

Synthesis of nanocrystalline CoFe_2O_4 using citrate-urea assisted combustion process for lithium battery anode

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ABSTRACT

Nanocrystalline CoFe_2O_4 particles are prepared using citric acid urea assisted combustion process by varying the metal ions, citric acid and urea ratio as 1:1:0.5, 1:1:1 and 1:1:2. The prepared sample is characterized using XRD, FTIR, DSC and SEM-EDS techniques. The impurity free, nano size (~15 nm) crystalline CoFe_2O_4 is obtained for M:CA: urea ratio 1:1:0.5 sample.

Keywords: Nanocrystalline CoFe_2O_4 , SEM-EDS, DSC, XRD, FTIR

1. INTRODUCTION

CoFe_2O_4 magnetic nanoparticles with high coercivity, moderate magnetization and very high magneto crystalline anisotropy having wide range of applications in the field of ferro fluids, magneto optics, spintronics, biomedical applications, data storage devices, catalysts, sensors, etc. Recently, CoFe_2O_4 nanostructures have also used as anode material in lithium ion battery and showed an improved electrochemical performance [1-3]. CoFe_2O_4 form normal, inverse spinel or mixed structure, according to the preparation temperature. CoFe_2O_4 nanoparticles exhibit variety of unusual magnetic properties when compared to the its bulk, which in turn will have wide range of commercial applications. Magnetization, hysteresis and phase transition temperature depend on the size of the magnetic nanoparticles. Magnetic nanoparticles can be prepared using sol-gel, co precipitation, polyol, combustion process, etc, [4-6]. Among the available wet chemical processes, combustion route is capable of producing nanocrystalline powder at a lower calcination temperature in a short time. In our present study, CoFe_2O_4 nanocrystals are prepared using combustion process by varying the metal ions, citric acid and urea fuel ratio as 1:1:0.5, 1:1:1 and 1:1:2. The synthesized sample is calcined at different temperatures and characterized using XRD, FTIR, DSC, SEM-EDS techniques to confirm the formation of CoFe_2O_4 nanocrystals.

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2. PREPARATION OF CoFe_2O_4 USING CITRIC ACID - UREA ASSISTED COMBUSTION PROCESS

Nanocrystalline CoFe_2O_4 powder sample was prepared using citric acid urea assisted combustion process by varying the metal ions, citric acid and urea ratio as 1:1:0.5, 1:1:1 and 1:1:2. All the analar grade precursor chemicals of Cobaltus nitrate, Ferric nitrate nanohydrate, citric acid and urea were used for the synthesis of Nanocrystalline CoFe_2O_4 powder. The required amount of metal nitrate solutions were taken and sonicated for 10 minutes. The mixture of solution was continuously stirred at 353 K for an hour. The required amount of citric acid and urea were added to the above solution on continuous stirring. The solution was evaporated at 353 K for 8 hours under constant stirring, which results the polymeric resin. The resins were further dried in an oven at 333 K for 24 hours to remove the excess water and the drying process caused the formation of dried foamy polymeric intermediate. Nanocrystalline CoFe_2O_4 powders were obtained by calcining the polymeric intermediates at 448 K and above. The complete process was investigated through XRD, FTIR, DSC and SEM techniques.

3. CHARACTERIZATION

The powder X-ray diffraction patterns were recorded on a PANalytical XPertPro X-ray diffractometer with $\text{Cu K}\alpha$ radiation of wavelength $\lambda=1.5418 \text{ \AA}$ and scanned from $80-10^\circ$. FTIR spectra were recorded on pellet samples using Shimadzu FTIR/8300/8700 spectrophotometer in the range of $4000 - 400 \text{ cm}^{-1}$ with 2 cm^{-1} resolution for 20 scans. Thin transparent pellet samples were prepared using the dried gel sample, heated from room temperature to higher temperatures (623 K), and grounded well with spectra pure KBr powder taken in 1:20 ratio. The DSC measurements were made on Mettler Toledo Star e System; module DSC 821e/500/575/414183/5278 under ambient air atmosphere. The polymeric intermediate sample, 3 mg, was taken in aluminium crucible and heated from 300 K to 773 K at a heating rate of 10K per minute. The microstructure of polymeric intermediate as well as the final size of the CoFe_2O_4 particles and their elemental distribution were

obtained through SEM – EDS measurements using Hitachi Scanning Electron microscope S 3400N.

4. RESULT AND DISCUSSION

4.1 XRD

Fig 2 shows the powder X-ray diffraction patterns of CoFe_2O_4 samples of three different compositions; 1:1:0.5, 1:1:1 and 1:1:2. From Fig 2, it was observed that the XRD patterns of as synthesized CoFe_2O_4 polymeric intermediates of composition 1:1:1 and 1:1:2 show the

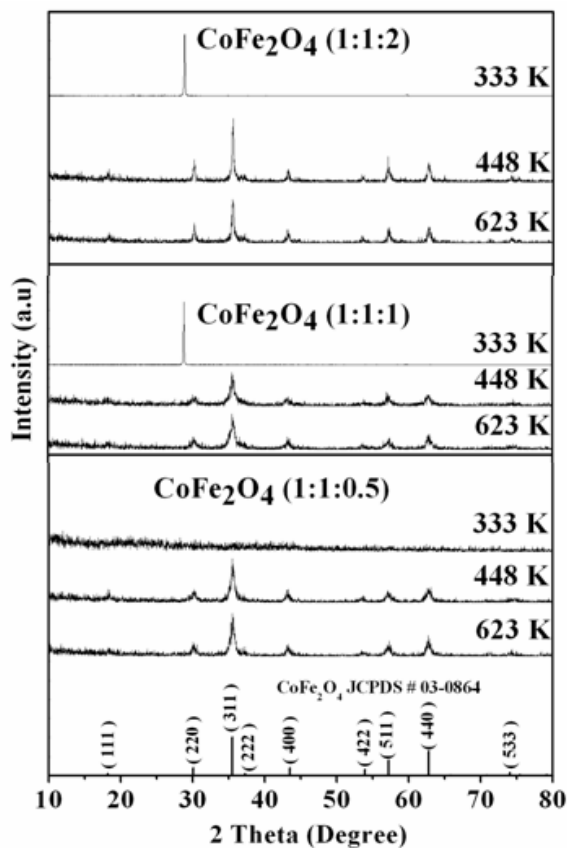


Fig. 1 XRD patterns of CoFe_2O_4 samples of three different compositions (M:CA:Urea = 1:1:0.5, 1:1:1 and 1:1:2).

characteristic diffraction patterns of ammonium nitrate. This indicates that the addition of excess urea to the sample is not participated in the formation of polymeric matrix, rather it forms ammonium nitrate. The XRD patterns of the as synthesized CoFe_2O_4 sample of composition 1:1:0.5 shows complete amorphous nature, which indicate that the added urea and citric acid are completely take part in the polymeric matrix formation and hence, showed amorphous nature. The XRD patterns of the calcined polymeric intermediate powders of

compositions 1:1:0.5, 1:1:1 and 1:1:2 show the characteristic diffraction patterns of the CoFe_2O_4 phase and further calcination increase the crystallite size of the sample. The formation of CoFe_2O_4 crystalline phase was confirmed by comparing the diffraction patterns with JCPDS # 03-0864 data. The crystallite size of the CoFe_2O_4 sample was calculated by using Scherer's formula and it is found to be 15 nm for 1:1:0.5, 12 nm for 1:1:1 and 30 nm for 1:1:2 samples, which confirm that the prepared crystalline CoFe_2O_4 samples are in nano size. The lowest crystallite size is observed for 1:1:1 composition of the CoFe_2O_4 sample.

4.2 FTIR

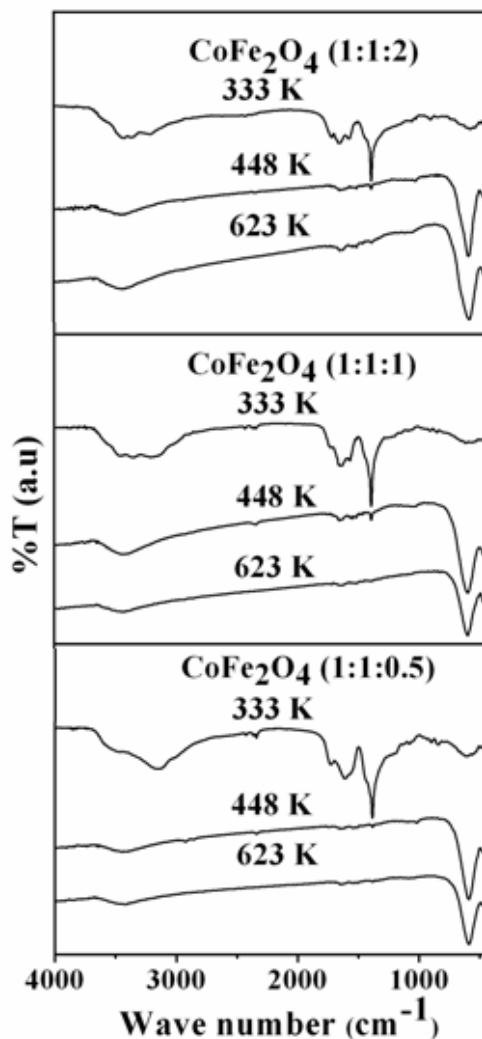


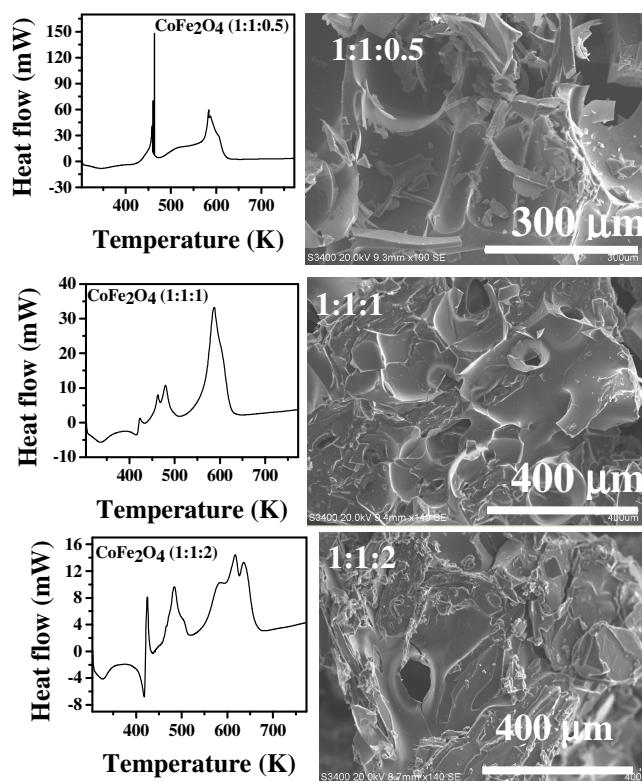
Fig. 2 FTIR spectra of CoFe_2O_4 samples of three different compositions (M: CA: Urea = 1:1:0.5, 1:1:1 and 1:1:2).

Fig. 2 shows the FTIR spectra of CoFe_2O_4 samples of three different compositions. From fig. 2, all the three different compositions of the synthesized samples showed the characteristic vibrational bands of organic groups and

nitrate at 3430, 3173, 1725, 1616, 1384, 1139, 1078, 901, 834 cm^{-1} . The above observed IR confirm the presence of citric acid and urea in the sample. The FTIR spectra of calcined samples of three different compositions showed the characteristic IR bands at 600 and 430 cm^{-1} , which correspond to the formation of tetrahedral and octahedral structured spinel CoFe_2O_4 and also confirms the removal of organic residuals [7-9]. Nanocrystalline CoFe_2O_4 sample with high purity was observed for 1:1:0.5 composition. The presence of organic impurities decreases the performance of lithium battery when this material is used as lithium battery anode. Hence organic impurity free CoFe_2O_4 sample is taken for further studies.

4.3 DSC

Fig 3 shows the DSC thermogram of CoFe_2O_4 sample of all compositions. From fig. 3, it was observed that the heat generation is more for 1:1:0.5 composition sample and all the organic fuels are completely burned around 473 K. There is no more exothermic peak observed in the sample after 620 K.



3

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Fig. 3 DSC thermograms, Fig. 4 SEM images of foamy polymeric intermediates of all compositions (M:CA:Urea = 1:1:0.5, 1:1:1 and 1:1:2) dried at 333 K.

The sample of composition 1:1:1 and 1:1:2 showed poor heat generation during combustion reaction. The sample showed two endothermic peaks one corresponds to

evaporation of water and other endotherm may be due to the melting of the sample before volume expansion. The poor exothermic reaction continues for a longer time and resulted unburnt carbon retain in the sample calcined around 623 K. The DSC result confirmed that the CoFe_2O_4 sample of composition 1:1:0.5 generate more heat during combustion reaction and resulted high pure fine powdered sample calcined at 623 K. For other composition, the prolonged exothermic reaction results in impurities. This result is also reflected in FTIR analysis

4.4 SEM

Fig 4 shows the SEM images of as synthesized polymeric intermediate of CoFe_2O_4 samples with different citric acid urea ratios. CoFe_2O_4 sample of composition 1:1:0.5 showed better polymerization, displayed very soft polymeric intermediate with high volume expansion and large pores. The CoFe_2O_4 samples of compositions 1:1:1 and 1:1:2 showed poor polymerization with less volume expansion and hard nature. The same is reflected as a crystalline form in XRD results. The SEM images of the above compositions CoFe_2O_4 samples showed the porous nature of as well as flakes. The porous nature will help for storing oxygen during combustion and better combustion was observed for the better polymerized sample with large pores. The same result is reflected in DSC results.

4.5 SEM-EDS

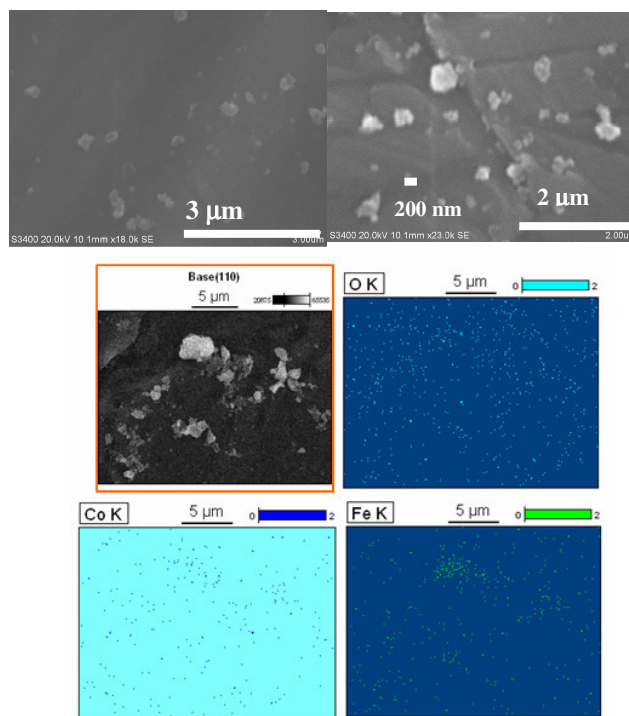


Fig. 4 SEM-EDS image of CoFe_2O_4 sample prepared with 1:1:0.5 composition

The fine powdered CoFe_2O_4 sample of composition 1:1:0.5 calcined at 623 K is dispersed in acetone and a little drop is dispersed over the aluminium stub and dried for SEM-EDS measurements.

<i>Element Line</i>	<i>Net Counts</i>	<i>Weight %</i>	<i>Atom %</i>	<i>Formula</i>
<i>O K</i>	0	27.52	57.41	Fe_2O_3
<i>Fe K</i>	84	49.58	29.63	
<i>Fe L</i>	0	---	---	
<i>Co K</i>	33	22.90	12.97	CoO
<i>Co L</i>	11	---	---	
<i>Total</i>		100.00	100.00	

Table 1 SEM-EDS results of CoFe_2O_4 sample prepared with 1:1:0.5 composition

Fig. 5 shows the SEM and EDS elemental mappings of CoFe_2O_4 sample of composition 1:1:0.5. From SEM image, the CoFe_2O_4 particles are dispersed uniformly and the particle size was varied from 150 to 250 nm. The elemental analysis confirmed the presence and uniform distribution of Co, Fe and O elements in the CoFe_2O_4 sample.

5. CONCLUSION

The nanocrystalline CoFe_2O_4 sample was prepared using citric acid and urea assisted combustion process. The metal ions, citric acid and urea fuel ratio was varied as 1:1:0.5, 1:1:1 and 1:1:2. The crystalline phase formation was confirmed from XRD results. The crystallite size was calculated using Scherer's formula and it is found to be 15 nm for 1:1:0.5, 12 nm for 1:1:1 and 30 nm for 1:1:2 composition sample. The FTIR results confirm the bond and structural formation of citric acid, urea and CoFe_2O_4 . The complete removal of impurity at 623 K for 1:1:0.5 composition is also confirmed from FTIR results. CoFe_2O_4 sample of composition 1:1:0.5 showed high pure final product at 623 K compared to other compositions. SEM image of as synthesized polymeric intermediate sample showed the porous nature of the sample. The SEM-EDS analysis of the sample of composition 1:1:0.5 showed the uniform elemental distribution. The particle size varied from 150 nm to 250 nm. The elemental result showed the presence and uniform distribution of Co, Fe and O elements in the CoFe_2O_4 sample.

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