Full Length Article

X-Ray Photoelectron Spectroscopic Characterization of Iron Oxide Nanoparticles

T. Radu [a,*], C. Iacovita [c], D. Benea [b], R. Turcu [a]

[a] National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat Street, 400293, Cluj Napoca, Romania
[b] Faculty of Physics, Babes Bolyai University, 400271, Cluj-Napoca, Romania
[c] Department of Pharmaceutical Physics-Biophysics, Faculty of Pharmacy, "Iuliu Hatieganu" University of Medicine and Pharmacy, 400349, Cluj-Napoca, Romania

ARTICLE INFO

ABSTRACT

We report X-ray photoelectron spectroscopy (XPS) results on iron oxide magnetic nanoparticle (Fe_3O_4) synthesized using solvothermal reduction in the presence of polyethylene glycol. The magnetite obtained was employed as precursor for the synthesis of γ-Fe_2O_3 (by oxygen dissociation) which in turn was transformed into α-Fe_2O_3. We confirmed the magnetite, maghemite and hematite structure by Fourier Transformed Spectroscopy (FTIR) and X-ray diffraction (XRD). The analysis of the XPS core level and valence band (VB) photoemission spectra for all investigated samples is discussed in terms of the degree of iron oxidation. This is of fundamental importance to better understand the electronic structure of the obtained iron oxide nanoparticles in order to control and improve their quality for specific biomedical applications. Moreover, theoretical band structure calculations are performed for magnetite and the separate contributions of Fe in tetragonal and octahedral environment are shown.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Magnetic nanoparticles (MNPs) are of large interest for biomedicine, biotechnology, magnetic fluids, magnetic resonance imaging, data storage as well as environmental depollution [1,2]. The key feature is new significant chemical, physical and biological properties of nanosized structured materials: nanocomposite, nanoparticles, nanotubes, etc. High surface to volume ratio provide for functionalization with specific ligands, coatings and other useful tools for many targeted applications. The most widely investigated magnetic nanoparticles mainly possessing superparamagnetic properties are iron oxides, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). The most frequently iron oxide polymorph found in nature is hematite (α-Fe_2O_3), which has a high thermodynamic stability. It has a hexagonal unit cell based on anion hcp packing [3]. Moreover, through its prevalence in nature, it has great importance in the study of transport of contaminants in water and the remediation of waste [4–6]. Similar to hematite, maghemite is a fully oxidized iron oxide polymorph where all Fe atoms are in

the Fe^{3+} state [7]. γ-Fe_2O_3 revealed a spinel crystal structure with the charge neutrality of the cell being guaranteed by the presence of cation vacancies. Its crystal structure has 2 and 1/3 vacant sites within its unit cell; if the vacant sites are randomly distributed over the crystal structure, then the γ-Fe_2O_3 has an inverse spinel crystal structure which is the most general case for this compound [8,9]. It is the second most stable polymorph of iron oxide. Unlike antiferromagnetic α-Fe_2O_3, γ-Fe_2O_3 exhibits ferrimagnetic ordering with a net magnetic moment (2.5 μB per formula unit) and a high Néel temperature ($\sim$950 K), which together with its chemical stability and low cost led to its wide application as magnetic pigment in electronic recording media since the late 1940's [10]. γ-Fe_2O_3 nanoparticles are also extensively used in biomedicine, because they are biocompatible and potentially non-toxic to humans and their magnetism allows manipulation with external fields [11,12]. Additional potential applications are in the field of spintronic, where it has been suggested that γ-Fe_2O_3 can be used as a magnetic tunnelling-barrier for room-temperature spin-filter devices [13,14]. Maghemite (γ-Fe_2O_3) is the allotropic form of magnetite, these two iron oxides being crystallographically isomorphous. The main difference between them is the presence of ferric Fe^{3+} ions only in γ-Fe_2O_3, and both ferrous, Fe^{2+} and Fe^{3+} in Fe_3O_4. The latter is ordered in inverse spinel structure; the ferric ions are distributed

* Corresponding author at: National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat Street, 400293, Cluj Napoca, Romania.
E-mail address: Teodora.Radu@itim-cj.ro (T. Radu).

equally between the tetrahedral and octahedral sites, reflected in the chemical formula $Fe^{3+}[Fe^{3+}, Fe^{2+}]O_4$.

Much research has been developed in the last decades for the synthesis of iron oxide MNPs, and many reports have described efficient synthesis approaches for producing shape controlled, stable, biocompatible, and monodispersed iron oxide MNPs. The most common methods for the synthesis of high quality of iron oxide MNPs are the following: co-precipitation, thermal decomposition, hydro-/solvothermal synthesis, microemulsion, sonochemical synthesis, and sonochemical synthetic route. In addition, these MNPs can also be prepared by other methods such as electrochemical synthesis laser pyrolysis techniques, microorganism or bacterial synthesis [2,15–19]. However, high quality MNPs in terms of crystallinity and magnetic properties are given by the thermal decomposition method of iron precursors in different types of solvents [20]. The use of polyol solvents, which act as reducing agents and surfactants as well, enable in one step the formation of water-dispersible iron oxide MNPs, with improved hyperthermia properties [21] or high r_1 and r_2 relativities [22]. In many cases the polyols are not chemically bound to the surface of MNPs, detaching in time and consequently the MNPs are prone to oxidation. The organic solvents, as oleic acid and oleylamine, assure a better protection of MNPs' surface from oxidation, but they render the MNPs hydrophobic.

According to literature iron ions all possess a very complex XPS lineshape [23–26], arising from: i) electron exchange interaction effects [23–30] which are known to determine the so-called "multiplet splitting" states, ii) electron correlation effects [29–31] which produce several "shake-up" and/or "shake-off" states, iii) the multiplet components of unpaired p-electrons that are aligned antiparallel to the unpaired 3d electrons which are in turn split by correlation interaction into several further components, resulting in many final-state electron configurations of differing energies [28,31–33,34]. Thus, as a result of combination of exchange and correlation phenomena, the iron oxides involve XPS spectra that always contain a "broad" leading signal, usually with an asymmetric tail to the high binding energy (BE) side plus some high-BE satellite signals [34,35]. It has been shown in previous studies that the peak positions of Fe $2p_{1/2}$ and Fe $2p_{3/2}$ depends on the ionic states of Fe [36–42]. Moreover, the positions of the satellite peaks for the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ peaks are also very sensitive to the iron oxidation states, therefore these peaks have been used for qualitative determination of the ionic states of iron.

In the present study we exploit the advantages of XPS technique to investigate the oxidation state of iron oxide MNPs surfaces, synthesized by polyol based technique in polyethylene glycol. The spectroscopic investigation has been extended to maghemite and hematite MNPs obtained from iron oxide MNPs by applying a thermal treatment. As a reference, we have introduced in the study, superparamagnetic Fe_3O_4 MNPs synthesized by thermal decomposition in organic solvents. X-ray diffraction and fourier transform infrared (FTIR) spectroscopy has been employed to confirm the formation of a particular phase of iron oxides MNPs.

Experimental and theoretical details

All the reagents employed in this study were of analytical grade and were used without any further purification. The synthesis of magnetic nanoparticles has been performed with the following products: iron(III) chloride hexahydrate ($FeCl_3$ $6H_2O$) (Roth, $\geq$98%), polyethylene glycol 200 (PEG200) (Roth, $\geq$99%), and sodium acetate trihydrate (NaAc) (Roth, $\geq$99.5%), Iron (III) acetylacetonate (Fe(acac)3) (Merck, $\geq$99%), oleic acid (Sigma Aldrich, $\geq$99%) oleylamine (Sigma Aldrich, $\geq$99%) and octylether (Sigma Aldrich, $\geq$99%), tetramethylammonium hydroxide 25% (TMAOH) (Merck, $\geq$99%),

hexane (Merck, $\geq$99%) ethanol (Merck, $\geq$99%). Ultrapure water (18.2 MO, Barnstead EASYPureROdi) was used for the preparation of aqueous solutions.

Synthesis methods

Magnetite sample: Polyhedral iron oxide MNPs have been synthesized according to the following procedure: $FeCl_3$ $6H_2O$ (0.675 g) and sodium acetate (NaAc) (1.8 g) were mixed and dissolved in 90 ml of PEG200. The solution was stirred thoroughly at room temperature for 30 min, transferred in sealed glass bottle, and heated at 240 °C for 12 h. The final temperature was reached at heating rate of 5 °C/min. The glass bottles were let to cool at room temperature, the excess liquid was discharged, and the obtained black precipitates were washed with ultrapure water, several times, in order to remove the excess of ligands and unreacted precursors. Finally, the black precipitates were dispersed and kept in ultrapure water for further analysis. Powder of iron oxide MNPs has been obtained by selecting the MNPs with a permanent magnet, discharging the water and drying them in a rota-evaporator.

Maghemite and hematite samples: The maghemite and hematite MNPs have been obtained by thermal annealing the powder of iron oxide MNPs obtained as described above, in an oven, at 250 °C for 4 h and at 550 °C for 6 h, respectively. These transformations are irreversible at ambient conditions. For TEM measurements the powders were dispersed in ultrapure water by repeated ultrasonication cycles of 30 minutes.

Considering the general synthetic procedure for the preparation of superparamagnetic Fe_3O_4 MNPs (SPION) 0.35 g of Fe(acac)3 were dissolved in a mixture of 1,6 ml of acid oleic, 2,6 ml of oleylamine and 2,6 ml of octylether. The solution was stirred thoroughly at room temperature for 10 minutes then transferred in sealed glass bottle and heated at 200° C for 2 h and finally at 300 °C for 1 h. The intermediary and final temperature has been reached with a heating rate of 3 °C/min. The glass bottle was let to cool at room temperature and the obtained black precipitates were washed several times with ethanol, separated by using permanent magnets, dispersed and kept in 10 ml of hexane. Powder sample has been obtained by chemical precipitation of Fe_3O_4 MNPs with ethanol and further drying in a rota-evaporator. The water transfer of hydrophobic Fe_3O_4 MNPs has been achieved by re-dispersion them in aqueous solution of 25% TMAOH.

Methods

TEM images of MNPs were taken on a Hitachi HT7700 (Hitachi Ltd. Tokyo, Japan) equipped with an 8 megapixel CCD camera and operating at 100 kV in high contrast mode. For TEM examination, 5 μl drop of MNPs solution was deposited on carbon-coated copper grids. After 2 minutes the excess water was removed by filter paper and the sample was left to dry under ambient air. XPS measurements were used to comparatively investigate the core-level and VB spectra of the different obtained samples (Table 1).

The XPS measurements were performed by using a SPECS XPS system with an Al Kα source (1486.69 eV) operated with a power of 280 W.

The background pressure during measurements was 7×10^{-9} mbar. A low-energy charge neutralizer was used to remove the charge shifts during photoemission. The BE scale was calibrated to that of the C1 s photoelectron peak (284.6 eV). Survey scans were recorded at a pass energy Epass = 100 eV, in steps of 1 eV, and high-resolution spectra with 0.5 eVstep and Epass = 30 eV. Analysis of the data was carried out with Casa XPS software. X-ray diffraction (XRD) measurements were carried out on powder samples at room temperature on a