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Chapter 4

Hydrothermally Produced Cobalt Oxide Nanostructures at Different Temperatures and Effect on Phase Transition Temperature and Threshold Voltage of Nematic Liquid Crystal Host

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.70946

Abstract

In this study, cobalt oxide $\text{Co}_3\text{O}_4$ nanostructured material is synthesized by hydrothermal method by using different concentration of cobalt acetate salt at unique hydrothermal reaction time for five different hydrothermal reaction temperatures 105, 120, 140, 160, and 180°C. The obtained nanoparticles are annealed at 300°C for 5 h. $\text{Co}_3\text{O}_4$ nanostructures are determined by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-vis spectroscopy. The hydrothermally produced samples were reannealed at 550°C, and morphological and structural properties were investigated deeply again. The effect of annealing temperature on morphologies and crystalline structure of cobalt oxide nanoparticle (NP) was also investigated. Nanopyramids and nanorods are two main morphologically obtained structures from the hydrothermal experiment. Nematic liquid crystal mixture E7 is doped with $\text{Co}_3\text{O}_4$ nanorod. Phase transition and threshold voltage of pure and $\text{Co}_3\text{O}_4$ NP-doped E7 LC are examined successfully. It reveals that for $\text{Co}_3\text{O}_4$ NP-doped E7 phase transition temperature and threshold voltage increased very slightly.

Keywords: cobalt oxide, hydrothermal synthesis, band gap, threshold voltage, thermal property

1. Introduction

“There is Plenty of Room at the Bottom” a titled lecture in 1959 was given by Richard Feynman, and this has opened a new era in the field of nanotechnology [1, 2], which can be
defined as the engineering of functional systems at the molecular level [3]. Nanoscience and nanotechnology have been growing rapidly due to the fact that nanomaterials are synthesized with new strategies and those synthesized materials are characterized and manipulated with new tools [4]. Nanostructures can be classified into three different categories according to their size and shapes: zero dimensional (0D), one dimensional (1D), and two dimensional (2D) [5, 6]. Nanodots-nanospheres, nanowires-nanorods, and nanosheets-nanoplates are some examples of different shapes and size nanomaterials for this classification. Nanomaterials, unlike to conventional materials, can be physically and chemically manipulated and used in different areas [7, 8] including biology and medicine [9–11], water treatment [12], electronics [13, 14], and optics [15–17].

Magnetic fields more or less impact a certain subclass of NP, which is called as magnetic nanoparticles (MNP) [18, 19]. MNPs have their own special properties, such as superparamagnetism [20], high mass transference [21], and high field irreversibility [22]. The second most popular MNP, considering to application areas, is cobalt oxide (Co3O4) since these nanoparticles are used in various fields from micro-electronics to drug delivery [7]. Co3O4 is one of the significant transition metal oxides, and the direct optical band gap of bulk Co3O4 is 2.19 eV.

Dispersion of nanomaterials into liquid crystals (LCs) has been a topic of great interest in recent years. There are many distinguished researchers investigating liquid crystals, and some of whose works are focused on doping nanomaterials into liquid crystals [23–29]. Gold, silver, zinc oxide, carbon, and quantum dots nanoparticles are some of the examples of guest nanoparticles. Co3O4 nanomaterials doped nematic liquid crystals (NLC) have only been investigated for spherical morphological Co3O4 nanoparticles to our knowledge [30].

Researchers have focused on synthesizing Co3O4 nanoparticles not only with diverse morphology but also with different methods since any change in production methods, particle size, shape, and structure of Co3O4 nanomaterials could lead producing new nanomaterials for potential applications with unique properties. Up to now, Co3O4 nanoparticles with various morphologies such as nanospheres [31, 32], nanorods [33–36], nanowalls [37], nanoneedles [38], nanobelts [39], nanoflowers [41], nanotubes [42, 43], nanofibers [44], nanodiscs [45], and nanochains [46] have been synthesized with different approaches, including urea precipitation [47], chemical vapor deposition [48], sol-gel [49], microwave-assisted process [50], wet chemical approach [51], and hydrothermal method [39, 52–54]. Hydrothermal methods are widely used to produce various different Co3O4 nanomaterials. Easily scaling up to industrial demand, requiring low temperature, no need for calcination, being inexpensive, and having a fairly uniform particle size and morphology are some of the advantages of this nanoparticle production method [55]. The term hydrothermal is used when water is used as a solvent, and solvothermal is used when organics are used as solvent [56]. In literature, the effect of hydrothermal reaction times and reaction temperature on morphologies of Co3O4 nanoparticles was examined [57–59].

In this study, new morphologies of Co3O4 have been synthesized by hydrothermal method using Cobalt(II) chloride hexahydrate precursor at different unique temperatures and hydrothermal reaction times. The influence of hydrothermal temperatures on crystal structures and particle morphologies was examined deeply. Five different hydrothermal temperature points were selected between 105 and 180°C, and the effect of annealing temperatures was also
investigated. The obtained particles were firstly annealed at 300°C for 5 h and then reannealed 500°C. The prepared Co$_3$O$_4$ NPs were characterized by XRD, SEM, and UV-vis. Moreover, we selected Co$_3$O$_4$ NPs obtained at 120°C hydrothermal reaction temperature to investigate how nanorod morphological Co$_3$O$_4$ NPs affect nematic liquid crystal phase transition and threshold voltages.

2. Materials and methods

2.1. Synthesis of Co$_3$O$_4$ NPs

All chemicals were used without further purification. A schematic diagram of the synthesis step is given in Figure 1. For the synthesis of the samples, 4.3983 g Cobalt(II) chloride hexahydrate
and 0.12 g Urea (CH$_4$N$_2$O) solution were mixed with 50 ml distilled water. The prepared solution was placed in the autoclave, and it waited in the furnace at 105, 120, 140, 160, and 180°C for 6 h. It was precipitated and washed several times with distilled water and dried at 60°C for 10 h. The obtained particles were annealed for 5 h at 300°C. Moreover, all obtained samples were also annealed at 500°C for 1 h to compare the effects of different annealing temperatures on XRD and SEM results of obtained Co$_3$O$_4$ samples.

2.2. Liquid crystal experiment

The LC used was commercially available eutectic mixture E7 (SYNTION Chemicals, Germany). The nematic to isotropic transition temperature for pure E7 is measured by using polarizing optical microscope integrated with hot stage, and it is found 58.6°C. The liquid crystal cells were made by indium-tin oxide-coated optical glass plates with a planar alignment layers. The thicknesses of cells were about 8 μm and an effective area of 1 cm$^2$. The cells were purchased from Instec, Inc. Hydrothermally produced Co$_3$O$_4$ sample at 120°C was selected to mixed in host E7 since the morphology of this sample contains nanorods. E7 nematic LC mixture and Co$_3$O$_4$ nanoparticles were dissolved in isopropanol followed by the ultrasonic bath. The mixture was left for 48 h in the furnace at 50°C to fully evaporate isopropanol. 0.05% doped sample was filled to LC cell at 60°C by capillarity action [25].

2.3. Characterization

The hydrothermally obtained Co$_3$O$_4$ samples’ crystalline structures were investigated by a Philips X’ Pert Pro X-ray diffractometer (XRD) with Cu-Kα radiation. The morphologies of the samples were examined by scanning electron microscope (Zeiss EVO 10LS). The optical

![Figure 2. Synthesis of Co$_3$O$_4$ samples and basic setup of LC light transmittance experiment.](image)
property samples were obtained by a Shimadzu UV-1800 ultraviolet visible spectroscopy (UV-vis) in the range of 200–900 nm using distilled water as a reference solvent. The samples were dispersed into distilled water solvent and ultrasonicated before the measurement. The textures of E7 and E7-doped sample were taken using polarizing optical microscope (Eclipse E200, Nikon, Japan) equipped with the digital camera. Temperature was controlled with heating stage (LTS 120, LinkamScientific Instruments, Ltd., England) with a temperature accuracy of ± 0.1°C controlled with PE95 LinkPad. Optical transmittance experiment designed and performed by laser, polarizer, analyzer, and photodiode and experimental scheme is described in detail in the literature [60]. Experimental detail about synthesis of Co₃O₄ samples and basic setup of liquid crystal optical transmittance experimental is given in Figure 2.

3. Results and discussion

X-ray diffraction pattern of Co₃O₄ samples annealed at 300°C for 6 h is given in Figure 3. The diffraction peaks of hydrothermally produced cubic structured sample at 120°C are suitable with the values in the standard card (PDF-2, reference code: 01-074-1656) and the Co₃O₄ particles produced at 180°C are partly suitable to this reference code as shown in Figure 3. The others produced Co₃O₄ particles’ apparent crystal structure patents were not observed. It is supposed that this was originated from hydroxide structures and chemical contaminant.
The obtained $\text{Co}_3\text{O}_4$ particles reannealed at 550°C for an hour and crystal structure of reannealed samples were investigated again. The effect of annealing temperature on the crystalline structure of obtained particles is shown in Figure 4. In this figure, XRD peaks of $\text{Co}_3\text{O}_4$ particles become clear, and all samples give at least some of the reference peaks of $\text{Co}_3\text{O}_4$. Hydroxide structures disappeared with reannealing at 550°C, and XRD peaks of $\text{Co}_3\text{O}_4$ particles are seen more clearly than samples annealed at 300°C.

The morphologies of particles that are produced using hydrothermal method at various temperatures and annealed at 300°C for 5 h are seen in Figure 5. In this figure, hydroxide and chemical waste structures are observed. Especially in Figure 5b, nanorod structures are seen. Nanosheet structures as layers are seen in Figure 5d. However, remarkable structures have not been observed for the samples produced at 105, 140, and 180°C, which are corresponding to Figure 5a, c, and e.

To observe the effect of annealing temperature, SEM pictures belonging to particles annealed within 550°C for 1 h are given in Figure 6. It was observed that the hydroxide compounds and chemical wastes decreased with the effect of the annealing. In Figure 6a and d, octahedral microparticles have been observed clearly, and in Figure 6b, nano-/microrods have been shown. Figure 6c shows the octahedral particles in nano level. In Figure 6e, agglomerated nanoparticles are dominantly seen.

Figure 4. XRD graph of $\text{Co}_3\text{O}_4$ samples annealed at 550°C.
The optical bad gap (Eg) for the direct transition was obtained using Tauc plot. Optical absorption graph of sampled annealed at 300°C is given in Figure 7, left column and optical absorption of sampled reannealed at 550°C is given in Figure 7, right column. The direct band gap of 300°C annealed Co$_3$O$_4$ NP changing between 3.1 and 3.5 eV; on the other hand, reannealed sampled band gaps were very close to 3.5 eV as interpreted in Figure 7. The measurement results of direct band gaps of reannealed nanoparticles were suitable with the literature [61, 62].
Polarizing optical microscope was used to investigate texture of pure and 0.05% nanoparticle-doped E7. The different magnification textures of pure E7 are given in Figure 8. The smallest magnification ratio of pure E7 is given in Figure 8a, and the most detailed texture of this LC is shown in Figure 8d.

Phase transitions of 0.05% cobalt oxide nanoparticle-doped E7 LC are illustrated in Figure 9a. The first drop of isotropic liquid appeared at 57.1°C, $T_{ NI }$, and the last drop nematic disappeared.
The average temperature of nematic-isotropic transition of doped sample is calculated by using equation $T_{NI} = 0.5(T_{N} + T_{I})$ [63], and found 58.85°C. The phase transition difference of pure E7 and NP-doped E7 is found as $\Delta T_{NI} = 0.2$°C. Figure 9b and c shows the optical picture of E7 LC without and with cross polarizers, respectively. The texture of pure and doped LC under 1 V applied voltage is given in Figure 9d and e.

Transmission versus voltage graph of pure and Co$_3$O$_4$ NP-doped LC is illustrated in Figure 10. The wavelength of used laser light in transmission experiment was 650 nm. The prepared LC cells are placed between cross polarizers, and the angle between cross polarizers and LC cell is adjusted to 45°, and the output signal was detected by a photodiode detector. Transmission voltage behavior of pure and doped sample is not very different from each other, which
implies that threshold voltage values are close to each other. The calculated threshold voltage for pure E7 and 0.05% Co$_3$O$_4$ NP-doped E7 are 0.8 V and 0.9 V sequentially.

4. Conclusion

In summary, Co$_3$O$_4$ nanostructures were synthesized using the hydrothermal method with unique hydrothermal reaction time at different temperatures. The crystalline structures, morphologies, and optical absorptions were investigated in detail with XRD, SEM, and UV-vis spectroscopy for two different annealed temperatures. The obtained samples were firstly investigated after being annealed at 300°C for 5 h, and the results of SEM and XRD separately indicated that cobalt hydroxide did not decompose fully to form cobalt oxide nanocrystalline. The samples were reannealed at 500°C for an hour to investigate deeply. The hydroxide compounds and chemical wastes are removed, and XRD peaks of Co$_3$O$_4$ particles become clear. Obtained morphologies of cobalt oxide nanostructures also changed with calcination. The particles, with a nanorod morphology, produced at 120°C hydrothermal reaction temperature and annealed at 500°C were selected to doped nematic LC mixture E7. Phase transition

Figure 10. Transmission vs. voltage graph for pure and NP-doped E7.
and the threshold voltage of pure and Co$_3$O$_4$ NP-doped E7 LC were examined successfully. It reveals that for Co$_3$O$_4$ NP-doped E7 phase transition temperature and threshold voltage increased very slightly.

Acknowledgements

The authors thank Kahramanmaras Sutcu Imam University for the continuous motivation to maintain this research. This work was financially supported by Kahramanmaras Sutcu Imam University, (KSU) Scientific Research Projects Coordination Department, under Project No. 2017/4-29D.

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References


[35] Zhang H et al. From cobalt nitrate carbonate hydroxide hydrate nanowires to porous Co₃O₄ nanorods for high performance lithium-ion battery electrodes. Nanotechnology. 2007;19(3):035711


[40] Gandha K et al. High energy product developed from cobalt nanowires. Scientific Reports. 2014;4:1-4
[41] Zhu Z et al. Application of cobalt oxide nanoflower for direct electrochemistry and
electrocatalysis of hemoglobin with ionic liquid as enhancer. The Journal of Physical
Chemistry C. 2011;115(25):12547-12553

[42] Lou XW et al. Self-supported formation of needlelike Co$_3$O$_4$ nanotubes and their appli-
cation as lithium-ion battery electrodes. Advanced Materials. 2008;20(2):258-262

[43] Xu J et al. Preparation and electrochemical capacitance of cobalt oxide (Co$_3$O$_4$) nanotubes
as supercapacitor material. Electrochimica Acta. 2010;56(2):732-736

[44] Mao Z et al. Electrosprinning synthesis of Co$_3$O$_4$@ C nanofibers as a high-performance
anode for sodium ion batteries. RSC Advances. 2017;7(37):23122-23126

[45] Yang J et al. Synthesis and characterization of cobalt hydroxide, cobalt oxyhydroxide, and

oxide nanochains: Morphology-dependent activity. ACS Catalysis. 2015;5(4):2017-2027

method as catalyst for the hydrolysis of sodium borohydride. Colloids and Surfaces A:
Physicochemical and Engineering Aspects. 2017;520:355-360

[48] Koumoulos EP et al. Tribological characterization of chemical vapor deposited Co and
Co$_3$O$_4$ thin films for sensing reliability in engineering applications. Tribology Interna-
tional. 2015;82:89-94

[49] Santos GA et al. Sol-gel synthesis of silica-cobalt composites by employing Co$_3$O$_4$ collo-
2012;395:217-224

[50] Jhung SH et al. Microwave effect in the fast synthesis of microporous materials: Which
stage between nucleation and crystal growth is accelerated by microwave irradiation?
Chemistry-A European Journal. 2007;13(16):4410-4417

[51] Li Y, Tan B, Wu Y. Mesoporous Co$_3$O$_4$ nanowire arrays for lithium ion batteries with high

[52] Liu F et al. Facile synthesis of ultrafine cobalt oxide nanoparticles for high-performance
supercapacitors. Journal of Colloid and Interface Science. 2017

[53] Wang G et al. Hydrothermal synthesis and optical, magnetic, and supercapacitance pro-
PERTIES of nanoporous cobalt oxide nanorods. The Journal of Physical Chemistry C.
2009;113(11):4357-4361

[54] Meher SK, Rao GR. Ultralayered Co$_3$O$_4$ for high-performance supercapacitor applica-

Advances in Applied Ceramics. 2016;115(6):354-376
[56] Li J, Wu Q, Wu J. Synthesis of Nanoparticles via Solvothermal and Hydrothermal Methods. Oak Ridge, TN (United States): Oak Ridge National Laboratory (ORNL); 2015


[60] Nayek P, Li G. Superior electro-optic response in multiferroic bismuth ferrite nanoparticle doped nematic liquid crystal device. Scientific Reports. 2015;5


