Journal of Alloys and Compounds 648 (2015) 53–58

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis and characterization of Ni–Cu alloy nanoparticles with a tunable Curie temperature

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ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form
1 June 2015
Accepted 8 June 2015
Available online 12 June 2015

Keywords:
Nickel–copper alloy
Sol–gel method
Magnetic nanoparticles
Curie temperature
Magnetic hyperthermia

ABSTRACT

A series of nickel–copper alloy magnetic nanoparticles with a range of Curie points from 51 °C to 63 °C were prepared by the reduction of intimately mixed nickel and copper oxides in a silica matrix using the sol–gel method. The silica matrix was subsequently removed with an etching solution, assisted by sonication. The alloy nanoparticles were characterized using X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA/SDTA), thermomagnetic analysis (TMA), transmission electron microscopy (TEM), magnetic measurements (SQUID, vibrating-sample magnetometer) and specific absorption rate measurements (SAR). The synthesized nanoparticles show a size in the range 15–20 nm, exhibited superparamagnetic behavior with a blocking temperature (T_B) of approximately 135 K and a room-temperature magnetization of 3–9 emu/g, depending on the composition. The nanoparticles showed a relatively high effective anisotropy constant (K_{eff}) and a significant heating ability in an alternating magnetic field. The synthesis method is straightforward and allows the preparation of homogeneous Ni–Cu alloy nanoparticles with a relatively narrow particle size distribution.

1. Introduction

Magnetic hyperthermia is a method whereby the heat obtained from the self-heating of magnetic nanoparticles in an alternating magnetic field (AMF) is used for the treatment of cancer. In the case of superparamagnetic nanoparticles the heat effect is a result of the Néel and/or Brown relaxation losses [1,2]. Today, the use of magnetic nanoparticles (mostly iron oxide) prevails in various technological and biomedical applications, for example, forward osmosis [3], cellular labeling, magnetic separation, drug delivery [4–6], and magnetic-mediated hyperthermia. One of the most promising uses of magnetic nanoparticles in biomedicine is as a cure for cancer with the use of magnetic-mediated hyperthermia (which is currently in clinical trials) [7–10]. At present, iron oxide superparamagnetic nanoparticles are the only magnetic nanoparticles that are approved for in-vivo applications [11]. In spite of the fact that ferromagnetic iron oxide nanoparticles are very promising for biomedical applications, their use in more demanding applications where the Curie temperature (T_c) plays an essential role, like in magnetic hyperthermia, is inappropriate. This is because the relatively high Curie point of magnetic iron oxides could lead to overheating and might damage the surrounding human tissue in the case of superparamagnetic iron-oxide nanoparticles (SPIONs) operating on the target tumor [12]. Here, the temperature of the target location must be constantly controlled in order to prevent any overheating of the surrounding tissue during the therapeutic treatment. Invasive thermometry has revealed that there can be relatively large temperature variations during hyperthermia treatments, which means that overheating of the tissue must be prevented by careful control of the conditions [13]. Another option is for the heat generated during the hyperthermia treatment to be controlled by using magnetic nanoparticles that exhibit a ferromagnetic-to-paramagnetic transition (FM/PM) near the therapeutic temperature, i.e., around 43 °C. No heating based on

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http://dx.doi.org/10.1016/j.jallcom.2015.06.067
0925-8388/

magnetization reversal is possible above the T_c, so that the Curie temperature acts as a temperature-controlling switch and preserves a constant temperature in the area of the tumor. In $Ni_{1-x}Cu_x$ alloys, for example, the T_c can be adjusted within the temperature range of interest by changing the magnetic atom composition (x), which influences the magnetic interactions [14]. Materials based on $Ni_{1-x}Cu_x$ alloys have been extensively studied in the past for a variety of applications, as catalysts [15], for multilayer ceramics capacitors [16] and for magnetic-mediated hyperthermia [17–19]. However, their most important use relates to hyperthermia, since they provide all the essential requirements for applications in self-regulating magnetic-fluid hyperthermia (SRMFH), with the exception of the material's biocompatibility with respect to the human body. This means that the nanoparticles must be covered by a leak-proof, biocompatible, protective layer. Recently, we reported on the "in-situ" synthesis of $Ni_{1-x}Cu_x$ alloy nanoparticles based on the sol–gel process, where we avoid the detritus coarsening during the thermal treatment of the precursors [20] and put the emphasis on adjusting the homogeneous nanoparticles. The main purpose of this investigation is to perform a systematic study of the synthesis route, the nanoparticles' morphology, and the magnetic properties of the superparamagnetic $Ni_{1-x}Cu_x$ nanoparticles with various compositions and Curie temperatures close to the therapeutic one and elucidate their influence on the heating efficiency when subjected to a high-frequency magnetic field.

2. Experimental

Chemicals: Tetraethyl orthosilicate (TEOS), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), sodium hydroxide (NaOH), hydrazine hydrate (80% solution), citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) and absolute ethanol were purchased from Sigma Aldrich. All the chemicals were used as received and without further purification.

The $Ni_{1-x}Cu_x/SiO_2$ samples with appropriate molar compositions were prepared according to a procedure published elsewhere [20], with some minor changes. Briefly, the synthesis procedure was as follows: the appropriate stock solution using the salt precursors $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ in appropriate ratios were prepared to fit the selected compositions. The citric acid was then admixed and dissolved in the stock solution. After that the appropriate amount of ethanol and TEOS were added and dissolved in the solution. This caused the formation of a green solution, which was mixed with a magnetic stirrer for 1 h. The product was left for three days in the air. The obtained products were green solid gels. Afterwards, the gel was calcinated in air at 800 °C for 6 h. The as-prepared powder was a solid solution of Cu_2O–NiO in a SiO_2 matrix. The next step was the reduction of the product in a H_2/Ar atmosphere for 6 h at 850 °C. The molar ratios of all the components were Ni:Cu:CA:TEOS:D.I.:ethanol = x:y:1.1:2.9:40.6:11.6, where $x + y = 1$. The molar ratios Ni:Cu (x:y) of the prepared samples are presented in Table 1. The silica matrix was removed with the etching solution (1 M NaOH/3% wt. hydrazine hydrate) assisted by sonification in an inert atmosphere. The resulting magnetic alloy nanoparticles were washed with an etching solution several times and finally re-dispersed in absolute ethanol.

Table 1
The molar ratio Ni:Cu (x:y) of the prepared samples.

Sample	Molar ratio Ni:Cu
A	0.675:0.325
B	0.625:0.375
C	0.600:0.400

The XRD diffraction data were obtained with a D5005 diffractometer (Bruker Siemens) and analyzed with Topas software (Bruker, AXS). The crystallite size was estimated from the XRD line broadening using the Scherrer equation. The nanoparticle size and the crystallinity were characterized by transmission electron microscopy (TEM) using a JEOL 2010F microscope. For the TEM investigation the nanoparticles were deposited on a copper-grid-supported, perforated, transparent carbon film. The Curie temperature was determined using a modified thermogravimetric analysis system (thermal demagnetization) on a TGA/SDTA 851 (Mettler Toledo). The room-temperature magnetization curves of the nanoparticles were measured with a Lake Shore 7307 vibrating-sample magnetometer (VSM). The temperature dependence of the magnetic susceptibility under zero-field (ZFC) and field cooling (FC) conditions were measured with a superconducting quantum interference device (SQUD) (Quantum Design MPMS SQUID). A device that generates an alternating magnetic field equipped with a calorimeter was used to measure the magnetic heating effect (Specific Absorption Rate - SAR) of the as-prepared solid powdered samples.

3. Results and discussion

The TG/SDTA, taken in the air atmosphere of the green gel of sample (A), is shown in Fig. 1. The diagram revealed endothermic peaks at 78 °C and 100 °C due to ethanol and water evaporation and a sharp exothermic peak at 150 °C due to the oxidation of the organic component (citric acid). At higher temperatures of 225 °C and 275 °C, two notable exothermic peaks accompanied with a weight loss can be observed, which can be related to the formation of copper oxide and nickel oxide, respectively, as identified by the XRD analyses. After heating the green gel at 500 °C a gray intimate mixture of nickel and copper oxides in a silica matrix was obtained, as identified by the XRD analysis in Fig. 2. The diffraction pattern of the product is identical to a physical mixture of monoclinic copper oxide (JPCDS file 5-0661) and nickel oxide (JPCDS file 47-1049). Here, it should be noted that instead of an oxide solid solution, the diffraction pattern of two separate oxides can be observed. The formation of an oxide solid solution in the SiO_2 matrix failed since the oxide crystal structure of the constitutive oxides is not compatible, i.e., the CuO exhibits a monoclinic structure, while the NiO has a fcc NaCl-type structure. On the other hand, the XRD of the product after the heat treatment in air up to 800 °C indicates the

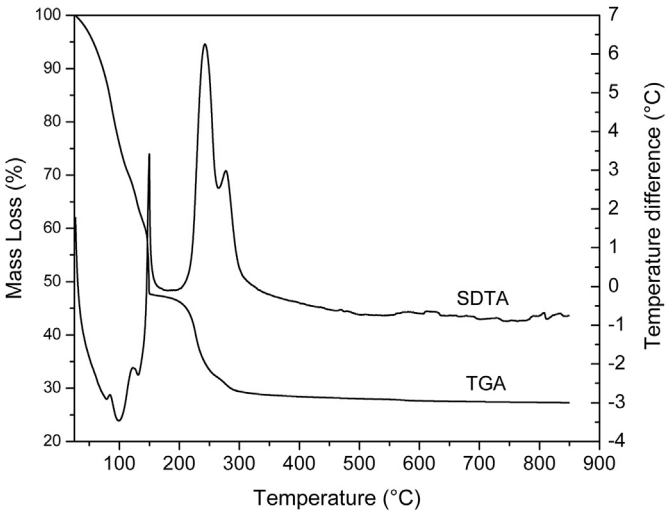

Fig. 1. TGA/SDTA spectra of green gel of sample (A) heated in an air atmosphere.