Chemical Engineering Journal 289 (2016) 261–269

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Synthesis of lightweight, hierarchical cabbage-like composites as superior electromagnetic wave absorbent

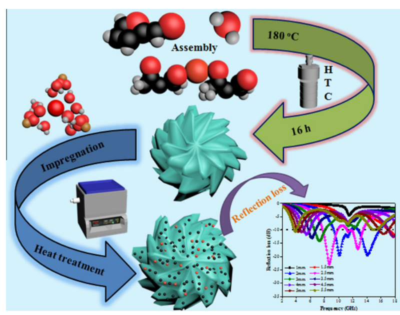
Jia-Liang Lv, Shang-Ru Zhai *, Ce Gao, Nan Zhou, Qing-Da An *, Bin Zhai

Faculty of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China

HIGHLIGHTS

- A new 3D hierarchical cabbage-like electromagnetic wave absorbent.
- The maximum reflection loss (RL) of Fe/CCMs-500 reached −22.9 dB.
- The effective absorption bandwidth (RL ⩽ −10 dB) was 4.32 GHz.
- Wide absorption frequency range, strong absorption ability and light weight.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 November 2015
Received in revised form 29 December 2015
Accepted 2 January 2016
Available online 7 January 2016

Keywords:
3D structure
Electromagnetic wave
Absorption
HTC
Iron

ABSTRACT

Three-dimensional (3D) hierarchical cabbage-like carbonaceous materials (Fe/CCMs-*X*, *X* means treating temperature) have been successfully prepared employing combinatorial processes of cobalt-assisted hydrothermal carbonization (HTC) of furfural and subsequent iron salt impregnation and thermal treatment. This new absorbent was characterized using powder X-ray diffraction (XRD), N_2 adsorption–desorption isotherms, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM) techniques. The maximum reflection loss (RL) of Fe/CCMs-500 reached −22.9 dB, and the effective absorption bandwidth (RL ⩽ −10 dB) was 4.32 GHz (7.76–9.84 GHz and 11.20–13.44 GHz) corresponding to an absorber thickness of 2.5 mm, a low loading amount of iron (6.83%) component and high carbon content (69.8%), clearly demonstrating its wide absorption frequency range and strong absorption ability. It is thus believed that the newly synthesized Fe/CCMs-500 can serve as light-weight electromagnetic wave absorbent and can be potentially used in practice.

1. Introduction

With the advent of the information age, increasing usage of electronic devices and communication facilities in applications, electromagnetic interference problems have caused environmental and health problems, such as the interference to the normal operation of electronic devices as well as harm to human bodies, which are becoming increasingly serious [1–3]. Within this context, it is

Abbreviations: CCMs, cabbage-like carbonaceous materials; Fe/CCMs-*X*, iron-containing cabbage-like carbonaceous composite materials (*X* means treating temperature); GO, graphene oxide; rGO, reduced graphene oxide; GN, graphene/poly (3,4-ethylenedioxythiophene) hybrid materials with Fe_3O_4 nanoparticles; CNT, carbon nanotube.

* Corresponding authors.

E-mail addresses: zhaisr@dlpu.edu.cn (S.-R. Zhai), anqingda@dlpu.edu.cn (Q.-D. An).

http://dx.doi.org/10.1016/j.cej.2016.01.003
1385-8947/

of great significance to absorb or reduce the electromagnetic wave radiation around us. To address these problems, significant efforts have been devoted in past decades toward exploring high-efficiency electromagnetic wave absorption materials that are usually required to have a wide absorption frequency range, strong absorption properties, low density, good thermal stability, and antioxidant capability [4–7].

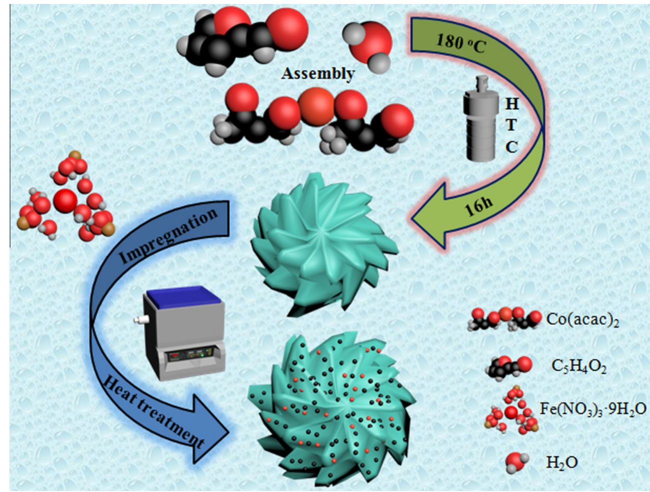
To the best of our knowledge, several materials such as ferrites, metals, carbons and conducting polymers can be applied for electromagnetic wave absorption, but they possess both advantages and disadvantages when applied alone [8–10]. For example, ferromagnetic metals such as Fe, Co and Ni as well as their alloys exhibit strong absorption intensity, while their frequency ranges are usually narrow [11]. By contrast, carbonaceous functional materials are of good lightweight dielectric absorbers, due to their low density, good conductive, chemical inertness and high temperature resistance [12–15]. Besides, iron and carbon are abundant, nontoxic and low-cost. Meanwhile, carbon based and iron based composite materials have good electromagnetic absorption properties and they can meet the strict requirements of electromagnetic wave absorption materials [16–20]. Therefore, iron oxides composited with carbon can become a promising candidate for lightweight microwave absorption materials. To date, the electromagnetic wave absorption property of iron particles have been extensively studied. For example, Liu et al. [21] synthesized GN/PEDOT/Fe_3O_4 nanocomposites and investigated their microwave absorption properties. The minimum reflection loss of the nanocomposites was up to −56.5 dB at 8.9 GHz and the absorption bandwidths exceeding −10 dB were 3 GHz with a thickness of 2.9 mm. Zhang and coworkers [22] synthesized hybrid 3D rGO/Fe_2O_3 composite hydrogel by a hydrothermal method with GO and Fe_3O_4 nanoparticles as the raw materials, and found that the composite exhibited both wider absorption band and a larger reflection loss. More recently, Yang et al. [23] synthesized Fe_3O_4/Ppy/carbon nanotube (CNT) composites by blending the CNTs with Fe_3O_4/Ppy composites and investigated their microwave absorption properties. Although there exists some work on carbon-based and iron-based absorbents toward the electromagnetic wave absorption, it is still a significant challenge to achieve deliberate control over the constituent and architecture of iron-containing carbonaceous composites in a simple and efficient manner.

Fortunately, in this work, a novel electromagnetic wave absorbent, i.e. 3D hierarchical magnetic cabbage-like carbonaceous materials (Fe/CCMs-*X*), has been synthesized utilizing successive procedures of cobalt-assisted HTC of biomass derivate-furfural and impregnation iron salts and subsequent heating treatment. As compared to previous work on carbonaceous materials for electromagnetic wave absorption, the proposed pathway method is relatively easy-to-handle, economic and environmentally friendly. The process of fabrication Fe/CCMs-*X* materials was depicted in Scheme 1. The prepared materials were characterized using various techniques to establish the relationship of structural variation and preparative conditions, and the electromagnetic wave absorption performance was investigated accordingly.

2. Experimental section

2.1. Materials

Furfural and cobalt acetylacetonate (Co(acac)$_2$) were supplied by Aladdin Chemical Co. China. Ethanol and $Fe(NO_3)_3 \cdot 9H_2O$ were purchased from Tianjin Kermel Chemical Reagent Factory, China. All of the Reagents were of analytical grade and were used as received without any further purification. Double distilled water was used throughout this study.



Scheme 1. Fabrication process of cabbage-like electromagnetic wave absorbent.

2.2. Preparation of 3D cabbage-like CCMs

The typical synthesis of the 3D CCMs was carried out as follows [24]: 0.0035 mol of cobalt acetylacetonate (Co(acac)$_2$) and 80 mL of distilled water were put into a beaker. Then, 2.7 mL of furfural was added with stirring until a homogeneous solution was obtained. The resulting solution was transferred into a stainless steel autoclave with capacity of 120 mL, then sealed and heated at 180 °C for 16 h. After that, the gray product was filtrated and washed to neutrality with distilled water and dried at 60 °C overnight. After then, the 3D CCMs were successfully prepared.

2.3. Preparation of Fe/CCMs-X

The iron-containing carbonaceous composite was synthesized by a simple impregnation method. Briefly, 0.0042 mol of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 50 mL ethanol, and was stirred at room temperature for 30 min. Then, 1.0 g of CCMs was added into the $Fe(NO)_3 \cdot 9H_2O$ solution, and the mixture was vigorously stirred for 2 h to make Fe^{3+} homogeneously distributed within carbonaceous materials. Thereafter, the mixture was placed in a water bath at 50 °C to completely evaporate ethanol, and the remaining solid powder was dried at 100 °C for 12 h in a drying oven. Afterwards, the resulting products placed in a tube furnace and was heated at a rate of 10 °C min^{-1} to a designed temperature (500, 600, 700 or 800 °C) in a N_2 atmosphere and kept for 4 h. After being cooled in flowing N_2, the obtained materials were denoted as Fe/CCMs-*X* (*X* = 500, 600, 700, 800), corresponding to varied heating temperatures.

2.4. Materials characterization

The surface morphologies and the particle distribution of Fe/CCMs-*X* were determined by field emission scanning electron microscopy (FESEM, JSM-6460LV, JEOL, Japan) and transmission electron microcopy (TEM, JEM-2000EX electron microscope, JEOL, Japan), respectively. Fourier transform infrared (FTIR, Perkin-Elmer, USA) spectra in the 4000–400 cm^{-1} region were acquired by using KBr pellets. The Raman spectra of the composites were measured with a Laser Raman spectrometer (InVia Reflex; Renishaw Company, London, England). The elemental composition of Fe/CCMs-800 was analyzed by an X-MaxN energy dispersive X-ray analyzer (EDS, OXFORD, UK). X-ray diffraction (XRD) patterns were conducted using a Shimadzu XRD-6100 diffractometer