

Variation in the crystallinity of cobalt oxide nanoparticles with increasing annealing temperature and pH

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This study is focused on the effects of annealing temperature and pH on the crystallinity of cobalt oxide (Co₃O₄) nanoparticles (NPs) synthesized via sol-gel method. X-ray diffraction (XRD) analysis was carried out to investigate the crystalline structure and size of the NPs. The results indicated that increasing the pH from 10 to 14 during NPs synthesis led to an increase in crystallinity, as evidenced by the appearance of Bragg reflections upon calcination. On the other hand, increasing the calcination temperature from 120°C to 800°C also increased the crystallinity of Co₃O₄ NPs, as seen by the appearance of additional Bragg reflections and an increase in crystallite size. These findings demonstrate the significance of pH and calcination temperature in controlling the crystallinity and properties of Co₃O₄ NPs.

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1. Introduction

Cobalt oxide exists in two main forms: CoO and Co₃O₄, among which CoO is a black, paramagnetic, and high melting point material that crystallizes in the rock salt structure [1]. The Co₃O₄ is a brownish-black mixed oxide that consists of both cobalt(II) and cobalt(III) ions, arranged in a spinel structure [2]. The Co₃O₄ has unique electronic, magnetic, and optical properties that arise from the presence of both oxidation states of cobalt [3]. The cobalt oxides are important transition metal oxides that have attracted significant interest due to their unique physical, chemical, and magnetic properties [4]. These oxides find applications in diverse areas, including catalysis, energy storage, gas sensing, and magnetic storage media [5]. Co₃O₄ can be synthesized through various methods, including solid-state reaction, precipitation, sol-gel, hydrothermal, and thermal decomposition [6,7]. The choice of the method depends on the desired properties of the final product, the level of control required over the particle size and morphology, and the ease of scale-up [8]. For example, CoO can be prepared by annealing cobalt hydroxide at high temperatures, while Co₃O₄ can be obtained by thermal decomposition of cobalt oxalate or by reacting cobalt salts with oxidizing agents under controlled conditions [9]. The use of surfactants and templates can also be employed to control the particle size and morphology of the Co₃O₄ NPs.

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In this article, we are reporting the synthesis of Co_3O_4 NPs via sol-gel method at different pH and was annealed at different temperature. The XRD analysis was carried out in order examined the effect of pH and calcination temperature on the crystalline structure and crystallite size of Co_3O_4 NPs. Although there are some studies on the effect of annealing temperature on the crystallinity of NPs, the investigation of the combined effect of annealing temperature and pH on Co_3O_4 NPs is a novel contribution to the field. This research can provide new insights into the synthesis and control of the crystallinity of Co_3O_4 NPs, which can have potential applications in various fields, such as catalysis, energy storage, and biomedical applications. Additionally, the findings of this study can serve as a basis for further research on the synthesis and modification of Co_3O_4 NPs with desired properties.

2. Experimental section

2.1. Materials used

The chemicals used in this research work are cobalt (II) nitrate hexahydrate, isopropyl alcohol, sodium hydroxide and distilled water, which were purchased from the Sigma-Aldrich and was used without further purification.

2.2. Preparation of Co_3O_4 NPs

For the typical synthesis of Co_3O_4 NPs, 30 mM solution of cobalt nitrate hexahydrates was prepared by dissolving 0.698 g in 80 mL of distilled water and was mixed with 20 isopropyl alcohol and the reaction mixture was heated ($60\text{ }^\circ\text{C}$) and stirred (300 rpm) for 15 min. The pH of the reaction mixture was adjust at 8 and the reaction was continue for an hour. Afterward, the reaction was cooled at room temperature for 6 h and was then was washed with distilled water thrice and dried at $120\text{ }^\circ\text{C}$. The same procedure was repeated for pH 10, 12 and 14 and the final product obtained was annealed at 400, 600 and $800\text{ }^\circ\text{C}$ in muffle furnace and stored in air tight polyethylene bottle for further process.

2.3. Characterization

The Panalytical X'pert pro equipped with a copper (Cu) X-ray source, which has a wavelength of 1.5406 \AA , which was run in the range of 10 to 80° with resolution of $0.002^\circ 2\theta$ was used for the phase identification, crystallite size determination, and texture analysis of the synthesized Co_3O_4 NPs.

3. Results and discussion

3.1. XRD analysis of Co_3O_4 NPs fabricated at pH-8

The XRD profile of Co_3O_4 NPs prepared at pH 8 and annealed at 120, 300, 600 and $900\text{ }^\circ\text{C}$ are presented in Fig. 1, where no Bragg reflections were seen for sample annealed at 120, 400, and $600\text{ }^\circ\text{C}$, suggesting non crystalline nature of the samples. Conversely, the XRD pattern of Co_3O_4 NPs annealed at $800\text{ }^\circ\text{C}$ exhibits a Bragg reflection at 36.85 due to the hkl plane (311), consistent with reference card 01-078-1969. The size of the crystallites, estimated from the FWHM of the Bragg reflection is 46.6 nm. The XRD results demonstrate that the crystallinity of Co_3O_4 NPs escalates with an increasing in annealing temperature.

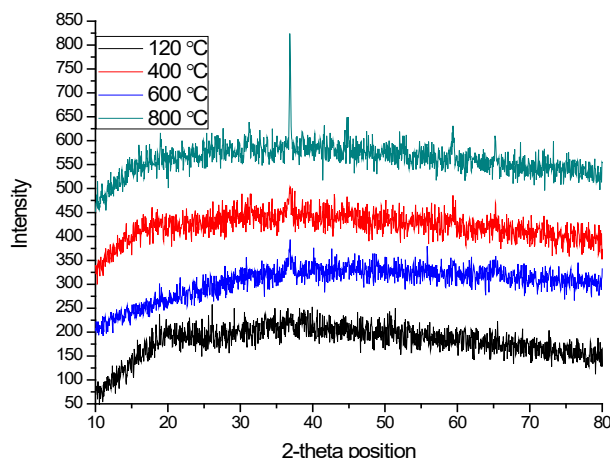


Fig. 1. XRD profile of Co_3O_4 NPs fabricated at pH-8.

3.2. XRD analysis of Co_3O_4 NPs fabricated at pH-10

The diffractogram of the Co_3O_4 NPs fabricated at pH 10 and dried at 120 °C reveals an amorphous sample with no Bragg reflections. However, upon calcination at 400 °C, the XRD profile has a Bragg reflection with respective miller plane i.e. 36.88(311), which correspond to JCPDS card 01-078-1969. Similarly, the diffraction bands at 36.85 in the XRD profiles of Co_3O_4 NPs annealed at 600 and 900 °C are due to the diffraction of X-rays from (311) hkl plane, which correspond to the JCPDS card 01-078-1969. The mean crystallite size was 23.3 nm and 34.90 nm for the Co_3O_4 NPs annealed at 600 and 900 °C respectively. It has been observed that the crystallite size is larger in case of the Co_3O_4 NPs annealed at higher temperature. Furthermore, the XRD analysis demonstrates that increasing the calcination temperature enhances both the crystallinity and crystallite size of Co_3O_4 NPs.

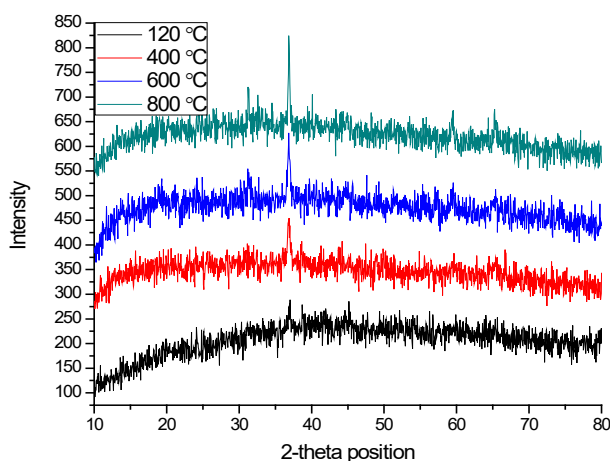


Fig. 2. XRD profile of Co_3O_4 NPs fabricated at pH-10.

3.3. XRD analysis of Co_3O_4 NPs fabricated at pH-12

The Co_3O_4 NPs synthesized at pH 10 and were dried at 120 °C has no Bragg's reflection in their XRD profile demonstrating the amorphous nature of the sample. However, upon annealing at 400 and 600 °C, a Bragg reflection at 36.88 appeared that was due to the miller plane (311) corresponding with JCPDS card 01-076-1802, and calculated crystallite sizes for the two Co_3O_4 NPs were 11.6 and 23.3 nm, respectively. The XRD pattern of the Co_3O_4 NPs annealed at 800 °C revealed the presence of three Bragg reflections at 2-theta positions i.e. 31.26, 36.88 and 65.27 which corresponding miller planes (220), (311) and (440) respectively. These Bragg reflections are in good agreement with that reported in the JCPDS card 01-078-1969, indicating the formation of crystalline

Co_3O_4 NPs. The mean crystallite size the Co_3O_4 NPs annealed at 800 °C was found to be 32.57 nm, which was larger than the Co_3O_4 NPs annealed at lower temperatures. Based on the XRD study, it can be inferred from the results that there is an increase in both the crystallinity and crystallite size of the NPs with an increase in annealing temperature.

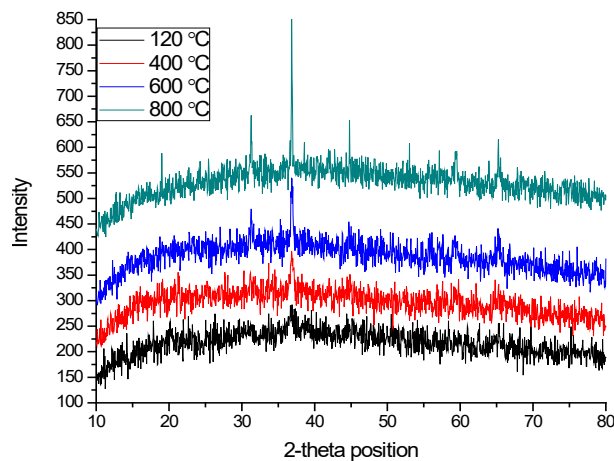


Fig. 3. XRD profile of Co_3O_4 NPs fabricated at pH-12.

3.4. XRD analysis of Co_3O_4 NPs fabricated at pH-14

The XRD profiles (Fig. 2) of the Co_3O_4 NPs prepared at pH 10 that was annealed at 120 and 400 °C possess the Bragg's reflection at 36.85 due to the diffraction of X-ray from the plane (311), which is matched with JCPDS card 01-078-1969. The calculated crystallite sizes for the both samples are were almost found similar (23.3 nm). Similarly, the XRD profile of Co_3O_4 NPs annealed at 600 °C displayed single diffraction band at 36.85 with a corresponding hkl value (311), which matched reference card 01-078-1969. However, the XRD profile of the Co_3O_4 NPs annealed at 800 °C shown two Bragg's reflections with corresponding hkl values of 36.85 (311) and 65.23 (440). These peaks were identical with those reported in JCPDS card 01-078-1969, indicating the formation of crystalline NPs. The crystallite size of NPs annealed at 800 °C was found to be 34.85 nm, which was larger than that of NPs annealed at lower temperatures. The peaks shown in the all XRD profiles discussed are assigned to the cubic geometry of the Co_3O_4 NPs having space group of $Fd\bar{3}m$ and space number 227. The XRD patterns of Co_3O_4 NPs annealed at different temperatures showed distinct differences in their crystallinity and crystallite size. Moreover, the increase in the peak intensity and emergence of a peak at 65.23 indicate that increasing the annealing temperature leads to enhanced crystallinity.

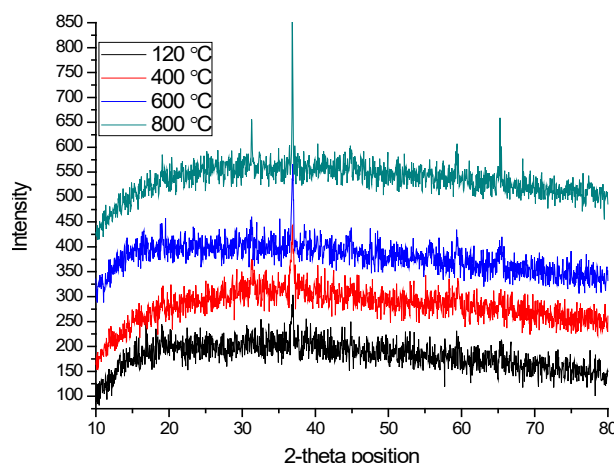


Fig. 4. XRD profile of Co_3O_4 NPs fabricated at pH-14.

3.4. Discussion

The crystallinity of Co_3O_4 NPs is influenced by various factors, including the pH of the reaction mixture. When the pH of the reaction mixture is increased, it can affect the rate of nucleation and growth of the NPs, resulting in increased crystallinity. At higher pH values, the concentration of hydroxide ions (OH^-) increases, which can lead to the formation of more stable intermediates during the synthesis process. These intermediates can act as nuclei for the formation of Co_3O_4 NPs with a higher degree of crystallinity [10]. Furthermore, the increased concentration of OH^- ions can promote the formation of a more stable cobalt hydroxide precursor, which can facilitate the formation of highly crystalline Co_3O_4 NPs upon subsequent calcination. Additionally, pH can also affect the surface charge of the NPs, which can influence the interaction between the NPs and the surrounding environment during synthesis. This can ultimately affect the growth and arrangement of the NPs, resulting in higher crystallinity at higher pH values [11]. However, it should be noted that the effect of pH on the crystallinity of Co_3O_4 NPs can also depend on other factors, such as the type of precursor used, the reaction temperature, and the concentration of other reactants in the reaction mixture. The pH of the reaction solution plays a crucial role in determining the properties of the resulting Co_3O_4 NPs [12].

Similarly, the annealing temperature has a significant influence on the crystalline nature of Co_3O_4 NPs. Annealing is the process of heating the NPs to a high temperature in a controlled atmosphere to remove any residual organic or inorganic compounds and promote crystallisation [13]. Generally, higher annealing temperatures can increase the degree of crystallinity of the Co_3O_4 NPs, resulting in larger and more well-defined crystal structures. For example, at a low annealing temperature of around 300°C , Co_3O_4 NPs are typically amorphous or partially crystalline, and the crystal structure is not well defined. However, at higher annealing temperatures (above 400°C), the Co_3O_4 NPs become more crystalline, with a higher degree of crystallinity achieved at higher temperatures [13,14]. The annealing temperature can also affect the crystal phase of the Co_3O_4 NPs. For instance, at lower temperatures, Co_3O_4 NPs may consist of a mixture of CoO and Co_3O_4 phases, whereas at higher temperatures, the NPs can transform into a single-phase Co_3O_4 structure [14]. Moreover, higher annealing temperatures can lead to an increase in the particle size of the Co_3O_4 NPs due to the sintering of the particles [10].

The results shows that both pH and calcination temperature have a significant impact on the crystallinity of Co_3O_4 NPs. A higher pH during the synthesis and a higher calcination temperature result in higher crystallinity, which in turn affects the properties and potential applications of these NPs. Therefore, careful optimization of these parameters is essential to achieve the desired properties and applications of Co_3O_4 NPs [15,16].

4. Conclusions

The crystallinity of Co_3O_4 NPs is greatly influenced by both the pH and calcination temperature during synthesis. It has been observed that as the pH increases, the crystallinity of Co_3O_4 NPs also increases due to the higher rate of nucleation and growth. On the other hand, as the calcination temperature increases, the crystallinity of Co_3O_4 NPs also increases due to the higher degree of thermal energy provided, leading to greater crystal growth and improved ordering of the atoms. The effect of pH and calcination temperature on the crystallinity of Co_3O_4 NPs is a crucial factor in determining their properties and potential applications in various fields.

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