Journal of Magnetism and Magnetic Materials 339 (2013) 175–181

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Surface stabilized GMR nanorods of silver coated CrO_2 synthesized via a polymer complex at ambient pressure

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ARTICLE INFO

Article history:
Received 10 November 2012
Received in revised form
2 March 2013
Available online 21 March 2013

Keywords:
CrO_2 nanorods
Chemical synthesis
Magnetoresistance
Spin dependent co-tunneling

ABSTRACT

Stable anisotropic nanorods of surface modified CrO_2 (~18 nm diameter) with a correlated diamagnetic layer (2–3 nm thickness) of silver efficiently tailors useful magnetic and magnetoresistance (MR) properties. Essentially, it involves a core-shell structure that is developed by displacing part of Cr^{4+} ions by Ag atoms on the CrO_2 surface (topotactic surface layer) via an etching reaction of a CrO_2-polymer complex with Ag^+ ions in hot water followed by heating the dried sample at 300–400 °C in air. The stable Ag-layer so obtained in the form of a shell protects CrO_2 such that it no longer converts to Cr_2O_3 in ambient pressure during the processing. X-ray diffractogram of the Rutile type tetragonal CrO_2 structure (lattice parameters $a=0.4429$ nm and $c=0.2950$ nm) includes weak peaks of a minority phase of an fcc-Ag ($a=0.4086$ nm). The silver surface layer, which manifests itself in a doublet of the $3d_{5/2}$ and $3d_{3/2}$ X-ray photoelectron bands of binding energies 368.46 eV and 374.48 eV, respectively, suppresses almost all Cr bands to appear in a measurable intensity. The sample exhibits a distinctly enhanced MR-value, e.g., (−) 7.6% at 77 K, than reported values in compacted CrO_2 powders or composites. Such a large MR-value in the Coulomb blockade regime (<100 K) arises not only due to the suppressed spin flipping at low temperature but also from a spin dependent co-tunneling through an interlinked structure of silver and silver coated CrO_2 nanorods.

1. Introduction

Chromium dioxide CrO_2 belongs to a specific class of half-metallic ferromagnetic compounds with wide range of potential applications in magnet technology, spintronics and magneto-optics, sensors, and spin-valve devices [1–14]. Useful magnetic and giant magnetoresistance (GMR) properties can be developed only in stable and ideal single domain CrO_2 particles with properly controlled size, shape, and surface structure. In this perspective, a simple synthesis technique that enables control over these attributes easily and leads to generate useful geometries with functional properties is highly desired in developing CrO_2 based magnet technology and GMR devices. Unfortunately, a pure CrO_2 with nascent surfaces is poorly stable in open air. Unless immobilized by some external means such as a thin adhesive surface layer, part of the CrO_2 from a free surface gets deteriorated to Cr_2O_3 (antiferromagnetic) at the surface, *viz.*, at an early temperature as 200 °C in 1 atm O_2 pressure [1,2]. Byproduct Cr_2O_3 grows at the expense of CrO_2. Moreover, a stable CrO_2 is often produced under high pressure with a highly interlinked $CrO_3 \rightarrow CrO_2 \rightarrow Cr_2O_3$ temperature–pressure phase diagram [5,15].

A controlled thermal or hydrothermal decomposition of CrO_3, CrO_2Cl_2, or $(NH_4)_2CrO_4$ is commonly used to derive CrO_2 in the form of a powder at an elevated temperature and pressure (typically 480 °C and 2 kbar) [2,5,16]. Single CrO_2 crystals were grown at still higher temperature 900–1300 °C (60–65 kbar) [16]. In this investigation, we developed a Cr^{4+}-polymer complex with polyvinyl alcohol (PVA) containing Ag^+ ions in hot water that yields a surface stabilized CrO_2 with silver when heated at 300–400 °C in ambient air. The Ag^+ species not only inhibit an unwanted $Cr^{4+} \rightarrow Cr^{3+}$ conversion but also promote CrO_2 to grow in single nanorods. Tailored magnetic and GMR properties of the sample Ag:CrO_2 nanorods are described here together with X-ray diffraction (XRD), microstructure and X-ray photoelectron spectroscopy (XPS) results.

2. Experimental procedure

Reactive PVA polymer molecules of refreshed surfaces able to form a polymer complex with Cr^{4+} ions were obtained by

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http://dx.doi.org/10.1016/j.jmmm.2013.03.011

magnetic stirring (10–15 h) a sample of 4.0 g/dl PVA (average molecular weight ~125,000) in hot water at 50–60 °C in air. An equal 100 ml volume of 40 g/dl sucrose in water was admixed to disperse PVA molecules via sucrose so that they can form a Cr^{4+}-PVA complex in presence of Cr^{4+} ions in small reaction centers. In water, the sucrose chelates small PVA molecules in a planar structure [9,17], which is required to shape a Cr^{4+}-PVA precursor of molecular plates in order to template a sample CrO_2 in shape of nanorods. To form a Cr^{4+}-PVA precursor, after 1 h of stirring a dispersion of PVA molecules via sucrose, the temperature was raised to 60–70 °C and then a cold CrO_3 (50 ml of 2.0 M solution in water) was injected to supply Cr^{6+} in small droplets by a syringe. An exothermic reaction proceeds in steps with a regular change in average color (see the photographs in Fig. 1a) from a blackish red (due to CrO_3) in the initial to a pale yellowish, an orange yellowish, and ultimately a dark blackish characteristic color of CrO_2 embedded in the polymer molecules.

CrO_2 remains stable inside the micellar enclosure of the PVA-sucrose molecules when cooled down to 5–10 °C (below the polymer glass transition [9,18]) just after the reaction in a hot condition. Upon 20–30 h of aging, a stable CrO_2-PVA/sucrose sample turned up that could preserve the CrO_2 when drying to a solid mass at a controlled temperature of 70–80 °C in air. Otherwise, the polymer layer piles off giving rise to uncoated CrO_2 that converts to Cr_2O_3 (greenish color) during the process. Annealing the pulverized powder at 100–120 °C in air yields a surface stabilized CrO_2 of tiny particles with carbon (amorphous) from a decomposed polymer. In order to obtain an Ag-coating of CrO_2 crystallites, a batch of 2.0 g powder so obtained was dispersed in an aqueous $AgNO_3$ (1.0 M, 100 ml) solution with continuous magnetic stirring at 50–60 °C in a dark place. After 20–30 min of reaction at this temperature, a recovered powder obtained by washing in hot water followed by drying in a reduced pressure (10–100 mbar) at 20–25 °C was annealed at 300–400 °C for 1 h in air. Stable Ag-coated CrO_2 formed in shape of nanorods no longer converts to Cr_2O_3 in ambient air.

The formation of Ag:CrO_2 nanorods was analyzed with XRD analysis, which was recorded with a Philips P.W.-1710 X-ray diffractometer using Cu K_α source of 0.15405 nm wavelength. The shape and size of the nanorods were studied with a field emission

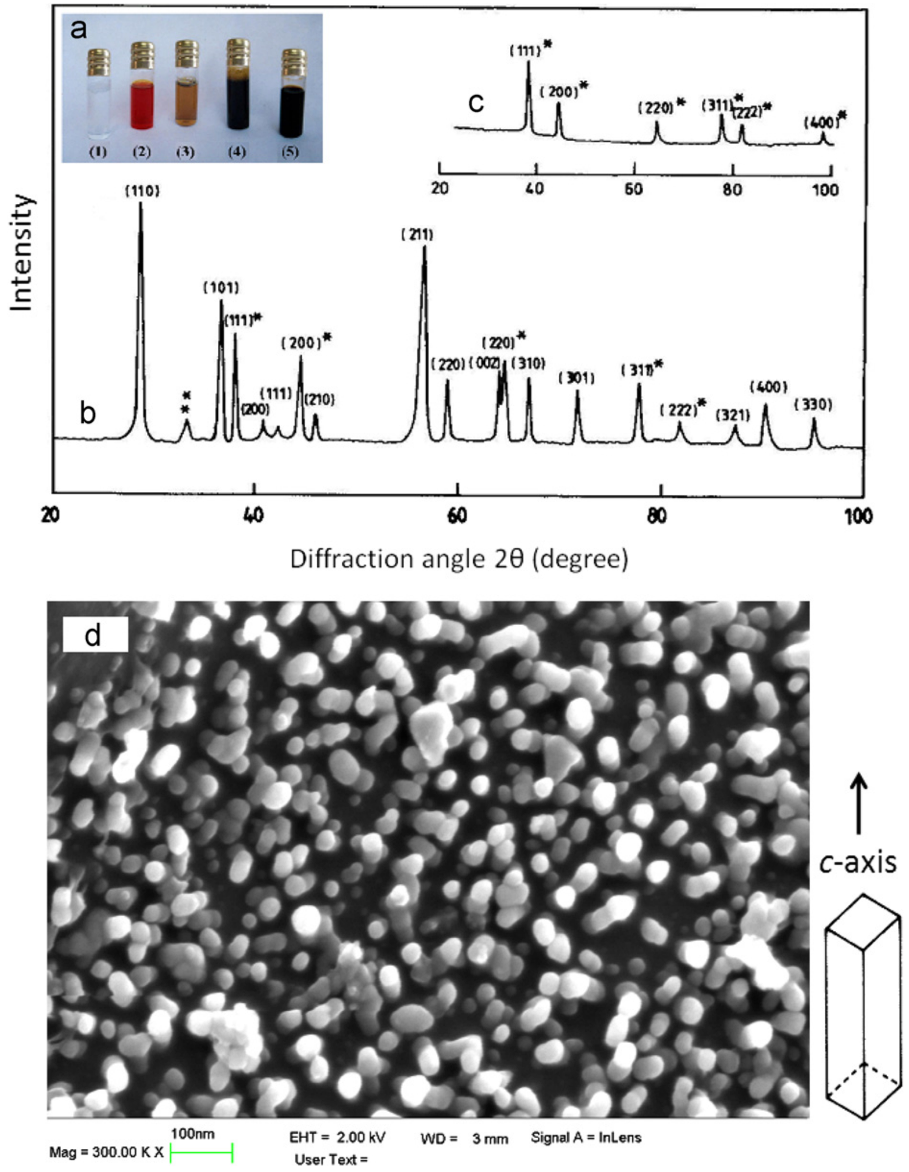

Fig. 1. (a) Colours recorded during the reaction of CrO_3 with PVA-sucrose in hot water, (1) 22 g/dl PVA-sucrose (1:10 ratio), (2) CrO_3 (2 M), and the product after (3) 1 min., (4) 5 min., and (5) 10 min reactions; (b) XRD pattern in obtained powder after heating an Ag-treated polymer complex with embedded CrO_2 of diffractogram (c) at 400 °C in air for 1 h (*Ag and * unidentified peaks), and (d) SEM image of the Ag-coated CrO_2 nanorods with a model shape in the right.