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Research Article

Crystallinity Improvement of Co_3O_4 by Adding Thiourea

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ABSTRACT

Tricobalt tetraoxide (Co_3O_4) 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 Co_3O_4 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 Co_3O_4.

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

Tiyoüre İlavesiyle Co_3O_4'ün Kristalleşmesinin Geliştirilmesi

ÖZET

Tiyoüre/Co molar oranı 0, 5 ve 10 olan trikobalt tetraoksit (Co_3O_4) numuneleri yaş kimyasal sentez ile hazırlandı. Tiyoüre içeriğinin Co_3O_4'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 Co_3O_4'ün kristal yapısıyla ilgili parametrelerinin kontrol edilmesinde kullanılabileceğini gösterdi.

Anahtar Kelimeler: *Kristal yapı, Elektron mikroskopisi, X-ışını teknikleri*

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I. INTRODUCTION

Cobalt oxide (Co_3O_4), which is a metal oxide semiconductor (p-type) having a normal spinel structure (AB_2O_4 type of $CoCo_2O_4$) 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]. Co_3O_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 Co_3O_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 Co_3O_4.

II. MATERIALS AND METHOD

Three Co_3O_4 samples with various thiourea ($CS(NH_2)_2$, Sigma-Aldrich, ≥ 99.0 %) /cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 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 Co_3O_4 sample, a solution of 50 mL of 0.05 M $Co(NO_3)_2 \cdot 6H_2O$ 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 Co_3O_4 was obtained. In the synthesis processes of the thiourea-containing Co_3O_4 samples, the appropriate amounts of the solutions of 0.25 M and 0.50 M $CS(NH_2)_2$ were added to $Co(NO_3)_2 \cdot 6H_2O$ solutions. The above process was repeated to have the thiourea-containing Co_3O_4 samples.

X-ray diffraction (XRD) data of the as-synthesized Co_3O_4 samples were collected by a Rigaku RadB-DMAX II model diffractometer using CuK_α 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 Co_3O_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]:

$$\beta \cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin\theta \quad (1)$$

where β, λ, θ and ε are the full width at half maximum, X-ray wavelength, Bragg angle and lattice strain, respectively. The ε and D values were estimated from the $\beta\cos\theta$ vs. $4\sin\theta$ plot given in Fig. 2.

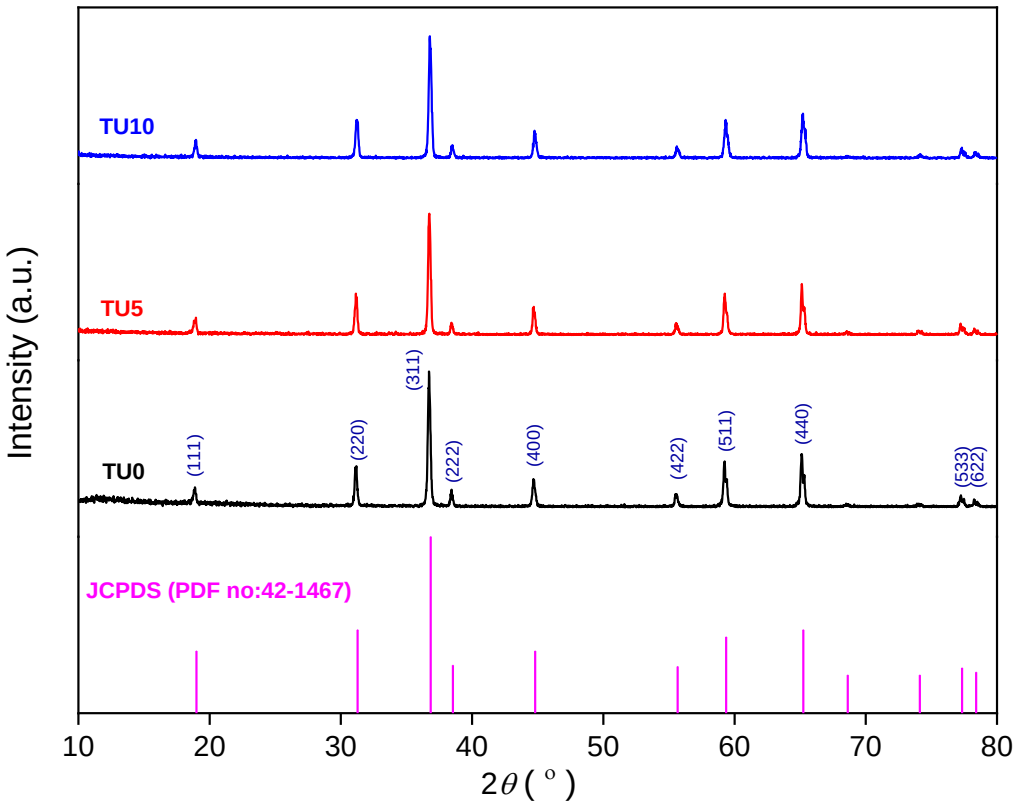

Figure 1. *XRD patterns of the as-produced samples*

The dislocation density (δ) was computed by using the following relation [11]

$$\delta = \frac{1}{D^2} \tag{2}$$

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

$$a = d\sqrt{h^2 + k^2 + l^2}\ , \tag{3}$$

$$V = a^3\ , \tag{4}$$

$$\rho_X = \frac{8M}{N_A a^3}, \tag{5}$$

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]:

$$SSA = \frac{6}{D\rho_X}, \tag{6}$$

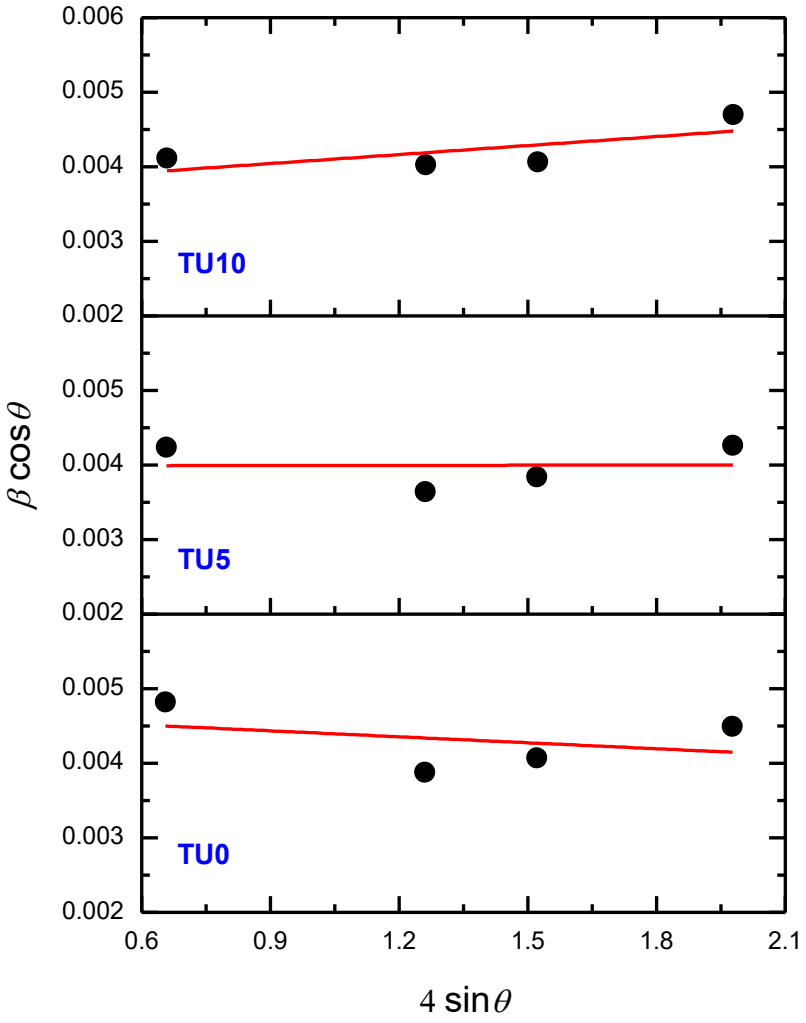

Figure 2. *Williamson-Hall plot of Co_3O_4 samples*

Table. 1. *The calculated values of the XRD related parameters of Co_3O_4 samples*

Sample	***D*** *(nm)*	***ε***	***δ*** *(m^{-2})*	X_C**%**	***a*** *(nm)*	***V*** *(nm^3)*	ρ_X *($kg\ m^{-3}$)*	***SSA*** *($m^2\ kg^{-1}$)*
TU0	29.63	-2.67×10^{-4}	11.39×10^{14}	92.1	0.8111	0.5336	5995	33,778
TU5	34.75	8.07×10^{-4}	8.28×10^{14}	93.6	0.8106	0.5326	6006	28,748
TU10	36.67	4.02×10^{-4}	7.44×10^{14}	94.0	0.8098	0.5310	6024	27,162

The as-calculated values of all the above-mentioned parameters are given in Table. 1. The X_C%, *D* and ρ_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].

B. FTIR ANALYSIS

The FTIR spectra for each Co_3O_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_3O_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].

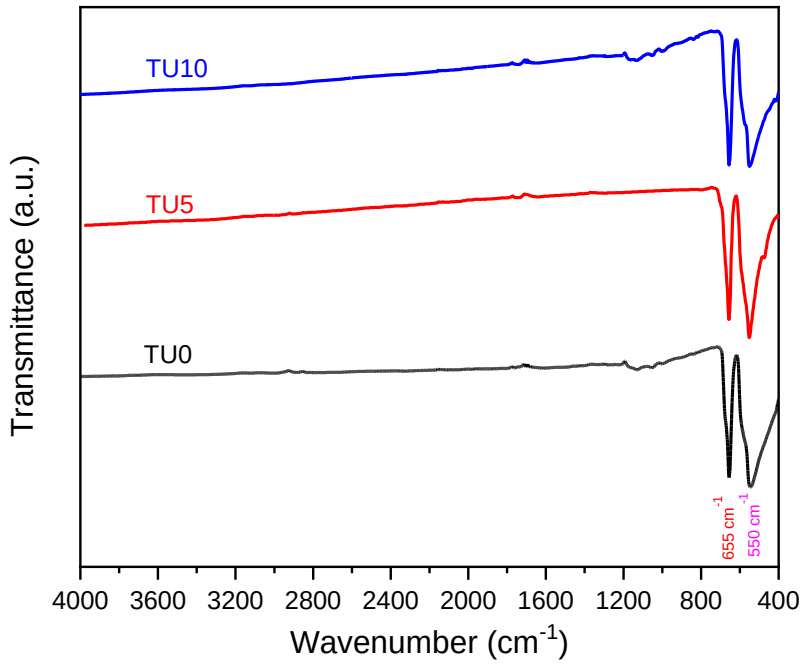

Figure 3. *The recorded FTIR spectra of Co_3O_4 samples*

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.

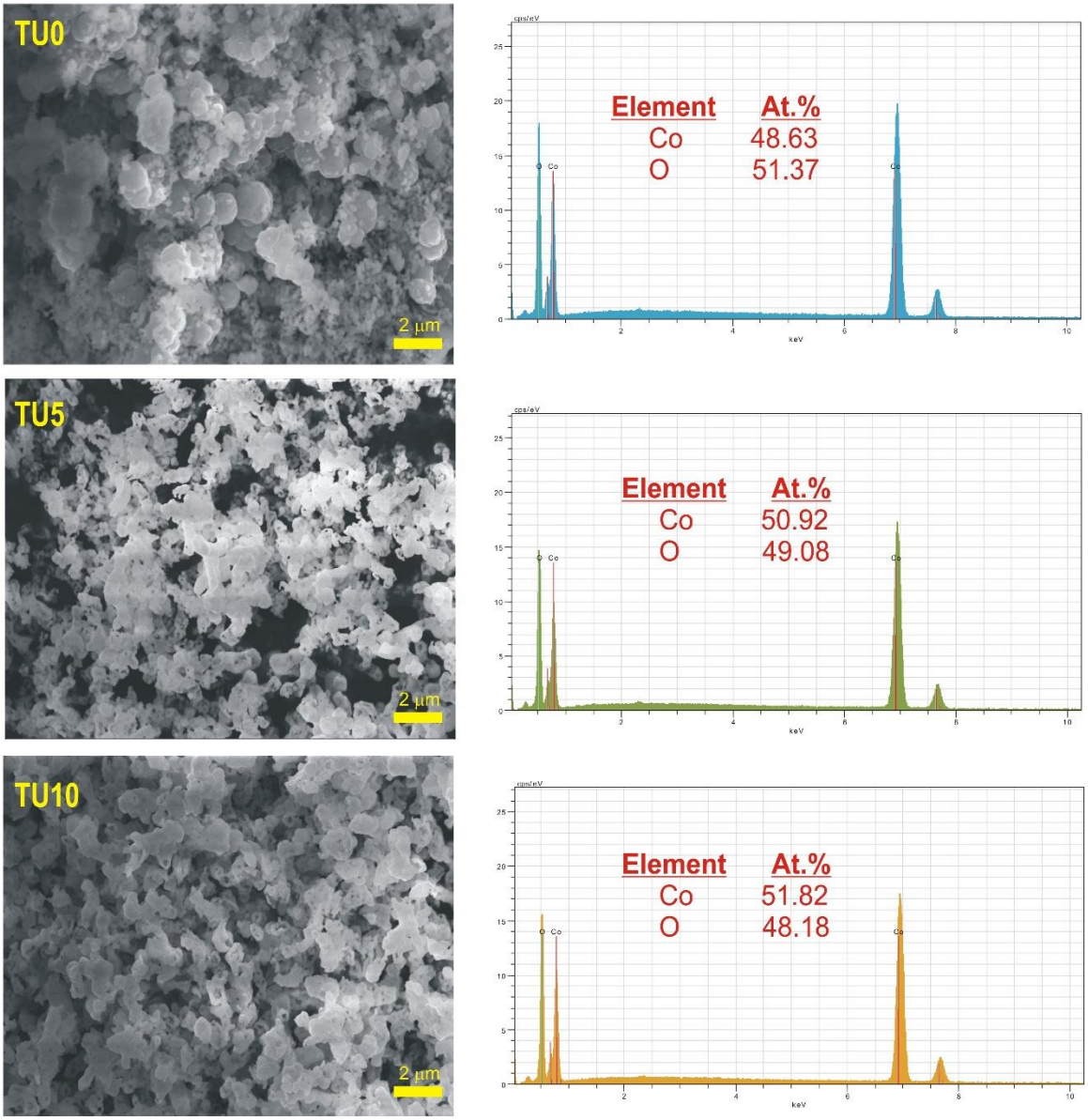

Figure 4. *Morphological observation and elemental analysis results of Co_3O_4 powders with various thiourea contents*

IV. CONCLUSIONS

In this study, Co_3O_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 Co_3O_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 Co_3O_4 can be improved and controlled by the amount of thiourea.

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