EPJ Web of Conferences **201**, 02002 (2019) https://doi.org/10.1051/epjconf/201920102002
AYSS-2018

Synthesis, characterization and promising properties of Fe_3O_4/CdSe nanocomposite

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Abstract Nowadays there is a continuously increasing worldwide concern for the utilization of magnetic semiconductor nanocomposites. We synthesized bifunctional magnetic–luminescent nanocomposites with Fe_3O_4 nanoparticles as the cores and CdSe as the shells by a facile direct precipitation method. Transmission electron microscopy (TEM) images revealed that the obtained bifunctional nanocomposites had a core–shell structure, in a spherical shape with a particle radius of about 10.3nm, and the shell thickness of about 2.2nm. The flower shape is due to the inhomogeneous growth of CdSe due to the presence of many active sites which turn to be nucleation centers for the CdSe on the surface of the nano-magnetite. The X-ray diffraction (XRD) patterns showed a cubic spinel structure of the Fe_3O_4 core. Magnetic measurements indicated that the presence of CdSe in the composite reduces its magnetic properties. Optical measurements of the Fe_3O_4/CdSe nanocomposite show that the prepared samples have dual functions, optical tunable band gap of the semiconductor quantum dots and the magnetic properties of magnetite. This type of composites would be considered as dilute magnetic semiconductors (DMS).

1 Introduction

The term “nanocomposite” is used in the study of multiphase material where at least one of the constituent phases has one dimension less than 100 nm [1]. The promising feature of nanocomposites lies in their multifunctionality. The challenges in reaching this promise are tremendous where the synthesis of hybrid nanostructures requires a great deal of control over the reaction parameters to generate functional materials with tunable properties [2]. A special class of particular interest of nanocomposite materials is core shell nanocomposites. These core/shell nanocomposites are highly functional materials consisting of thin coatings (1-20 nm) of one particular material deposited on core particles of another different material. The interest in synthesis and characterization of core/shell nanoparticles raised from the varied attributes of functional activities involving optical, electronic, magnetic, catalytic and chemical/biological phenomenon [3].

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Now it is possible to synthesize these nanocomposites in desired size and shape and with controlled improved properties such as increased stability, surface area, magnetic, optical and catalytic properties. Core shell composites can be synthesized practically using any material by utilizing the approach, known as controlled precipitation; where the synthesis of shell particles can be achieved in the presence of cores. The core particles act as nuclei and hydrolyzed shell material gets condensed on these cores forming nanoshells. Reactant concentrations and the amount of added core particles play an important role in deciding the shell thickness. Additionally, core particles can be coated with a shell to obtain a single nanoshell or even multishells. These structures show tunable optical properties from the visible to infrared region of the electromagnetic spectrum by choosing different combinations of core and shells.

The choice of a suitable pair for the core and shell composites requires the understanding of individual properties of core and shell single material. The core particles should withstand the process used for coating of the shell material. Core and shell particles should not interdiffuse and surface energies of the core and shell particles must be similar, so that the probability of heterogeneous nucleation is more than that of homogeneous nucleation [4]. The present work has been devoted to prepare hybrid magnetic-semiconductor nanocomposite (Fe_3O_4-CdSe) in order to study the coupling between magnetic and semiconductor nanoparticles. The novelty in the present paper is preparing Fe_3O_4/CdSe nanocomposite -(a composite which is not investigated before)- by a so much easy procedure – (not published before)- giving promising results to be applied in the areas of biolabeling, bioseparation, immunoassays, and other diagnostic applications. Also, this easy procedure may facilitate future investigations for the use of this nanocomposite in solar energy storage.

2 Preparation of Fe_3O_4/CdSe nanocomposites

The first step was the preparation of magnetite nanocrystals by co-precipitation method [5]. To use the Fe_3O_4 nanocrystals their surface was modified at first by oleic acid. 4 ml of this dispersion was transferred into a three-necked flask containing additional 1.2 ml of oleic acid and 0.12 g of CdO. The mixture was heated to 170 °C under a constant flow of nitrogen. Then 2.0 g of trioctyphosphine oxide (TOPO) and 2.0 g hexadecylamine (HDA) were added and the temperature was allowed to elevate to 200 °C. Se powder (0.12 g) in 3 ml TOP was added to the reaction mixture swiftly with vigorous stirring. The reaction mixture was held at reflux for a further 15 min for the reaction to be completed. After those 15 minutes, 1 ml of the composite has been drawn using a glass pipet each two minutes. Each sample then was washed by toluene for further investigations.

3 Results and discussion

3.1 Characterization of Fe_3O_4 nanoparticles

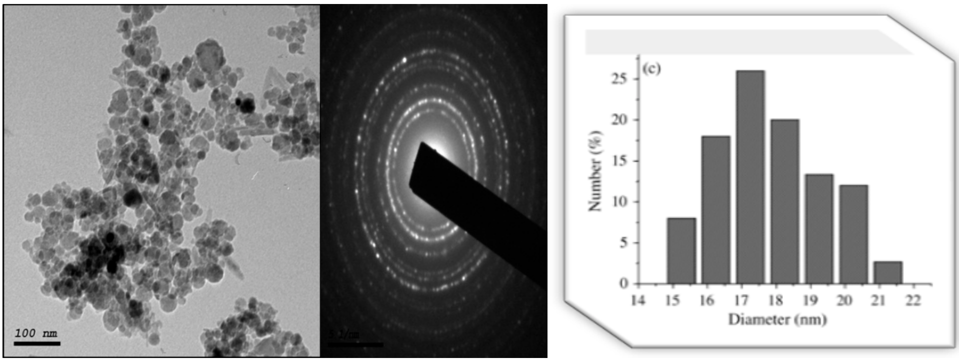
The prepared magnetite nanoparticles were characterized via XRD, TEM and their magnetic properties were investigated by the vibrating sample magnetometer (VSM).

3.2 X-ray diffraction results of Fe_3O_4

The XRD analysis of the prepared Fe_3O_4 nanoparticles confirmed the formation of the required cubic ferrite without other unwanted phases in fair consistency with standard cards and with XRD patterns published in literature [6-7].

3.3 Transmission electron microscopy of Magnetite (Fe_3O_4)

In Fig. 1 the TEM image shows that the prepared magnetite nanoparticles are almost spherical shape. The particles have tendency to aggregate because of their magnetic properties. The average particle size as determined from the histogram is ~ 17 nm. The electron diffraction shows that the sample is completely crystalline as confirmed from the XRD.



(a) **(b)** **(c)**

Fig. 1. a) TEM images and b) Electron diffraction of the prepared magnetite nanoparticles. c) The average size as shown from the histogram is ~ 17.6 ± 3 nm.

3.4 Characterization of the Fe_3O_4/CdSe Nancomposites

Different sizes of hybrid Fe_3O_4/CdSe nanocomposites have been prepared using Fe_3O_4 as a core and CdSe was added in order to form core shell particles. The infleunce of nano Fe_3O_4 on the growth of CdSe shells has been studied. The obtained particles have been characterized by TEM and the magnetic properties by means of VSM. It is clear from the TEM images shown in Fig. 2. that the particles has nearly flower like shape. This structure consists of a core from magnetite nanoparticles with dark contrast, and arms from CdSe nanocrystals with low contrast around it.

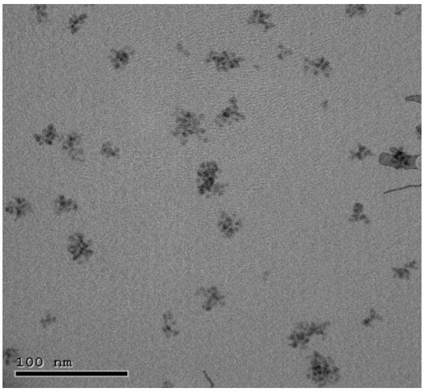


Fig. 2. The TEM images and HR-TEM images of the flower like-shaped Fe_3O_4/CdSe nanocomposite

By using the HR-TEM mode, the interplaner spacing of the core particle was determined to be ~0.16 nm referring to the Bragg reflection of (511) plane of Fcc crystallographic structure of Fe_3O_4, while the interplaner spacing for one arm is also ~0.16 nm referring to the Bragg reflection of (202) plane of WZ crystallographic structure of CdSe. The average particle size was determined too. Since the average particle size of the magnetite core is about 10.3 nm. This means that CdSe shell around the Fe_3O_4 partilces is about 2.2 nm. The flower shape is due to the imhougenous growth of CdSe due to the presence of many active sites which turn to be nucleation centers for the CdSe on the surface of the nano-magnetite.

To confirm these results, another sample prepared after 5 minutes has been imaged by using the TEM; where the average particle size has been determined to be about 13.5 nm. The same nano Fe_3O_4 core has been used, this means that the CdSe layer is about 3.2 nm.

3.5 Magnetic properties of the pure Fe_3O_4 and the Fe_3O_4/CdSe

The magnetic properties of the core/shell nanocomposite have been measured by the VSM and compared to that of the pure Fe_3O_4 nanostructure.

Table 1. The magnetic parameters of Fe_3O_4/CdSe nanocomposite compared to those of pure Fe_3O_4.

Magnetic parameters	Magnetite nanoparticles Fe_3O_4	Fe_3O_4/CdSe nanocomposite
Saturation magnetization σ_S (emu/g)	~ 53.5	~ 34.9
The coercivity H_c (Oe)	19.1	27.97
The retentivity (emu/g)	1.713	4.971

It is clear from Table 1 that the presence of CdSe in the composite reduces its magnetic properties. These types of composite would be considered as dilute magnetic semiconductor (DMS).

3.6 Optical Properties of the Fe_3O_4/CdSe nancomposites

The prepared nanostuctures have dual functions, optical tunable band gap similar to the semiconductor quantum dots and magnetic properties due to Fe_3O_4 nanoparticles.

Table (2) Optical constants of the prepared samples of hybrid Fe_3O_4/CdSe nanostructures (samples taken at different times from the beginning of the formation).

Samples at different time from the beginning of formation (min.)	Absorption wavelength (nm)	Emission wavelength (nm)	Stokes shift (nm)	Quantum yield %
1	515	565	50	17
3	525	585	60	17.2
4	540	570	30	16.5
5	550	575	25	12.6
7	560	625	65	6.7
8	565	623	58	4.9
10	575	635	48	3.2
12	579	627	48	3.15

To ensure the formation of the composite nanostructure, a strong magnet has been used to collect the nanocomposite Fe_3O_4/CdSe. This confirms that all the CdSe particles are attached to the magnetite nanoparticles. The calculated size of CdSe shell on the surface of Fe_3O_4 as calcualated from the absorption spectra using Burs' effective mass equation [8] is ranged from 2.0 nm up to 4.6 nm. Here, it may be useful to clarify what Stokes' shift is the difference (in wavelength or frequency units) between positions of the band maxima of the absorption and emission spectra (fluorescence and Raman being two examples) of the same electronic transition. It is named after Irish physicist George G. Stokes [9].

It is clear that the quantum yield of the Fe_3O_4/CdSe nanocomposites has larger quantum yield values than those of pure CdSe QDs [10] may be due to the fact that magnetic nanoparticles facilitate the electron hole recombination and enhance the emission from the quantum dots. It is known that the emission from quantum dots is due to the electron hole recombination from the dark exciton state, which is a forbidden state. The electron has to flip its spin in order to recombine with the hole. For this reason, the life time of the quantum dots becomes long and the Stockes shift is large. The presence of magnetic particles attached to the CdSe enhances the coupling between the hole and the electron. This means the emission is enhanced greatly upon loading CdSe QDs on Fe_3O_4 nanocrystals.

4 Conclusions

Fe_3O_4 nanoparticles has been successfully prepared by the co-precipitation method. The prepared particles have been investigated via XRD, TEM and VSM. The XRD confirms the formation of the required cubic ferrite without other unwanted phases. The Fe_3O_4 particles have been used as seeds or as core to grow CdSe nanoshells around. The obtained hybrid Fe_3O_4 nanostructure has flower shape particles. The Fe_3O_4/CdSe nanocomposites has larger quantum yield values than those of pure CdSe QDs may be due to the fact that magnetic nanoparticles facilitate the electron hole recombination and enhance the emission from the quantum dots. In other words, the presence of Fe_3O_4 enhances the optical properties of CdSe quantum dots. The prepared nanocomposites have dual functions, optical tunable band gap similar to the semiconductor quantum dots and magnetic properties due to Fe_3O_4 nanoparticles.

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