Materials Research Bulletin 48 (2013) 4039–4047

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

High coercivity sized controlled cobalt–gold core–shell nano-crystals prepared by reverse microemulsion

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ARTICLE INFO

Article history:
Received 3 October 2012
Received in revised form 10 June 2013
Accepted 12 June 2013
Available online 20 June 2013

Keywords:
A. Magnetic materials
A. Nanostructures
B. Chemical synthesis
B. Magnetic properties
C. X-ray diffraction

ABSTRACT

Size-controlled cobalt–gold core–shell nanoparticles were synthesized via the reverse-micelle microemulsion method. In order to control the size of the nanoparticles, the nucleation and growth process were performed within a confined space by adjusting the water to surfactant ratio of reverse micelles solution during synthesis. The crystallinity percentage and percentage of phases presented in Co–Au core–shell nanoparticles were calculated using X-ray diffraction data. The results from transmission electron microscopy provide direct evidence for core–shell structure nanomaterials. Magnetic properties of the samples were investigated using a vibrating sample magnetometer. The as-prepared samples showed significant coercivity at room temperature. The intrinsic blocking temperature was experimentally deduced from zero-field-cooled warmed (ZFC-W) curves by a simple method without employing an external magnetic field. The *B*-field dependence temperature data of Co–Au nanoparticles exhibited an intrinsic blocking temperature at 45 K. Annealing these samples at 400 °C caused an increase in particle size, crystallinity percentage and further enhanced their magnetic properties.

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1. Introduction

Through the past several decades, amorphous and more recently nano-crystalline materials have been investigated for applications in many fields. An example is the high density magnetic recording media technology which has grown due to its potential to store more data, access the data faster and also to use less power than current memory devices. To achieve these goals, the applied materials should have high coercivity and high magnetic anisotropy energy. The problem is how to retain the magnetization of the medium despite thermal fluctuations that are occurring at the superparamagnetic edge? This problem could be solved by preparing magnetic nanoparticles with blocking temperature near room temperature that contain less superparamagnetic domains and show single domain ferromagnetic behavior at room temperature [1,2]. Many researchers have been looking for the ways to solve this problem by preparing high quality and homogeneous particles via controlling of the preparation conditions. Increasing the storage density requires more strict control over the morphology of the magnetic material and strong reduction of its dimensions, down to the sizes of the single domain materials. In nano-region size the crystallinity percentage plays an important role and affects the properties of nanoparticles. Moreover, as a large portion of atoms in nanocrystals are located at the surface, the modification of the surface atoms has been recognized as one of the most advanced methods to improve the reactivity of surface and enhance the stability of the material. Since agglomerations and coalescence of the nanoparticles during the synthesis may cause the material to lose most of its characteristic properties therefore special organic compound such as surfactants, polymers and stabilizing ligands are used to passivate the surface of nanoparticles and prevent them from agglomeration. Advance research on nanotechnology brings new structures such as core–shell nanoparticles. These structures are applied specially in medicine for drug delivery by encapsulating cancer target inside the shells which are not harmful to the human body [3]. Core–shell structure nanoparticles have a macrostructure consisting of the surface and internal part. As compared with the single core nanoparticles, core–shell nanoparticles have shown improvement in the functional properties and oxidative stability.

Modern techniques allow fabricating different kinds of core shell nanoparticles with well-defined structural properties such as mean size, morphology and crystallography. It is often difficult to say which technique is better for synthesizing nanoparticles but

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0025-5408/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2013.06.021

chemical methods are used frequently because of their convenience and rapidity. The basic principle of chemical synthesis of nano-structured materials is to initiate chemical reactions to control the nucleation and growth of the nanoparticles. Among various chemical synthesis methods, the microemulsion based method creates stable colloids with good size dispersion and is typically carried out at relatively low annealing temperature. A restricted reverse-micelle microemulsion (water-in-oil) environment allows synthesis of nanomaterials encapsulated in tiny droplets of water dispersed in oil as the main phase. Water droplets of these reverse-micelles act as nano-reactors for performing simple reaction of synthesis, and the size of the nano-crystals is determined by the size of these droplets. The size of the water pools could be controlled by the molar ratio of water to surfactant in the system.

Among magnetic materials cobalt has attracted much attention as magnetic recording media due to its very high magnetocrystalline anisotropy, high Curie temperature and chemical stability. Since cobalt nanopaticles are sensitive to oxidation and their sensitivity increases with decreasing particle size, it would be appreciated to coat them with different materials such as silica [4], metal oxides [5] and gold [6]. It is important to choose the shell material based on the required application. For example, using silica as a shell causes reduced crystalinity of nanoparticles since silica has an amorphous phase [7]. Also exchange biasing at the interface between ferromagnetic Co core and antiferromagnetic CoO shell reduces the magnetic properties of Co nanoparticles [5]. In contrast, gold particles show high thermal and electrical conductivity, and also have high corrosion and oxidation resistance even in the nanometer size region [8]. Therefore coating a gold shell on cobalt nanoparticles can effectively reduce the oxidation of magnetic cobalt cores and could maintain most of its favorable magnetic properties [9,10]. In addition, controlling the shell thickness is a delicate point in the fabrication of core shell nanoparticles. A very thin shell causes an inefficient passivation of the core particles and leads to instability. conversely, if the shell is too thick, the strain and defect states may deteriorate properties of the resulting core–shell nanoparticles [11].

In this work cobalt–gold core–shell nanoparticles (NPs) were synthesized using the reverse-micelle microemulsion method. The average size of nanoparticles was successfully controlled by adjusting the water droplet size. Moreover the effect of ω (the molar ratio of water to surfactant) on particle size, structure, crystallinity percentage and magnetic properties of cobalt–gold nanoparticles were investigated.

2. Methodology

2.1. Preparation of cobalt–gold core–shell NPs

The Co–Au core shell nanoparticles were synthesized in a two-step route: initial synthesis of core nanoparticles and the subsequent shell growth reaction. The compositions of the used microemulsion systems are summarized in Table 1. Cobalt core nanoparticles were synthesized by preparing two microemulsion solutions. Microemulsion II was slowly added into microemulsion I under argon atmosphere during stirring, and continuously mixed for 20 min. Cobalt nanoparticles formation was indicated by an appearance of black colored precipitates. A portion of the precipitates was put aside to produce, later, purely cobalt nanoparticles without shells. The remaining precipitates were used in the next step. Microemulsion III followed by microemulsion IV was slowly added into this remainder solution to get the gold-shell. The resulting precipitates as well the purely cobalt precipitates were separately centrifuged, and washed with a mixture of methanol and chloroform (volume ratio 1:1) several times and dried at room temperature. The core–shell and cobalt nanoparticles were to be compared later.

Table 1
Composition of the microemulsions.

	Surfactant phase	Oil phase	Aqueous phase
Microemulsion I	CTAB + 1-butanol	n-Octane	$Co(NO_3)_2{\cdot}6H_2O$
Microemulsion II	CTAB + 1-butanol	n-Octane	$NaBH_4$
Microemulsion III	CTAB + 1-butanol	n-Octane	$AuCl_3$
Microemulsion IV	CTAB + 1-butanol	n-Octane	$NaBH_4$

CTAB: N-cetyl-trimethylammonium bromide.

2.2. Size controlled nanoparticles

Controlling the size of particles with microemulsion method was performed by changing the molar ratio of water to surfactant (ω = [water]/[surfactant]) from 5 to 20 to control the water droplet size in the main phase (oil).

Moreover controlling the shell thickness was performed by a calculation of the required amount of the shell precursor. Assuming all the shell material is used for deposition on the existing core nanoparticles, the amount of precursor for the growth of a shell with the desired thickness of δ can be calculated as follows [11,12]:

$$V_{\text{shell}} = \frac{nM}{N_{\text{core}}\rho_{\text{shell}}} = \frac{\pi}{6}((d_{\text{core}} + 2\delta)^3 - d_{\text{core}}^3) \quad (1)$$

where V_{shell} is the shell volume, d_{core} is the core diameter, n is the number of moles of shell material that can formed by reaction; M and ρ_{shell} are the molecular weight and density of shell material, respectively, and N_{core} is the number of core nanoparticles.

2.3. Heat treatment of Co–Au NPs

Some parts of the as-prepared powders were sintered at 400 °C for 2 h under argon gas.

2.4. Characterization methods

X-ray diffraction (XRD) spectra was obtained using a Philips Diffractometer, model 7602 EA Almelo, equipped with a graphite monochromator, operating at 40 kV and 30 mA CuKα radiation source with a wavelength λ = 1.5418 Å. The XRD run was performed at a scanning rate of 5°/min in the 2θ range 4–90°. Transmission electron microscope (TEM) was performed by a Hitachi (H-7100) electron microscopy with an accelerating voltage of 120 kV. Particle size measurement and distribution graphs were calculated over at least 150 particles per sample. Energy dispersive X-ray spectroscopy (EDX) and field emission electron microscopy (FESEM) measurements were carried out on powder samples by using a Joel-Jsm-7600F field emission SEM. Hysteresis loops measurements were obtained by a Lake Shore model 7407 vibrating sample magnetometer (VSM) at room temperature with the maximum applied magnetic field of 10 kOe on powder form samples. The blocking temperature was measured at a cusp of the magnetic field B produced by the sample in the B versus the temperature curve, during warming up of the sample from a very low temperature (15 K) to room temperature in the absence of applied magnetic field.

3. Results and discussion

Cobalt nanoparticles are extremely sensitive to oxidation [13], therefore after removing the surfactant in the washing process, the color of products changed from black to green indicating oxidation

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