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Original Research Paper

# Effect of fuel/oxidizer ratio and the calcination temperature on the preparation of microporous-nanostructured tricobalt tetraoxide

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ABSTRACT

Microporous tricobalt tetraoxide, $Co_3O_4$, nanoparticles (NPs) clusters have been successfully fabricated using a simple but efficient controlled solution combustion route. Such a synthesis involves combustion reaction of cobalt nitrate with cetyl trimethylammonium bromide (CTAB). The combustion process has been analyzed by simultaneous thermal analysis. The resultant powders were characterized by means of X-ray diffraction technique (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and nitrogen adsorption at −196 °C. The morphology and specific surface area of the obtained $Co_3O_4$ nanoparticles clusters have proved to be strongly dependent on the fuel (F)/oxidizer (O) molar ratio and the calcination temperature. It was found that both the crystallite size and the lattice parameter nanocrystalline $Co_3O_4$ increase with increasing the F/O molar ratio as well as the calcination temperature. X-ray diffraction confirmed the formation of CoO phase together with spinel $Co_3O_4$ using F/O ratio of 1. The concentration of such phase increases with increasing the F/O ratio. Moreover, when the calcination is applied at 900–1000 °C traces of CoO was obtained together with $Co_3O_4$ as a major phase.

## 1. Introduction

Tricobalt tetraoxide, $Co_3O_4$, is an important magnetic p-type semiconductor with the normal spinel structure represented as $AB_2O_4$ in which A ions, $Co^{2+}$ ($3d^7$), occupying tetrahedral sites and B ions, $Co^{3+}$ ($3d^6$), are located in octahedral sites [1,2]. $Co_3O_4$ have direct optical band gap at 2.18–3.52 eV [3]. In recent years, there has been great research interest in synthesis and applications of nanostructured $Co_3O_4$. This is due to the fact that cobalt oxides with different nanostructures and morphologies have attracted more attention due to their unique applications as catalysts for selective catalytic reduction of NO by ammonia [4], Fischer–Tropsch synthesis [5], hydrogenation of carbonyl sulfide [6], and photocatalytic degradation of reactive black [7], methyl orange [8], and methylene blue [9] dyes. More recently, nanocrystalline $Co_3O_4$ showed promising potential applications as anode material for lithium-ion batteries [10,11] and superior specific capacitance for supercapacitors [12–14].

$Co_3O_4$ is conventionally synthesized via the thermal decomposition of cobaltous salts at elevated temperatures under oxidizing conditions [15]. This approach usually leads to grain growth or sintering and unlikely to produce high surface area particles with special morphological character [16]. To date, various $Co_3O_4$ nanostructures have been prepared by using different synthesis methods. In this context, $Co_3O_4$ nano-cubes have been synthesized using solution precursor plasma spray [13], thermal decomposition of cobalt malonate [17], solvothermal transformation of hexagonal β-$Co(OH)_2$ [18], and hydrothermally by mixing high temperature water (sub-, near to supercritical) with an aqueous cobalt acetate precursor at high pressure [19]. Nano-crystalline $Co_3O_4$ rods were prepared via thermal decomposition of its oxalate salt [20] or using ethylene glycol route and subsequent thermal process [4,6]. $Co_3O_4$ nanowires were synthesized from the decomposition of the corresponding nanowires of $CoC_2O_4{\cdot}2H_2O$ [11], β-$Co(OH)_2$ [21], and $Co(OH)_{1.0}(CO_3)_{0.5}{\cdot}0.11H_2O$ [22]. Spherical $Co_3O_4$ nanoparticles were prepared using sol–gel [23], aerosol flame [24], and hydrothermal [25] syntheses. Quasi-spherical $Co_3O_4$ nanoparticles were prepared by the decomposition of the hexamminecobalt (III) nitrate complex, $[Co(NH_3)_6](NO_3)_3$, at 200 °C [1,3]. Concurrently, hierarchical urchin-like hollow spheres were obtained throughout the decomposition of their carbonate and hydroxyl–carbonate precursors [7,26]. Novel $Co_3O_4$ nanoflower structures were fabricated by hydrothermal method using hexadecyltrimethyl ammonium Bromide (CTAB) [27] and polyvinylpyrrolidone [28] as surfactants and hereafter with a post-calcination process in air. Other morphologies such as nanosheets, nanorings, nanobelts, nanofibers,

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and nanowalls have also been recently synthesized by various routes [2,12,14,29–32].

Combustion reaction is one of the most accessible, fast and low-energy soft methods for the synthesis of variety of advanced ceramics, catalysts and nanomaterials [33–37]. Combustion synthesis (CS) methods can be classifies on the basis of physical nature of reaction mixture itself into three categories: (i) flame synthesis or gas phase combustion, (ii) heterogeneous condensed phase combustion synthesis and (iii) solution combustion synthesis (SCS) [33]. Focusing our attention to the SCS route, it involves a self-sustained exothermic reaction between an oxidizer (e.g. metal nitrate) and a fuel (e.g. urea, glycine, hydrazides, carbohydrazide, etc.). The mechanism of combustion reaction is quite complex and influenced by several parameters including type of fuel, fuel to oxidizer ratio, ignition temperature and water content of the precursor mixture [37]. As a consequence, the particle morphology, crystalline phase, surface area and other particular properties of the final solid products could be directed only by adjusting these parameters. A literature survey indicates that SCS based techniques have been used in the production of a wide variety of nanomaterials such as, Ni–Fe–Cu–O catalysts, $CaAl_2O_4$, $\alpha$-$Al_2O_3$, $ZnAl_2O_4$, $Mg_{1-x}Co_xAl_2O_4$, and $Mg_{1-x}Ni_xAl_2O_4$ [33,34,36,38–40].

In the open literature, there are several reports on the formation of tricobalt tetraoxide by the SCS method [36,41–43]. In the work cited, a series of fuels (aspartic acid, glycine, and urea) was employed. CTAB is known to be utilized as a template in the synthesis of mesoporous materials [27,44]. To the best of our knowledge, there are no studies on the synthesis of nanocrystalline $Co_3O_4$ employing CTAB as fuel. For this reason, in the current work, we report on the synthesis of microporous nanocrystalline $Co_3O_4$ clusters via the solution combustion reaction employing cobalt nitrate as oxidizer and CTAB as fuel with various F/O ratios. A series of characterization techniques were employed to study the crystal structure, surface properties and the morphologies of the as-prepared $Co_3O_4$ samples. We also report the effectiveness of the calcination temperature in controlling the morphology and the crystallite size of the obtained $Co_3O_4$ NPs.

## 2. Experimental

### 2.1. Preparation procedure

Cobalt nitrate, $Co(NO_3)_2{\cdot}6H_2O$, and CTAB, $((C_{16}H_{33})N(CH_3)_3Br$, were of analytical grade reagents and were used without further purification. Distilled water was used in all of preparations. Two series of samples were prepared. In the first one, we have investigates the influence of changing the F/O ratio, 0.5, 1, 2, 5, 8 and 16, on the texture, morphology, and crystallite size of $Co_3O_4$. In a typical procedure, the required amounts of cobalt nitrate and CTAB, for each F/O mixture, were weighed to the nearest milligram. The fuel and the oxidizer were dissolved in 100 ml of distilled water to form a pink homogeneous solution; the solution was then evaporated by heating over a hotplate at around 100 °C leading to the formation of a viscous gel. Such gel was, finally, calcined in muffle furnace at 400 °C for 3 h in a static air atmosphere. In series II, we have investigated the effect of changing the calcination temperature, 350–1000 °C employing the same procedure and a CTAB/cobalt molar ratio of 0.5.

### 2.2. Characterization

Simultaneous TGA and DTA curves were recorded with a Shimadzu DTG-60 instrument apparatus using a heating rate of 10 °C $min^{-1}$ in air atmosphere (flow rate 40 ml/min). Powder X-ray diffraction (XRD) patterns were recorded using Philips diffractometer (type PW 103/00) with Cu K$\alpha$ radiation ($\lambda$ = 1.5405 Å) at 35 kV and 20 mA with a scanning rate in 2$\theta$ of 0.06 $min^{-1}$. FTIR spectra were performed employing the KBr disc technique in the wavelength range 4000–400 $cm^{-1}$, using Thermo-Nicolet-6700 FTIR spectrophotometer. Nitrogen adsorption isotherms, measured at −196 °C, were constructed using Quantachrome (Nova 3200 series) multi-gas adsorption apparatus. Surface areas were calculated by BET analysis of the corresponding adsorption isotherms whereas the external surface areas were calculated using the $V_a$–$t$ plots of de Bore [45]. Scanning electron micrographs were obtained using a JEOL scanning microscope (model JSM-5400 LV). Transmission electron images were taken using JEOL transmission microscope (model JEMTH-100 II).

## 3. Results and discussion

### 3.1. Effect of changing the F/O ratio

Fig. 1 shows the TGA–DTG and DTA curves of the uncalcined CTAB/cobalt nitrate precursor having CTAB/Co of 0.5. Several weight loss (WL) steps can be observed upon heating the dried precursor from ambient temperature till 1000 °C (Fig. 1(a)). The first WL step starts from ambient till around 150 °C associated with

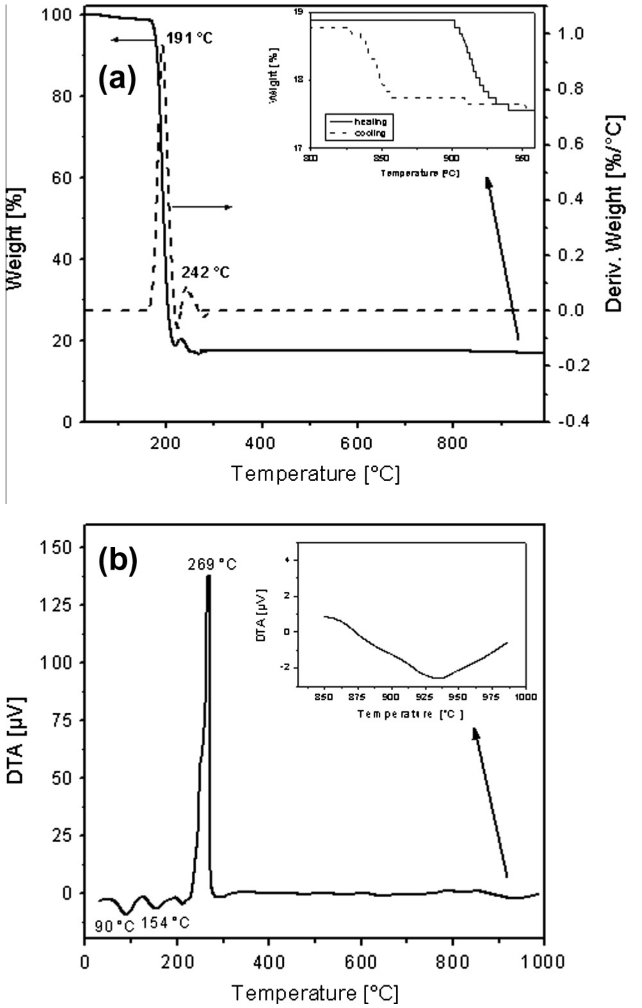

**Fig. 1.** TGA–DTG (a) and DTA (b) curves obtained by heating the dried CTAB/cobalt nitrate precursor having F/O ratio equal 0.5 in air atmosphere as (heating rate 10 °C/min).