

# Magnetic Behavior of Size-Controlled $\text{Co}_3\text{O}_4$ Nanoparticles Synthesized in the Pores of Functionalized Silica

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**Abstract** — Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) nanoparticles were prepared by reducing cobalt sulfate heptahydrate with sodium borohydride using functionalized SBA-15 mesoporous silica as a hard template. Functionalization of both external and internal silica walls leads to the infiltration and reaction of the reagents inside the silica framework. Heat treatment of the impregnated silica at 500 °C in air resulted in formation of cobalt oxide nanoparticles inside silica pores. Cobalt oxide nanoparticles with an average diameter of  $2.9 \pm 0.5$  nm were obtained by dissolution of the silica template using a solution of NaOH. The  $\text{Co}_3\text{O}_4$  nanoparticles were characterized by X-ray diffraction, and transmission electron microscopy. Magnetic properties of  $\text{Co}_3\text{O}_4$  nanoparticles were determined with a Quantum Design MPMS SQUID magnetometer. The blocking temperature ( $T_B$ ) observed at 6 K indicates a superparamagnetic behavior.

**Index Terms**— SBA-15 silica, cobalt oxide, nanoparticles, functionalization, magnetic properties.

## I. INTRODUCTION

In recent years nanostructured materials have been intensively explored because of their unique physicochemical properties, which make them desirable in many technological applications. Among all the functional materials that synthesized in size of nanometer, metal oxides nanoparticles are particularly attractive from both technological and scientific point of view. The unique characteristics of metal oxides such as, electronic, magnetic, optical, photoelectronic, and electrical properties, which almost covering all aspects of materials science and solid state physics, make them one of the most important class of materials [1].

The magnetic properties of magnetic nanoparticles (MNPs) make them extensively used in many applications, for instance nanoparticles of magnetic metal oxides have been used to enhance the contrast in Magnetic Resonance Imaging (MRI) [2, 3], also MNPs have been considered as one of the best candidates for

future magnetic recording media [4]. Furthermore, MNPs are demonstrated to be functional elements in photonic crystals, sensors based on giant magnetoresistance, and magneto-optical switches [5].

Synthesis of metal oxides nanoparticles with well-defined shapes, sizes, and crystallinity has received significant attention due to their potential applications in many areas e.g., sensors, catalytic supports, and solar cells [6-9]. Among the various types of metal oxides, cobalt oxide ( $\text{Co}_3\text{O}_4$ ) is a promising material for many applications, such as gas sensor, microbatteries, electrochromic devices, and in various catalytic applications [10-13].

Cobalt oxide in different morphologies like nanotubes, nanorods, nanocubes, spherical particles, and nanoporous structures can be obtained by different methods, such as sol-gel, reduction-oxidation, polymer combustion, mechanochemical, pulsed laser deposition, and solvothermal [11, 14-19]. However, controlling size and shape of the synthesized materials remain subject to explore.

In this study, the preparation of cobalt oxide nanoparticles with well-controlled and narrow size distribution is reported. Moreover, the magnetic behavior of the obtained nanoparticles is investigated.

## II. EXPERIMENTAL SECTION

### A. Materials

Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Aldrich), tetraethyl orthosilicate (TEOS) (reagent grade, 98 %, Aldrich), hydrochloric acid (purity  $\geq 37$  %, puriss. p.a., Fluka, ACS Reagent, fuming), Trimethylchlorosilane (TMCS  $\geq 99$  %, Aldrich), 3-Aminopropyl-trimethoxysilane (APTMS 97 %, Aldrich), sodium hydroxide pellets (purity  $\geq 97$  %, purum. p.a., Fluka), toluene (anhydrous 99.9%), cobalt (II) sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , 99%, Aldrich), sodium borohydride ( $\text{NaBH}_4$ , 99%, Aldrich), were used as received.

### B. Synthesis

Monodispersed mesoporous silica SBA-15 with a hexagonal pore arrangement was synthesized and used as molds for templating of  $\text{Co}_3\text{O}_4$  nanoparticles. The detailed description of the synthesis route was reported

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by Sayari et al. [20], where the triblock copolymer Pluronic P123 was used as a structure directing agent, and tetraethyl orthosilicate TEOS as silica source in acidic condition. The obtained silica sample is labeled as (S1).

The external surface of the (S1) sample was functionalized by trimethylchlorosilane (TMCS) according to the earlier procedure developed by Zhang et al. [21]. Typically, 1.0 g of as-synthesized silica (S1) was stirred into 100 mL of toluene in a round bottom flask for 30 min at room temperature. Subsequently, 15 mL of trimethylchlorosilane was added and heated at 80 °C for 8 h under stirring. The filtrated solid was washed twice with toluene and dried at room temperature. The obtained sample was labeled (S2). After that, and to remove P123 from the pores, the functionalized silica (S2) was calcinated at 300 °C for 5 h. This sample is labeled (S3).

The modification of the internal walls of the silica, and the reduction of cobalt salt sources inside pores of the silica were carried out according to the procedure reported by Escalera et al. [22]. For the modification of the internal walls, typically, 0.5 g of (S3) sample was suspended for 30 min in 80 mL of toluene, and then 5.0 mL of APTMS was added and stirred at room temperature for 24 h. Subsequently, the solid was refluxed for 5 h by soxlet extraction in 80 mL of toluene in order to remove the physical sorption of APTMS. The obtained sample was labeled (S4).

The method to reduce cobalt salt sources inside channels of the silica was performed as follows: 0.5 g of dried (S4) sample was transferred to a round bottom flask and mixed with 30 mL of cobalt (II) sulfate solution (0.02M), and sonicated for 15 min at room temperature. In order to remove the excess of cobalt precursor the sample was filtered and dried, and subsequently 30 mL of  $\text{NaBH}_4$  aqueous solution (0.1M) was added drop wise during magnetic stirring for 20 min to reduce the cobalt ions; the mixture was then kept in a sonication bath for 15 min at room temperature. The sample was labeled (S5).

By heat treatment of the sample (S5) in air formation of the cobalt oxide nanocrystals was achieved. The temperature was increased with a heating rate of 10 °C/min to 500 °C and held for 5 h. Finally, to remove the silica template, a solution of NaOH (0.25M) was mixed with the sample and sonicated at 55 °C for 5 h; the synthesized nanoparticles were collected using centrifugation (4100 rpm/15 min).

### C. Characterization

The crystalline structure was determined by powder X-ray diffractometry (XRD) using a Siemens D 5000 diffractometer and  $\text{Cu K}\alpha$  radiation. Transmission electron microscopy (TEM) was performed with an FEI Tecnai G2 microscope operated at 200 kV. For preparing TEM samples, the product of interest was dispersed in acetone and then deposited onto carbon copper grids and allowed to dry before analysis.

The magnetic behavior of the nanocrystals was analyzed with a Quantum Design MPMS SQUID magnetometer in the temperature range 2-25 K and in a magnetic field of 20 Oe.

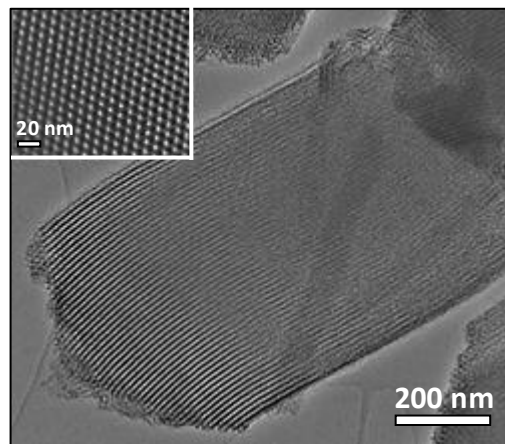


Figure 1. TEM micrograph of the silica template (S1); the inset represents the pore structure.

### III. RESULTS AND DISCUSSION

Monodispersed mesoporous silica SBA-15 has been used as a template for confined growth of cobalt oxide nanoparticles. The overall morphology and pore structure of this template are shown in Figure 1. The particles are rodlike shaped with a diameter of 0.4–0.5  $\mu\text{m}$  and a length of 1–1.5  $\mu\text{m}$ . Hexagonally ordered mesoporous channels run along the length of the particles, with a pore size of about 10 nm (see the inset).

The external surface of the synthesized SBA-15 silica (S1) was first modified with trialkylsilane ( $-\text{Si}(\text{CH}_3)_3$ ). Thereby a highly hydrophobic surface was achieved, which proved to be sufficient to avoid formation of large cobalt particles outside the silica channels.

Calcination of the obtained sample (S2) at 300 °C has previously been shown to be enough for successfully remove of P123 from SBA-15 pore channels [22, 23], and at the same time the attached functional groups remain intact on the modified surface [22]. After removal of P123 from the pores, silanol ( $\text{Si}-\text{OH}$ ) groups on the internal surface will react with APTMS, thus the internal surface is functionalized with amino group ( $-\text{NH}_2$ ). When the cobalt salt was dissolved in water the cations are hydrated  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . Therefore, hydrated cobalt ions will form a stable complex with amino groups. The attraction of cobalt ions to the silica pores is enhanced because the anchored amino groups provide a stronger negative charge than the silanol groups [17]. The X-ray diffractogram of this sample (S5) after heat treatment at 500 °C in air is presented in Figure 2. All peaks can be

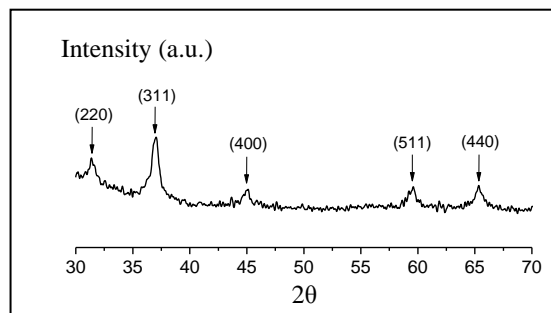


Figure 2. Powder X-ray diffractogram of SBA-15 silica infiltrated with cobalt salt after heat treatment at 500 °C in air

assigned to the crystal structure of  $\text{Co}_3\text{O}_4$  [24] suggesting that the impregnated precursor transformed to a large degree to the aimed oxide. The broadening of the diffraction peaks is due to the small crystallite size of the formed nanoparticles as indicated by the TEM micrograph represented in Figure 3.

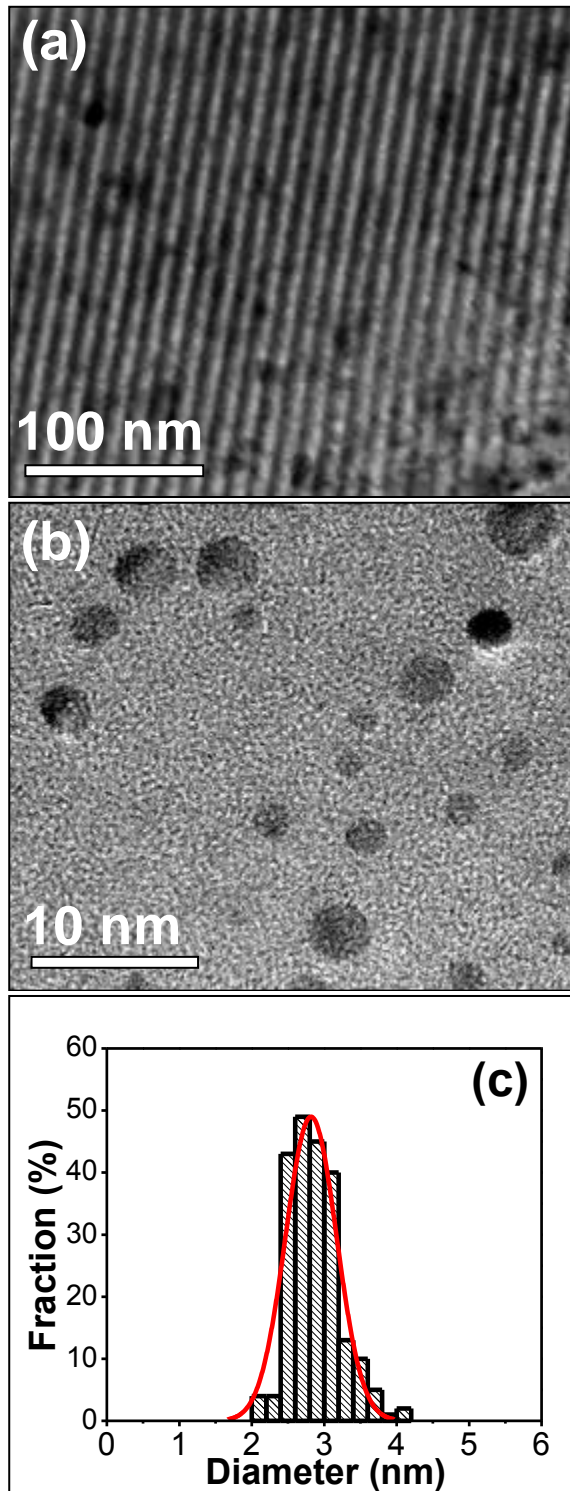


Figure 3. TEM micrographs of (a) mesoporous silica with cobalt oxide nanoparticles inside the pores (b) cobalt oxide nanoparticles on a Cu/carbon grid after silica removal, and (c) particles size distribution histogram of the obtained nanoparticles and corresponding Gaussian fit (solid line).

Transmission electron microscopy (TEM) provides direct observation of the formed cobalt oxide nanoparticles inside the silica mold as shown in Figure 3a. It is clear that the mesoporous channels maintain their well-ordered structure after nanoparticle formation. The cobalt oxide nanoparticles seen as dark spots dispersed in the silica matrix. No bulk aggregation of the cobalt oxide on the outer surface could be observed, which indicates that the  $\text{Co}_3\text{O}_4$  is confined to the pores. It is also clear from Figure 3a that the channels are only partially occupied by cobalt oxide nanoparticles, and no formation of nanowires could be found. Figure 3b shows ultra-fine cobalt oxide nanoparticles with a uniform spherical shape ranging in size between 2 and 4 nm, these nanoparticles were recovered after mild dissolution of the silica template in a solution of NaOH. The average particle size was determined by image analysis of TEM micrographs by measuring the diameter of more than 200 particles using DigitalMicrograph™ 3.9.3 software for GMS 1.4.3 by Gatan Software Team. The result is plotted in Figure 3c as a size distribution histogram. From the fit of a Gaussian function to the histogram the average diameter of the particles was determined to be  $2.9 \pm 0.5$  nm. The size distribution is narrow and the size of the obtained nanoparticles is small in comparison with that obtained using other techniques [14, 25].

The temperature dependence of the magnetisation in field-cooling (FC) and zero-field-cooling (ZFC) is shown in Figure 4, and a superparamagnetic behavior is observed with a blocking temperature  $T_B=6$  K.

The superparamagnetic behavior occurs when the crystals are smaller than the magnetic domains of the material, and the blocking temperature is also size dependent, as shown by e.g. Ichiyangi and Yamada [26]. The blocking temperature can be expressed by the equation:

$$T_B = KV/k_B \ln(\tau_{\text{obs}}/\tau_0)$$

where  $V$  is the volume of one particle,  $K$  is an anisotropy constant,  $k_B$  is the Boltzmann constant,  $\tau_{\text{obs}}$  is the measurement time and  $\tau_0$  is a characteristic time constant. The low value of  $T_B$  indicates small particles, but the blocking temperature is also dependent of the magnetic field [27].

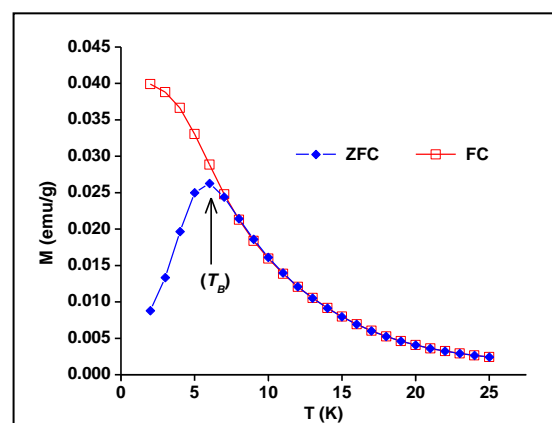


Figure 4. The magnetisation in field-cooling (FC) and zero-field-cooling (ZFC).

## IV. CONCLUSION

A wet chemical process was successfully performed to synthesize cobalt oxide nanoparticles with controlled size using NaBH<sub>4</sub> as the reducing agent, and SBA-15 mesoporous silica with both external and internal functionalized surfaces as a template. The magnetic behavior of the obtained nanoparticles was investigated. The results concluded that the ultra-fine cobalt oxide particles exhibited super paramagnetic behavior.

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