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Cite as: AIP Advances 9, 125033 (2019); https://doi.org/10.1063/1.5130425
Submitted: 18 October 2019. Accepted: 21 November 2019. Published Online: 23 December 2019

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Magnetic properties and hyperthermia behavior of iron oxide nanoparticle clusters

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Note: This paper was presented at the 64th Annual Conference on Magnetism and Magnetic Materials.

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ABSTRACT

In this study, Iron Oxide nanoparticle clusters have been synthesized utilizing individual Fe3O4 nanoparticles with different sizes as building blocks. The synthesis was accomplished by encapsulation of the individual Fe3O4 nanoparticles in an oil in water emulsion via hydrophobic interactions between cetyltrimethylammonium bromide (CTAB) and the nanoparticle’s surface aliphatic capping agents. It has been observed that the time, temperature and CTAB concentration were three crucial factors for controlling the size, shape and collective behavior of the clusters. Powder X-Ray Diffraction study shows that both individual Fe3O4 and the corresponded nanoparticle clusters have the Fe3O4 cubic spinel structure. Dynamic Light Scattering (DLS) shows that the hydrodynamic diameter of cluster is in the range of 100 to 200 nm. Transmission electron microscopy (TEM) images illustrate that different sizes of clusters can be effectively synthesized by using different concentration of CTAB and the results are consistent with the DLS values. Magnetic measurements show that the saturation magnetization of clusters can be changed from 56.7 emu/g to 70.1 emu/g by just changing the size of primary individual nanoparticles from 7.1 nm to 11.5 nm. Also, the blocking temperatures for Fe3O4 clusters were increased to higher temperatures which confirms the stronger collective behavior in the case of larger nanoparticles. The magnetic hyperthermia behavior of the clusters has also been studied, and the data shows that the Specific Absorption Rate (SAR) values are increased by both the clustering and the size of the primary nanoparticles.

INTRODUCTION

Recently the self-assembly of nanoparticles into three dimensional clusters has been popular for biomedical applications.1-6 The properties of individual nanoparticles can be combined by clustering the particles, and it can result to new properties which were not present in the original constituents. In other words, these clusters can have some collective properties which individual nanoparticles do not have.9 Moreover, the interparticle interactions can be changed by changing parameters such as the spatial arrangement and interparticle spacing of the constituting nanoparticles.10-12 Since synthesis of a large number of individual nanoparticles have been studied so far, there is a great potential of clustering approaches for the creation of new nanoparticle based functional material. The particle size is also one of the most important parameters that affects the magnetic properties of these clusters. However, in the case of oil-in-water emulsion evaporation method, there are no studies on the influence of primary nanoparticles’ size on intrinsic properties of the clusters.

In this study, we use a method in which the hydrophobic iron oxide nanoparticles are assembled together which results in the formation of hydrophilic spherical nanoparticle clusters (NPCs).
Although there are limited research works in the literature for the individual nanoparticles clustering through similar emulsion routes, the effect of the size of individual nanoparticle in the clustering process using this method has not been considered yet. Thus, in this work, two clusters with different nanoparticle sizes are synthesized and their magnetic and structural properties have been studied. Furthermore, our results suggest that clustering the larger Fe$_3$O$_4$ nanoparticles enhances their magnetic hyperthermia behavior significantly.

**EXPERIMENTAL METHODS**

The clusters were formed following the procedure discussed below. First, individual Fe$_3$O$_4$ nanoparticles were synthesized by thermolytic decomposition of Fe(acac)$_3$ in a 1/20 v/v oleic acid/oleyl amine solution, under the air atmosphere. Once the inorganic iron precursor was completely dissolved, the temperature was raised to 300°C and was kept there for 2 hours. The solution was then cooled down to room temperature and was precipitated by the addition of ethanol and hexane and then separated with centrifuge. In the case of larger nanoparticles, the heating procedure was repeated two more times and the oleyl amine-oleic acid mixture was kept at 300°C for another 4 hours.
In the second step, 15 mg of as-made Fe$_3$O$_4$ nanoparticles was dissolved in chloroform following by the addition of 10 ml cetyltrimethylammonium bromide (CTAB) water solution (2 mg/ml) and the mixture was sonicated for 20 minutes for emulsification. Finally, in order to completely remove the organic phase, the solution was heated to 85 °C for 1 hour and then washed with the addition of ethanol and water.

The size and morphology of as-prepared NPCs were characterized by using transmission electron microscopy (TEM). All the TEM images were obtained using a JEOL 3010 transmission electron microscope, operated at an accelerating voltage of 300 kV. X-ray diffraction analysis of the prepared nanoparticles was done using a Rigaku Ultima IV X-ray diffractometer. The magnetic properties of individual and clustered nanoparticles were carried out using vibrating sample magnetometry (VSM, Quantum Design model VersaLab). Hyperthermia measurements were performed using a G2-D5 Series Multi-mode 1500W Driver from Nanoscale Biomagnetics. Hydrodynamic size measurements were determined by using a Wyatt Möbius Dynamic Light Scattering.
RESULTS AND DISCUSSION

The X-ray diffraction patterns of two different sizes of Iron Oxide nanoparticles are shown in Figure 1, which indicates that all of the peaks can be attributed to the Fe$_3$O$_4$ cubic spinel structure. It can be seen in TEM results that the nanoparticle clusters are all spherical and their building blocks are two different sizes of Fe$_3$O$_4$ nanoparticles with average diameter of 7.1 and 11.5 nm, respectively (Figure 2, 3). It is observed that the size of the clusters can be precisely controlled with changing the time, temperature and CTAB concentration. For example, the average radius of clusters with 7.1 nm primary nanoparticles can be decreased from 86.9 nm to 71.3 nm by just increasing the CTAB concentration from 20 mg to 30 mg.

The room temperature hysteresis loops of the corresponding samples are shown in Figure 4. It has been observed that by increasing the size of nanoparticles from 7.1 nm to 11.5 nm, the saturation magnetization is increased from 56.7 emu/g to 70.1 emu/g. Moreover, for both sizes the saturation magnetization of clusters and individual nanoparticles are equal. Additionally, both types of nanoparticles showed no coercivity at room temperature which confirms their superparamagnetic behavior.

The zero-field cooled (ZFC) and field cooled (FC) curves for both types of the samples are shown in Figure 5. The data shows that for both sizes, the blocking temperatures significantly shift toward higher temperature. This increase confirms the larger magnetic dipole-dipole interactions in the case of clusters which is because of the shorter interparticle spacing. Such interactions slow the magnetic relaxation and increase blocking temperature, as reported in the literature.

Hyperthermia measurements of these two different sizes of Fe$_3$O$_4$ and their clusters (Figure 6), indicate that the Specific Absorption Rate (SAR) for clusters of each size is higher than the SAR of individual nanoparticles and this is because of the collective magnetic behavior arising from multiple Fe$_3$O$_4$ nanoparticles assembled in each cluster. In these 3D spherical assemblies of Fe$_3$O$_4$ nanoparticles, the interparticle interactions can lead to such collective magnetic behavior similar to the cluster-assembled magnetic nanoparticle films and closed packed nanoparticle arrays.

Also, it was observed that the SAR for clusters with larger individual nanoparticles are much higher than SAR for clusters with smaller nanoparticles. This can be explained by considering the significant role of size in decreasing the spin canting effect in nanoparticles (Figure 7).

CONCLUSIONS

In this work, a general method for making nanoparticle clusters has been developed. It has been observed that by using CTAB and an oil in water emulsion system, the hydrophobic individual nanoparticles assemble together leading to the formation of hydrophilic spherical clusters. The size of the clusters can be precisely controlled by changing the CTAB concentration. Moreover, two types of clusters were made from two different sizes of primary individual nanoparticles and the structural and magnetic properties of them...
were measured. For both types of clusters, it was demonstrated that the dipole interactions inside the clusters improve their heating performance because of the stronger correlation between magnetic moments of the clusters in comparison with the individual nanoparticles. Hence, the collective behavior of clusters makes them a better choice for biomedical applications such as magnetic hyperthermia.

ACKNOWLEDGMENTS

Part of this work was supported by the project MIS 5002567, implemented under the “Action for the Strategic Development on the Research and Technological Sector”, funded by NSRF 2014-2020 and co-financed by Greece and the European Union (European Regional Development Fund). Additionally, Dr Ahmed Elgendy acknowledges financial support by his startup and rising stars fund by UTEP.

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