



Hydrothermal synthesis of cobalt carbonates using different counter ions: An efficient precursor to nano-sized cobalt oxide (Co₃O₄)

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ABSTRACT

Synthesis of submicrometer crystalline particles of cobalt carbonate was achieved hydrothermally using different cobalt salts and urea with a molar ratio from 1:3 to 1:20 (cobalt salt:urea) in aqueous solutions at 160 °C for 24–36 h, in the presence of cetyltrimethylammonium bromide (CTAB) as a surfactant. Nanoparticles of Co₃O₄, with an average size from 30 to 39 nm, were obtained by thermal decomposition of CoCO₃ samples at 500 °C for 3 h in an electrical furnace. The as-synthesized products were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV–Vis spectra and thermal analysis. Studying the optical properties of the as-prepared cobalt oxide nanoparticles showed the presence of two band gaps, the values of which confirmed the semiconducting properties of the prepared Co₃O₄.

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1. Introduction

Over the past several years, considerable attention has been paid to nanomaterials, including their synthesis, characterization, chemical and physical properties. This considerable interest is due to their unique electrical, magnetic, optical and catalytic properties compared with those of the bulk materials [1–7]. Moreover, control of the morphologies has drawn a keen interest of researchers because materials with the same compositions but different morphologies and microstructures exhibit substantial differences in their properties [8–11]. As such, many synthetic methods have been developed to prepare nano-sized materials with different morphologies and architectures, such as nanotubes [12], nanobelts [13], nanorods [14], nanoparticles [15] and other nanoarchitectures [16].

Metal carbonates have been intensively investigated in recent years because they are an important class of inorganic materials, and they are extensively used as a standard model systems in industry because of their abundance in nature and their wide applications (such as in the paper, plastic, paint and rubber industries) [17]. Carbonates comprise a class of minerals in which a metal ion is coordinated by the CO₃²⁻ carbonate molecule. Carbonate mineral structures are either hexagonal rhombohedral, orthorhombic or monoclinic, depending on whether the metal ion is small (rhombohedral) or large (orthorhombic), or whether the carbonate is hydrous (monoclinic) [18]. Generally, sodium carbonate or carbon dioxide is used for the preparation of carbonate

salts such as CaCO₃, PbCO₃, BaCO₃ and MnCO₃ [19–22]. Moreover, cadmium carbonate with different morphologies was prepared via wet chemical methods [23,24]. Additionally, other metal carbonates such as CaCO₃, and BaCO₃ were synthesized by the reverse micelle method [25]. Recently, the hydrothermal method has attracted the attention of some researchers due to its effectiveness in the synthesis of different inorganic materials with different morphologies. As such, MnCO₃ hollow microspheres and nanocubes have been successfully synthesized via an ionic liquid-assisted hydrothermal synthetic method [26]. Moreover, the structural and optical properties of CuO layered hexagonal discs synthesized by a low-temperature hydrothermal process have been investigated [27]. Also, the structural, optical and photocatalytic properties of alpha-Fe₂O₃ nanoparticles have been studied [28].

CdCO₃ nanowires and nanoparticles were reported to be synthesized using the hydrothermal method [29,30]. However, to the best of our knowledge, the hydrothermal synthesis of cobalt carbonate and using it to generate Co₃O₄ is rare [29,30]. Cobalt(II,III) oxide (Co₃O₄) has a normal spinel structure in which Co²⁺ and Co³⁺ ions are at the centers of tetrahedral and octahedral sites, respectively [31]. Co₃O₄ nanomaterials are widely used in lithium-ion batteries and chemical sensors [32], heterogeneous catalysts [33], and magnetic and optical materials [34,35], where their properties are strongly dependent on their size and morphology. As such, many novel synthetic methods have been developed recently to make nanostructured Co₃O₄ with different morphologies such as nanorods [36], nanowires [37], nanocubes [33], nanotubes [38], nanofibers [34], nanowalls [39] and nanoplatelets [40]. Additionally, flower-like nanomaterials [41–43], microspheres [29,44] and hollow spheres [45] have also been made. Among them, a two-step

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process is often adopted to fabricate Co_3O_4 crystals with different shapes; namely, (i) solid cobalt precursors are first synthesized, and (ii) the precursors are then calcinated to produce Co_3O_4 [29]. Cobalt hydroxyoxide, cobalt hydroxide, cobalt-nitrate-hydroxide and cobalt-nitrate-carbonate-hydroxide have been synthesized and proved to be effective solid cobalt precursors to make Co_3O_4 [46–49,44,50], but as mentioned above, reports on the synthesis of CoCO_3 as a solid cobalt precursor and then using it to fabricate Co_3O_4 are rare [29,30]. To the best of our knowledge, reports on

the synthesis of uniform CoCO_3 with particle sizes in the sub-micrometer range are also rare [30].

Herein we report a facile hydrothermal procedure to synthesize submicro cobalt carbonate crystals by a hydrothermal method using different cobalt salts (such as cobalt chloride, cobalt acetate and cobalt nitrate, separately), cetyltrimethylammonium bromide (CTAB) as a surfactant and urea, a low cost and environmentally benign chemical employed as a carbonate source. The as-prepared cobalt carbonate was then thermally converted to phase-pure

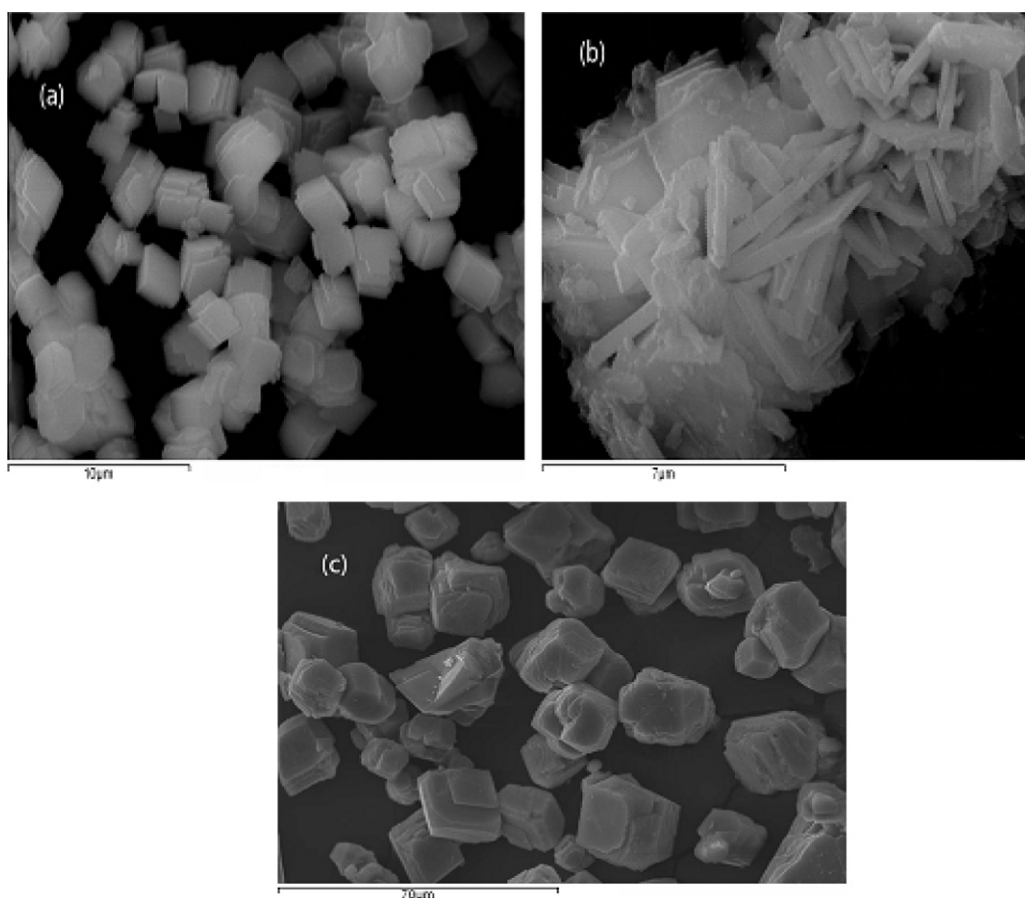


Fig. 1. (a–c) SEM images of the prepared cobalt carbonate samples.

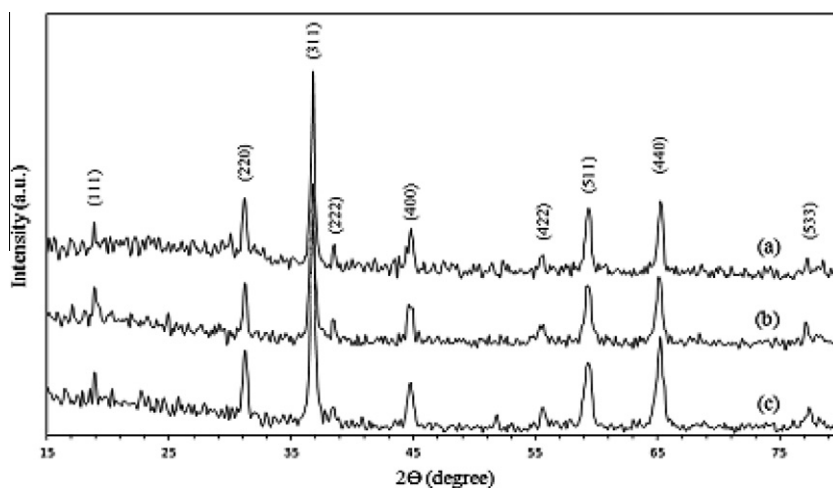


Fig. 2. (a–c) XRD patterns of the prepared cobalt carbonate samples.

Co₃O₄. The intermediate products were investigated by means of XRD, FT-IR, TGA and SEM. The cobalt oxide product was characterized by using XRD, FT-IR, UV–Vis spectra and TEM.

2. Experimental

2.1. Materials and reagents

All reagents were of analytical grade and were purchased and used as received without further purification: cobalt acetate (Co(CH₃COO)₂·4H₂O; Fluka), cobalt chloride (CoCl₂·6H₂O; Sigma–Aldrich), cobalt nitrate (Co(NO₃)₂·4H₂O; Sigma–Aldrich), cetyltrimethylammonium bromide (CH₃(CH₂)₁₅N(CH₃)₃Br; CTAB; MW = 364.45 g/mol; Sigma–Aldrich), urea (0.15–3 g; CO(NH₂)₂; Fluka).

2.2. Preparation of cobalt carbonate

In a typical hydrothermal synthesis, 2.5 mmol cobalt salt: 0.62 g of cobalt acetate (Co(CH₃COO)₂·4H₂O), 0.6 g of cobalt chloride (CoCl₂·6H₂O) or 0.64 g cobalt nitrate (Co(NO₃)₂·4H₂O), independently, 0.1 mmol (36.5 mg) of cetyltrimethylammonium bromide (CH₃(CH₂)₁₅N(CH₃)₃Br; CTAB; MW = 364.45 g/mol) and a varying amount of urea (0.15–3 g; CO(NH₂)₂) were dissolved in 60 mL distilled water in an Erlenmeyer flask, and vigorously stirred for about 10 min for complete mixing. The reaction mixture was then transferred to a Teflon-lined stainless steel autoclave (capacity 100 mL). Finally, the autoclave was closed and kept inside an electric oven at 160 °C for a certain reaction period, typically from 3 to 24 h, when cobalt chloride or cobalt acetate was used as a cobalt ion source; and from 3 to 72 h, when cobalt nitrate was used. After the reactions, pink solid products of cobalt carbonates (CoCO₃); or mauve solid products, depending on the reaction conditions, were washed with deionized water and ethanol several times via centrifugation–redispersion cycles, and then dried in an oven at 60 °C for 24 h.

2.3. Preparation of nano-structure of tricobalt tetroxide (Co₃O₄)

The thermal decomposition of the as-prepared CoCO₃ (A, B and C) to tricobalt tetroxide (Co₃O₄) was performed at 500 °C for 3 h in an electric furnace.

2.4. Characterization

The as-prepared samples were characterized by X-ray powder diffraction (XRD) using a 18 kW diffractometer (Bruker; model

D8 Advance) with monochromated Cu K α radiation (λ) 1.54178 Å. The SEM images were taken on a scanning electron microscope (JEOL; model JSM-5410). The TEM images were taken on a transmission electron microscope (JEOL; model 1200 EX) at an accelerator voltage of 80 kV. FT-IR spectra were recorded using a FT-IR spectrometer (Bomen; model MB157S) from 4000 to 400 cm⁻¹ at room temperature. The thermal analysis (TGA and DTA) measurements were carried out on a thermal analyzer instrument (Shimadzu; model TA-60WS) with a heating rate of 15 °C/min in nitrogen gas. Note, the CoCO₃ and Co₃O₄ samples obtained from cobalt acetate, cobalt chloride and cobalt nitrate will be referred to as A, B and C, respectively.

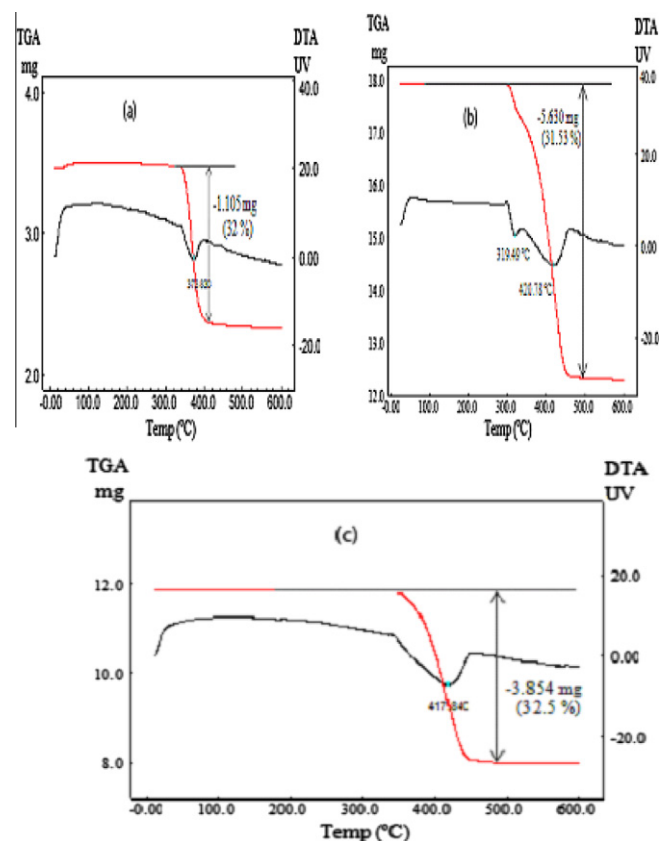


Fig. 4. (a–c) TGA and DTA curves of the prepared cobalt carbonate samples.

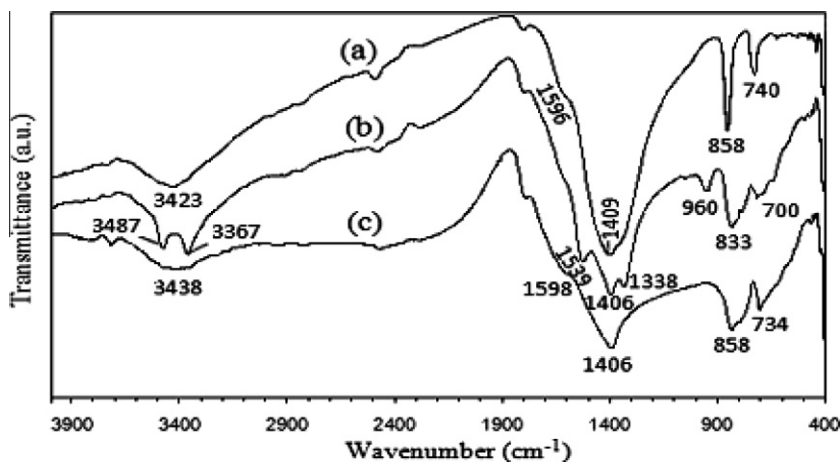


Fig. 3. (a–c) FT-IR spectra of the prepared cobalt carbonate samples.

3. Results and discussion

3.1. Morphology and XRD study

The morphologies of the as-prepared CoCO_3 submicrometer crystals were investigated with SEM. Fig. 1a–c show some typical images of the SEM of the as-prepared CoCO_3 products. When different counter ions, such as acetate, chloride and nitrate, were used during the preparation of cobalt carbonate, CoCO_3 submicrometer crystals with different morphologies were obtained. The obtained cobalt carbonate crystals from cobalt acetate or cobalt nitrate were almost uniform, but the ones obtained from cobalt chloride were not. From the micrograph, it was observed that the cobalt carbonate particles were quasi cubes with an average diameter of $2.8 \mu\text{m}$ (Fig. 1a), tetragonal with an average length of $7 \mu\text{m}$ and an average width of $1.3 \mu\text{m}$ (Fig. 1b), and flakes congregated and stacked more compactly into irregular cubes with an average diameter of $25 \mu\text{m}$ (Fig. 1c), for A- CoCO_3 , B- CoCO_3 and C- CoCO_3 , respectively.

The crystal phases of the as-prepared cobalt carbonate samples prepared by using the previously mentioned counter ions were examined by XRD patterns as shown in Fig. 2. The intensities of the sharp diffraction peaks indicated that the obtained product has good crystallinity. All of the diffraction peaks in the XRD

patterns can be indexed as a pure hexagonal phase of CoCO_3 with cell constants: $a = 4.661 \text{ \AA}$, and $c = 14.96 \text{ \AA}$ (space group $R\bar{3}c$, JCPDS card 78-0209); these data are in agreement with the ones published by Cong et al. [31]. No other peaks for impurities were detected. The average size of the nanocrystallites was also estimated using the Debye–Scherrer formula [51]:

$$D = 0.9\lambda / \beta \cos \theta_B \quad (1)$$

where λ , β , θ_B are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle respectively. The estimated crystallite size from XRD data is found to vary from 127 nm (for A- CoCO_3) to 207 nm (for C- CoCO_3). From both SEM and XRD data it seems that the CoCO_3 submicrometer crystals were formed by aggregation of smaller crystallites during the synthesis process. The three CoCO_3 samples with a single phase could be prepared in an autoclave with a reaction time of 24 h when acetate or chloride counter ions were used, and in 36 h when the nitrate counter ion was used. It is worthy to mention that when the reaction time was reduced to less than the indicated ones, the urea–cobalt salt reactions sometimes gave basic cobalt carbonates and in other cases it gave a mixture of cobalt oxide and cobalt carbonate. The growth and nucleation mechanism of the CoCO_3 submicrometer crystals can be explained by a

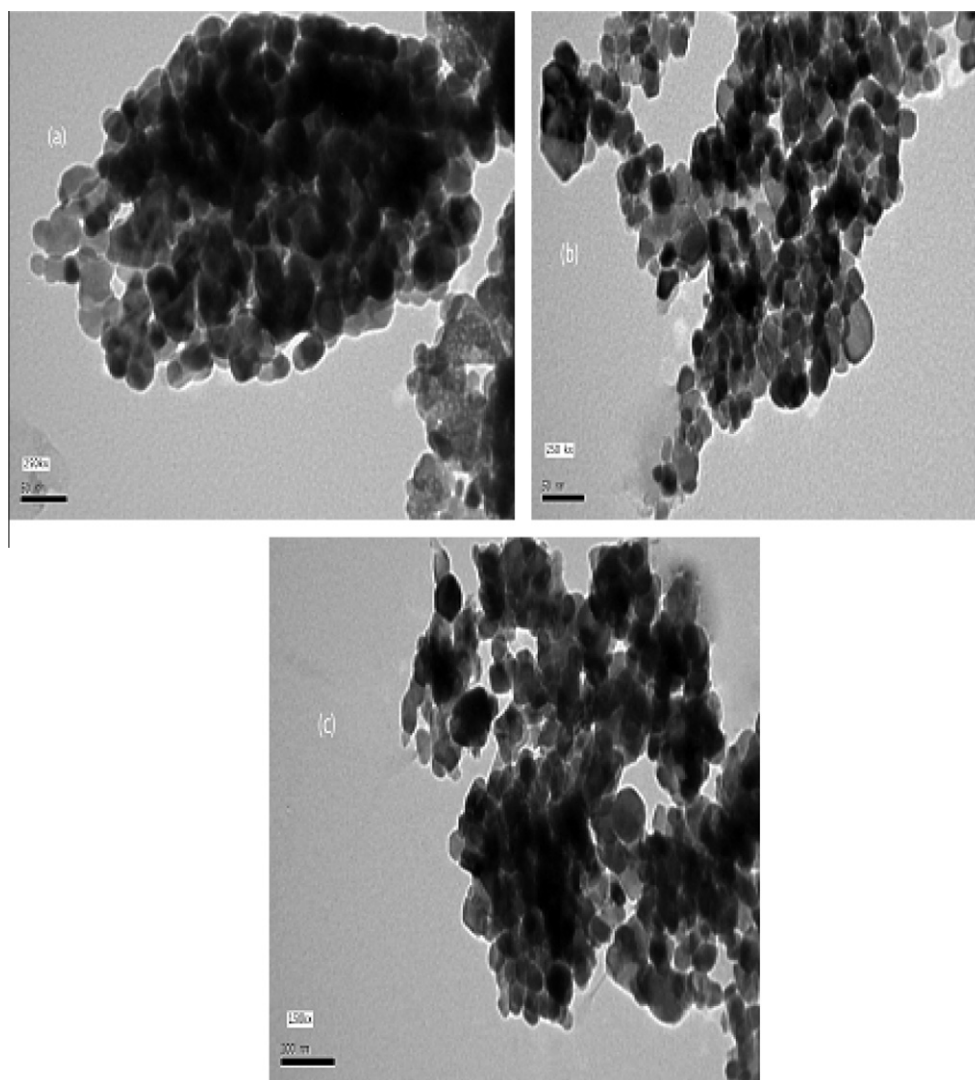
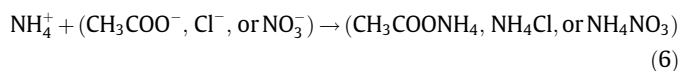
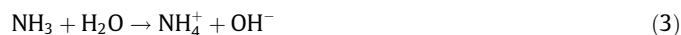
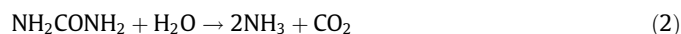


Fig. 5. (a–c) TEM images of the prepared Co_3O_4 samples.

precipitation–dissolution–renucleation–growth–aggregation mechanism [30]. At the beginning, when the reaction mixture solution reaches its supersaturation, primary precipitates are instantaneously formed. After that, this process is followed by dissolution of unstable precipitates which then give renucleation and growth of crystallites [20,29,44,52]. The produced crystallites aggregate and coagulate into final crystals, as described in mineralization processes [53]. The formation mechanism of cobalt carbonate can be proposed based on the reactions (2)–(6) [54]. Urea in these reactions serves mainly as a carbonate source because urea decomposes into carbon dioxide and ammonia in aqueous solutions at temperatures higher than 80 °C [55]. Carbon dioxide then reacts with hydroxide ions to generate carbonate ions [56], which finally react with cobalt ions to form cobalt carbonate products.



3.2. FT-IR-spectra

The bonding and chemical composition of the cobalt carbonate were investigated using FT-IR. Fig. 3 shows the IR spectra of the as-prepared A-CoCO₃, B-CoCO₃ and C-CoCO₃ samples. The IR spectra show bands around 3423, 3487 and 3423 cm⁻¹ for the A-CoCO₃, B-CoCO₃ and C-CoCO₃ samples, respectively, which can be attributed to the stretching vibration of the O–H group of surface molecular water and O–H hydrogen-bonds O–H [30]. A band appearing at 3367 cm⁻¹ for B-CoCO₃ is attributed to the O–H group interacting with carbonate anions of CoCO₃ [29,57]. The evidence for the presence of CO₃²⁻ in the CoCO₃ samples can be confirmed by its fingerprint peaks of D_{3h} symmetry at 1409, 858 and 740 cm⁻¹ for A-CoCO₃, at 1406, 833 and 690 cm⁻¹ for B-CoCO₃, and at 1406,

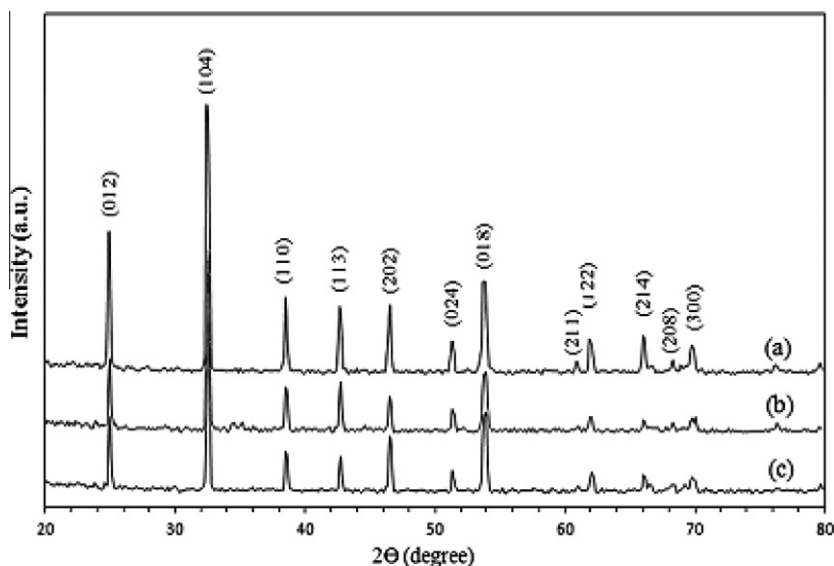


Fig. 6. (a–c) XRD patterns of the prepared Co₃O₄ samples.

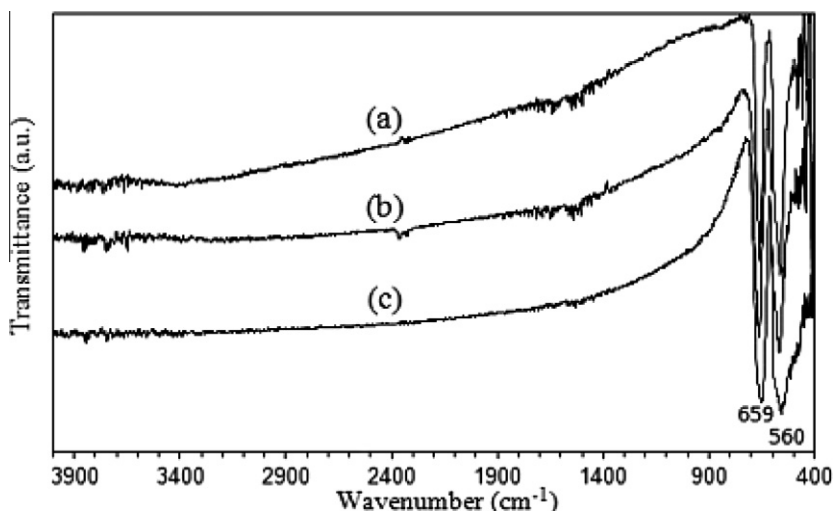
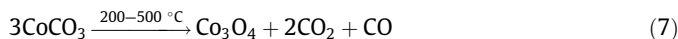


Fig. 7. (a–c) FT-IR spectra of the prepared Co₃O₄ samples.

858 and 734 cm^{-1} for C- CoCO_3 , which are assigned for each prepared carbonate sample to the vibrational modes $\nu_3(E')$, $\nu_2(A_2'')$ and $\nu_4(E'')$, respectively, according to normal modes of vibration of planar XO_3 molecules/ions ($\text{X} = \text{carbon}$ in the present case) [58–60]. The shoulder appearing at 1596 cm^{-1} for A- CoCO_3 and at 1598 cm^{-1} for C- CoCO_3 , and the peak appearing at 1539 cm^{-1} for B- CoCO_3 may be assigned to the bending vibration of adsorbed water molecules [61]. The peak appearing at 3367 cm^{-1} for B- CoCO_3 is attributed to the O–H groups interacting with the carbonate anions of CoCO_3 [30]. There are two peaks at 960 and 1338 cm^{-1} for B- CoCO_3 which may be assigned to the presence of the CTAB surfactant as an impurity in a very small quantity.

3.3. TG-DTA analysis

The thermal behavior of the as-prepared CoCO_3 samples has been investigated by TGA and DTA techniques as shown in Fig. 4a–c. The TGA curves show that there is one weight loss step in the temperature range 320–390 °C, two merged steps in the range 290–460 °C and one step in the range 320–450 °C for A- CoCO_3 , B- CoCO_3 and C- CoCO_3 , respectively. The actual weight loss of CoCO_3 to Co_3O_4 in this thermal process was about 32%, 31.53%, and 32.5% for A- CoCO_3 , B- CoCO_3 and C- CoCO_3 , respectively, which is close to the theoretically calculated value (32.5%). Hence, the as-prepared cobalt carbonate samples in our report are more pure than the ones prepared by others [29,30]. Moreover, the thermal decomposition of the as-prepared cobalt carbonate samples under nitrogen gas can be represented by the following equation:



Additionally, the DTA thermal analyses show that the thermal decomposition of the as-prepared cobalt carbonates is an endothermic process, as seen in Fig. 4a–c.

On the basis of the TGA results, the temperature for the calcinations of the CoCO_3 precursor to Co_3O_4 particles was set at 500 °C for 3 h to ensure the complete decomposition of the CoCO_3 precursor. Morphologies of Co_3O_4 particles were investigated with TEM. Some of the TEM images of the obtained Co_3O_4 are presented in Fig. 5a–c. From the micrograph, it was observed that the Co_3O_4 particles show dense bulk agglomerates, and the particles have both rounded and squared shapes with an average diameter of 35, 29 and 29 nm, for A- Co_3O_4 , B- Co_3O_4 and C- Co_3O_4 , respectively. The crystallographic phase of this spinel oxide was confirmed by the XRD method, as displayed in Fig. 6. All the diffraction peaks in the XRD patterns can be assigned to the cubic phase of Co_3O_4 samples (A- Co_3O_4 : space group $Fd\bar{3}m$, lattice constant $a = 8.084$ Å, JCPDS card 43-1003; B- Co_3O_4 : space group $Fd\bar{3}m$, lattice constant $a = 8.085$ Å, JCPDS card 78-1970; and C- Co_3O_4 : space group $F\bar{4}3m$, lattice constant $a = 8.065$ Å, JCPDS card 71-0816). No other peaks for impurities were detected. The average size of the nanocrystallites was also estimated using the Debye–Scherrer formula (Eq. (1)) and it was found to be 39, 31.8 and 30.1 nm for A- Co_3O_4 , B- Co_3O_4 and C- Co_3O_4 , respectively, and these values are close those obtained from the TEM analysis. The FT-IR spectra (Fig. 7) show two strong absorption bands at 659 and 560 cm^{-1} which confirms the spinel structure of Co_3O_4 . The first peak is attributed to the stretching vibration mode of M–O in which M is Co^{2+} and is tetrahedrally coordinated, and the second peak can be assigned to M–O in which M is Co^{3+} and is octahedrally coordinated [62,63].

3.4. Optical absorption

UV–Vis absorption spectra were carried out in order to characterize the optical absorbance properties of the cobalt oxide

samples, as presented in Fig. 8(i) a–c. The band gap E_g can be calculated from Eq. (8) [64,65]:

$$(\alpha h\nu) = K(h\nu - E_g)^n \quad (8)$$

where α is the absorption coefficient, K is a constant, E_g is the band gap and n equals either 1/2 for a direct allowed transition or 2 for an indirect allowed transition. In this case, $(\alpha h\nu)^2$ is plotted versus $h\nu$, as shown in Fig. 8(ii)a–c. The value of $h\nu$ extrapolated to $\alpha = 0$ gives the absorption band gap energy. The curves in Fig. 8(ii)a–c can be linearly fitted into two lines with intercepts at: 2.15 and 1.5 eV, 1.9 and 1.48 eV, and 1.94 and 1.49 eV, respectively. The band gap of 2.15, 1.9 and 1.94 eV for A- Co_3O_4 , B- Co_3O_4 and C- Co_3O_4 , respectively, can be assigned to a Co^{2+} , O^{2-} charge transfer process (basic optical band gap energy or valence to conduction band excitation), while the band gap of 1.5, 1.48 and 1.49 eV for A- Co_3O_4 , B- Co_3O_4 and C- Co_3O_4 , respectively, can be assigned to a Co^{3+} , O^{2-} charge transfer (the Co^{3+} level located below the conduction band). The best fit of Eq. (2) gives $n = 1/2$, suggesting

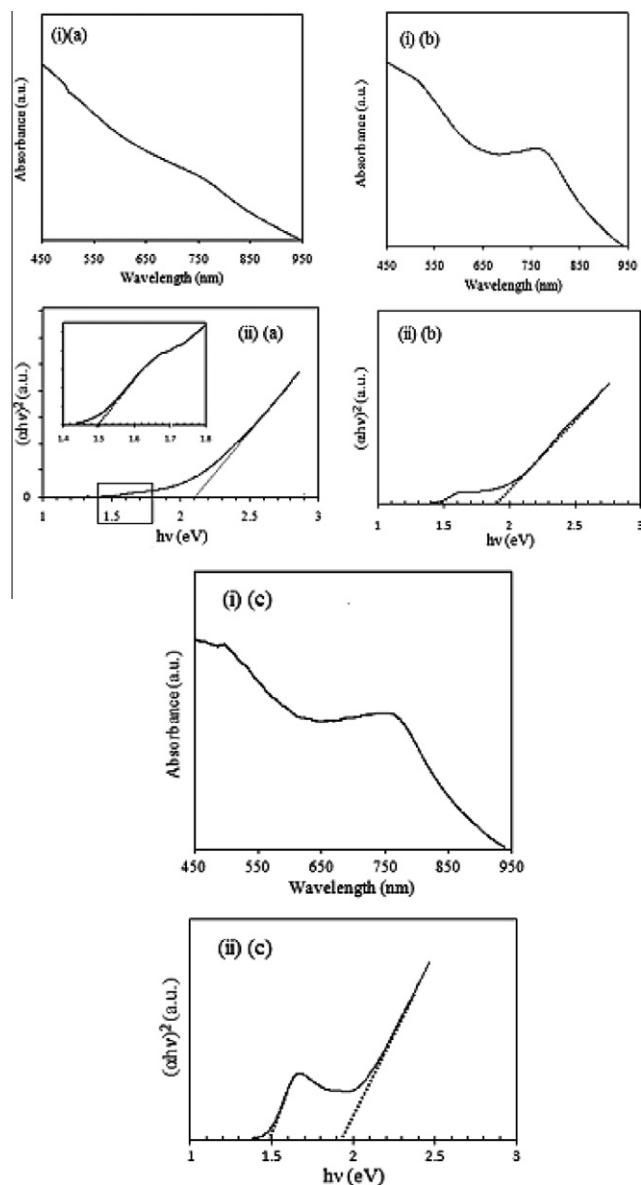


Fig. 8. (a–c) (i) UV–Vis absorption spectra and (ii) $(\alpha h\nu)^2 \sim h\nu$ curve for the prepared cobalt oxide using different counter ions: a – cobalt acetate, b – cobalt chloride, and c – cobalt nitrate.

that the obtained Co_3O_4 nanoparticles in all cases are semiconducting with a direct transition. Additionally, the presence of two band gaps with the specific determined values proves the purity of the prepared Co_3O_4 , and these data are in agreement with those previously reported [34,65–68].

4. Conclusion

Submicrometer crystalline particles of cobalt carbonate with different morphologies can be prepared by a hydrothermal process using cobalt acetate, cobalt chloride or cobalt nitrate and urea, in presence of cetyltrimethylammonium bromide (CTAB) as a surfactant. Squared-shape nanoparticles of Co_3O_4 , with an average size from 30 to 39 nm can be produced by calcination of the CoCO_3 samples at 500 °C for 3 h. The as-prepared cobalt oxide nanoparticles show some optical properties such as the presence of two band gaps with values in range 1.94–1.49 eV, which confirm the semiconducting properties of the prepared Co_3O_4 nanoparticles.

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