

Hybrid nanostructure for bifunctional application in an aqueous room temperature method

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Abstract : Combining fluorescent and magnetic objects in one system is of special interest for various types of applications where it is necessary to monitor and manipulate at the same time. Growth of CdS shell on the seeds of iron oxide nanoparticles, a two-step process, was accomplished in a chemical bath using thiourea, cadmium chloride and ammonium chloride at room temperature. Growth of the shell nanoparticles on iron oxide was restricted to few nanometer in thickness by in-situ monitoring. The crystalline nature of the prepared core, shell and decorated structure was analyzed by powder X-ray diffraction. The as prepared particles have also been characterised by transmission electron microscopy, photoluminescence spectroscopy and optical absorbance. The absorption onset in all the Fe_3O_4 nanoparticles was shown to be broad and independent of the particle size. A significant result of this onset was a substantial enhancement in the observed photoluminescence following formation of a CdS shell on the Fe_3O_4 nanoparticle cores. Such hybrid nano structures can be useful in wide variety of bids where both magnetic response and luminescence responses are desired.

Keywords : Nanomaterials, Superparamagnetic, Hetero nanostructures, Hybrid nanostructures.

Introduction

The ability to combine diverse functional constituents into a single nanostructure has enormous potential for improving efficiency and adaptability in the many applications of nanomaterials in everyday life. Among the well-established nanomaterials, both magnetic and semiconducting nanoparticles (NPs) have found amazing and widespread applications in medical diagnostics and spintronics [1]. Whereas the earlier have been used as magnetic resonance imaging (MRI) agents to diagnose a variety of disorders, including malignancies, the semiconductor are gaining popularity as fluorescent probes for observing biological processes [2].

Linking fluorescent and magnetic things in a single entity is particularly appealing for a variety of applications that require simultaneous monitoring and manipulation. Iron oxides, both magnetite and maghemite, are generally opted for the functional magnetic items. Iron oxides are superparamagnetic, however, there is no inherent luminescent possessions. On the other hand Cadmium sulphide (CdS), famous

for its wide range of applications, is a widely accepted semiconductor. CdS semiconductor is unquestioned for its narrow forbidden gap due to which it is recognized as one of the best visible light operate photocatalysts. These hetero structures combine the capabilities of its constituent elements to create a multifunctional tool that can do multiple jobs at once.

Bawendi M.G et. al demonstrate an easy method for synthesizing magneto fluorescent core shell NPs [3]. In another study, Singh et. al reports the possibility of decorating CdS NPs on the exterior of different ferrite NPs[4]. Novel magneto fluorescent nanobowls with mandrel-exoderm architecture were successively explained by Tang et.al in 2016[5]. However, number of reports on growth of hybrid nanostructure employing magnetite as core and CdS as shell via different methods is very less. Green methods to synthesize hybrid nanostructure with a CdSe/CdS- Fe_3O_4 structure under mild conditions have been explained by Zhou et.al [6]. Fe_3O_4 -CdS complex structure has been prepared by Shim et al in a relatively high temperature route in 2006 [7]. Magnetic recyclable $\text{Fe}_3\text{O}_4/\text{ZnxCd1-xS}$

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hybrid nanostructures have been prepared by Qian et al under hydrothermal condition[s].

In all the studies it has been noticed that the magnetic responses of the iron oxide nanoparticles were defined to be deteriorated by the non magnetic outer shells to a certain extent. Moreover, combined studies which comprise of dual functionality, magnetic and photo luminescence, on a single entity to confirm hybrid function have also been missing. A co precipitation method in room temperature establishing hetero nanostructures will be technically sounder. Hence there is a pressing need to develop a relatively room temperature, aqueous preparation method for such a hybrid nanostructures for the scientifically advancement. In this study, we have offered an elaborated report on the facile method and characterization of hybrid superparamagnetic magnetite nanoparticles decorated with cadmium sulphide shell using a wet synthesis method.

Experimental Techniques

A close to room temperature aqueous bath was used to synthesize uncoated magnetite NPs in co precipitation method. Ferric and Ferrous chloride were used for iron salts in the molar ratio 2:1. Ammonia solution was served as the base agent and pH maintained 11 during the synthesis. Mercaptoethanol used as stabilizing agent for the restriction of particle agglomeration. All the precipitates were collected by centrifugation followed by magnetic separation and then dried to remove water content at close to room temperature.

The CdS nanoparticles were synthesized by a reaction matrix comprised of NH_4Cl , thiourea and CdCl_2 in 3:7:1 molar ratio mixed in triply ionized water. The ammonium solution was used to make precipitate by adding drop wise until the pH was reached at 9 in the bath. The size of the particle was monitored using a predetermined quantity of mercapto ethanol as capping agent. The as prepared NPs were collected from the reaction matrix and washed systematically in distilled water.

Growth of CdS on Fe_3O_4 NPs was furnished in a reaction bath using CdCl_2 , thiourea and ammonium chloride in molar ratio 1:7:3 at room temperature aqueous method. The pH was maintained at 9 by the systematic addition of an ammonical solution. An uncoated iron oxide nanoparticles was inserted timely into the matrix during vigorous stirring. The shell growth on iron oxide nanoparticles was continuously monitored by the help of different spectroscopy.

Centrifugation and magnetic separation was used to collect the precipitate quickly from the bath and washed thoroughly in triple distilled water.

Result and Discussion

The crystalline landscape of the as synthesized nano core, shell and decorated structure was analyzed by powder X-ray diffraction using XRD-6000 and the attained diffraction outline shows in figure 1. The uncoated iron oxide NPs display 7 peaks in between 18° to 65° . The experimental X-ray patterns can be consigned to the different planes of the cubic spinel structure of iron oxide. All the detected diffraction peaks were in noble agreement with the usual JCPDS [9].

The as-synthesized Fe_3O_4 NPs was in high purity as reveals by figure 1a. The presence of wide diffraction peaks shows that the uncoated iron oxide is in nano-crystalline nature. The crystallites size is calculated using Scherrer's formula as 7 nm. The preferred growth was in the direction of (311) plane as observed from the pattern.

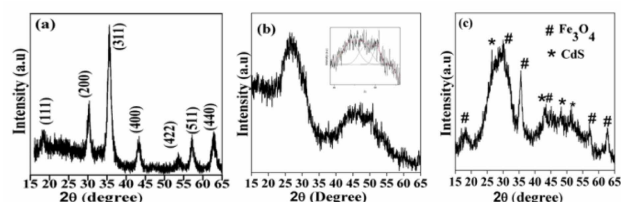


Fig. 1 —XRD reflexes of (a) Uncoated Fe_3O_4 NPs, (b) CdS NPs and (c) their hetero structure.

The shell particles (CdS) are also examined with XRD for the comparison and the obtained diffraction spectra presented in figure 1b. The obtained pattern for CdS is characterized by two wide peaks centered at 26.60° and 47.6° . The peak at $2\theta = 26.60^\circ$ is mainly owing to the reflexes from the (111) planes of the cubic CdS. The second peak observed at 47.6° was relatively feeble in intensity and may be contributed by diffraction from different planes of CdS crystal structure. Hence the later peak was deconvoluted for getting accurate peak position. The theoretically measured interplanar values were well matched with standard data for cubic CdS. Table 1 shows the comparative d values along with customary values for different nanoparticles. The crystalline diameter of the Cadmium Sulphide NPs was measured using Sherrer's equation as 1.7 nm.

The as prepared hybrid nanostructure using bare iron oxide and CdS NPs were characterized by the help of X-Ray Powder Diffractometer for structural analysis and the obtained XRD pattern depicts in figure

1c. The observed pattern consist of 5 broad peaks at different position. The first prominent visible peak at $2\theta = 18.37^\circ$ was due the reflexes from (1 1 1) planes of cubic magnetite. The asymmetric behavior of the second peak positioned at $2\theta = 30^\circ$ is due to various reasons. The broadening of this peak as a result of particle size decrease and their merger made distinct structural assignment more challenging. The peaks at 26.34° , 30.14° could be consigned to CdS and Fe_3O_4 cubic phase respectively. The symmetric nature of the peak at 35.62° could be consigned to the (3 1 1) planes of Fe_3O_4 . The reflexes at $2\theta = 50^\circ$, was very broad due to particle size reduction, has been decovoluted for deeper insight and for better assignment of different peaks. The as determined peak position was at $2\theta = 43.87^\circ$, 48.12° , 51.47° and 57.07° .

Table 1: Comparative XRD results of Fe_3O_4 , CdS and their heterostructure.

Name of sample	2 θ (degree)	d value (\AA)		Relative Intensity		[hkl] Plane	Component	Structure	Grain Size
		Obs	Std	Obs	Std				
Core Fe_3O_4	18.33	4.83	4.85	14	08	(111)			7
	30.23	2.96	2.97	35	30	(220)			
	35.59	2.52	2.53	100	100	(311)			
	43.20	2.09	2.10	20	20	(400)	Fe_3O_4	Cubic	
	53.60	1.70	1.71	6	10	(422)			
	57.13	1.61	1.62	22	30	(511)			
	62.82	1.47	1.48	25	40	(440)			
Shell (CdS)	26.63	3.35	3.36	100	100	(111)			1.7
	43.96	2.06	2.05	59	40	(200)			
	47.55	1.91	1.89	60	50	(103)	CdS	Cubic	
	50.34	1.81	1.75	60	60	(311)			
	55.77	1.65	1.68	41	10	(222)			
Core-Shell ($\text{Fe}_3\text{O}_4/\text{CdS}$)	18.17	4.88	4.85				Fe_3O_4		
	26.36	3.37	3.36				CdS		
	30.19	2.95	2.97				Fe_3O_4		
	35.62	2.52	2.53				Fe_3O_4		
	43.87	2.06					$\text{Fe}_3\text{O}_4/\text{CdS}$	Cubic	
	48.12	1.89	1.89				CdS		
	51.47	1.77	1.75				CdS		
	57.07	1.61	1.62				Fe_3O_4		
	62.84	1.48	1.48				Fe_3O_4		

High-resolution transmission electron microscopy (HRTEM) was also deployed for the structural confirmation of as synthesized core shell nanoparticles. Magnetically separated as prepared hetero structures have been characterized by HRTEM and the typical image depicts in Figure 2. Formation of clear lattice fringes with bright and dark contrast shows the existence of hetero structure with CdS shell in connection with seeds of Fe_3O_4 NPs. The values corresponds for the different interplanar distances is in good agreement the corresponding standard values of most preferred orientation, (111) planes, of CdS and

Fe_3O_4 . Seed of iron oxide nanocrystals and later grown CdS shell could thus be distinguished, suggesting good nano crystallinity.

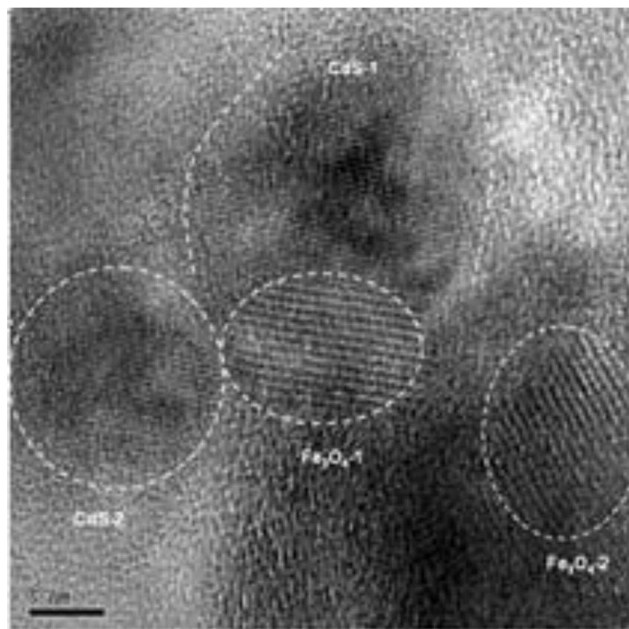


Fig. 2 — High Resolution TEM image of hetero nanostructures

Since the shell thickness perform a substantial role in the field of hybrid application level, we employed UV Vis spectroscopy in the hetero structures and the corresponding graph is shown in figure 3 below. The typical absorption spectra of as prepared Q-CdS sample, having particle size 1.7 nm has a sharp onset of absorption at 365nm.

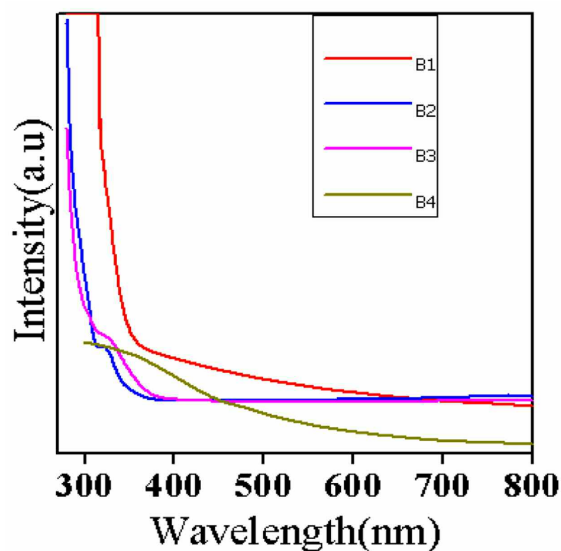


Fig.3 — In situ monitored optical absorption spectroscopy of uncoated Fe_3O_4 (B4) and $\text{Fe}_3\text{O}_4/\text{CdS}$ heterostructure.

The curve B4 was measured for the uncoated Fe_3O_4 . Generally the uncoated Fe_3O_4 NPs exhibit wide absorption behaviour with any distinct onset [10]. The shell nanoparticles are now allowed to grow on bare iron oxide by the controlled precipitation of the shell constituent, generated absorption lines represented by way of B1, B2 and B3, in figure 3 recorded at different interval time. A remarkable absorption onset witnessed at 364.5 nm for B1 due to the absorption by the Cadmium Sulphide (shell)[11]. It is noteworthy to observe a considerable redshift in the absorption peak recorded at different time for peaks B1 to B3 when the evolution of CdS coating over magnetite is proceeded.

In situ monitored photoluminescence graph of the uncoated magnetite and the hetero NPs were deployed for the detection of luminescence response. The response were recorded at different interval of time as we did in the case of absorption graph of uncoated Fe_3O_4 (P4) and following 15 (P1) minute, 35 (P2) minute, and 120 (P3) minute of the development of CdS shell have been shown in figure 4. The inherent photon response of uncoated iron oxide NPs are negligible (P4), interestingly, the new hetero nano structure bring in an improved luminescence response at 380.5 nano meter. A red shifted PL peaks from 380.5 nm to 407 nm was observed when we are allowing to grow the shell particles on core nanoparticles. The radiative recombination of both electron and hole originated from the CdS shell can be assigned to the sharp response of the luminescence.

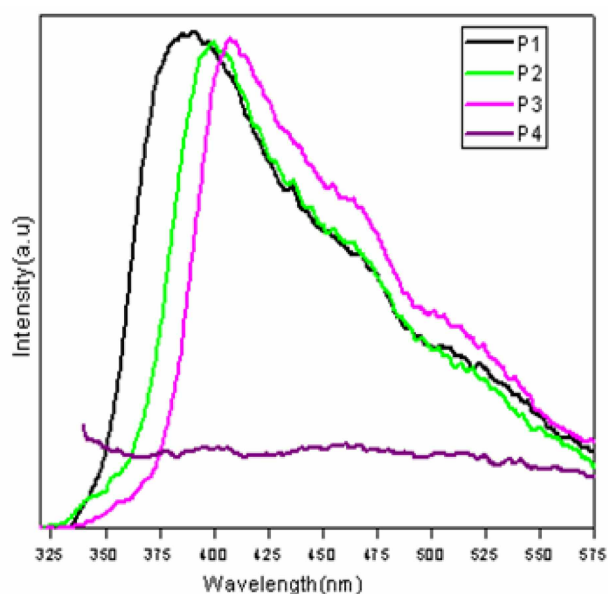


Fig. 4. Luminescence behavior of as prepared core and hetero structure.

The observed luminescence response shows a broad tail towards higher wave length with two bands centered at 431nm and 495nm. The interpretation of our sample's luminescence data is complicated due to different sulfur, cadmium vacancies, interstitial cadmium and sulfur vacancies, presence of polyvalent entrap in Cadmium Sulphide and the occurrence of imperfections in surface [12, 13]. The various transitions in between the localized levels scattered within the Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital slit of Cadmium Sulphide NPs, in general, are responsible for the detected asymmetric nature of photoluminescence response. The interstitial sulfur vacancies with in the CdS NPs are attributable for the luminescence peak observed at 495 nm [12]. The later peak witnessed at 431 could be arised from an interstitial site [13-15].

Conclusion

Fe_3O_4 and CdS NPs were synthesized in room temperature by an aqueous method. Particle sizes of both NPS were controlled using an appropriate amount of mercapto ethanol. The core/shell structures were developed on Fe_3O_4 by the systematic growth of CdS shell. HRTEM and XRD techniques were employed for the structural confirm of the formation of hybrid nanostructure. Luminescence spectroscopy and absorption response reveals the formation of hetero structure. The absorption and luminescence spectra shows the as prepared nanoparticles have strong optical response in contrary to its core nanostructure.

Thus our outcome points to an innovative economic aqueous method for tuning new properties which comprises both magnetism and luminescence. These types of novel hybrid nanostructures can be consider as a promising candidate for future bids where boosted luminescence along with magnetic replies are anticipated.

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