Crystallinity Improvement of Co₃O₄ by Adding Thiourea

Omer KAYGILI a, Niyazi BULUT a, I.S. YAHIA b,c, Ismail ERCAN d, Filiz ERCAN e, Tankut ATES a, Hanifi KEBIROGLU a,e, Riyadh Saeed AGID f, Bahroz Kareem MAHMOOD g

a Department of Physics, Faculty of Science, Firat University, 23119 Elazig, TURKEY
b Advanced Functional Materials & Optoelectronic Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, SAUDI ARABIA
c Nanoscience Laboratory for Environmental and Bio-medical Applications (NLEBA), Semiconductor Lab., Department of Physics, Faculty of Education, Ain Shams University, Roxy, 11757 Cairo, EGYPT
d Institute for Research and Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, Dammam, SAUDI ARABIA
e College of Science, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam, 31441, SAUDI ARABIA
f Department of Physics, College of Science, Salahaddin University,44002 Erbil, IRAQ
g Physics Department, College of Science, University of Halabja, Halabja 46018, IRAQ
* Corresponding author’s e-mail address: hanifi007@hotmail.com
DOI: 10.29130/dubited.654169

ABSTRACT
Tricobalt tetraoxide (Co₃O₄) samples having different thiourea/Co molar ratio of 0, 5 and 10 were prepared by wet chemical synthesis. The effects of thiourea content on the crystal structure-related parameters of Co₃O₄ were determined. The increase in the amount of thiourea caused a gradual decrease in the lattice parameters and specific surface area and an increase in the crystallinity and crystallite size. The experimental analysis results showed that thiourea content can be used to control the crystal structure-related parameters of Co₃O₄.

Keywords: Crystal structure, Electron microscopy, X-ray techniques

ÖZET
Tiyoüre/Co molar oranı 0, 5 ve 10 olan trikobalt tetraoksit (Co₃O₄) numuneleri yaş kimyasal sentez ile hazırlanıdı. Tiyoüre içeriğinin Co₃O₄’ün kristal yapısıyla ilgili parametreleri üzerine etkileri belirlendi. Tiyoüre miktarındaki artış, örgü parametreleri ve spesifik yüzey alanında kademeli bir düşüşe, kristalleşme ve kristal büyüklüğünde bir düşüşe neden oldu. Deneysel analiz sonuçları, tiyoüre içeriğinin Co₃O₄’ün kristal yapısıyla ilgili parametrelerinin kontrol edilmesinde kullanılabilirliği gösterdi.

Anahtar Kelimeler: Kristal yapı, Elektron mikroskopisi, X-ışını teknikleri
I. INTRODUCTION

Cobalt oxide ($\text{Co}_3\text{O}_4$), which is a metal oxide semiconductor (p-type) having a normal spinel structure (AB$_2$O$_4$ type of CoCo$_2$O$_4$) has got a lot of tremendous properties such as high catalytic reactivity, fast redox behavior, high electrochemical stability, low cost and environmentally friendly and has been used as a gas sensing material owing to its abundant oxygen adsorption and multivalence properties, an anode material for lithium-ion batteries and an electrode for high performance supercapacitors and a catalyst for the oxygen evolution reaction [1-6]. $\text{Co}_3\text{O}_4$ has been prepared via several methods including polyol, hydrothermal, sol-gel, combustion, microemulsion, chemical vapor deposition, sol-flame, solvothermal and sonochemical [7,8].

In the present paper, we aimed to prepare the $\text{Co}_3\text{O}_4$ powders via a wet chemical method using the precursor of thiourea, which has been used as a sulfur-contained inexpensive organic fuel [9], of various amounts, and we reported the effect of the addition of thiourea on the crystal structure-related parameters of $\text{Co}_3\text{O}_4$.

II. MATERIALS AND METHOD

Three $\text{Co}_3\text{O}_4$ samples with various thiourea (CS(NH$_2$)$_2$, Sigma-Aldrich, ≥ 99.0 %) /cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich, ≥ 99.0 %) molar ratio of 0, 5 and 10 were produced by wet chemical synthesis, and these samples were referred to as TU0, TU5, and TU10, respectively. To prepare the thiourea-free $\text{Co}_3\text{O}_4$ sample, a solution of 50 mL of 0.05 M Co(NO$_3$)$_2$·6H$_2$O in the distilled water was prepared and stirred at 100 °C for 1 h. Then, this mixture was dried in an oven at 150 °C for 15 h and calcined in an electric furnace at 750 °C for 2 h. In this way, the thiourea-free $\text{Co}_3\text{O}_4$ was obtained. In the synthesis processes of the thiourea-containing $\text{Co}_3\text{O}_4$ samples, the appropriate amounts of the solutions of 0.25 M and 0.50 M CS(NH$_2$)$_2$ were added to Co(NO$_3$)$_2$·6H$_2$O solutions. The above process was repeated to have the thiourea-containing $\text{Co}_3\text{O}_4$ samples.

X-ray diffraction (XRD) data of the as-synthesized $\text{Co}_3\text{O}_4$ samples were collected by a Rigaku RadB-DMAX II model diffractometer using CuK$_\alpha$ radiation. Fourier transform infrared (FTIR) data were recorded by a PerkinElmer Spectrum One spectrophotometer in the mid-infrared spectral range using the KBr pellet technique. A LEO EVO 40xVP scanning electron microscope (SEM) equipped with a Röntech xflash energy dispersive X-ray (EDX) analyzer was used to investigate the morphology and chemical composition of the as-observed areas.

III. RESULTS AND DISCUSSION

A. XRD RESULTS

The XRD patterns shown in Fig. 1 represent the polycrystalline structure for each sample, and all the as-observed peaks on these patterns are perfectly matched with the reported pattern belonging to the standard pattern of $\text{Co}_3\text{O}_4$ (JCPDS PDF No: 42-1467).

The estimation of the crystallinity percent ($X_C$ %) can be found in elsewhere [10]. The crystallite size was calculated by using the Williamson-Hall equation as $D$ [10]:

$$\beta \cos \theta = \frac{0.9 \lambda}{D} + 4 \varepsilon \sin \theta$$
where $\beta$, $\lambda$, $\theta$ and $\epsilon$ are the full width at half maximum, X-ray wavelength, Bragg angle and lattice strain, respectively. The $\epsilon$ and $D$ values were estimated from the $\beta \cos \theta$ vs. $4 \sin \theta$ plot given in Fig. 2.

**Figure 1. XRD patterns of the as-produced samples**

The dislocation density ($\delta$) was computed by using the following relation [11]

$$\delta = \frac{1}{D^2}$$  \hspace{1cm} (2)

The lattice parameter ($a$), unit cell volume ($V$) and X-ray density ($\rho_X$) of the cubic crystal system were calculated using the following relations, respectively [12,13]:

$$a = d \sqrt{h^2 + k^2 + l^2},$$  \hspace{1cm} (3)

$$V = a^3,$$  \hspace{1cm} (4)

$$\rho_X = \frac{8M}{N_A a^3},$$  \hspace{1cm} (5)

where $h$, $k$ and $l$ are the Miller’s indices, $M$ is the molecular weight and $N_A$ is the Avogadro’s constant. The specific surface area (SSA) for each sample was calculated using the following relation [13]:

$$SSA = \frac{6}{D \rho_X},$$  \hspace{1cm} (6)
The as-calculated values of all the above-mentioned parameters are given in Table 1. The \( X_C \), \( D \) and \( \rho_X \) increase with an increasing amount of thiourea, while the \( a \), \( V \) and \( SSA \) decrease. These findings are in a very good harmony with the results belonging to the fuels of aspartic acid, glycine and sucrose [14-16]. The changes reported in Table 1 verify that the fuel to oxidizer ratio effects all the as-calculated parameters. This result is in a good agreement with Venkateswara Rao and Sunandana [17]. Carvalho et al. [18] reported that the excessive amount of the combustion fuel of urea improves the crystallinity. As can be seen from Table 1, our results are in a good agreement with their report. The as-obtained negative lattice strain for the sample TU0 indicates that the unit cell under compressive stress, and its positive value means that the unit cell under the tensile stress [19].

**Figure 2.** Williamson-Hall plot of \( \text{Co}_3\text{O}_4 \) samples

**Table 1.** The calculated values of the XRD related parameters of \( \text{Co}_3\text{O}_4 \) samples

| Sample | \( D \) (nm) | \( \varepsilon \) | \( \delta \) \( (m^2) \) | \( X_C \% \) | \( a \) (nm) | \( V \) \( (nm^3) \) | \( \rho_X \) \( (kg/m^3) \) | SSA \( (m^2/kg) \) |
|--------|--------------|----------------|----------------|----------|---------|-------------|----------------|--------------|
| TU0    | 29.63        | -2.67\( \times \)10\(-4\) | 11.39\( \times \)10\(14\) | 92.1     | 0.8111  | 0.5336      | 5995           | 33,778       |
| TU5    | 34.75        | 8.07\( \times \)10\(-4\) | 8.28\( \times \)10\(14\) | 93.6     | 0.8106  | 0.5326      | 6006           | 28,748       |
| TU10   | 36.67        | 4.02\( \times \)10\(-4\) | 7.44\( \times \)10\(14\) | 94.0     | 0.8098  | 0.5310      | 6024           | 27,162       |
B. FTIR ANALYSIS

The FTIR spectra for each Co$_3$O$_4$ sample are shown in Fig. 3. Two sharp bands, which are related to the vibration modes occurred between metal and oxygen bonds [20], are observed in the as-mentioned spectra for each sample. The bands indicating the formation of Co$_3$O$_4$ structure are detected at 655 and 550 cm$^{-1}$, and these are assigned to O-Co-O bridging vibration and Co-O stretching vibrations, respectively [21,22].

![FTIR spectra of Co$_3$O$_4$ samples](image)

*Figure 3. The recorded FTIR spectra of Co$_3$O$_4$ samples*

C. MORPHOLOGICAL OBSERVATIONS

The SEM images of the samples shown in Fig. 4 point out that all the samples have fine-sized particle distribution, and the thiourea content affects the morphology. The particle size distributions are found to be in the ranges of 85–1,638 nm for TU0, 48–1,830 nm for TU5 and 55–1,990 nm for TU10, respectively. The as-observed particle size distributions are in an agreement with Bazrafshan et al. [23]. The EDX data support that all the samples are composed of Co and O and no impurity is detected.
IV. CONCLUSIONS

In this study, \( \text{Co}_3\text{O}_4 \) powders with a different amount of thiourea were easily prepared. After analyzing the experimental data, it can be reached the following results. The crystallite size, crystallinity, lattice parameter, unit cell volume and X-ray density increase with the increase in the thiourea content, whereas the specific surface area and dislocation density decrease. The XRD and FTIR results confirm the formation of \( \text{Co}_3\text{O}_4 \) without any impurity. The morphology is affected by the thiourea content. The grain size distributions are found to be in the range of about 50-2,000 nm. It is found that the structural properties of \( \text{Co}_3\text{O}_4 \) can be improved and controlled by the amount of thiourea.

Figure 4. Morphological observation and elemental analysis results of \( \text{Co}_3\text{O}_4 \) powders with various thiourea contents
V. REFERENCES

[1] T. Zhou, T. Zhang, J. Deng, R. Zhang, Z. Lou and L. Wang, “P-type Co$_3$O$_4$ nanomaterials-based gas sensor: Preparation and acetone sensing performance,” Sensors and Actuators B: Chemical, vol. 242, pp. 369-377, 2017.

[2] N. Sheibani, M. Kazemipour, S. Jahani and M. Foroughi, “A novel highly sensitive thebaine sensor based on MWCNT and dandelion-like Co$_3$O$_4$ nanoflowers fabricated via solvothermal synthesis,” Microchemical Journal, vol. 149, pp. 103980, 2019.

[3] F. Qu, T. Thomas, B. Zhang, X. Zhou, S. Zhang, S. Ruan M. Yang, “Self-sacrificing templated formation of Co$_3$O$_4$/ZnCo$_2$O$_4$ composite hollow nanostructures for highly sensitive detecting acetone vapor,” Sensors and Actuators B: Chemical, vol. 273, pp. 1202-1210, 2018.

[4] L. Wang, Y.F. Yuan, Y.Q. Zheng, X.T. Zhang, S.M. Yin and S.Y. Guo, “Capsule-like Co$_3$O$_4$ nanocage@ Co$_3$O$_4$ nanoframework/TiO$_2$ nodes as anode material for lithium-ion batteries,” Materials Letters, vol. 253, pp. 5-8, 2019.

[5] S.A. Pawar, D.S. Patil and J.C. Shin, “Transition of hexagonal to square sheets of Co$_3$O$_4$ in a triple heterostructure of Co$_3$O$_4$/MnO$_2$/GO for high performance supercapacitor electrode,” Current Applied Physics, vol. 19, no. 7, pp. 794-803, 2019.

[6] J. Koza, Z. He, A. Miller and J. Switzer, “Electrodeposition of crystalline Co$_3$O$_4$—A catalyst for the oxygen evolution reaction,” Chemistry of Materials, vol. 24, no. 18, pp. 3567-3573, 2012.

[7] J. Jang and L. Li, “Synthesis of sphere-like Co$_3$O$_4$ nanocrystals via a simple polyol route,” Materials Letters, vol. 61, no. 27, pp. 4894-4896, 2007.

[8] B. Zhang, X. Zhou, C. Jiang, F. Qu and M. Yang, “Facile synthesis of mesoporous Co$_3$O$_4$ nanofans as gas sensing materials for selective detection of xylene vapor,” Materials Letters, vol. 218, pp. 127-130, 2018.

[9] X. Luo, W. Cao and M. Xing, “Preparation of nano Y$_2$O$_3$:Eu phosphor by ethanol assisted combustion synthesis method,” Journal of Rare Earths, vol. 24, no. 1, pp. 20-24, 2006.

[10] O. Kaygili, C. Tatar, S. Keser and N. Bulut, “Preparation and characterization of monetites co-doped with Ni/Al, Ni/Mn and Al/Mn,” Materials Letters, vol. 201, pp. 39-42, 2017.

[11] A.B. Vennela, D. Mangalaraj, N. Muthukumarasamy, S. Agilan and K.V. Hemalatha, “Structural and optical properties of Co$_3$O$_4$ nanoparticles prepared by sol-gel technique for photocatalytic application,” International Journal of Electrochemical Science, pp. 3535-3552, 2019.

[12] B.D. Cullity, Elements of X-ray Diffraction. 2nd Edition, Massachusetts, USA: Addison–Wesley Publishing Company, 1978, p. 102.

[13] J. Pal and P. Chauhan, “Study of physical properties of cobalt oxide (Co$_3$O$_4$) nanocrystals,” Materials Characterization, vol. 61, no. 5, pp. 575-579, 2010.

[14] M.C. Gardey Merino, M. Palermo, R. Belda, M.E. Fernández de Rapp, G.E. Lascalea and P.G. Vázquez, “Combustion synthesis of Co$_3$O$_4$ nanoparticles: Fuel ratio effect on the physical properties of the resulting powders,” Procedia Materials Science, vol. 1, pp. 588-593, 2012.
[15] M. Th. Makhlouf, B. M. Abu-Zied and T. H. Mansoure, “Direct fabrication of cobalt oxide nano-particles employing glycine as a combustion fuel,” Physical Chemistry, vol. 2, no. 6, pp. 86-93, 2013.

[16] M. Makhlouf, B. Abu-Zied and T. Mansoure, “Direct fabrication of cobalt oxide nanoparticles employing sucrose as a combustion fuel,” Journal of Nanoparticles, vol. 2013, pp. 1-7, 2013.

[17] K. Venkateswara Rao and C.S. Sunandana, “Co3O4 nanoparticles by chemical combustion: Effect of fuel to oxidizer ratio on structure, microstructure and EPR,” Solid State Communications, vol. 148, no. 1-2, 32-37, 2008.

[18] L. Carvalho, V. Melo, E. Vitor Sobrinho, D. Ruiz and D. Melo, “Effect of urea excess on the properties of the MgAl2O4 obtained by microwave-assisted combustion,” Materials Research, vol. 21, no. 1, 2017.

[19] A. Khorsand Zak, W. Abd Majid, M.E. Abrishami and R. Yousefi, “X-ray analysis of ZnO nanoparticles by Williamson–Hall and size–strain plot methods,” Solid State Sciences, vol. 13, no. 1, 251-256, 2011.

[20] G. Anandha Babu, G. Ravi, Y. Hayakawa and M. Kumaresavanji, “Synthesis and calcinations effects on size analysis of Co3O4 nanospheres and their superparamagnetic behaviors,” Journal of Magnetism and Magnetic Materials, vol. 375, 184-193, 2015.

[21] M. Galini, M. Salehi and M. Behzad, “Structural, magnetic and dielectric properties of Dy-doped Co3O4 nanostructures for the electrochemical evolution of oxygen in alkaline media,” Journal of Nanostructures, Vol. 8, no. 4, pp. 391-403, 2018.

[22] S. Bhagade, S. Chaurasia and B. Bhanage, “Reductive-hydroformylation of 1-octene to nonanol using fibrous Co3O4 catalyst,” Catalysis Today, vol. 309, pp. 147-152, 2018.

[23] H. Bazrafshan, R.S. Touba, Z.A. Tesieh, S. Dabirnia and B. Nasernejad, “Hydrothermal synthesis of Co3O4 nanosheets and its application in photoelectrochemical water splitting,” Chemical Engineering Communications, vol. 204, no. 10, 1105-1112, 2017.