Composites Science and Technology 134 (2016) 168–174

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Facile preparation of amorphous iron nanoparticles filled alginate matrix composites with high stability

Jian-Fei Huang [a], Yong-Tao Li [b], Jin-Hua Wu [c], Xian-Ming Dong [a], Piao-Yang Cao [a], Yong-Lin Liu [a], Zuan-Tao Lin [d], Gang-Biao Jiang [a], *

[a] *College of Materials and Energy, South China Agricultural University, Guangzhou, 510642, China*
[b] *College of Natural Resources and Environment, South China Agricultural University, Guangzhou, 510642, China*
[c] *School of Environment and Energy, South China University of Technology, Guangzhou, 510006, China*
[d] *Department of Biomedical Engineering, University of Houston, Houston, TX, 77204-5060, USA*

ARTICLE INFO

Article history:
Received 4 February 2016
Received in revised form
14 August 2016
Accepted 20 August 2016
Available online 22 August 2016

Keywords:
Amorphous materials
Polymer-matrix composites
Interface
Sol-gel methods

ABSTRACT

Zero-valent iron nanoparticles have poor chemical stability due to their intrinsic crystal structure and surface energy that greatly limit their practical applications. However, significant improvements can be made *via* preparation of iron nanoparticles in amorphous structure. In this study, we provide a facile strategy to prepare amorphous iron nanoparticles filled alginate matrix composites. Sodium alginate, as the biopolymer matrix of the composites, can successfully inhibit the crystallization of iron nanoparticles and control their formation. In the presence of the alginate matrix, the amorphous iron nanoparticles can be prepared and act as the fillers of the composites. In the stability experiment, the air-exposed composites still remained 89.7% capability under the atmosphere with a relative humidity of 45% at 15 °C for 30 days. The result demonstrated that the amorphous iron nanoparticles of the composites exhibited high stability. Hence, the amorphous iron nanoparticles filled alginate matrix composites are very promising to be used in many fields.

1. Introduction

Iron nanoparticles are widely used in chemical catalyst, electrical conductor and water treatment. However, the crystalline iron nanoparticles have been associated with plenty of drawbacks, including easy corrosion and loss of reactivity, strong tendency to aggregate [1], inhomogeneous properties in microstructure [2] and crystal inherent imperfections such as crystal dislocation, vacancies and phase boundaries [3]. These drawbacks result in their poor stability, greatly limiting their practical applications. Extensive efforts have been devoted to enhance the stability performance of the crystalline iron nanoparticles. For instance, clay had been used as a supporting matrix [4]. Indeed, the dispersion of the nanoparticles can be improved greatly without severe agglomeration by virtue of the support of the solid material, yet the nanoparticles still suffered from corrosion and loss of reactivity when an inert atmosphere, such as a glove box, was not available [5]. Thus, it is worthwhile to explore iron nanoparticles with high stability to meet fast-growing demand of various fields.

Apart from the common crystalline structure, amorphous structure is inherently different, yet it seems not to reached current focus area. Among amorphous materials, amorphous alloys, also called amorphous glasses, are well-known for their high-performance catalytic ability due to their catalytically efficient activity and unique selectivity [6]. Significantly, amorphous phase, has many unique properties that its crystalline counterpart never have. The unique properties are attributed to short-range ordered structure. The short-range ordering means the local ordering that the nearest local atomic configuration including interatomic distances and coordination numbers is constant [7], rather than long-range ordered structure of crystalline phase. By virtue of the special structure of short-range ordered, the short-range ordered structure results in the absence of crystalline structural characteristics, less structural confinement to be isotropic and homogeneous structure, thus is structurally stable at room temperature [8]. Hence, iron nanoparticles in amorphous phase may overcome the limitations derived from crystalline structure.

---

* Corresponding author.
E-mail address: jgb3h@163.com (G.-B. Jiang).

http://dx.doi.org/10.1016/j.compscitech.2016.08.018
0266-3538/

Currently, the preparation of metal in amorphous structure remains a challenge, it is mainly because the amorphous phase is hard to retain during the synthetic process. Although metal-metalloid interactions can raise the structural stability of amorphous structure [9], yet the amorphous phase can be retained *via* the incorporation of the metalloid element (B,P) in the synthetic process, resulting in amorphous alloys (such as Fe-B), rather than amorphous element metal.

Since biopolymer can provide effective means for nanoparticle location control, metal nanoparticle stabilization [10] and nanocomposite creation, in this study, we provide a facile strategy for preparation amorphous iron nanoparticles filled alginate matrix composites (AB-amorphous iron) with high stability. Sodium alginate was selected as the supporting matrix for the in situ preparation of amorphous iron nanoparticles because it can form a specific "egg-box" structure with metal cation [11]. The "egg-box" structure indicates the appropriate interactions between the oxygenic groups of sodium alginate and the Fe^{III} cation. The Fe^{III}-oxygenic group complex acts as the amorphous iron precursor, which can lead to the suppression of crystalline phase nucleation and growth during the reduction process, and controls the nanoparticles growth. Subsequently, the alginate-based amorphous iron nanoparticles can be obtained through sodium borohydride reduction. Moreover, we have evaluated the stability of AB-amorphous iron through their performance in heavy metal removal from solution. Since industrial materials should ideally have high stability and be easy to fabricate, this composites can be considered as one of the candidates.

2. Experimental section

2.1. Chemicals

Chemicals for the AB-amorphous iron: Sodium alginate, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), calcium chloride ($CaCl_2$) anhydrous and sodium borohydride ($NaBH_4$). All of the reagents used were purchased from Guangzhou chemical reagent factory (Guangzhou, China). They were of analytical grade.

2.2. Preparation of the AB-amorphous iron

2.0 g of sodium alginate was dissolved in 100 mL of distilled water and heated to 60 °C. After stirring for about 30 min, sodium alginate solution was dropped into the $CaCl_2$ solution which was prepared by dissolving 10.0 g of $CaCl_2$ into 200 mL of distilled water, by using a cylindrical separating funnel to prepare droplets. Then the framework (AB-Ca^{II}) was formed and immediately transferred into the $FeCl_3 \cdot 6H_2O$ solution which was prepared by dissolving 4.0 g of $FeCl_3 \cdot 6H_2O$ into 200 mL of distilled water, followed by shaking in a shaker and then kept for overnight. After filtration, the amorphous iron precursor (AB-Fe^{III}) was formed and then transferred into $NaBH_4$ solution under the N_2 protection for 30 min. Through reduction by the $NaBH_4$ solution, the amorphous iron nanoparticles of the composites were formed. The as-prepared AB-amorphous iron were filtered and washed thoroughly with absolute acetone, followed by a drying process.

2.3. Characterizations

The structures of the AB-amorphous iron, the AB-Fe^{III} and the AB-Ca^{II} were examined by X-ray diffraction (XRD, Mini Flex 600, Rigaku) with Cu Kα radiation. The specific morphologies of the AB-amorphous iron, the AB-Fe^{III} and the AB-Ca^{II} were examined with field emission scanning electron microscope (FESEM, Ultra 55, Zeiss). The surface morphology of AB-amorphous iron was also observed by using transmission electron microscope (TEM, Tecnai 12, FEI). The elemental composition of AB-amorphous iron surface was determined by energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax 200). The infrared spectra of the AB-amorphous iron, the AB-Fe^{III}, and the sodium alginate were measured by a fourier transform infrared spectrometer (FTIR, Nicolet 6700, Thermo Fisher Scientific). X-ray photoelectron spectroscopy (XPS) spectrum was recorded with a photoelectron spectrometer (K-Alpha, Thermo Scientific) using Al Kα radiation. The charging effect was calibrated using C 1s = 284.8 eV as a reference.

2.4. Pyrolysis experiment

The AB-Fe^{III} was carbonized at a muffle furnace under ambient

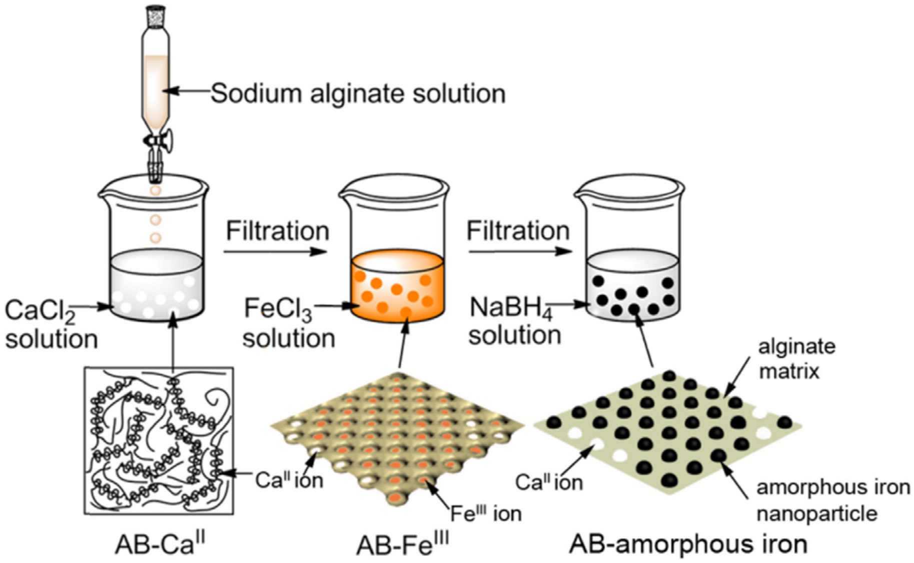

Fig. 1. Schematic illustration of the amorphous iron nanoparticle growth in the alginate substrate.