

Comparative Study between Magnetite Nanoparticles and Magnetite/Silver as a Core/Shell Nanostructure

Nabiha I. Abdo

Higher Institute of Engineering and Technology, New Borg Al Arab City, Alexandria, Egypt Email: nabiha_ibrhim@yahoo.com

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Abstract

Magnetite nanoparticles (MNPs) and magnetite/silver nanoparticles (M/Ag NPs) were synthesized by chemical co-precipitation of Fe^{2+} and Fe^{3+} . In case of M/Ag NPs, MNPs (core) were separately coated by silver metal (shell) in presence of glucose as a reducing agent. The particle size and morphology of the nanoparticles were characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM). Magnetic properties were investigated by vibrating sample magnetometry (VSM). The superparamagnetic natures of the nanoparticles were confirmed by the absence of the hysteresis loop. Coverage with silver produced a core-shell heterostructure which weakens magnetization of MNPs, inducing an inert character to the final nanostructure. The surface conjugation of MNPs with silver metal has been employed in order to improve the compatibility of magnetite nanoparticles to overcome their limitations in practical applications.

Keywords

Magnetite Nanoparticles (MNPs), Fe $_3O_4$, Silver Metal, Core/Shell, DLS, SEM, VSM

1. Introduction

During the last few years, magnetite (Fe_3O_4) nanoparticles have been attracting interest, especially in the area of clinical-oriented medical applications, such as diagnosis [1] [2], hyperthermia cancer treatment [3] or combating iron deficiencies [4]. This was possible due to their properties like biocompatibility [5] [6] [7] [8], biodegradability [9] [10] [11], magnetic behaviour [12] [13] and the possibility of easy functionalization [14] [15]. Other possible uses of these

nanoparticles might be in fields like catalysis [16] [17], environmental remediation [18] [19] [20] [21], electronics [22] [23] [24].

The chemical methods for synthesis offer the advantage that the resulting nanoparticles can be functionalized at the end of the process, which ensures improved stability compared to non-functionalized materials and conservation of magnetic properties. One of the most common and easiest chemical methods for magnetite nanoparticles synthesis is the co-precipitation developed by Massartin 1981 [25].

Metallic bonds are chemical bonds that form between metal elements. It is very rare that this interaction takes place between the Fe atoms in the oxide structure of magnetite and other metals, when developing core-shell metallic nanoparticles. So, the current study purposed to synthesize and then characterize MNPs and M/Ag NPs [(Fe₃O₄) core-(Ag) shell] by using DLS, SEM and VSM as a comparative study.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate (FeCl₃· $6H_2O$), ferrous sulphate hexahydrate (Fe-SO₄· $6H_2O$), ammonia solution, silver nitrate and glucose were purchased from Sigma-Aldrich. All chemical reagents used in the experiments were used without any further purification.

2.2. Preparation of Magnetite Nanoparticles (MNPs) and M/Ag NPs [(Fe₃O₄) Core-(Ag) Shell]

Magnetite nanoparticles (MNPs) and magnetite/silver nanoparticles (M/Ag NPs) were prepared as reported previously [26] [27]. Magnetite nanoparticles (MNPs) were synthesized by chemical coprecipitation of Fe^{2+} (1 mol) and Fe^{3+} (2 mol) with the addition of NH₄OH (30 wt%). M/Ag NPs [(Fe₃O₄) core-(Ag) shell] is by directly reducing Ag⁺ ions on the surface of the Fe₃O₄ nanoparticles, using reducing agents such as glucose.

2.3. Characterization

2.3.1. Dynamic Light Scattering

The average size was examined by means of dynamic light scattering (DLS, Zetasizer Nano-ZS, Malvern Instruments, London, UK).

2.3.2. Scanning Electron Microscopy

The morphology of powder sample of Fe_3O_4 nanoparticles was analyzed using scanning electron microscopy (JEOL SEM, JSM-636OLA, Japan) at an accelerated voltage 20 kV.

2.3.3. Vibrating Sample Magnetometer

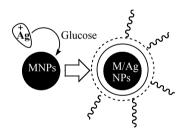
Magnetic characteristics were measured by VSM (Lake Shore-7410 vibrating sample magnetometer, USA), magnetic field up to 30,000 Oe.

3. Results and Discussion

Dynamic Light Scattering (DLS): DLS, also known as photon correlation spectroscopy, is one of the most popular methods used to determine the size of MNPs. During the DLS measurement, the MNPs suspension is exposed to a light beam (electromagnetic wave), and as the incident light impinges on the MNPs, the direction and intensity of the light beam are both altered due to a process known as scattering [28].

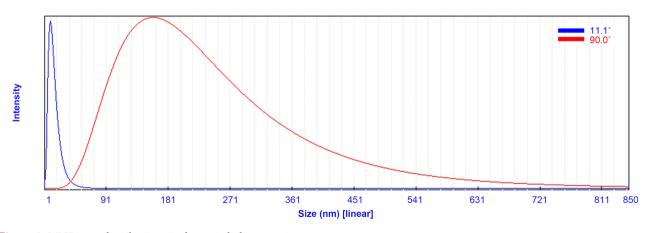
The hydrodynamic radius is the radius of a sphere that has the same diffusion coefficient within the same viscous environment of the particles being measured. It is directly related to the diffusive motion of the particles.

MNPs and M/Ag NPs size distributions via dynamic light scattering are shown in **Figure 1** and **Figure 2**. The mean particle size measured at angle (forward angle 11°) of synthesized MNPs and M/Ag NPs were 10.6 and 20 nm, respectively. Hydrodynamic size of M/Ag NPs greater than MNPs, which is a strong evidence for extra layers attached on the surface of magnetite core. Measurement at angle (side scattering 90°), it found that the mean particle size of each has a higher value with a broad range (the variation of the intensity with time) which means high distribution range of particles after silver coating on MNPs surface.



I.dat Unimodal Results Summary

Angle	Mean (nm)	P.I.	Diff.Coef (m²/s)	Counts/s	Baseline Error	Overflow
11.1°	10.6	-3.656	4.05e-11	4.28e+05	0.11%	0
90.0°	177.0	-1.386	2.42e-12	4.04e+06	0.00%	0





/	Angle	Mean (nm)	P.I.	Diff.Coef (m²/s)	Counts/s	Baseline Error	Overflow
	11.1°	20.0	-0.705	2.14e-11	2.10e+06	0.78%	0
	90.0°	1009.8	-12.184	4.24e-13	4.56e+06	0.44%	0

Dimodal Results Summary

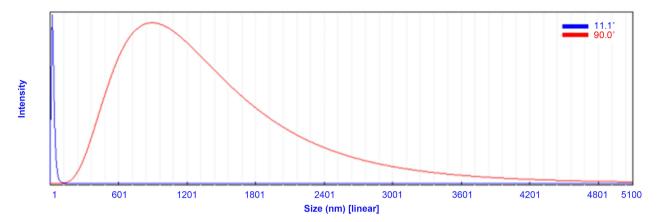


Figure 2. M/Ag NPs size distribution via dynamic light scattering.

Based on particle size, small particles move quickly with fast decay (driving forces on them are the same) but large particles move more slowly and therefore the decay is delayed (larger friction force with solvent) which is related to their diffusion coefficients [29]. So, coating silver may promote surface properties with good dispersion and aggregation stability to MNPs core carrier. Additionally, indicating good physical contacts between the target materials and the hybrid nanoparticles which consider useful in many applications.

SEM analysis: The SEM micrographs of MNPs and M/Ag NPs are shown in **Figure 3(a)** and **Figure 3(b)**. The scanning electron micrograph of MNPs (**Figure 3(a)**) shows smooth clusters of particles together and the aggregates are slightly spherical in shape. The micrograph of M/Ag NPs (**Figure 3(b)**) shows more compact particles aggregates with an improved surface. Clearly, the SEM data serve as visual and descriptive evidence for the formation of Fe_3O_4/Ag core-shell nanoparticles.

Magnetic analysis (VSM): Magnetic properties of MNPs and M/Ag NPs were studied previously [26] [27] with a magnetometer with vibrating sample (a maximum applied field of 30 k Oe) at ambient temperature. The changes in the magnetization with the applied magnetic field are presented in Figure 4.

The superparamagnetic natures of the nanoparticles were confirmed by the absence of the hysteresis loop. There was a decrease in the saturation magnetization after coating MNPs (core) with Ag (shell). This indicates that the coverage with silver weakens magnetization of MNPs, which diminishes magnetic properties for the M/Ag NPs and inducing an inert character to the final nanostructure.

The superparamagnetic of MNPs (core) with silver (shell) can be a potential candidate to effectively applications with recyclable capability and minimum release into environment.

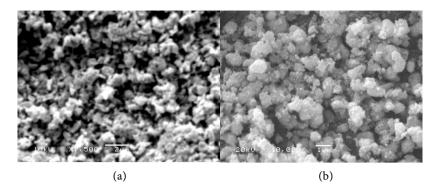


Figure 3. SEM micrographs: (a) Pure MNPs; (b) MNPs after coating Ag metal.

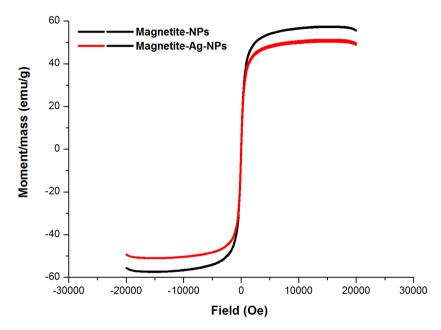


Figure 4. The relation between the applied magnetic field (H) (Oe) and the magnetization (M) (emu/g) of MNPs and M/Ag NPs.

4. Conclusion

Magnetite nanoparticles (MNPs) were synthesized using the coprecipitation method. The direct route to obtaining this type of nano-composites M/Ag NPs $[(Fe_3O_4) \text{ core-}(Ag) \text{ shell}]$ is by directly reducing Ag⁺ ions on the surface of the Fe₃O₄ nanoparticles, using reducing agents such as glucose. According to DLS, coating silver may promote surface properties with good dispersion and aggregation stability to the MNPs core carrier. SEM data serve as visual and descriptive evidence for the formation of Fe₃O₄/Ag core-shell nanoparticles. Coverage with silver produced a core-shell heterostructure which weakens magnetization of MNPs, inducing an inert character to the final nanostructure.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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