Colloids and Surfaces A 529 (2017) 239–245

Contents lists available at ScienceDirect

Colloids and Surfaces A

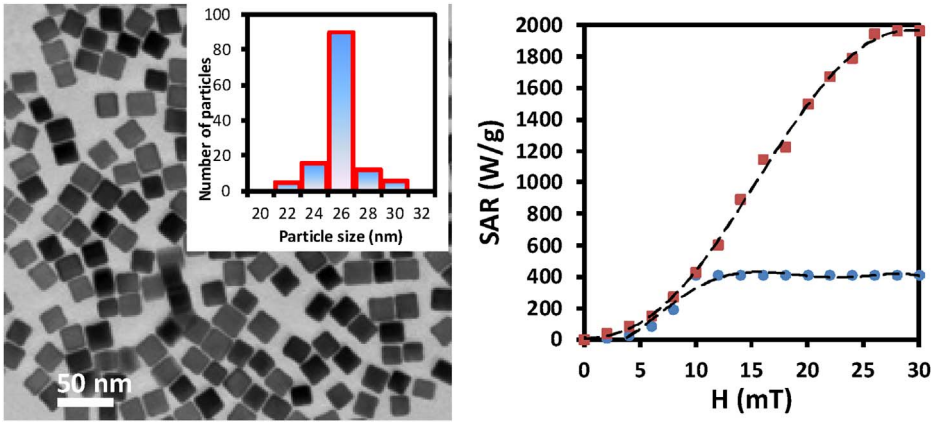
journal homepage: www.elsevier.com/locate/colsurfa

A novel approach for rapid green synthesis of nearly mono-disperse iron oxide magnetic nanocubes with remarkable surface magnetic anisotropy density for enhancing hyperthermia performance

W.E.M. Elsayed[a], Farag S. Al-Hazmi[a], Leena S. Memesh[a,*], Lyudmila M. Bronstein[a,b]

[a] King Abdulaziz University, Faculty of Science, Physics Department, Jeddah, Saudi Arabia
[b] Indiana University, Department of Chemistry, Bloomington, IN, 47405, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Nanocrystalline materials
TEM
Crystal growth
X-ray techniques
Magnetic materials

ABSTRACT

Magnetic nanoparticles have received considerable attention because of their fascinating applications in nano-catalysts, magnetic resonance imaging (MRI), drug delivery and hyperthermia. The development of robust techniques of their syntheses became of paramount concern for enhancing their magnetic properties. This would allow their use as a clinical tool instead of the conventional materials. Herein, for the first time, we report a simple but efficient and green method to develop nearly monodisperse iron oxide nanocubes via a β-amyrin assisted solvothermal method. The magnetic nanoparticles prepared were characterized using X-ray powder diffraction, transmission electron microscopy and superconducting quantum interference magnetometry. The method developed allows for a fast and facile formation of pure cubic spinel Fe_3O_4 nanostructures. Moreover, in the presence of β-amyrin, monodisperse Fe_3O_4 nanocubes with a mean diameter 26 ± 3 nm were formed, while in the absence of this compound, Fe_3O_4 nanospheres of the same size were prepared. The iron oxide nanocubes showed superior magnetic properties and the enhanced hyperthermia performance for a cancer treatment because of their higher magnetic anisotropy density compared to iron oxide nanospheres.

* Corresponding author.
E-mail address: lsmemish@yahoo.com (L.S. Memesh).

http://dx.doi.org/10.1016/j.colsurfa.2017.06.008
Received 13 February 2017; Received in revised form 29 May 2017; Accepted 5 June 2017
Available online 08 June 2017
0927-7757/

1. Introduction

Iron oxides are well known materials, which are important from technological point of view owing to their magnetic properties and applications in magnetic refrigeration, hyperthermia, catalysis, drug delivery, information storage and ion exchangers [1–6]. Among these applications, magnetic nanoparticles received considerable attention in a cancer treatment with AC hyperthermia. The efficiency of this type of thermotherapy has been examined on various kinds of cancer tumors such as prostate cancer, breast carcinoma and brain tumor [7]. Unfortunately, in many cases the treatment required a large amount of magnetic nanoparticles exceeding the toxicity limit before reaching a therapeutic temperature [7]. Therefore, to reach the therapeutic temperature at low concentrations in tissue, the magnetic nanoparticles should exhibit a high inductive specific absorption rate (SAR). It was reported that the value of SAR mainly depends on the shape, size, magnetic anisotropy and saturation magnetization of magnetic nanoparticles [8]. Thus, tuning the morphologies of magnetic nanoarchitectures during syntheses is of high significance to improve the heat generation amount. Iron oxides nanoparticles with various morphologies have been developed by various synthetic routes [9–11]. Recently, magnetic iron oxide nanoparticles have shown promising hyperthermia applications [12]. From this point of view, magnetite nanocubes seem to be promising hyperthermia probes. However, the nanocube sizes should be between 15 and 50 nm for easy penetration through the mammalian cell membranes [13]. Numerous chemical routes have been reported for syntheses of iron oxide nanocubes [14,15]. For example, Jiang and coworkers [16] have used a microwave-assisted solvothermal method to synthesize iron oxide nanocubes by thermal decomposition of iron oleate complex in the presence of oleic acid, followed by Ostwald ripening procedures. These iron oxide nanoparticles have been transformed to crystalline α-Fe_2O_3 with a trace amount of Fe_3O_4 when aged at 180 °C.

It is noteworthy that the majority of the developed recipes for producing magnetic nanocubes require expensive chemicals, while the nanocubes obtained consist of a mixture of magnetite and maghemite that might hinder the rate of heat generation under an AC magnetic field. Moreover, the majority of papers report magnetic properties, but not the hyperthermia performance. In this paper we focused on developing a green, fast, and low cost synthetic method to prepare magnetite nanocubes by using β-amyrin in a one-step reaction. β-amyrin belongs to Pentacyclic triterpenes commonly extracted from medicinal plants such as Bursera or Protium of the Burseraceae family [17]. These compounds have shown anti-microbial, anti-inflammatory and other interesting biological activities [18,19]. The presence of a hydroxyl group in β-amyrin (olean-12-en-3beta-ol, $C_{30}H_{50}O$) allows for strong affinity to iron oxides. The other advantages of β-amyrin are its low toxicity and biocompatibility [17–19].

We demonstrate that magnetic nanocrystals with cubic shape exhibit superior magnetic properties and enhanced hyperthermia performance compared to iron oxide nanospheres of approximately the same size. By performing systematic AC magnetic measurements in an aqueous solution, we show that, the SAR is strongly related to the shape and surface magnetic anisotropy density as well as the concentration of magnetic nanostructures.

2. Experimental

In a three neck flask, 0.35 g of iron acetylacetonate was dissolved in 30 mL of dibenzyl ether at 60 °C for 30 min under nitrogen bubbling. After a clear solution was obtained, 0.3 mL of 2 mM of trimethylamine N-oxide dissolved in 10 mL of mercaptoethanol was injected via a gastight syringe and left stirring for further 10 min at the same temperature. The mixture was transferred to a stainless steel autoclave and introduced into an electric oven at 200 °C with a heating ramp of 3.2 °C/min, and kept at this temperature for 3 h. Then it was left to cool down and followed by addition of 20 mL of acetone. The supernatant was discarded after centrifugation at 7000 rpm and the solid was redispersed in hexane. This process was repeated except that 0.2 g of β-amyrin was added together with iron acetylacetonate and the heating ramp was adjusted to 1.3 °C/min. Since the magnetic nanopowders obtained are hydrophobic, these nanopowders were further dissolved in a mixture of dimethylsulfoxide (DMSO) and water with the 1:1 vol ratio. DMSO was selected because of a low price and non-toxicity. It is also considered an excellent pharmaceutical agent recognized as a well-tolerated excitatory modulator in the management of cancer pain [20]. Moreover, DMSO can be easily absorbed and distributed through the biological systems. Therefore, biocompatibility is guaranteed for future medical applications.

The products were investigated by transmission electron microscopy (TEM) using JEOL-JEM-2100. The crystalline structure was examined by Rigaku-Ultima diffractometer with Cu Kα radiation (λ = 1.5418 Å). The superconducting quantum interference magnetometer (SQUID-MPMS XL-7T) was employed for assessment of magnetic properties, i.e., to obtain hysteresis curves and zero field cooling (ZFC) and field cooling (FC) curves. ZFC measurements were performed upon warming with an applied magnetic field of 50 Oe after cooling the samples in a zero applied field. The FC curves were obtained when cooling was carried out in the same applied magnetic field. The AC magnetic hyperthermia experiments were conducted using a 30 mm diameter three-turn induction coil connected with an AC generator with a power of 5 kW at a constant frequency of 276 kHz. The amplitude of the applied AC magnetic field was tuned from 0 to 28 mT, which was determined by a pick-up coil connected to the oscilloscope. The generated temperature was measured by a fiber optic probe (model: OpSens PicoM GaAs). This fiber optic was immersed in a vial tube containing 0.7 mg/mL of iron oxide nanoparticles suspended in water. SAR values were estimated by subtracting the solvent background signal and the heat losses to the environment.

3. Results and discussion

Fig. 1 depicts the XRD pattern of the prepared iron oxide nanoparticles in the absence and presence of β-amyrin. All diffraction peaks matched well the standard card (JCPDS-75-0033) of the cubic spinel crystal structure of Fe_3O_4. No other peaks were detected, confirming the high purity of the products. However, the spinel peaks were broad, implying that nanocrystals were obtained. The crystallite size, D, of the Fe_3O_4 nanostructures was determined using the Debye-Scherrer formula [21–37]

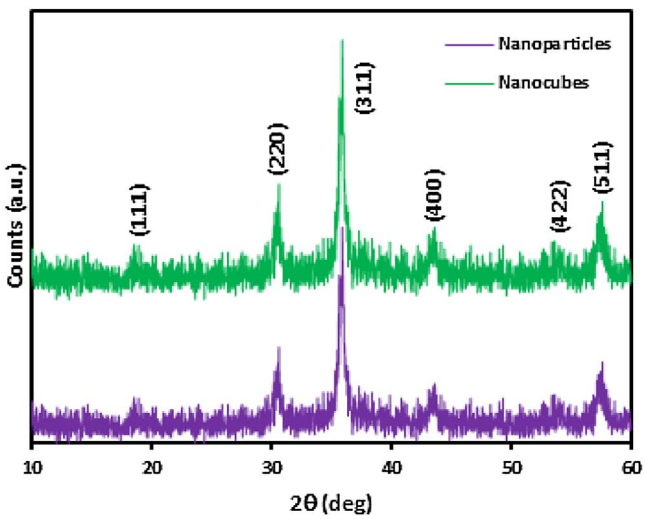


Fig. 1. XRD patterns of iron oxide nanocubes and nanospheres.