From Egg Shell Wastes (ESWs) into Advanced Materials: A Rapid and Simple Synthesis of $CaO/Ca_2Fe_2O_5$ as a Novel Nanocomposite-Derived ESW Biomaterial

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ARTICLE INFO

Article history:

Received 25 April 2018
Accepted 20 October 2018
Available online 5 November 2018

Keywords:

$Ca_2Fe_2O_5$
Eggshell waste
CaO
Nanocomposite
Biomaterial
Calcination

ABSTRACT

ESW as a natural byproduct, although non-hazardous and contains calcium, magnesium carbonate and protein, is commonly disposed in landfills without any pretreatment because it was traditionally useless. In this regards, we wish to report the synthesis of a novel $CaO/Ca_2Fe_2O_5$ nanocomposite based on ESW. At the first, eggshell (ES) nanopowder was prepared by ball-milling. Then, the $CaO/Ca_2Fe_2O_5$ nanocomposite as a novel and heterogeneous nanomaterial was synthesized by simply adding an aqueous solution of $FeSO_4$ on the ES nanopowder. After coating the $FeSO_4$ on the surface of the ES powder, the precipitate was collected and calcinated. The synthesized nanocomposite was fully characterized by FTIR, FESEM, TEM, TGA, EDX and XRD analysis. The result was shown that the porous structure of the ESW as a cheap and biomaterial source of Ca was provided good contact area for growing the Fe nanoparticles. The suggested strategy for the synthesis of $CaO/Ca_2Fe_2O_5$ nanocomposite is very interesting due to use of green and low cost starting materials and its simple and clean preparation procedure. The present procedure was successfully provided a useful application of ESW from the environment to synthesis the novel nanomaterials.

1-Introduction

ESW, a bio-ceramic composite, contains different minerals such as $CaCO_3$ (94%), $MgCO_3$ (1%), $Ca_3(PO_4)_2$ (1%) in an organic matrix (4%) like sulfated polysaccharides, other polypeptides and collagen [1, 2]. This material belongs to the most abundant household waste produced by food industry [3]. Chicken ES world production is 50000 tons per year [4]. ESW is a by-product, and its disposal constitutes a serious environmental hazard. Environment pollution due to the ESW of industries encourages our societies to use this bio-waste (BW) product in our research. The advantage of using ES BW is its availability in bulk quantity with lightweight and being environmental friendly [5]. The synthesis of the cheap biomaterials based on ESW is interesting because of the potential to lower cost design of new and advanced materials from BW.

The importance of oxide materials containing Fe has attracted much attention during the last decades due to the exhibition of various applications as pigment [6], anode materials in lithium batteries [7] and catalytic material [8]. CaO–FeO compounds are an important class of

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multi metal oxide materials which composed of the alkaline metals core agent such as Ca, Sr or Ba [9]. Among the CaO–FeO systems, calcium ferrites ($Ca_2Fe_2O_5$) are the well-known compounds with general formula of $A_2B_2O_5$ (A=Ca, Sr; B=Fe, Al) [9]. The brown millerite structure of $Ca_2Fe_2O_5$ has an orthorhombic crystal, which is composed of a three dimensional framework of corner-sharing FeO_6 octahedron and FeO_4 tetrahedron with two oxygen [8]. Despite of considerable importance of calcium ferrites, there are a few reports for synthesis of these materials such as physical mixing method [10, 11], heating the mechanical activated of $Ca(OH)_2$/α-FeOOH mixture [12] and thermal decomposition of $Ca[Fe(CN)_5NO]_4H_2O$ [13]. Also, calcination of Fe_2O_3/CaO or $CaCO_3$ mixture has been reported for the synthesis of $Ca_2Fe_2O_5$ nanoparicles (NPs) [14-16]. Unfortunately, these protocols suffer from different drawbacks such as several heating steps with long reaction times and some impurities. Considering the high cost of preparation of this class of nanomaterials and the complicated and harsh synthetic procedure, a cheaper but efficient method is expected.

According to the best of our knowledge, there is not any report for the application of natural product and especially ESW as a support for synthesis of $Ca_2Fe_2O_5$ NPs. The surface area of natural ES as we reported in our previous research [17] is about 0.0253 m^2g^{-1}, which indicated that ES processed average porosity, whereas, the surface area of pure $CaCO_3$ is 0.0145 m^2 g^{-1} that processed low porosity. So, in the present work, the synthesis of novel $CaO/Ca_2Fe_2O_5$ nanocomposite with maximum Ca/Fe ratio was discussed using ESW as abundant and biomaterial source of Ca by co-precipitation and thermal decomposition methods.

2-Experimental Section

2-1-Materials and methods

IR spectra were obtained with MATSON 1000 FT-IR spectrophotometer. X-ray diffraction (XRD) with an X-Pert Philips PW340/60 diffract meter (40kV and 30mA) and Cu $_{K\alpha}$ radiation (λ=0.154 nm) was used to analyze the crystal structure of the nanocomposite. TGA experiments were carried out using a STA 409 PC Luxx thermal analysis machine (NETZSCH, Germany). The morphology of the cross section of the film was examined with a scanning electron microscopy (FESEM) (Seron Tech. AIS 2100) and transition electron microscopy (TEM) (Philips, CM 120).

2-2-Preparation of $CaO/Ca_2Fe_2O_5$ nanocomposite

The initial ESW nanostructure powder preparation was performed according to our previous method [17]. Following, 1.0 g of the prepared ES powder was mixed with100.0 mL of $FeSO_4$ solution in the concentration of 1000 mg L^{-1} in a baker and shaken in 60ºC. After completion of the reaction (20 min), the as-synthesized nanocomposite (ES/Fe_3O_4) was separated from aqueous solution by using an external magnet. Then the black precipitate of ES/Fe_3O_4 was washed with distilled water and undergone thermal treatment at 900 ºC for 2 h to produce $CaO/Ca_2Fe_2O_5$nanomaterial (Fig. 1).

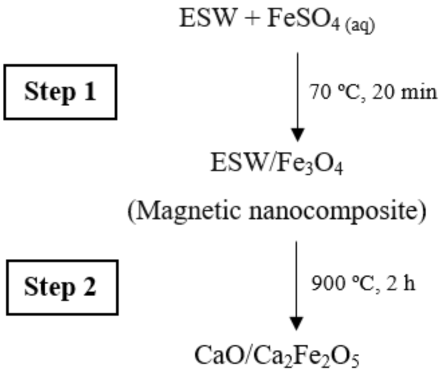

Fig. 1. Schematic preparation procedure of $CaO/Ca_2Fe_2O_5$ nanocomposite.

3-Results and discussion

3-1-Characterization of $CaO/Ca_2Fe_2O_5$ nanocomposite

For the synthesis of $CaO/Ca_2Fe_2O_5$ nanocomposite, first, $CaCO_3/Fe_3O_4$ was simply prepared using heterogeneous stirring an aqueous $FeSO_4$ solution with ESW support as cheap starting materials. ESW acts as bifunctional agent (alkali and support) to precipitate Fe^{2+} without any use of more external alkali, whereas, the literature survey was shown that the magnetic nanoparticles were usually prepared by using a mixture of Fe^{2+} and Fe^{3+}salts and an alkali under protective atmosphere to produce the Fe_3O_4 intermediate [18, 19]. In the present procedure, the Fe_3O_4 crystal was grew on the porous and basic surface of the ESW according to the following reaction (eq. 1). Then the black precipitate of $CaCO_3/Fe_3O_4$was calcined to produce CaO-FeO system. The multi metal oxide system contains CaO and Fe_2O_3 phases which derived from decomposition of $CaCO_3$ and Fe_3O_4respectively [20-22]. The mixture of multi metal oxides was undergone further thermo-chemical reaction to produce $Ca_2Fe_2O_5$[23].

$$FeSO_4 + 2H_2O \rightarrow H_2SO_4 + Fe(OH)_2(aq)$$

$$ESW + Fe(OH)_2(aq) \overset{\Delta}{\rightarrow} CaCO_3/Fe_3O_4$$

$$CaCO_3 \overset{\Delta}{\rightarrow} CaO + CO_2$$

$$Fe_3O_4 + O_2 \overset{\Delta}{\rightarrow} Fe_2O_3$$

and

$$3CaO + Fe_2O_3 \rightarrow CaO/Ca_2Fe_2O_5 \qquad \text{(eq. 1)}$$

3-1-1-XRD analysis

The structure of the obtained nanocomposite derived ESW was characterized by XRD pattern and deduced from comparison with those of known literature [9, 10, 23-25]. Figure 2a shows the XRD results of the calcined ES and the as-synthesized nanocomposite at 900 ºC. The main peak at 2θ =34.2 was identified as the phase of CaO in the both structures of the pure calcined ES and the as-synthesized nanocmposite [21]. The new diffraction peaks that are obviously different from those of calcined ES are related to the major phase of $Ca_2Fe_2O_5$ [25-27]. It indicates that after calcinations, composite metal oxide phase containing Fe^{3+} and Ca^{2+}cations have developed. All the diffraction peaks arising from the structure of the nanocomposite are according to the reported literatures [25-27].

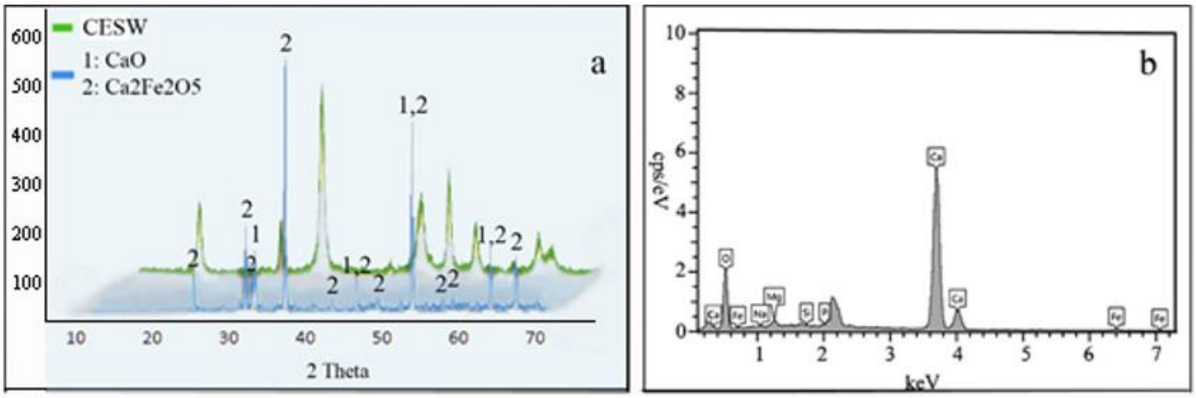

Fig. 2. (a) XRD pattern of nano $CaO/Ca_2Fe_2O_5$ (blue line) and calcined ESW(green line); (b) Energy dispersion x-ray (EDX) analysis of $CaO/Ca_2Fe_2O_5$ nanocomposite.

Further, the chemical composition of the nanocomposite was investigated with energy dispersion x-ray (EDX) analysis of nanocomposite (Fig. 2b) that showed the presence of Ca, O and Fe as major elements. Also, the XRD investigation revealed that the as-synthesized $CaO/Ca_2Fe_2O_5$ has an orthorhombic structure and the mean crystalline size of CaO is 42 nm that calculated by using Scherrer equation ($D=K\lambda /(\beta \cos\theta)$, where λ is the X-ray wavelength in nanometer (nm), β is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and K is a constant related to crystallite shape, normally taken as 0.9).

3-1-2-FTIR spectra and TGA analysis

The FTIR spectra of $CaO/Ca_2Fe_2O_5$ nanostructure and the calcined ES (CaO) (Fig. 3) show the existence of peak at 3430 cm^{-1} which is due to OH in $Ca(OH)_2$ formed during adsorption of water by CaO. The strong bands at around 1150 and 680 cm^{-1} correspond to the Ca-O band. The IR spectrum of the nanocomposite (Fig. 3a) appeared at the same wave number of the calcined ES (Fig. 3b) [21]. The band at 590 cm^{-1} was just observed for $CaO/Ca_2Fe_2O_5$ that indicates the incorporation of metal ion and the formation of the stretching mode of Fe–O in 590 cm^{-1}.

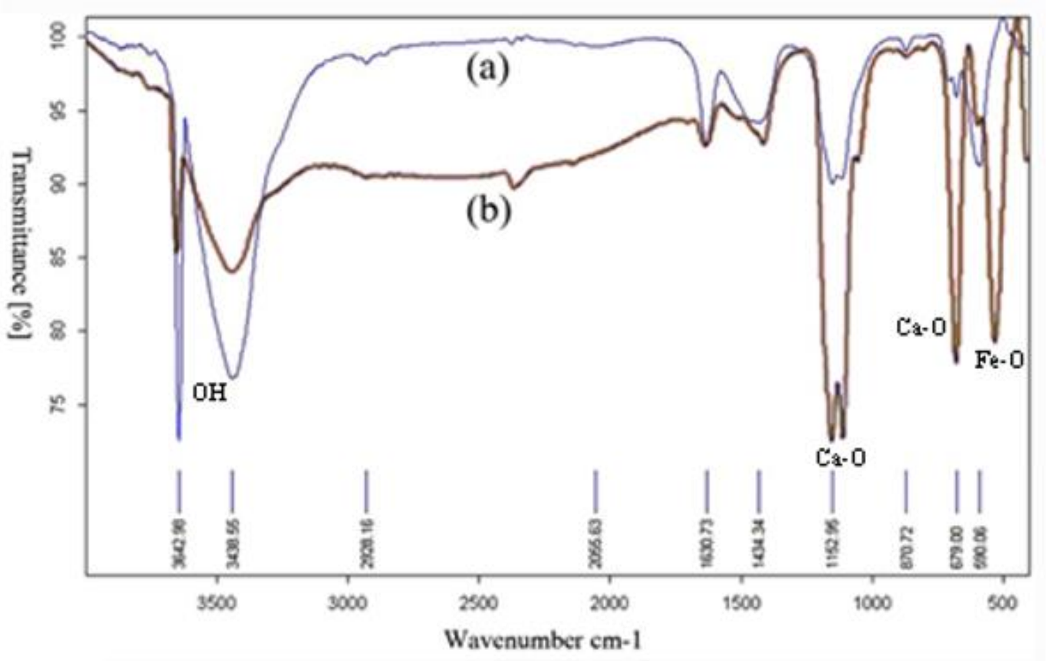

Fig. 3. FTIR spectra of (a) Nano $CaO/Ca_2Fe_2O_5$ and (b) Calcined ESW.

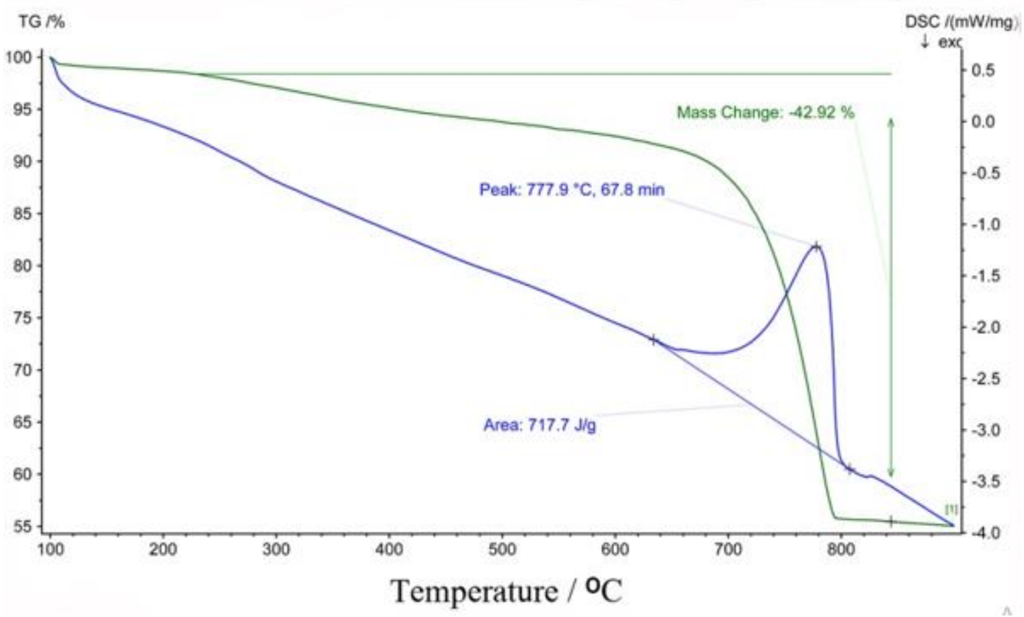

Fig. 4. TGA curves of nano ES supported Fe_3O_4 nanoparticles.

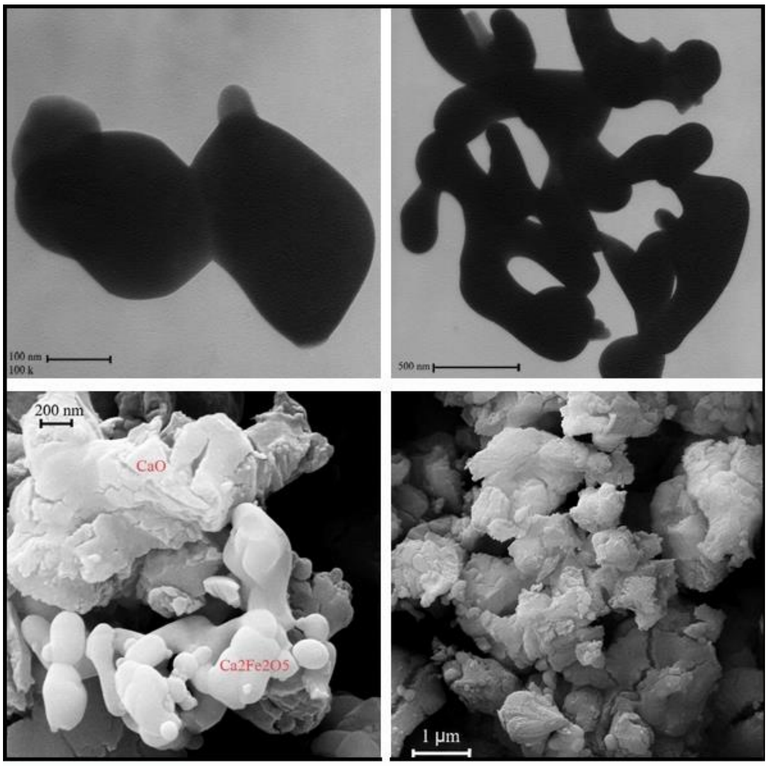

Fig. 5. TEM and FESEM images of $CaO/Ca_2Fe_2O_5$ nanocomposite.

The thermal stability of the nanocomposite was investigated by TGA analysis from room temperature to 900 °C in air (Fig. 4). The thermal decomposition analysis was carried on the $CaCO_3/Fe_3O_4$ to form the desired nanocomposite. The sharp endothermic DSC peak around 778ºC with the main weight loss of 42.92% is related to the decomposition of $CaCO_3$ and Fe_3O_4 to give CaO and $Ca_2Fe_2O_5$ phases and revealed CO_2 and excess O_2 [17,18].

3-1-3-Electron microscopic investigation

TEM and FESEM have provided in order to analyze the surface morphology of the nanocomposite (Fig. 5). The FESEM image shows that the nanoporous structure of ES provided a great surface and large contact area to deposition and grow the Fe^{2+} crystals as cubic. As shown in TEM image, the nanocomposite $CaO/Ca_2Fe_2O_5$ has been synthesized in the form of shell/core like material with high degree of crystallinity and crystallite size of less than100 nm.

The $Ca_2Fe_2O_5$ NPs were usually synthesized via multi steps thermo or mechano-chemical procedures under harsh reaction conditions and in very long time (Table 1) with some impurities [9, 10, 12]. In addition, the previous reports were usually used an additive modifier or alkali such as ammonium or NaOH to raise the *p*H of the reaction suspension up to 9 (Table 1, entries 2-4, 11). It could be achieved from Table 1 that the Fe_2O_3 is more reactive than the other Fe ions and intensively reacts with CaO derived from calcination of $CaCO_3$ to produce $Ca_2Fe_2O_5$. So, the most procedures were used commercially available calcium salts and Fe_2O_3 as starting materials. Also, the $Ca_2Fe_2O_5$ was reported as a magnetic material [25, 26, 31-36], while, the low magnetic property of the $Ca_2Fe_2O_5$ is related to a few impurity of α-Fe_2O_3 which remains from unreacted starting materials [9, 10, 36]. It is due to the use of stochiometric amount of starting materials, whereas, the ratio of 2:1 for Ca/Fe should be used according to the eq. 2:

$$Ca^{2+} \xrightarrow{thermal\ treatment} CaO$$

$$2CaO + Fe_2O_3 \overset{\Delta}{\rightarrow} Ca_2Fe_2O_5$$

eq. 2

Table 1. A comparison of various methods in the synthesis of $Ca_2Fe_2O_5$ phase.

Entry	Starting materials	Procedure	Total time	Reference
1	Fe_2O_3, $CaCO_3$	Calcination: 1100 ºC, 24 h	24 h	28
2	$Fe(NO_3)_3.9H_2O$, $Ca(NO_3)_2.4H_2O$	1: Co-precipitation: 50 ºC (step 1) and NaOH, 100 ºC, 2 h (step 2) 2: Drying: 120 ºC, 20 h 3: Calcination: 600 ºC	>22 h	26
3	$CaCl_2$, $FeSO_4$, dl-Serine	1: Co-precipitation: NaOH, 100 ºC, 2 h 2: Drying: 100 ºC, 1 h 3: Ignition in silica crucible: 500 ºC, 4 h 4: Purification in EtOH: 3-4 times	7 h	29
4	$Ca(NO_3)_2$, $Fe(NO_3)_3$	1: Co-precipitation: Urea, 408 K, 12 h 2: Settling: 368 K, 12 h 3: Drying: 353 K, 48 h in a vacuum drier 4: Calcination: 1073 K, 5 h in a muffle furnace	77 h	25
5	Fe_2O_3, $CaCO_3$	1: Calcination: 500 ºC, 2 h (step 1) and 950 °C, 16 h (step 2) 2: Sintering: 1050 °C, 6 h	27 h	9
6	Fe_2O_3, CaO	1: Calcination: 1000 ºC, 3 h	3 h	10
7	Fe_2O_3, $CaCO_3$	1: Grounding, pressing and then heating at 1273 K, 20 h. 2: Heating 1473 K., 50 h.	70 h	30
8	$Ca(OH)_2$, FeOOH	1: Ball mill, 10 min 2: Calcination: 400-1100 ºC 3: Evacuation: 500 ºC, 0.5–1 h	unknown	31
9	Fe_2O_3, $CaCO_3$	1. Solid-state reaction at 1000 ºC, 24 h 2. a) Cooling; b) regrinding 3. Re-heating, 1100 ºC, 24 h 4. Cooling (3 ◦C/min)	>58 h	32
10	Fe_2O_3, $CaCO_3$	1. Drying starting materials 200-500 ºC, 2 h 2. Decarbonation, 700-1050 ºC, 16 h 3. Firing, 1350 ºC, 2 days	66 h	33
11	$Fe(NO_3)_3$, $Ca(NO_3)_2$, Citric acid	1. Mixing, ammonia, 70 ºC 2. polymerization under IR irradiation, >10 h 3. Drying 4. Calcination, 450 ºC, 2 h 5. Heating, 800 ºC, 4 h	>16 h	34
12	$Fe(NO_3)_3\cdot9H_2O$, CaO	1. a) DriyingCaO, 120 ºC, 10 h; b) Calcination 900 ºC, 4 h. 2. Mixing the suspension 3. Drying, 110 ºC, 12 h 4. Calcination: 900 ºC, 5 h	31 h	27
13	Fe_2O_3, $CaCO_3$	1. Thermal treatment,1223 K, 24 h 2. Annealing with grinding, 1473 K, 24 h.	48 h	35
14	Fe_2O_3, $CaCO_3$	1. a) Grinding, b) Calcination, 950 ºC, 24 h 2. a) Regrounding b) sintering, 1150 ºC, 24 h 3. a) Regrounding b) Pressing, 400 atm 4. Sintering, 1200 ºC, 20 h 5. Crystal growing in IR-heated image furnace	>68 h	36
15	ESW, $FeSO_4$	1: Co-precipitation: 60 ºC, 20 min 2: Calcination: 900 ºC, 2 h	2.3 h	Present work

In this regards, we used ESW as cheap source of $CaCO_3$ with high porosity and wide nucleation sites for the growing NPs under mild reaction conditions at the lowest time. The ES has a basic nature which can provide an alkaline media with *p*H of 9.5 by forming $Ca(OH)_2$ in its surface structure. More addition, the Fe_2O_3 was synthesized in-situ and undergone further thermal reaction to produce $Ca_2Fe_2O_5$ without any impurity (eq. 1). So, we could success to decrease the steps of the procedures to two steps with total time of 2.3 h without an external alkali by using simple starting materials.

4. Conclusion

In summary, high efficient, convenient and alkali-free synthesis of $CaO/Ca_2Fe_2O_5$ nanocomposite has been established by simply heterogeneous stirring $FeSO_4$ aqueous solution with ESW as coating and cheap biomaterial via a thermal co-precipitation and then calcination method. Moreover, the $CaO/Ca_2Fe_2O_5$ NPs has been synthesized in orthorhombic and brownmillerite structure without the Fe_2O_3 or Fe_3O_4 impurity. The structure of the nanocomposite was characterized and approved by FTIR. Also, XRD and EDX analysis were dedicated the chemical composition of the nanocomposite. TEM and FESEM images were shown the particles size less than 100 nm. Also, the images were shown the smooth and great surface for the novel nanocomposite. Furthermore, The TGA analysis was approved the synthesis of the nanocomposite by showing a sharp endothermic DSC peak around 778ºC with the main weight loss of 42.92% related to the decomposition of $CaCO_3$ and Fe_3O_4 to give CaO and $Ca_2Fe_2O_5$ phases. Finally, the present research introduced the fast, clean and facile method for the synthesis of $CaO/Ca_2Fe_2O_5$ nanocomposite regarding to the previous literature.

Acknowledgments

The financial support of the Graduate University of Advanced Technology are gratefully acknowledged (project 94/2244).

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