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Surfactant Assisted Growth and Optical Studies of $NiCo_2O_4$ Nanostructures through Microwave Heating Method

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Abstract: A fast and facile method has been imposed for the preparation of $NiCo_2O_4$ nanostructures using metal nitrate as a precursor material and CTAB as a surfactant. The prepared samples were characterized by Powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM), Raman and PL spectroscopy. It was found that the synthesis route proposed in this work favored the formation of $NiCo_2O_4$ spinel phase at low temperature. The surfactant CTAB was chosen to control over the nucleation, growth and agglomeration nature of observed $NiCo_2O_4$ nanocrystalline products. With the effect of surfactant, the obtained $NiCo_2O_4$ has been used for various promising potential applications. Based on the observed experimental observations and analysis, a possible microwave reaction mechanism is proposed to synthesis $NiCo_2O_4$ nanostructured materials to enrich the structural, morphological and optical properties of $NiCo_2O_4$ nanostructures.
Key Words: Nanostructures, X-ray diffraction, Crystal structure, Surfactant, Optical.

1. INTRODUCTION

The presence of two metals in the same molecule largely affects both the physical and chemical properties and it has wide range of applications in various fields like electrocatalysts, chemical sensors, magnetic and biomedical applications [1]. The binary cobaltites of transition metals with the general formula MCo_2O_4, where M is a divalent cation of a d element, Ni, Cu and Zn cobaltites are of definite interest due to their significant modification in the individual properties of the metals which do not occur in monometallic compounds [2]. Nickel cobaltite ($NiCo_2O_4$) is one of the important metal oxides in the family of cobaltite materials which has a spinel structure AB_2O_4. Basically the incorporation of nickel ion into cobalt oxide would strongly enhance the properties of the prepared samples towards many applications [3]. In the recent years, large number of chemical methods were adopted and used for the preparation $NiCo_2O_4$ nanoparticles such as sol–gel process [4], co-precipitation [5], microwave [6], solid state [7] and solvothermal [8]. Recently, the microwave method has been most widely used for $NiCo_2O_4$ nanoparticles because of effectiveness of fast reaction and shorter heating time. In this paper, we report that the effect of calcination temperature on structural, optical, morphological and compositional analysis of nanocrystalline $NiCo_2O_4$ powders by a fast and facile microwave method using CTAB as a surfactant. This process is an effective way to produce nanoparticles with enhanced properties by using the effectiveness of CTAB towards various applications.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of Nickel Cobaltite

Nickel cobaltite ($NiCo_2O_4$) was synthesized from microwave reaction using the precursor materials of Co $(NO_3)_2.6H_2O$, Ni $(NO_3)_2.6H_2O$ and the surfactant CTAB. In this reaction, 3 g of Ni $(NO_3)_2.6H_2O$ was added to the 50 ml distilled water. Then 6g of Co $(NO_3)_2.6H_2O$ was mixed with nickel nitrate solution and 2.5 g of CTAB was added to the precursor solution. Finally 3ml of ammonia was added to maintain the pH value around 9-10. The solution was treated with microwave reaction with the power of 180 W in 15 min. The precipitate was collected and dried at hot air oven with 80 °C for 24 hours. Then the powder was calcined at different temperatures namely 400 °C, 600 °C and 800 °C

3. RESULTS AND DISCUSSION

3.1. Structural and Functional Analysis

Figure 1A(a1-a3) shows the XRD patterns of $NiCo_2O_4$ spinel structure calcined at three different temperatures such as 800 °C, 600 °C and 400 °C respectively. Characteristic diffraction lines of the NiCo2O4 spinel structure were well matched with standard JCPDS (73-1702) in all calcined samples [9]. The peaks related to NiO phase were also identified from the XRD spectrum. It was observed from the XRD patterns that the crystallite size grows when the calcination temperature increases. At higher calcinations of 800 °C shown in figure A (a1), crystalline nature was increases compared to lower calcination temperatures. It is strongly concluded that, the formation of $NiCo_2O_4$ at lower calcination temperature is less and it increases with higher calcination temperature with increasing particle size. The lattice parameters were calculated and tabulated in table 1. The FTIR spectra of the $NiCo_2O_4$ nanoparticles were displayed in figure 1B(b1-b3) for three calcined samples. In this analysis, two strong absorption bands in the region 650-665 cm^{-1} and 550-560 cm^{-1} corresponding to the metal-oxygen stretching from tetrahedral and octahedral sites respectively, which are the characteristics of cobaltites. Only the Co–O and Ni–O vibrations of $NiCo_2O_4$ samples are detected, no signal corresponding to OH group is observed, indicating the cobalt and nickel metallic salts are completely decomposed after calcination. The peak positions were shifted to higher side with respect to increase of calcination temperatures. No other peaks were obtained in the FTIR spectrum indicates that the purity of $NiCo_2O_4$ nanoparticles is good without other species in the samples [10&11].

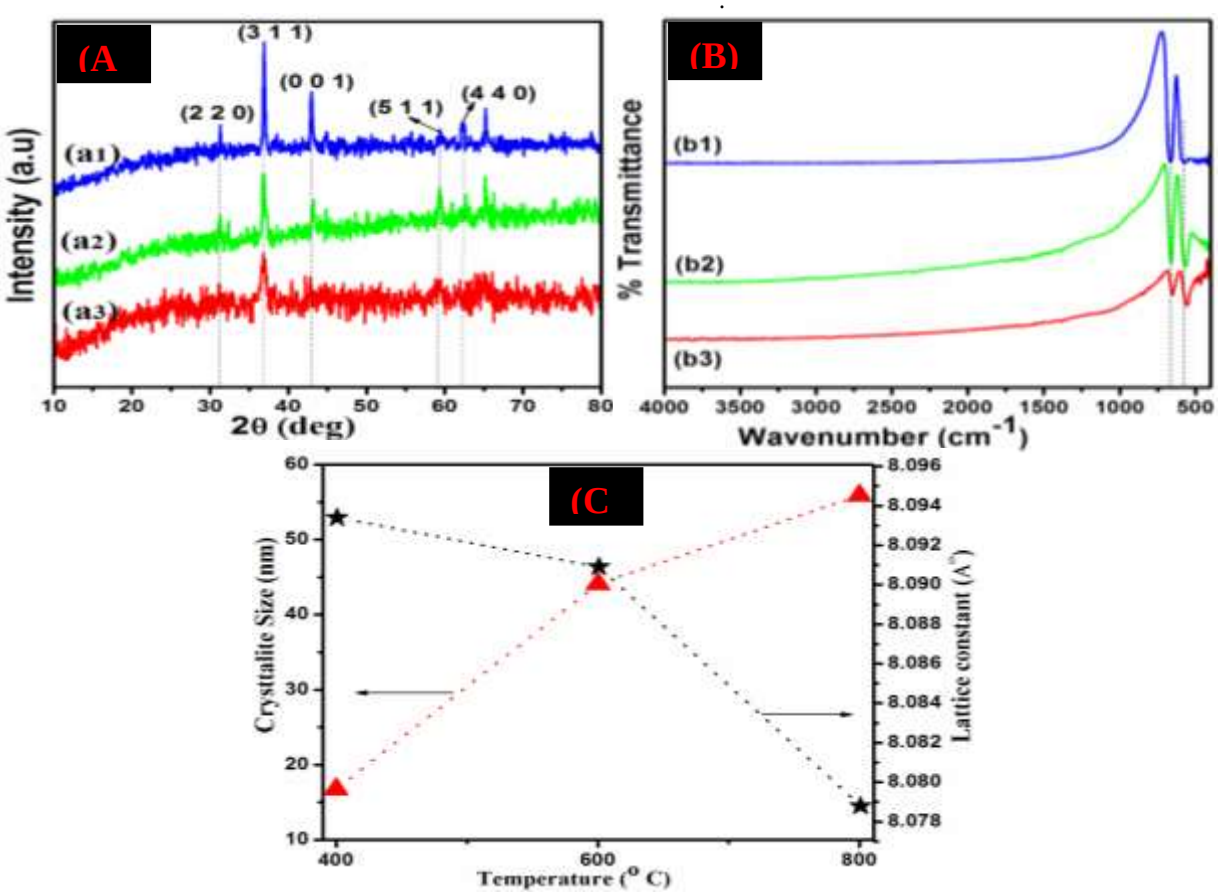


Figure 1. A) X-ray diffraction pattern of $NiCo_2O_4$ for a1) 800 °C, a2) 600°C and a3) 400°C, B) FTIR spectra for b1) 800 °C, b2) 600°C and b3) 400°C respectively and C) Comparison graph of particle size and lattice parameter.

Figure 1C gives the comparison of particle size, lattice constant variation with the calcination temperatures. It is observed from the figure that, increase of calcinations temperature increases the particle size but lattice constant is found to be decreased.

Table 1. Structural parameters of $NiCo_2O_4$ calcined at three different temperatures.

Calcination Temperature (° C)	Grain Size(nm)	Dislocation Density 10^{14} lines/cm^2	Lattice constant (a) Å	Volume (V) (Å)^3	Lattice distortion (V_o-V)
400	16.75	0.3563	8.0934	530.15	0.0076
600	44.10	5.1451	8.0909	529.65	0.0085
800	55.90	3.2056	8.0788	527.28	0.0129

3. Morphological and Compositional Analysis

The morphological variations of $NiCo_2O_4$ spinel structure with the effect of calcination temperatures are shown in Figure 2. The images of $NiCo_2O_4$ calcined at 400 °C displayed highly agglomerated nanoparticles (Fig.2 (a&b)). When the calcination temperature increases to 600 °C, (Figure 2(c & d)), particles are formed into irregular quasi spherical shape with increasing size. In further increase of calcination temperature (800 °C), particles are grown into uniform morphology with spherical shape shown in figure 2 (e&f). The particles size obtained from higher calcined sample is in the range of 50-100 nm which is higher than lower calcinated samples. By increasing the calcination temperature, the shape of particles is changed into uniform size with better morphology which is clearly observed in the SEM micrographs. EDS analysis were performed to identify the elemental composition of $NiCo_2O_4$ nanoparticles and the corresponding images are displayed in figure 3(a-c) for the different calcinated samples.

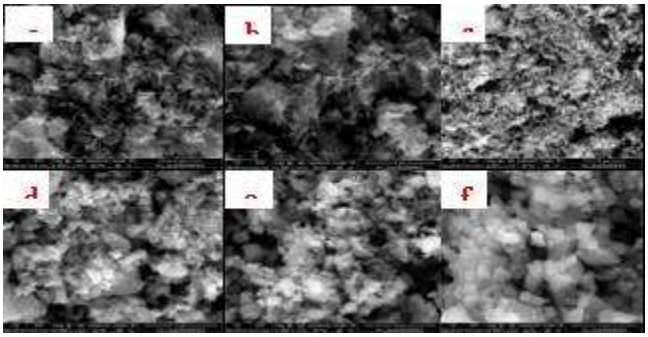


Figure 2. Low and high magnification SEM images of $NiCo_2O_4$ nanoparticles for 400 °C (a&b), 600°C (c&d) and 800°C (e&f) calcinated samples

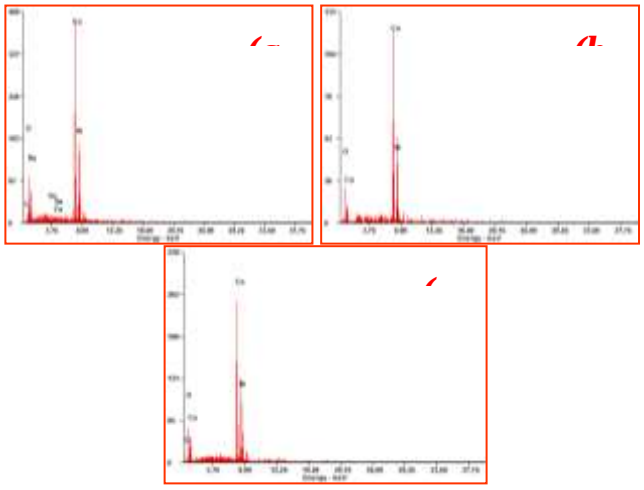


Figure 3. EDAX spectra of $NiCo_2O_4$ nanoparticles for a) 400 °C, b) 600°C and c) 800°C calcinated samples.

3.3 Optical Analysis

The photoluminescence spectrum of $NiCo_2O_4$ nanoparticles is shown in figure 4(a-c) for the corresponding calcination temperatures of 400 °C, 600 °C and 800 °C. This spectrum displayed two strong emission peaks at 360 and 490 nm for all the three samples with increasing peak intensity with calcination temperatures. The band gap energies of the $NiCo_2O_4$ nanoparticles are calculated and it gives 3.45 eV and 2.53 eV for the corresponding emission peaks of 360 and 490 nm [12].

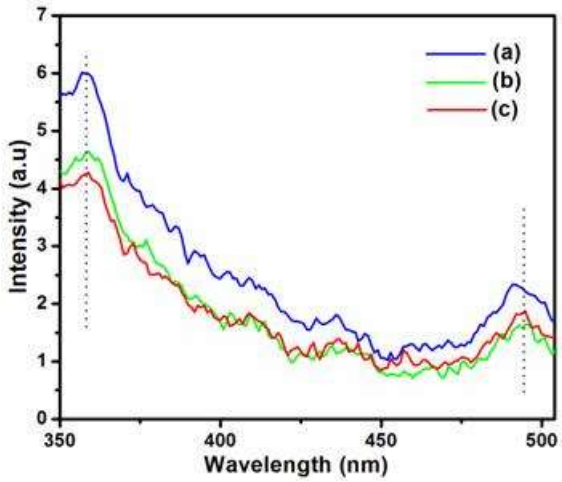
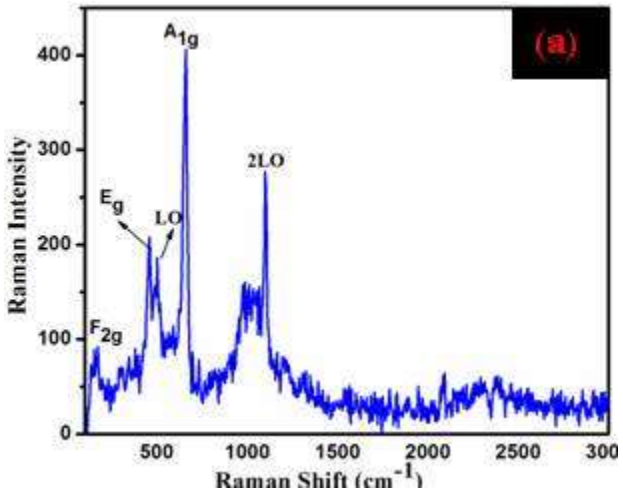


Figure 4. PL spectra of $NiCo_2O_4$ nanoparticles for a) 800 °C, b) 600°C and c) 400°C respectively

In order to further understand the composition and structure of these $NiCo_2O_4$ samples, Raman spectrum was taken which is shown in Figure 5. With respect to the as-prepared $NiCo_2O_4$ samples, the peaks at 152, 455.2, 505.2, 657.2 and 1097.3 cm^{-1} correspond to F_{2g}, E_g, LO, A_{1g} and 2LO modes of $NiCo_2O_4$, respectively. These results are well consistent with previously reported literatures [13&14].



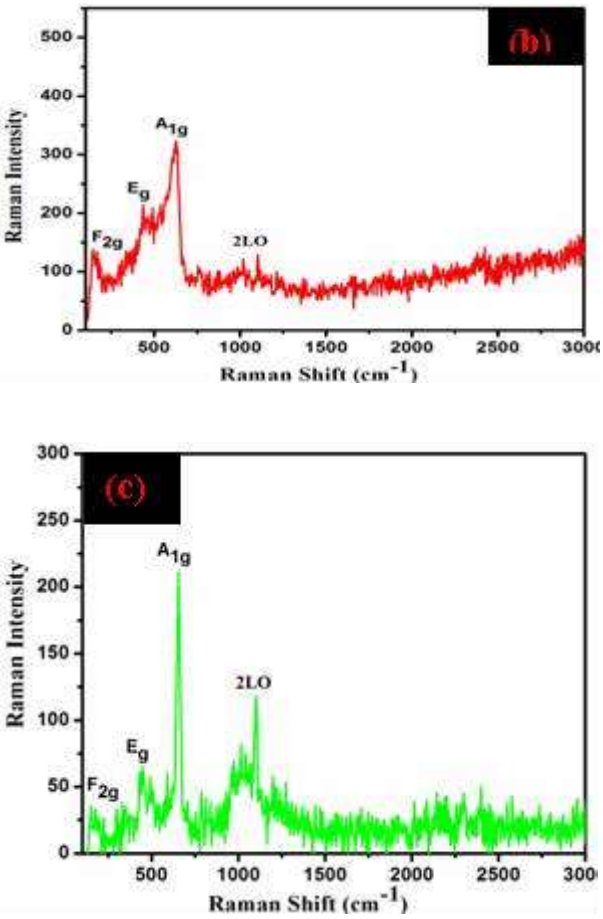


Figure 5. Raman spectra of $NiCo_2O_4$ nanoparticles for a) 800 °C, b) 600°C and c) 400°C calcinated samples

4. CONCLUSION

It was found that the microwave route proposed in this work favored the formation of $NiCo_2O_4$ spinel phase confirmed from the X-ray diffraction with increasing particle size with calcination. It produced uniform spherical shaped particles at higher calcination with size around 50-100 nm than other low temperature calcinated samples. EDS results confirmed the presence of elements Co, Ni and O in $NiCo_2O_4$. PL results showed that the band gap of $NiCo_2O_4$ nanoparticles are 3.45 and 2.53 eV and Raman spectrum emerges the Co–O and Ni–O vibrations in $NiCo_2O_4$ samples. The calcination effect was used to study the nucleation, growth and agglomeration nature of $NiCo_2O_4$ nanoparticles with the effect of surfactant CTAB. The uniform sized $NiCo_2O_4$ can be used for various promising potential applications.

5. ACKNOWLEDGMENT

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6. REFERENCES

[1] Niculescu, M., Birzescu, M., Raluca Dumitru, Şişu, E., and Budrugeac, P., 2009, *Thermochimica Acta*. 193, 1-5.

[2] Chun-Tsung Hsu and Chi-Chang Hu, 2013, *Journal of Power Sources*. 242, 662-671.

[3] Swathi, T., and Buvaneswari, G., 2009, *Materials Letters*, 62, 3900–3902

[4] Nivedita, S. Chaubal and Vishal Y. Joshi, 2011, *J Porous Mater*. 18, 177–183.

[5] Sook-Keng Chang, Zulkarnain Zainal, Kar-Ban Tan, Nor Azah Yusof, Wan Mohamad Daud Wan Yusoff and S.R.S. Prabaharan, 2012, *Sains Malaysiana*. 41, 465-470.

[6] Chi-Chang Hu, Chun-Tsung Hsu, Kuo-Hsin Chang and Hsiang-Yu Hsu, 2013, *Journal of Power Sources*, 238, 180-189.

[7] Rui Ding, Li Qi and Hongyu Wang, 2012, *J Solid State Electrochem*, 16, 3621–3633.

[8] Zhao-Qing Liu, Kang Xiao, Qi-Zhi Xu, Nan Li, Yu-Zhi Su, Hong-Juan Wanga and Shuang Chen, 2013, *RSC Adv*, 3, 4372–4380.

[9] Peres, A.P.S., Lima, A.C., Barros, B.S., Melo, D.M.A., 2012, *Materials Letters*, 89, 36-39.

[10] Yang Ren and Lian Gao, 2010, *J. Am. Ceram. Soc*, 93, 3560–3564.

[11] Saeid Farhadi and Kolsoum Pourzare, 2012, *Materials Research Bulletin*, 47, 1550–1556.

[12] Bai Cui, Hong Lin, Yi-zhu Liu, Jian-bao Li, Peng Sun, Xiao-chong Zhao and Chuan-jie Liu, 2009, *J. Phys. Chem. C*, 113, 14083–14087.

[13] Tyczkowski, J., Kapica, R., and Łojewska, J., 2007, *Thin Solid Films*, 515, 6590–6595.

[14] Charles.F. Windisch.Jr. and Gregory J. Exarhos, 2002, *J. Appl. Phys*, 92, 5572-5574.