stable aliphatic carbon chains that are normally present in hydrothermal carbon produced at lower temperatures. The O 1s spectra fitted to four component peaks (Figure 3C and supporting materials Figure S2C,G). Peak I (530.2 eV) corresponds to the C=O or quinone groups, Peak II (531.5 eV) to the C-O-C groups, peak III (532.2 eV) to the C-OH groups, and peak IV (533.2) to the -O-C=O groups [28,29]. The O-C=O contribution to the O 1s profile (peak IV) decreases significantly from 95.6% ($\text{EAcNH}_3\text{-}180$) to 21.7% ($\text{EAcNH}_3\text{-}280$), which is probably due to a reduction of the carboxyl group under acidic conditions. Clearly, the O 1s spectra are consistent with the C 1s profiles, corroborating that there was an increase in the hydroxyl groups on $\text{EAcNH}_3\text{-}280$. From the Fe2p high-resolution spectra (Figure 3D and the supporting materials in Figure S2C,G), there are two peaks at 724.4 and 711.4 eV corresponding to the $\text{Fe}2\text{p}^{1/2}$ and $\text{Fe}2\text{p}^{3/2}$ in Fe_3O_4 [30], respectively.

Figure 3. Original XPS spectrum of the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles EAc_{NH_3} -280 (A), XPS spectrum of C 1s peak (B), XPS spectrum of O 1s (C), XPS spectrum of Fe 2p (D).

Table 2. Experimental C 1s and O1s binding energy (BE eV)/chemical state assignments for the as-synthesized nanoparticles.

Samples	C1	C2	C3	C4	C5	O1	O2	O3	O4
	Carbide C	C-C	C-O	C=O	O=C-O	C=O	C-O-C	C-O	O-C=O
EAc_{NH_3} -180		284.8/11.9%	285.3/21.4%	286.7/55.0%	288.0/11.7%	530.6/5.4%	-	-	533.1/95.6%
EAc_{NH_3} -230	284.2/26.6%	284.8/38.6%	285.3/22.4%	286.3/12.4%	-	530.2/15.1%	531.9/63.5%	-	533.3/21.4%
EAc_{NH_3} -280	284.2/21.2%	284.8/34.3%	285.3/32.3%	286.3/12.2%	-	530.2/23.0%	531.2/26.9%	532.2/28.4%	533.2/21.7%

3.3. SEM and TEM

The as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ hybrids were further characterized using SEM, TEM, and HRTEM images, and SAED patterns. The ILs' dissolution process affects the morphology of the final products greatly. It can be seen that W_{NH_3} -280 displayed non-spherical particles with irregular surface (Figure 4A) and aggregated strongly on the 2D plates (Figure 4B,C). By comparison, the nanoparticles EAc_{NH_3} -280 and ACl_{NH_3} -280 formed spherical aggregation clusters connected by carbonaceous materials (Figure 4D and supporting material Figure S3), which were further confirmed by the TEM image (Figure 4E). An individual particle EAc_{NH_3} -280 at higher magnification clearly shows that the particle has a core-shell structure with an average core size in the range of 6 to 10 nm. It can be seen that the $\text{Fe}_3\text{O}_4@\text{C}$ -EmimAc and $\text{Fe}_3\text{O}_4@\text{C}$ -AmimCl consist of well-dispersed round/ellipsoidal shape nanoparticles. The carbon shell was amorphous, and the core exhibited a single crystalline with homogeneous diffraction rings (inset of Figure 4F). From the HRTEM image, the lattice fringe spacing of 0.252 nm corresponds to the (311) plane of the face-centered structure Fe_3O_4 , indicating that the as-synthesized products were well-crystallized with a high degree of crystallinity.

Figure 4. SEM and TEM images of the Fe₃O₄@C nanoparticles W_{NH3}-280 (A–C), EAc_{NH3}-280 (D–F) and EDS element (C, Fe, O) mapping (G).

3.4. TGA

The TGA–DTA (thermogravimetry analysis and differential thermal analysis) profiles of the thermal behavior between 80 °C and 600 °C for selected samples are presented in Figure 5 and the supporting material Figure S4. A prominent weight loss occurred at a temperature ranging from 300 to 350 °C, which was observed in the Fe₃O₄@C nanoparticles hydrocarbonized at 180 °C. There was still ~35% and ~30% solid residue left at 600 °C, respectively. It has been confirmed that hemicelluloses started decomposition easily, with the weight loss mainly happening at 220–315 °C, and cellulose pyrolysis was focused at a higher temperature range (315–400 °C) [31]. Thus, due to the pyrolysis occurring under nitrogen protection, the dramatic weight loss for EAc_{NH3}-180 and ACl_{NH3}-180 was mainly due to the thermal degradation of the hemicelluloses and partial cellulose [32], though it displayed a thermal curve with a single weight loss dip when a one-step oxidative degradation process of crystalline carbon with oxygen occurred [33]. When the HTC temperature was higher than 230 °C, almost all the holocelluloses were converted into amorphous carbon, with a very high solid residue reaching 65% and 60% for the EAc_{NH3}-280 and ACl_{NH3}-280 samples. Obviously, a higher pretreatment temperature increases the thermal stability of the resultant materials.

Figure 5. TGA (solid line) and DTA (dash line) analysis of $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles EAC_{NH_3} (A) and ACl_{NH_3} (B) hydrocarbonized at different temperatures.

3.5. VSM

Figure 6 shows the magnetic hysteresis loops of the W_{NH_3} and EAC_{NH_3} ; the corresponding M_s , M_r , and H_c values of each sample are tabulated in Table 1. It is clear that the series of EAC_{NH_3} nanoparticles produced by the simultaneous Fe_3O_4 deposition and holocelluloses regeneration process exhibited higher magnetic properties than that of the W_{NH_3} (supporting materials), mainly due to their higher Fe_3O_4 loading. Furthermore, increasing the HTC temperature was found to be beneficial in obtaining $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles with higher magnetic performance, which is attributable to an increase in the crystallinity [34]. By mixing the iron solution with rattan sawdust or rattan charcoal, Hu et al., (2017) prepared a series of magnetic rattan biochar with the saturation magnetization value ranging from 1.52 and 27.11 emu g^{-1} and found that magnetite dominates the crystal phases of the magnetic biochar pyrolyzed at 600–800 °C [35]. Comparatively, the synthesizing procedure in the present work has the potential to prepare magnetic carbon materials with higher saturation magnetization.

Figure 6. VSM magnification curves of $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles W_{NH_3} (A) and EAC_{NH_3} (B) hydrocarbonized at different temperatures.

3.6. Proposed Growth Mechanism of Series $\text{Fe}_3\text{O}_4@\text{C}$ Nanoparticles

Based on the above discussion and the characterization results of a series of nanoparticles, a possible mechanism of the formation process of the carbon-encapsulated iron-core nanoparticles is proposed (Figure 7). When holocelluloses are dissolved in ILs (EmimAc and AmimCl), the intra- and intermolecular H-bonds in the cellulose are completely

cleaved [36,37]. During this process, the anion of the ILs is incorporated into the cellulose surface, attracting the surrounding iron ions. Subsequently, when $\text{NH}_3 \cdot \text{H}_2\text{O}$ is added into the homogeneous systems, the iron ion absorbed on the holocellulose surface will react with the $\text{NH}_3 \cdot \text{H}_2\text{O}$ to form Fe_3O_4 , which is deposited on the surface of the holocellulose. Similar to the mechanisms of pure carbohydrates hydrocarbonization [38–40], regenerated rattan holocelluloses are hydrolyzed into sugars under acidic conditions obtained via the decomposition of H_2O when hydrothermally treated at 180°C . Then, polymerization and condensation reactions may be induced by intermolecular dehydration, dehydrogenation, or aldol condensation. The Fe_3O_4 nanoparticles attached on the surface of the holocelluloses are then combined with small carbonaceous colloids through coulombic interactions with the surface functional groups (e.g., OH and $\text{C}=\text{O}$) and condense to form $\text{Fe}_3\text{O}_4\text{-in-C}$. This is then further assembled to $\text{Fe}_3\text{O}_4\text{@C}$ core/shell nano-spheres via further intermolecular dehydration of the surface functional groups. Stable surface functional groups, such as ether or quinone, are also formed. Once the growth process is stopped, the nano-carbon shells, which cover nano Fe_3O_4 particles, are completed.

Figure 7. Schematic growth models of the as-obtained $\text{Fe}_3\text{O}_4\text{@C}$ nanoparticles.

Actually, the formation of the Fe_3O_4 nanoparticles after the ILs dissolving process is divided into two parts: (1) the iron ions are absorbed on the holocelluloses surface by electrostatic attraction and complexation, and part of the Fe_3O_4 nanoparticles are formed under the basic condition created by the ILs themselves; (2) during the regeneration process, other parts of the Fe_3O_4 nanoparticles are formed by the reaction between the absorbed iron ions and OH^- from $\text{NH}_3 \cdot \text{H}_2\text{O}$. Clearly, the latter process plays a critical role in the formation of Fe_3O_4 , evidenced by the excellent magnetization property of $\text{EAC}_{\text{NH}_3-280}$ (Figure 6B) compared to that of $\text{EAC}_{\text{H}_2\text{O}-280}$ (Figure S5B). In terms of the type of ILs, basic ILs (Figure S1A) favored the formation of Fe_3O_4 nanoparticles in the dissolving process, which could be simultaneously adsorbed on the surface of holocelluloses. Under the same alkaline condition, the magnetic products from ILs-treated holocelluloses, even in acidic ILs (Figure S5A), performed much higher magnetization than those dispersed in water (Figure 6A).

4. Conclusions

In conclusion, a very simple and scalable pathway towards the synthesis of $\text{Fe}_3\text{O}_4\text{@C}$ nanoparticles has been explored. It has been demonstrated that the ILs dissolution and $\text{NH}_3 \cdot \text{H}_2\text{O}$ regeneration procedure was in favor of manufacturing samples with high yields and saturation magnetization. Stable magnetic carbon-encapsulated nano-composites with an average core size in the range of 6 to 10 nm were obtained, which displayed a maximum saturation magnetization of 42.6 emu/g and the highest yields of 37.9%. This method has the potential to provide a simple, energy-efficient, and environmentally friendly approach for preparing carbon-coated nanomaterials, and the proposed mechanism may open a new avenue for the development of carbon-encapsulated iron oxide-based magnetic nanoparticles.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/coatings11111397/s1>, Figure S1: XRD patterns of the Fe₃O₄@C nanoparticles EAcH₂O (A) and ACIH₂O (B) hydrocarbonized at different temperatures, Figure S2: XPS spectra of the Fe₃O₄@C nanoparticles EAcNH₃ hydrocarbonized at 180 °C (A–D) and 230 °C (E–H), respectively, Figure S3: TEM and HRTEM images of the Fe₃O₄@C nanoparticles EAcNH₃-230 (A,B), ACINH₃-230 (C,D), and ACINH₃-280 (E,F), Figure S4: TGA analysis EmimAc dissolved holocelluloses regenerated by hot water, Figure S5: VSM magnification curves of Fe₃O₄@C nanoparticles derived from AmimCl dissolved holocelluloses regenerated by NH₃·H₂O and EmimAc dissolved holocelluloses regenerated by hot water.

Author Contributions: Conceptualization and methodology, X.L.; software and formal analysis, Z.J.; investigation, L.D.; methodology, L.F.; writing—original draft preparation, L.D.; writing—review and editing, Z.L.; funding acquisition, J.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for grants from the Fundamental Research Funds of ICBR (Grant No 1632020013, 1632019028).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Saygılı, H. Hydrothermal synthesis of magnetic nanocomposite from biowaste matrix by a green and one-step route: Characterization and pollutant removal ability. *Bioresour. Technol.* **2019**, *278*, 242–247. [\[CrossRef\]](#)
2. Lee, S.Y.; Lee, J.H.; Kim, Y.H.; Rhee, K.Y.; Park, S.J. Roles of london dispersive and polar components of nano-metal-coated activated carbons for improving carbon dioxide uptake. *Coatings* **2021**, *11*, 691. [\[CrossRef\]](#)
3. Radwan, A.; Jin, H.; Liu, B.; Chen, Z.; Wu, Q.; Zhao, X.; He, D. 3D-ZIF scaffold derived carbon encapsulated iron nitride as a synergistic catalyst for ORR and zinc-air battery cathodes. *Carbon* **2021**, *171*, 368–375. [\[CrossRef\]](#)
4. Zhao, Z.; Zhu, Z.; Zhang, H.; Fang, W.; Jiang, W.; Lin, S.; Yang, Y. Polyurethane sponge-derived nitrogen-doped carbon-encapsulation composite for enhanced lithium-ion battery performances. *Appl. Surf. Sci.* **2020**, *534*, 147631. [\[CrossRef\]](#)
5. Wu, T.; Liu, Y.; Zeng, X.; Cui, T.; Zhao, Y.; Li, Y.; Wang, S. Facile hydrothermal synthesis of Fe₃O₄/C core-shell nanorings for efficient low-frequency microwave absorption. *ACS Appl. Mater. Interfaces* **2016**, *8*, 7370–7380. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Zhang, Z.; Liu, S.; Tian, X.; Wang, J.; Xu, P.; Xiao, F.; Wang, S. Facile synthesis of N-doped porous carbon encapsulated bimetallic PdCo as a highly active and durable electrocatalyst for oxygen reduction and ethanol oxidation. *J. Mater. Chem. A* **2017**, *5*, 10876–10884. [\[CrossRef\]](#)
7. Huang, S.; Meng, Y.; He, S.; Goswami, A.; Wu, Q.; Li, J.; Tong, S.; Asefa, T.; Wu, M. N-, O-, and S-tridoped carbon-encapsulated Co₉S₈ nanomaterials: Efficient bifunctional electrocatalysts for overall water splitting. *Adv. Funct. Mater.* **2017**, *27*, 1606585. [\[CrossRef\]](#)
8. Gupta, A.K.; Naregalkar, R.R.; Vaidya, V.D.; Gupta, M. Recent advances on surface engineering of magnetic iron oxide nanoparticles and their biomedical applications. *Nanomedicine* **2007**, *2*, 23–29. [\[CrossRef\]](#)
9. Dos Reis, G.S.; Larsson, S.H.; Thyrel, M.; Pham, T.N.; Claudio Lima, E.; de Oliveira, H.P.; Dotto, G.L. Preparation and application of efficient biobased carbon adsorbents prepared from spruce bark residues for efficient removal of reactive dyes and colors from synthetic effluents. *Coatings* **2021**, *11*, 772. [\[CrossRef\]](#)
10. He, X.; Zhu, J.; Wang, H.; Zhou, M.; Zhang, S. Surface functionalization of activated carbon with phosphonium ionic liquid for CO₂ adsorption. *Coatings* **2019**, *9*, 590. [\[CrossRef\]](#)
11. Rehman, A.; Park, M.; Park, S.J. Current progress on the surface chemical modification of carbonaceous materials. *Coatings* **2019**, *9*, 103. [\[CrossRef\]](#)
12. Zhang, X.; Navarathna, C.M.; Leng, W.; Karunaratne, T.; Thirumalai, R.V.K.G.; Kim, Y.; Pittman, C.U., Jr.; Mlsna, T.; Cai, Z.; Zhang, J. Lignin-based few-layered graphene-encapsulated iron nanoparticles for water remediation. *Chem. Eng. J.* **2021**, *417*, 129199. [\[CrossRef\]](#)
13. Zhang, Z.; Wen, G. Synthesis and characterization of carbon-encapsulated magnetite, martensite and iron nanoparticles by high-energy ball milling method. *Mater. Charact.* **2020**, *167*, 110502. [\[CrossRef\]](#)
14. Zhao, N.; Wu, S.; He, C.; Wang, Z.; Shi, C.; Liu, E.; Li, J. One-pot synthesis of uniform Fe₃O₄ nanocrystals encapsulated in interconnected carbon nanospheres for superior lithium storage capability. *Carbon* **2013**, *57*, 130–138. [\[CrossRef\]](#)
15. Suma, D.; Deng, D. Facile synthesis of Fe₃O₄@g-C nanorods for reversible adsorption of molecules and absorption of ions. *ACS Sustain. Chem. Eng.* **2015**, *3*, 133–139. [\[CrossRef\]](#)

16. Wang, Y.; Sun, H.; Duan, X.; Ang, H.M.; Tadé, M.O.; Wang, S. A new magnetic nano zero-valent iron encapsulated in carbon spheres for oxidative degradation of phenol. *Appl. Catal. B Environ.* **2015**, *172*, 73–81. [\[CrossRef\]](#)
17. Liu, J.; Xie, L.; Wang, Z.; Mao, S.; Gong, Y.; Wang, Y. Biomass-derived ordered mesoporous carbon nano-ellipsoid encapsulated metal nanoparticles inside: Ideal nanoreactors for shape-selective catalysis. *Chem. Commun.* **2020**, *56*, 229–232. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Barin, G.B.; de Fátima Gimenez, I.; da Costa, L.P.; Souza Filho, A.G.; Barreto, L.S. Hollow carbon nanostructures obtained from hydrothermal carbonization of lignocellulosic biomass. *J. Mater. Sci.* **2014**, *49*, 665–672. [\[CrossRef\]](#)
19. Sevilla, M.; Fuertes, A.B. The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon* **2009**, *47*, 2281–2289. [\[CrossRef\]](#)
20. Ahsan, M.A.; Puente Santiago, A.R.; Rodriguez, A.; Maturano-Rojas, V.; Alvarado-Tenorio, B.; Bernal, R.; Noveron, J.C. Biomass-derived ultrathin carbon-shell coated iron nanoparticles as high-performance tri-functional HER, ORR and Fenton-like catalysts. *J. Clean. Prod.* **2020**, *275*, 124141. [\[CrossRef\]](#)
21. Liu, Y.; Li, X.; Haridas, A.K.; Sun, Y.; Heo, J.; Ahn, J.-H.; Lee, Y. Biomass-derived graphitic carbon encapsulated Fe/Fe₃C composite as an anode material for high-performance lithium ion batteries. *Energies* **2020**, *13*, 827. [\[CrossRef\]](#)
22. Wang, Q.; Liang, X.; Qiao, W.; Liu, C.; Liu, X.; Zhan, L.; Ling, L. Preparation of polystyrene-based activated carbon spheres with high surface area and their adsorption to dibenzothiophene. *Fuel Process. Technol.* **2009**, *90*, 381–387. [\[CrossRef\]](#)
23. Cuesta, A.; Dhamelincourt, P.; Laureyns, J.; Martinez-Alonso, A.; Tascón, J.D. Raman microprobe studies on carbon materials. *Carbon* **1994**, *32*, 1523–1532. [\[CrossRef\]](#)
24. Pawlyta, M.; Rouzaud, J.N.; Duber, S. Raman microspectroscopy characterization of carbon blacks: Spectral analysis and structural information. *Carbon* **2015**, *84*, 479–490. [\[CrossRef\]](#)
25. Wang, Y.; Alsmeyer, D.C.; McCreery, R.L. Raman spectroscopy of carbon materials: Structural basis of observed spectra. *Chem. Mater.* **1990**, *2*, 557–563. [\[CrossRef\]](#)
26. Laszlo, K.; Tombacz, E.; Josepovits, K. Effect of activation on the surface chemistry of carbons from polymer precursors. *Carbon* **2001**, *39*, 1217–1228. [\[CrossRef\]](#)
27. Pittman, C.U., Jr.; Jiang, W.; Yue, Z.R.; Gardner, S.; Wang, L.; Toghiani, H.; y Leon, C.L. Surface properties of electrochemically oxidized carbon fibers. *Carbon* **1999**, *37*, 1797–1807. [\[CrossRef\]](#)
28. Enterría, M.; Martín-Jimeno, F.J.; Suárez-García, F.; Paredes, J.I.; Pereira, M.F.R.; Martins, J.I.; Martínez-Alonso, A.; Tascón, J.M.D.; Figueiredo, J.L. Effect of nanostructure on the supercapacitor performance of activated carbon xerogels obtained from hydrothermally carbonized glucose-graphene oxide hybrids. *Carbon* **2016**, *105*, 474–483. [\[CrossRef\]](#)
29. Li, B.; Dai, F.; Xiao, Q.; Yang, L.; Shen, J.; Zhang, C.; Cai, M. Nitrogen-doped activated carbon for a high energy hybrid supercapacitor. *Energy Environ. Sci.* **2016**, *9*, 102–106. [\[CrossRef\]](#)
30. Descostes, M.; Mercier, F.; Thromat, N.; Beaucaire, C.; Gautier-Soyer, M. Use of XPS in the determination of chemical environment and oxidation state of iron and sulfur samples: Constitution of a data basis in binding energies for Fe and S reference compounds and applications to the evidence of surface species of an oxidized pyrite in a carbonate medium. *Appl. Surf. Sci.* **2000**, *165*, 288–302. [\[CrossRef\]](#)
31. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [\[CrossRef\]](#)
32. Quan, C.; Gao, N.; Song, Q. Pyrolysis of biomass components in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and product characterization. *J. Anal. Appl. Pyrol.* **2016**, *121*, 84–92. [\[CrossRef\]](#)
33. Kumar, A.; Kostikov, Y.; Orberger, B.; Nessim, G.D.; Mariotto, G. Natural laterite as a catalyst source for the growth of carbon nanotubes and nanospheres. *ACS Appl. Nano Mater.* **2018**, *1*, 6046–6054. [\[CrossRef\]](#)
34. Kang, S.; Li, X.; Fan, J.; Chang, J. Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, D-xylose, and wood meal. *Ind. Eng. Chem. Res.* **2012**, *51*, 9023–9031. [\[CrossRef\]](#)
35. Hu, X.; Xu, J.; Wu, M.; Xing, J.; Bi, W.; Wang, K.; Ma, J. Effects of biomass pre-pyrolysis and pyrolysis temperature on magnetic biochar properties. *J. Anal. Appl. Pyrol.* **2017**, *127*, 196–202. [\[CrossRef\]](#)
36. Clough, M.T.; Geyer, K.; Hunt, P.A.; Son, S.; Vagt, U.; Welton, T. Ionic liquids: Not always innocent solvents for cellulose. *Green Chem.* **2015**, *17*, 231–243. [\[CrossRef\]](#)
37. Raj, T.; Gaur, R.; Dixit, P.; Gupta, R.P.; Kagdiyal, V.; Kumar, R.; Tuli, D.K. Ionic liquid pretreatment of biomass for sugars production: Driving factors with a plausible mechanism for higher enzymatic digestibility. *Carbohydr. Polym.* **2016**, *149*, 369–381. [\[CrossRef\]](#)
38. Falco, C.; Baccile, N.; Titirici, M.M. Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons. *Green Chem.* **2011**, *13*, 3273–3281. [\[CrossRef\]](#)
39. Kruse, A.; Funke, A.; Titirici, M.M. Hydrothermal conversion of biomass to fuels and energetic materials. *Curr. Opin. Chem. Biol.* **2013**, *17*, 515–521. [\[CrossRef\]](#)
40. Titirici, M.M.; Thomas, A.; Yu, S.H.; Müller, J.O.; Antonietti, M. A direct synthesis of mesoporous carbons with bicontinuous pore morphology from crude plant material by hydrothermal carbonization. *Chem. Mater.* **2007**, *19*, 4205–4212. [\[CrossRef\]](#)