Radiation Physics and Chemistry 137 (2017) 108–115

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Local structure of cobalt nanoparticles synthesized by high heat flux plasma process

P.B. Orpe [a,b], E. Paris [c,d], C. Balasubramanian [a], B. Joseph [e], S. Mukherjee [a], D. Di Gioacchino [f], A. Marcelli [f,g], N.L. Saini [c,*]

[a] FCIPT Division, Institute for Plasma Research, Sector 25, Gandhinagar 382016, India
[b] Nirma University, S-G Highway, Chandlodia, Gota, Ahmedabad, Gujarat 382481, India
[c] Dipartimento di Fisica, Università di Roma "La Sapienza", P. le Aldo Moro 2, 00185 Rome, Italy
[d] Center for Life NanoScience@Sapienza, Istituto Italiano di Tecnologia, V. le Regina Elena 291, 00185 Rome, Italy
[e] Elettra, Sincrotrone Trieste, Strada Statale 14, km 163.5, Basovizza, Trieste, Italy
[f] INFN Laboratori Nazionali di Frascati, Via E. Fermi, 40, 00044 Frascati (RM), Italy
[g] RICMASS, Rome International Center for Materials Science Superstripes, Via dei Sabelli 119A, 00185 Rome, Italy

H I G H L I G H T S

- Co-nanoparticles synthesized by a high flux plasma process.
- The morphology of the nanoparticles depends on the plasma current.
- The local structure of Co-nanoparticles studied by X-ray absorption spectroscopy.
- Production of CoO nanoparticles and Co-metal nanoparticles at low and high plasma currents.

A R T I C L E I N F O

Article history:
Received 18 October 2015
Received in revised form
29 December 2015
Accepted 15 January 2016
Available online 1 February 2016

Keywords:
Co-nanoparticles
Plasma synthesis
EXAFS
Local disorder

A B S T R A C T

We have used high heat flux plasma synthesis process to grow Co those for the morphology, stoichiometry and the local structure as a function of plasma current. We find that the nanoparticles produced by the thermal plasma method have different shapes and size distribution with the plasma current being a key parameter in controlling the formation of composition, morphology and crystalline structure. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at Co K-edge have revealed formation of metal and metal oxide nanoparticles with the composition mainly depending on the arc current. While low plasma current appears to produce nanoparticles solely of CoO with a small amount of Co metal, the high plasma current tends to produce nanoparticles of CoO and Co_3O_4 oxides with increased amount of Co metal. The results are consistent with the morphological and structural analysis, showing nanoparticles of different shapes and size depending on the arc current.

1. Introduction

Magnetic nanoparticles have vast application potential in the fields of biology and medicine, e.g., magnetic drug targeting, magnetic resonance imaging, hypothermia, separation/purification of nucleic acids, proteins and cells (Gupta and Gupta, 2005; Gu et al., 2006). Apart from these, other applications include high density magnetic recording devices (Gangopadhyay et al., 1992), magnetic detectors and magneto-optical devices (Cahn, 1992). Study of these materials is also of scientific interest as it gives an insight into the mechanism that determines their magnetic properties (Balasubramanian et al., 2014).

Among others, iron oxide nanoparticles have been in the lime light for their biomedical applications (Laurent et al., 2008), however, metal nanoparticles like cobalt, studied to a lesser extent, can be highly useful for the purpose. Metallic nanoparticles, e.g., Co, Fe, FeCo can be of large significance due to the fact that they can be produced with smaller size and a narrow size distribution unlike the oxide nanoparticles for which direct synthesis often results in rather broad particles' size distributions (Lu et al., 2007). In addition, metal nanoparticles exhibit a high saturation magnetization (e.g., the saturation magnetization (M_s) of bulk

* Corresponding author.
E-mail address: Naurang.Saini@roma1.infn.it (N.L. Saini).

http://dx.doi.org/10.1016/j.radphyschem.2016.01.023
0969-806X/

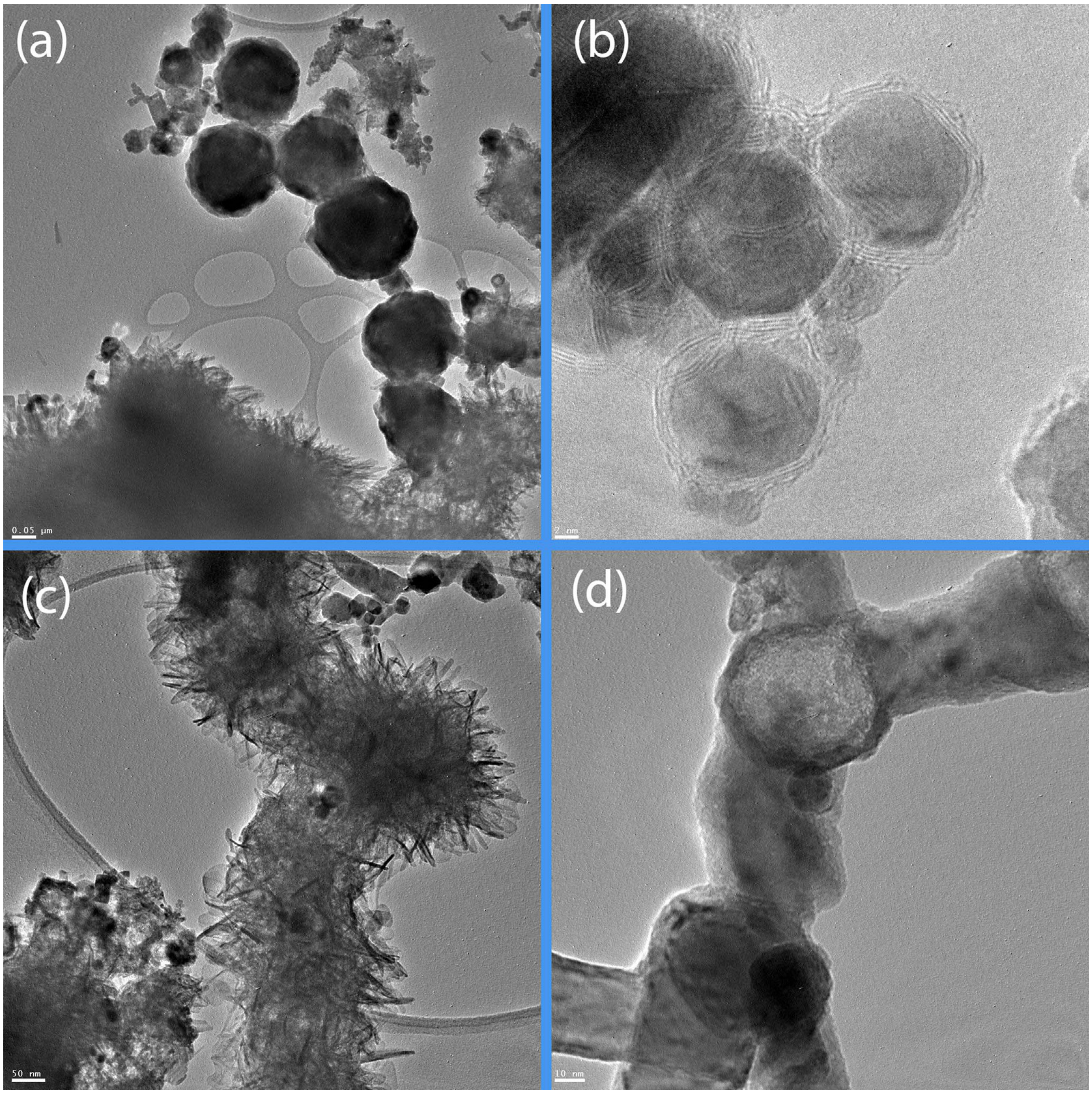

Fig. 1. TEM images of cobalt nanoparticles synthesized using high temperature plasma process with the arc current of 80 A. The white scale bars are of 0.05 μm, 2 nm, 50 nm and 10 nm respectively in the (a), (b), (c) and (d) panels.

cobalt is ~162 Am^2/kg) in comparison with oxide nanoparticles (Matoussevitch et al., 2007). Indeed, higher magnetization and hence higher specific power loss make cobalt a potential candidate for applications in hyperthermia (Zeisberger et al., 2007). On the other hand, metal nanoparticles have a tendency to get oxidized easily when exposed to ambient atmosphere, altering its magnetic properties. It is also known that cobalt nanoparticles are soft materials with very high saturation magnetization, low coercivity, high permeability and high Curie temperature and can be used in turbine engine components, magnetic bearings etc. However, owing to their high surface area they also have higher susceptibility to oxidation, affecting its magnetization. Indeed, cobalt easily oxidizes in air producing CoO (heat of formation ~237.9 kJ/mol) and Co_3O_4 (heat of formation ~891.0 kJ/mol). In many cases a thin oxide layer (of few nm) forms on the metal nanoparticles that acts as a passivating layer preventing it from further oxidation (Smardz et al., 1992).

Like for other magnetic nanoparticles, there have been several methods adopted for the synthesis of Co nanoparticles. Chemical process like co-precipitation is a commonly used method (Lee and Nakatani, 1999; Wagener et al., 1999). On the other hand, physical methods (Wagener and Gunther, 1999), based on vaporization and sputtering or thermal decomposition of carbides and halogens, followed by vapor condensation, have also been practiced. Incidentally, in the physical methods, nanoparticles' production rate has been reported to be much higher (~10 times) than usually used in chemical methods.

In this work, we have reported the use of thermal plasma for the synthesis of Co nanoparticles. The process involves vaporization followed by condensation of metal in a chamber containing high temperature of the arc zone coupled with sharp thermal gradients outside of the arc column. This process yields nanoparticles which are not only highly crystalline in nature but also can be controlled in different shapes and sizes. We have studied the effect of plasma current on the product morphology and the stoichiometry, and investigated the local structure of these nanoparticles with the aim to optimize conditions for their bulk production. Alongwith the morphological characterization by transmission electron microscopy (TEM), we have exploited capabilities of atomic site-selective experimental probe, X-ray absorption spectroscopy (Prins and Koningsberger, 1988), to study the local structure and valence electronic states of thermal plasma route synthesized cobalt nanoparticles.