



ANNEXURE III

UNIVERSITY GRANTS COMMISSION
(SELECTION & AWARDS BUREAU)
BAHADUR SHAH ZAFAR MARG
NEW DELHI -110002

FORM FOR SUBMITTING ACCOUNTS OF CONTINGENCY GRANTS AND
THE UTILISATION CERTIFICATE

1. Name of awardee : Dr. Pritam Deb
2. Award letter number and date : F.30-1/2014/RA-2014-16-GE-WES-5629(SA-II)
Dated.20.2.2015
3. Name of the scheme under which he/she is working : UGC Research Award
4. Period for which the accounts of contingency grant relates : 2017-2018
5. Expenditure : From : 01.4.2017 to 31.3.2018. Amount : Rs.1,50,000.00
 - a) Research staff : NIL
 - b) Book and allied items : NIL
 - c) Typing (tracing & ammonia printing) : NIL
 - d) Stationary : NIL
 - e) Postage : NIL
 - f) Chemical and electrical goods : Rs.1,50,000.00
6. Period for which the contingency grant is payable : 2017-2018

Certified that the expenditure of **Rs. 1,50,000.00 (Rupees one lakh fifty thousand only)** out of the contingency grant of **Rs.1,50,000.00 (Rupees one lakh fifty thousand only)** sanctioned vide commission letter number F.30-82/2015(SA-II) dated 30.5.2016 in respect of **contingency** has been utilized for the purpose for which it was sanctioned in accordance with the terms and condition laid down by the University Grants Commission.

If, as result of check or audit objection, some irregularity is noticed at a later stage, action will be taken to refund, adjust or regularized the objected amount.

(P. Deb)

Professor
Dept. of Physics
Tezpur University
Professor

(N. Das)

Head of Deptt.
Dept. of Physics
Tezpur University
Prof. & Head

Finance Officer
Tezpur University
15/07/19
Finance Officer
Tezpur University

Registrar
Tezpur University
Registrar
Tezpur University



Ref no. F-11-13/Per/2004/phy/864

Dated 16th May, 2017

To
Dr. Sunita Siwach
Deputy Secretary
University Grants Commission
Bahadur Shah Zafar Marg
New Delhi 110002

Subject: UGC Research Award 2014-16 (Physics)

Madam,

This is reference to the release of Grant-in-aid in respect of research award towards research grant for the year 2015-16 vide letter no. F.30-81/2015(SA-II) dated 30.05.2016. I had submitted the i) Utilization certificate towards the 1st year salary grant, ii) Utilization certificate and Statement of expenditure towards 1st year contingency grant, iii) Monthwise salary statement for 2015-17 and iv) Mid-term progress report as per suggestion. I have not yet received the sanctioned grant for salary and also the 2nd year contingency grant. Without the fund, it will be difficult to achieve the research goals approved by UGC under this award within the stipulated period. Therefore, may I put forward the request to you to enable me the sanctioned grant at the earliest possible.

Looking forward to your kind action.

Thanking you,

Yours sincerely,


16/05/2017
(Pritam Deb)

Dr. P. Deb
Professor
Department of Physics
Tezpur University (Central University)
Tezpur 784028
Tel: 03712-275560
Fax: 03712-267005/6
E-mail: pdeb@tezu.ernet.in

Ref. No. F.19.10/Pro/2013/Phy

Date: 27.08.2019

To,

Prof. Rajnish Jain,
Secretary,
University Grants Commission,
Bahadur Shah Zafar Marg
New Delhi - 110002

Subject : Submission of UC, SE, and Progress Report of my UGC Research Award 2014-16

- Ref. no. 1. UGC Award letter no. F.30-1/2014/RA-2014-16-GE-WES-5629 (SA-II)
dated. 20.2.2015
2. UGC Grant release letter no. F.30-82/2015(SA-II) dated 30.5.2016

Sir,

I am glad to inform that I was selected for UGC Research Award (2014-16) without undertaking any research guidance. During the period of award, I was paid full salary and contingency grant without any additional remuneration under the award from University Grant Commission, New Delhi.

This career award was very rewarding for me and my research career received a boost due to this generous support. I acknowledge the research outcomes in last few years in my career to this award support. **I would like to request University Grants Commission to consider an extension of this award support for another two years if the progress outcome is found suitable.**

Looking forward for your kind consideration.

Yours sincerely,

(Pritam Deb)
UGC Research Awardee
Professor
Department of Physics
Tezpur University(Central University)





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2. Award letter number and date : F.30-1/2014/RA-2014-16-GE-WES-5629(SA-II)
Dated.20.2.2015
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 - a) Research staff : NIL
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 - d) Stationary : NIL
 - e) Postage : NIL
 - f) Chemical and electrical goods : Rs.1,50,000.00
6. Period for which the contingency grant is payable : 2017-2018

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Tezpur University
Professor

(N. Das)
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Tezpur University
Prof. & Head

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Registrar
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ANNEXURE IV

UNIVERSITY GRANTS COMMISSION
(SELECTION & AWARDS BUREAU)
BAHADUR SHAH ZAFAR MARG
NEW DELHI -110002

PROGRESS REPORT

1. Name of awardee : Dr. Pritam Deb
2. Award letter number and date : F.30-1/2014/RA-2014-16-GE-WES-5629(SA-II)
dated 20.2.2015
3. Topic of research work : strongly correlated magnetic nanosystems
4. Is the Awardee working on the topic for the award of a doctorate degree: No
5. Total number of working days during the period : 435
6. Number of days the awardee remained on leave (with dates):
 - a) With salary, number of days : 146 days (for vacation and holidays)
 - b) Without salary, number of days : Nil
7. Number of days the awardee remained out of station for fieldwork / travel, with dates and place of visited :
 - a) Number of days : Nil
 - b) Places visited : N.A.
8. Number of days the awardee remained present at the University/Institution: 435
9. Publications during the period under report (please enclose a reprint of each) :
Annexure I
10. Title of the monograph written during the period under the report. : Nil
11. A detailed account of the work done during the period (a separate sheet may be attached for the purpose) : Annexure II


(P. Deb)
Professor
Dept. of Physics
Tezpur University


(N. Das)
Head of Dept.
Dept. of Physics
Tezpur University


Finance Officer
Tezpur University
18/07/19
Finance Officer
Tezpur University


Registrar
Tezpur University
Registrar
Tezpur University



ANNEXURE V

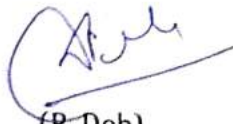
UNIVERSITY GRANTS COMMISSION
(SELECTION & AWARDS BUREAU)
BAHADUR SHAH ZAFAR MARG
NEW DELHI -110002


UTILISATION CERTIFICATE

Certified that an amount of Rs. **1643359.00 (Rupees sixteen lakh forty three thousand three hundred fifty nine only)** has been utilized out of the sanctioned grant of **Rs. 1643359.00 (Rupees sixteen lakh forty three thousand three hundred fifty nine only)** for the purpose for which it was sanctioned in accordance with the terms and conditions laid down by the UGC in respect of **Dr. Pritam Deb** under the scheme of Research Award, sanctioned vide letter number **F.30-1/2014/RA-2014-16-GE-WES-5629(SA-II) Dated.20.2.2015 to the Tezpur University, Tezpur, Assam.**

The unspent balance of Rs..... has been carried forward/ refunded vide demand draft number dated for Rs.....

If, as result of check or audit objection, some irregularity is noticed at a later stage, action will be taken to refund, adjust or regularized the objected amount.


(P. Deb)
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Deptt. of Physics
TEZPUR UNIVERSITY


Finance Officer
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Tezpur University


Registrar
Tezpur University
Registrar
Tezpur University



Awardee letter no: F.30-1/2014 RA -2014-16-GE-WES-5629(SA-II) Dated 20.2.2015.

UGC Research Awardee : Dr. Pritam Deb, Dept. of Physics, Tezpur University
Month wise salary statement

Period : 1st April 2015 to 31st March 2016

Financial Year : 2015-16

Sl.no	Year	Month	Amount Rs.
1	2015	April	130655.00
2	2015	May	130655.00
3	2015	June	130655.00
4	2015	July	137892.00
5	2015	August	137892.00
6	2015	September	137892.00
7	2015	October	137892.00
8	2015	November	137892.00
9	2015	December	137892.00
10	2016	January	141314.00
11	2016	February	141314.00
12	2016	March	141414.00
		Total Rs.	1643359.00

Rupees sixteen lakh forty three thousand three hundred fifty nine only

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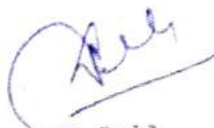
ANNEXURE V


UNIVERSITY GRANTS COMMISSION
(SELECTION & AWARDS BUREAU)
BAHADUR SHAH ZAFAR MARG
NEW DELHI -110002

UTILISATION CERTIFICATE

Certified that an amount of Rs. 1771155.00 (Rupees seventeen lakh seventy one thousand one hundred fifty five only) has been utilized out of the sanctioned grant of Rs. 1771155.00 (Rupees seventeen lakh seventy one thousand one hundred fifty five only) for the purpose for which it was sanctioned in accordance with the terms and conditions laid down by the UGC in respect of Dr. Pritam Deb under the scheme of Research Award, sanctioned vide letter number F.30-1/2014/RA-2014-16-GE-WES-5629(SA-II) Dated.20.2.2015 to the Tezpur University, Tezpur, Assam. The unspent balance of Rs..... has been carried forward/ refunded vide demand draft number datedfor Rs.....

If, as result of check or audit objection, some irregularity is noticed at a later stage, action will be taken to refund, adjust or regularized the objected amount.


(P. Deb)
Professor
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TEZPUR UNIVERSITY


Finance Officer
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15/10/19
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Tezpur University


Registrar
Tezpur University
Registrar
Tezpur University



Awardee letter no: F.30-1/2014 RA -2014-16-GE-WES-5629(SA-II) Dated 20.2.2015.

UGC Research Awardee : **Dr. Pritam Deb, Dept. of Physics, Tezpur University**
Month wise salary statement

Period : **1st April 2016 to 31st March 2017**

Financial Year : **2016-17**

Sl.no	Year	Month	Amount Rs.
1	2016	April	141414.00
2	2016	May	141414.00
3	2016	June	141414.00
4	2016	July	149657.00
5	2016	August	149657.00
6	2016	September	149657.00
7	2016	October	149657.00
8	2016	November	149657.00
9	2016	December	149657.00
10	2017	January	149657.00
11	2017	February	149657.00
12	2017	March	149657.00
		Total Rs.	1771155.00

Rupees seventeen lakh seventy one thousand one hundred fifty five only

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Tezpur University

Low temperature dynamics in strongly correlated magnetic nanosystems

Award letter no. F.30-1/2014/RA-2014-16-GE-WES-5629 (SA-II)

Progress report of 2015-2016

**Name of the awardee: Dr. P. Deb,
Associate Professor,
Department of Physics
Tezpur University (Central University)
Tezpur-784028**

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG,
NEW DELHI-II0002**

Approved objectives of the proposal with time lines

6 month	<ul style="list-style-type: none">➤ Literature Survey
12 month	<ul style="list-style-type: none">➤ Synthesis of magnetic nanoparticles as primary building blocks and their characterizations.➤ Investigation of different chemical factors in controlling the assembly formation of the
18 month	<ul style="list-style-type: none">➤ Controlled assembly of magnetic nanoparticles and their preliminary characterizations for structural investigations.➤ Low-temperature magnetic and magneto-transport measurements of the secondary nanostructures
24 month	<ul style="list-style-type: none">➤ Comparative magnetic and magneto-transport measurements of the secondary nanostructures➤ Memory and aging study of the assembled systems and their comparison with primitive systems.➤ Compile and summarize the results.

As per the time line of the proposal flowing objectives have been achieved.

Achieved Objectives

- Two systems of magnetic nanoparticles have been developed and also their microstructural characterizations have been performed.
- Effect of surfactant concentration was investigated in obtaining iso-oriented secondary structures of the nanoparticles.

Result and discussions

1. Iron oxide nanoparticles and their secondary structures formation

In this work, we have tried to develop secondary structures of iron oxide nanoparticles using surfactants and polymers in the post synthesis stage of the nanoparticles. The intension was to develop the spatially independent arrangement of magnetic nanoparticles for understanding organization dependent collective magnetic properties. In this progress report, we have shown the developed primary nanoparticles and their secondary structures formation and few surface and microstructure related characterizations, as per the time line of the submitted proposal.

1.1 Development of iron oxide nanoparticles

Iron oxide nanoparticles were synthesized using a co-precipitation method. To control the growth and colloidal stability of the particles, oleic acid was employed. DMSO (Dimethyl sulfoxide) was employed as the solvent, which also acted as the oxidizing agent to oxidize a fraction of ferrous salt to ferric. The co-precipitation reaction occurred when the pH of the solution was increased to basic pH with the addition of TMAOH (Tetramethylammonium hydroxide). The black coloured precipitate was washed for many times for the removal of extra oleic acid and dried. Transmission electron microscopy showed uniformly distributed nanoparticles of average size 5 nm (shown in the Figure1 (a)). The capping characteristic of oleic acid is known from the FTIR spectra (shown in the figure 1(c)). The bidentate binding of the oleic acid carboxylic group COOH to the nanoparticle surface is confirmed from the stretching vibrations at 1560 cm^{-1} and 1413 cm^{-1} in the FTIR spectrum [1]. These peaks are due to the COO^- asymmetric and symmetric stretching vibrations respectively. The characteristic peak of Fe-O stretching is observed at around 630 cm^{-1} and 573 cm^{-1} [2]. In addition, other characteristic peaks like, CH_2 symmetric and asymmetric stretching bands at around 2924 cm^{-1} and 2851 cm^{-1} respectively of oleic acid have been also observed for this sample [2]. The maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phase of the developed nanoparticles is confirmed from the characteristic peaks at around 350 cm^{-1} , 500 cm^{-1} and 670 cm^{-1} in the Raman spectrum (shown in the figure 1d) [3]. The maghemite phase of the particles has been confirmed by indexing the diffraction rings on the SAED pattern also. Moreover, the interplanar spacing measured in the HRTEM image well matches with the interplanar spacing of 2.5 \AA for the (311) of the maghemite phase (shown in the figure 1b).

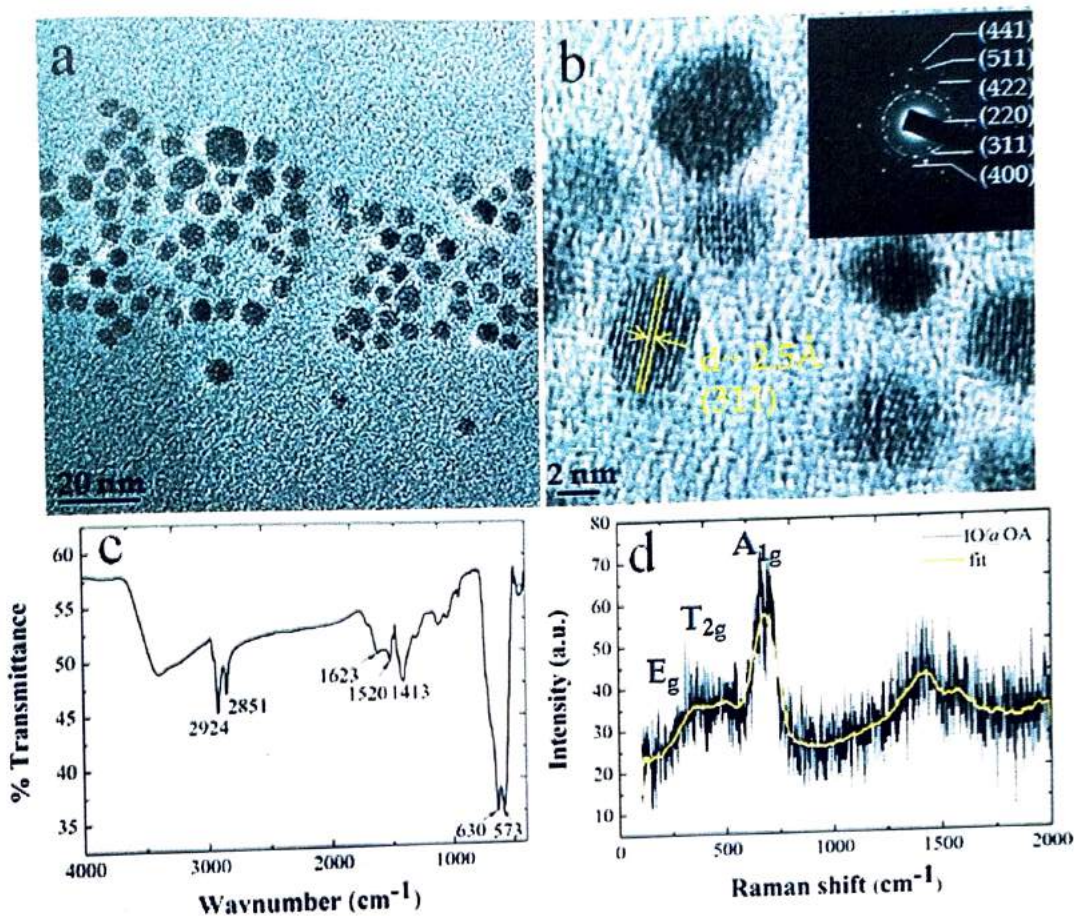


Figure 1: TEM image (a), HRETEM with SADED pattern (b), FTIR spectrum (c) and Raman spectrum of the developed oleic acid capped iron oxide nanoparticles.

1.2 Development of secondary nanostructures from the iron oxide nanoparticles for using post functionalization steps

Developed hydrophobic nanoparticles were functionalized with CTAB (Cetyltrimethylammonium bromide) and subsequently with PAA (Polyacrylic acid) for the formation of anisotropic aggregation and cluster structures respectively. Figure 2(a) and (b) show the TEM images of these two systems. From the TEM micrographs, it is clear that after CTAB functionalization the nanoparticles get aggregated with branching morphology and after PAA addition, separated clusters were obtained. The confirmation of CTAB and PAA functionalization can be known from the comparative FTIR spectra of these two samples (shown in the figure 2 (c)). The peaks at around 3014 cm^{-1} and 1473 cm^{-1} are due to bending vibration of N^+ - $(\text{CH}_3)_3$ [4]. The obtained aggregation is obvious, because, due to the strong hydrophobic-hydrophobic interaction through long carbon chains of oleic acid and CTAB, few oleic acid molecules can be detached from the nanoparticles surface during the functionalization. This can be confirmed from the noticeable intensity increment of the peak for $\text{C}=\text{O}$ vibration at around 1731 cm^{-1} and its higher wave

number shifting in comparison to that for the oleic acid capped nanoparticles system. After PAA functionalization, it is observed that the intensities of characteristic peaks CTAB in the FTIR spectra have been decreased; however, no shifting is observed. Additionally, the peak for C=O vibration becomes more prominent, signifying that the PAA functionalization results abundance of COOH groups to the system. The measured zeta potential for the so-prepared CTAB functionalized nanoparticles is +40.54 mV (shown in the figure 2(d)). However, the resultant solution of PAA functionalized nanoparticles has showed the zeta potential value +28.36 mV. The peaks at 962 cm^{-1} and 910 cm^{-1} are due to the quaternary ammonium mode of CTAB [5]. Zeta potential measurement also shows that after PAA addition the value of zeta potential decreases, which signifies the neutralization of a fraction positive charge of the CTAB by negatively charged PAA. COOH group of PAA is argued to be bound to the polar head group ($\text{N}^+(\text{CH}_3)_3$) of CTAB, exposed outward. Raman spectra of these two samples have confirmed that after functionalization steps also retained maghemite phase like that in the primary particle system (shown in the figure 2 (e)).

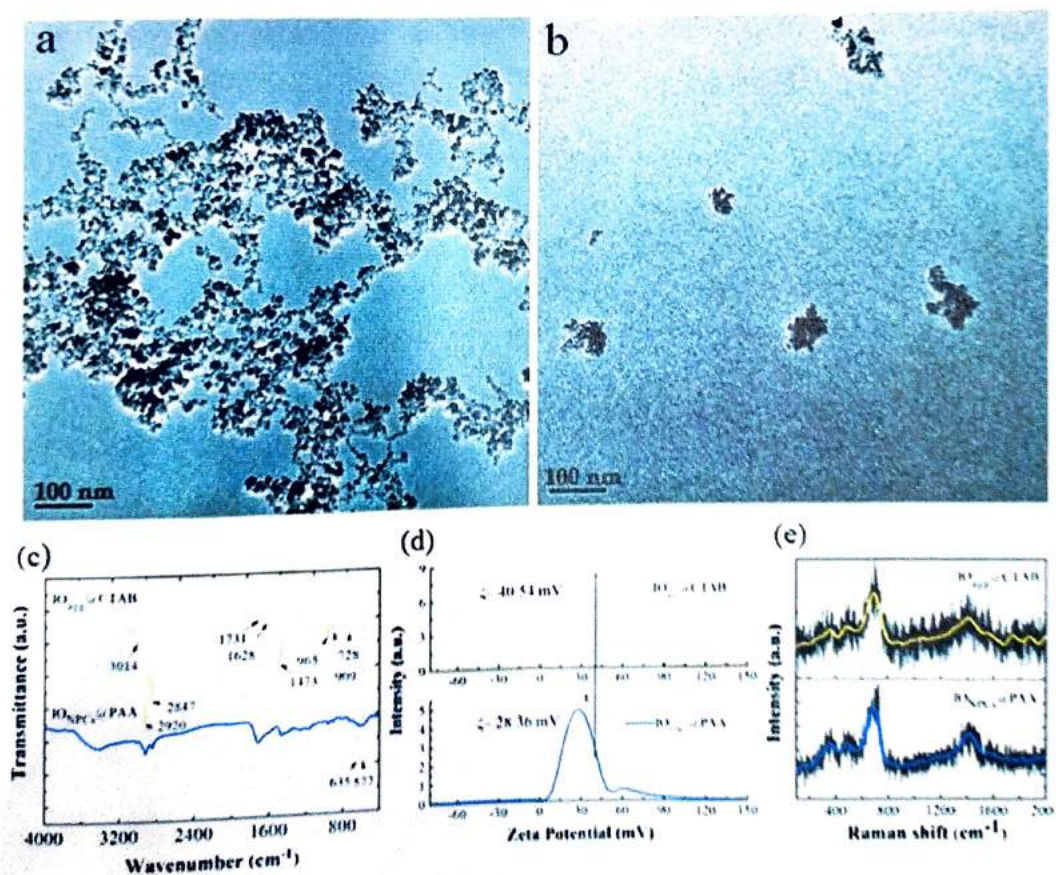


Figure 2: TEM image of (a) anisotropic aggregation and (b) nanoparticles cluster of iron oxide nanoparticles; (c) comparative FTIR, (d) Zeta distribution plot and (e) Raman spectra of the aggregate and cluster systems.

Observed variation in the arrangement of the particles in these two systems would effect on the collective spin dynamics and hence in the collective magnetic properties.

2. Controlled secondary growth of CoFe_2O_4 nanoparticles for the formation of their iso-oriented assemblies

Controlling the self-assembly process of primary nanoparticles and subsequent secondary growth mechanism is the key aspect for achieving such ordered structures. In this work, we introduce a new insight on achieving hierarchical assemblies of CoFe_2O_4 nanoparticles based on the temporal stability of the primary nanoparticles, where, the growth and stability of the primary particles are controlled by using oleic acid. It is found that the developed particles, at a critical concentration of oleic acid, prefer a secondary growth process, rather than promoting their individual growth. Domination of the attractive hydrophobic interaction over steric repulsion among the primary particles at this critical concentration of oleic acid is found to be the key factor for the initial aggregation of the primary particles, which eventually leads to the formation of spherical hierarchical assemblies via oriented attachment. It is also realized that at an extremely good or extremely poor stability condition of the primary particles do not prefer this secondary growth process.

2.1 Effect of oleic acid concentration on the secondary growth of CoFe_2O_4 nanoparticles

Three systems of CoFe_2O_4 nanoparticles have been developed using the three concentration of oleic acid. The method employed was similar to that used for the iron oxide nanoparticles. Only difference is that here Co precursor was also added with a stoichiometric ratio. The samples prepared with 0.07 M, 0.14 M and 0.21 M concentrations have been coded as CF1, CF2 and CF3 respectively.

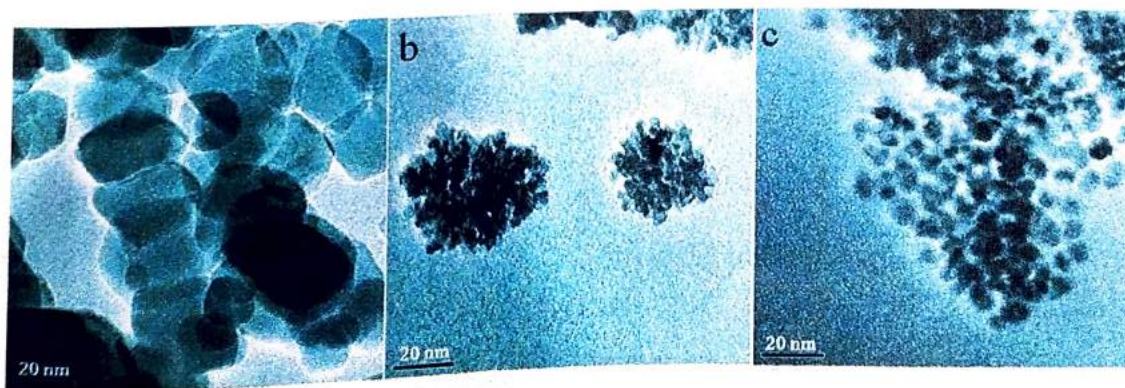


Figure 3: TEM images show the state of the CoFe_2O_4 nanoparticles prepared with 0.07 M (a) 0.14 M (b) and 0.21 M (c) concentration of oleic acid. The figure b clearly shows the secondary structures of the particles.

To identify the nature of oleic acid binding to the nanoparticle surface and to quantify the amount adsorbed oleic acid at different concentrations FTIR and TGA analysis were performed. Figure 4(a) shows the comparative FTIR plots of the three systems. The common peak observed at 1630 cm^{-1} for all three samples corresponds to the H-O-H scissoring from free or adsorbed water molecules [6]. The intense absorption peaks around 578 cm^{-1} for all three samples are attributed to Fe-O or Co-O vibrations [7]. The absence of characteristic C=O stretching vibration peak around 1700 cm^{-1} in the Figure 4(a) FTIR spectra witnesses the lack of pure, unmodified oleic acid in all the three nanopowders. Instead of this, two new peaks have appeared at 1569 cm^{-1} and 1415 cm^{-1} , corresponding to asymmetric and symmetric COO⁻ stretching vibrations respectively [8]. However, both of these two peaks are observed to be distinct for the CF3 sample only. The obtained separation ($\Delta=154\text{ cm}^{-1}$) between these two peaks corresponds to the bridging bidentate type of interaction of COO⁻ with the nanoparticles' surface metal atoms (Fe and Co) [9]. For CF1 and CF2, though the COO⁻ symmetric stretching peak is observed distinctly, the asymmetric peak is observed as a weak shoulder peak. This signifies that in CF3 sample only, oleic acid molecules are effectively bonded to the nanoparticles surface, which could be justified as the consequence of higher oleic acid concentration used in this sample. This is also supported by the higher intensities of CH₂ symmetric and asymmetric peaks at 2923 cm^{-1} and 2852 cm^{-1} respectively for this sample [2]. However, escaping this usual trend of intensity variation with oleic acid concentration, CF2, i.e. the assembly sample shows two highest intense peaks at 1115 cm^{-1} and 949 cm^{-1} , which are attributed to C-O stretching and out-of-plane O-H bending vibrations [8]. Moreover, one additional peak is observed for this sample at 1482 cm^{-1} which is ascribed to the in-plane O-H bending vibrations [10]. Thus, the observed intense peak of C-O stretching and O-H bending vibrations for the CF2 sample means that, there might be a fraction of oleic acid molecules which are in quasi-bonding state.

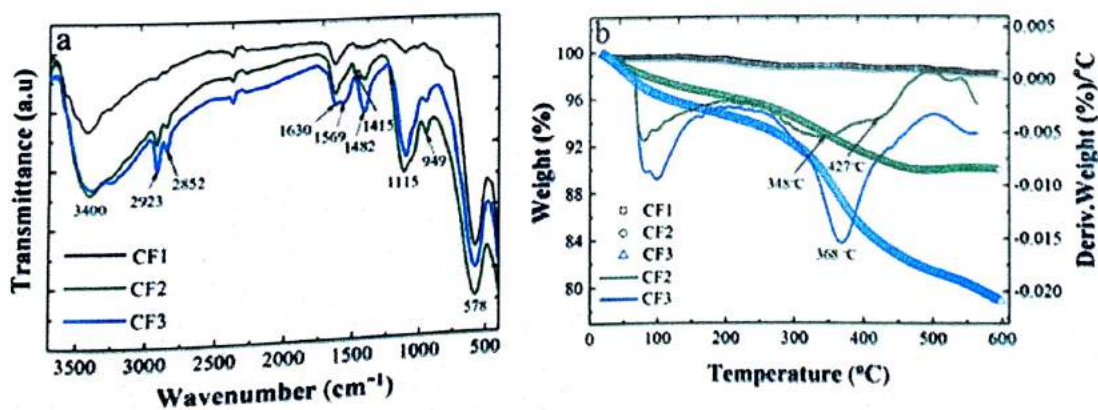


Fig. 4 Surface compositional analysis: (a) FT-IR spectra and (b) TGA of the CF1, CF2 and CF3 samples. Figure b also shows the DTG plots of the CF2 and CF3 samples.

The observed anomaly in FTIR can be further understood based on the TG analysis. Figure 4(b) shows the comparative TGA plots of the three systems. In the TGA plots, the CF1 sample shows significantly low weight loss ($\sim 2\%$), while for CF2 and CF3 samples around $\sim 11\%$ and $\sim 22\%$ of weight losses are obtained respectively. However, the TGA plots of CF2 and CF3 show respective $\sim 2\%$ and $\sim 3\%$ weight losses up to 100°C due to the removal of adsorbed water molecules. It is obvious to observe higher percentage of weight loss for the samples prepared with higher concentrations of oleic acid. It is also known that depending on the availability of oleic acid in the system, monolayer or bilayer can be formed over the nanoparticles. However, here, for none of the samples the formation of oleic acid bilayer was observed. This is supported by the absence of any characteristic peak of C=O stretching in the FTIR spectra [11]. Oleic acid bilayer is usually formed through physisorption of oleic acid molecules over the first chemisorbed layer, where, the physisorbed oleic acid molecules possess the hydrophobic tails towards the first layer and the COOH groups remain undisturbed pointing outward from the nanoparticles surface. The derivative TGA plot of CF2 sample shows two step weight loss (348°C and 427°C), which again contradicts the affirmation based on the FTIR spectra interpretation that in these cases results only monolayers. But, it is not always true that only the bilayer can result two step weight losses in the temperature range ($200^\circ\text{C} - 600^\circ\text{C}$). Few reports are there showing the two step weight loss and the explanation was given as the possibility of two types of binding strength due to the chemisorption process itself. Another possible reason could be given as the contribution of the van der Waal interaction among the neighbouring hydrophobic chains of the already chemisorbed oleic acid molecules in *cis* form. But, in that case the question is that why it will happen only for the CF2 sample. The CF3 sample which is uniformly capped by oleic acid should have higher probability for this type of van der Waal interaction among the chemisorbed molecules. Therefore, in the case of CF2 sample, the already mentioned explanation of dual binding strength can be put forwarded to interpretate the DTG plot. If we see the first peak of CF2 sample, it is coming a little bit lower temperature than that of the single peak of CF3 sample. Moreover, this peak of CF2 sample is noticeably broad. This observation implies that in the CF2 sample a major fraction of oleic acid molecules are not chemisorbed uniformly and effectively over the particles like that of the CF3 sample. The possible reason behind this could be the secondary growth process of the particles in the CF2 sample. During this process oleic acid molecules can detach from the particles' surface at the interface regions.

The developed iso-oriented structure can be interesting for study the interaction dependent collective magnetic properties.

Future objectives

1. Detail magnetic properties study of the developed assemblies and understanding their modified properties. Particularly, low temperature magnetic phenomena, like spin glass, memory effect etc. will be tried to understand for these assembly systems.
2. Development of more secondary nanostructures of other ferrite materials and their comparative properties study.

Publications from this award

Two papers have been published in peer-reviewed journal from this award

1. Organization dependent collective magnetic properties of secondary nanostructures with differential spatial ordering and magnetic easy axis orientation, K. Saikia, D.D. Sarma, **P. Deb**, Journal of Magnetism and Magnetic Materials, 408, 2016, 127-136.
2. Fatty acid as structure directing agent for controlled secondary growth of CoFe_2O_4 nanoparticles to achieve mesoscale assemblies: A facile approach for developing hierarchical structures, K. Saikia, S.D. Kaushik, D. Sen, S. Mazumder, **P. Deb**, Applied Surface Science, 379, 2016, 530-539.
3. Progressive freezing of interacting spins in isolated finite magnetic ensembles, K. Bhattacharya, V. Dupuis, D.L. Roy, **P. Deb**, Journal of Physics: Condensed Matter 29, 2016, 045002.

References

- [1] Bloemen, M. et al. Improved functionalization of oleic acid-coated iron oxide nanoparticles for biomedical applications, *J. Nanopart Res.* **14**, 1100 (pp.10), 2012.
- [2] Predoi, D. et al. A study on iron oxide nanoparticles coated with dextrin obtained by coprecipitation, *Dig. J. of Nanomate. Biostruct.* **2**, 169--173, 2007.

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Low temperature dynamics in strongly correlated magnetic nanosystems

Award letter no. F.30-1/2014/RA-2014-16-GE-WES-5629 (SA-II)

Progress report of 2016-2019

Name of the awardee: Dr. P. Deb,
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UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG,
NEW DELHI-II0002

Approved objectives of the proposal with time lines

6 month	➤ Literature Survey
12 month	➤ Synthesis of magnetic nanoparticles as primary building blocks and their characterizations. ➤ Investigation of different chemical factors in controlling the assembly formation of the
18 month	➤ Controlled assembly of magnetic nanoparticles and their preliminary characterizations for structural investigations. ➤ Low-temperature magnetic and magneto-transport measurements of the secondary nanostructures
24 month	➤ Comparative magnetic and magneto-transport measurements of the secondary nanostructures ➤ Memory and aging study of the assembled systems and their comparison with primitive systems. ➤ Compile and summarize the results.

As per the time line of the proposal flowing objectives have been achieved.

Achieved Objectives

- The three systems (i) assembly($IO_{NPs}@OA$) (ii) network aggregate($IO_{agg}@CTAB$) and (iii) cluster ($IO_{NPCs}@PAA$) of iron oxide nanoparticles ($\gamma-Fe_2O_3$) have been developed and their magnetic properties have been performed.
- The secondary structure of maghemite ($\gamma-Fe_2O_3$) nanoparticles (NPs) assembly in mesoporous silica spheres have been developed and their magnetic properties have been observed.
- Effect of surfactant concentration was investigated in obtaining iso-oriented secondary structures of the nanoparticles.

Results and discussions

1.1 Development of Three systems of iron oxide nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$):

In this work, the three systems defining as (i) $\text{IO}_{\text{NPs}}@OA$; an assembly (ii) $\text{IO}_{\text{agg}}@CTAB$; a network aggregation, (iii) $\text{IO}_{\text{NPCs}}@PAA$; an identical clusters of iron oxide nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$) have been developed by simply changing the solvent evaporation conditions. Here, assembly of the synthesized nanoparticles have been developed by separating the same nanoparticles at a measureable spacing. For the development of a network aggregation of the same nanoparticles, the synthesized nanoparticles are placed by taking close together and facing the same way. All the synthesized three systems have kept the same phase and they are polydispersity of primary particles.

1.2 Magnetic effects developed three systems of iron oxide nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$):

In this work, we have observed the magnetic properties of secondary structures of iron oxide nanoparticles. The variation in easy axes orientations and spatial ordering of the synthesized iron oxide nanoparticles in the three developed systems is noticed to be liable for the remarked deviation in the dipolar direction. It can be observed from magnetic measurements that the stacking accretion morphology results the significant improvement of coercivity and remanence values for the aggregate system and vice-versa for cluster system due to random orientation of easy axis. The field dependent magnetization measurements of the three systems with respect to temperatures is shown by the figure 1. Magnetic measurements show that partial alignment of the easy axes of the particles in the aggregate system can result in perceptible non-monotonic field dependence of ZFC peak temperature (T_{peak}). The trend of blocking temperature for the three systems of iron oxide nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$) is utterly engrossing in which the cluster system shows the lowest blocking temperature (T_B) relevant to the lowering of effective energy because of strongest magnetic field. Temperature dependent magnetization measurements (FC and ZFC) for the three developed systems is shown in figure 2. The FC memory effect of the three systems is shown in figure 3. It can be observed that FC memory effect is independent of the type of dipolar interaction (positive or negative) which is present in the system, but it is dependent only on the resultant strength of dipolar interaction.

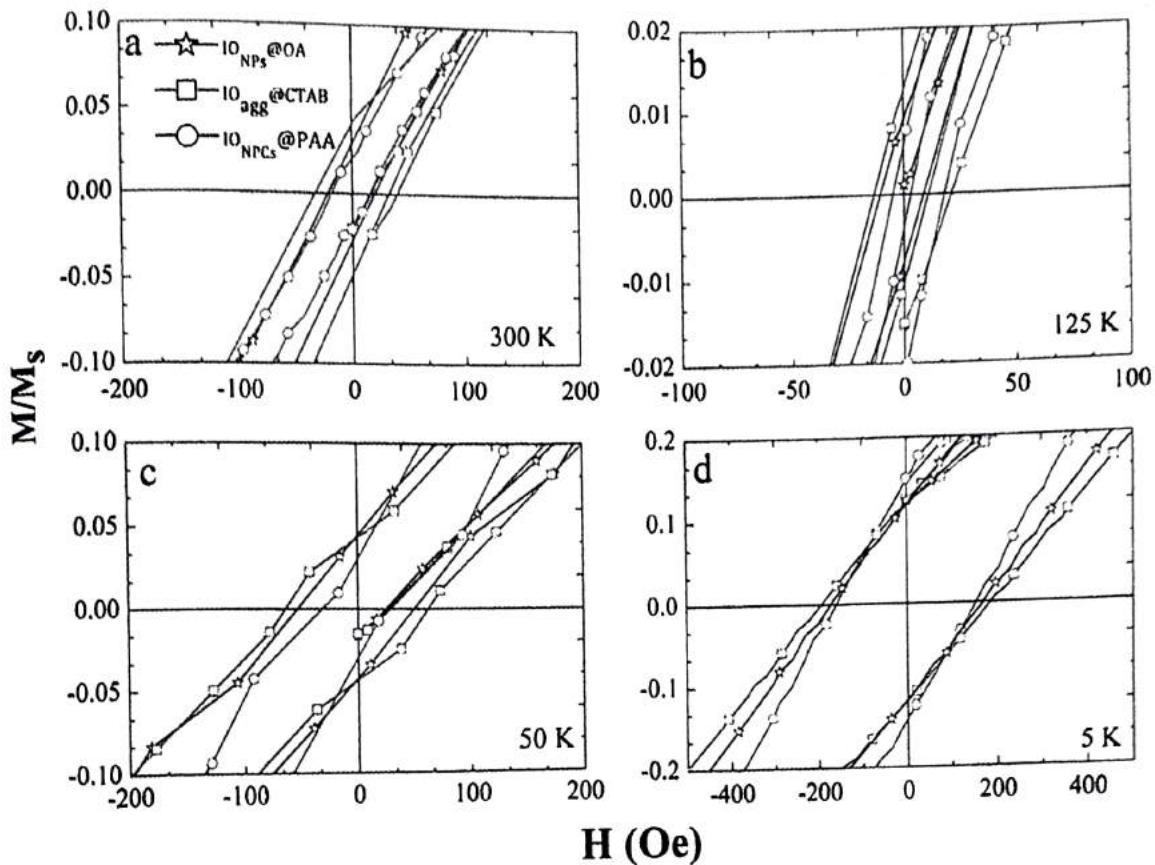


Figure 1: M-H plots of the three systems showing coercivities and reduced remanences at temperatures (a) 300 K, (b) 125 K, (c) 50 K and (d) 5 K

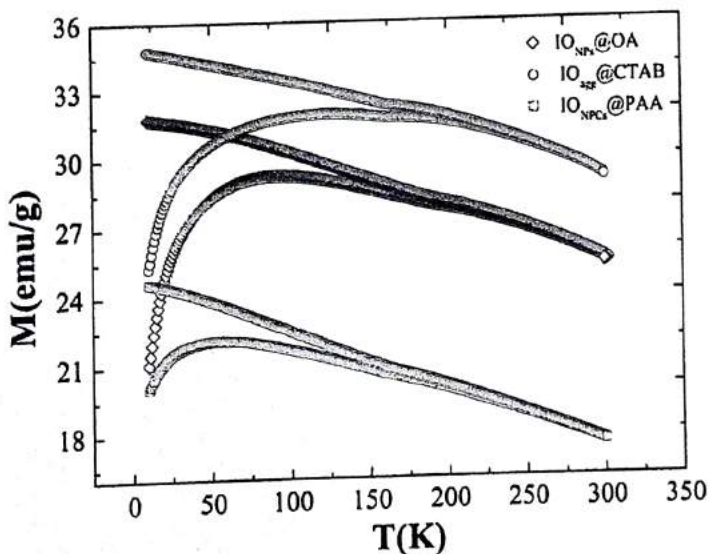


Figure 2: M-T measurements (FC and ZFC) of the three systems with probe field 500 Oe.

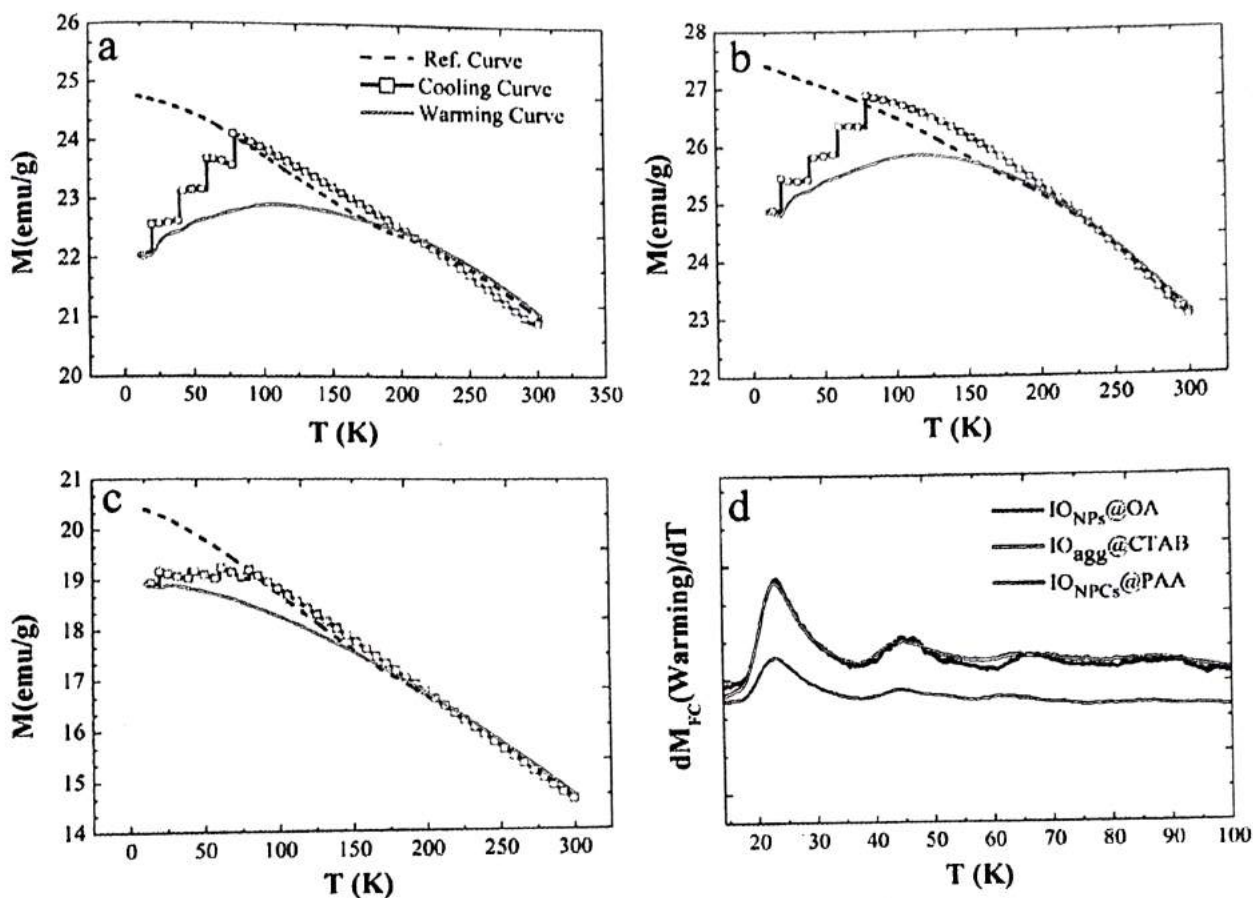


Figure 3: (a–c) FC memory effect for the three systems and (b) shows the temperature derivative of FC warming curves

2 Development of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles (NPs) assembly loaded mesoporous silica spheres:

In this work, mesoporous silica loaded dense assembly structure of maghemite nanoparticles have been developed by controlled solvent evaporation process where the NPs having higher size than pore diameter get enmeshed inside the porous silica spheres. Only silica spheres can enmesh the iron oxide NPs the mesoporous so that silica pore is suitable for this mechanism. Also, the developed magnetic assembly system can have superparamagnetic property of the NPs. Here, we have studied the DLS and zeta potential measurements for the three silica samples and silica coated nanoparticles samples have been plotted shown in figure 4. It can be observed from DLS measurements that the NPs loaded silica samples have lower value of the polydispersity index than that of the pure silica system (S1) while the polydispersity index has increased for the other two samples after conjugating NPs because of morphological non-uniformity structure. Whereas Zeta potential values for the NPs loaded silica system (S1@IO) increases crucially than that of pure silica system (S1) due to enhance stability of mesoporous silica spheres while zeta potential values for the other two systems decrease moderately due to non-occurring of the enveloping process and formation of separate aggregations of NPs outside the silica sphere. The complete and the high resolution XPS spectra of Fe^{2p} , O^{1s} and C^{1s} for both the two samples has been shown in

the figure 5 (a) and 5 (b) respectively. The comparative field dependent magnetization (M-H) plots for iron oxide nanoparticles and iron oxide nanoparticles loaded silica spheres has been plotted in figure 6(a) and (b) respectively. It is observed that coercivity and remanence values for both the samples are very small which clearly signifies the superparamagnetic property. Also, the coercivity value for composite sample is smaller than that for separated iron oxide nanoparticles and vice-versa is observed for reduced remanence. Since, the $\gamma\text{-Fe}_2\text{O}_3$ NPs assembly have strong collective magnetization and the secondary nanostructures are highly penetrable for the water protons which can pass across the pores, so they show a significant improvement in MRI transverse relaxivity which is twice as high as that for isolated primary $\gamma\text{-Fe}_2\text{O}_3$ NPs. Higher dimensional designed secondary nanostructures have been developed by fabrication method and enhanced magnetic effects of secondary nanostructures can be observed.

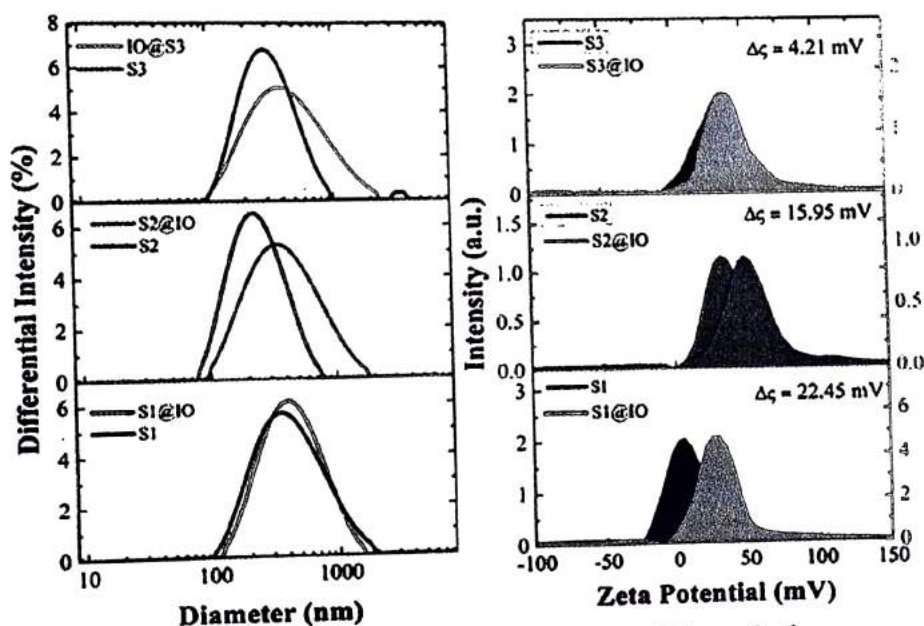


Figure 4: Comparative size distribution plots from DLS and the comparative Zeta potential plots the three silica samples and silica-nanoparticles conjugate samples

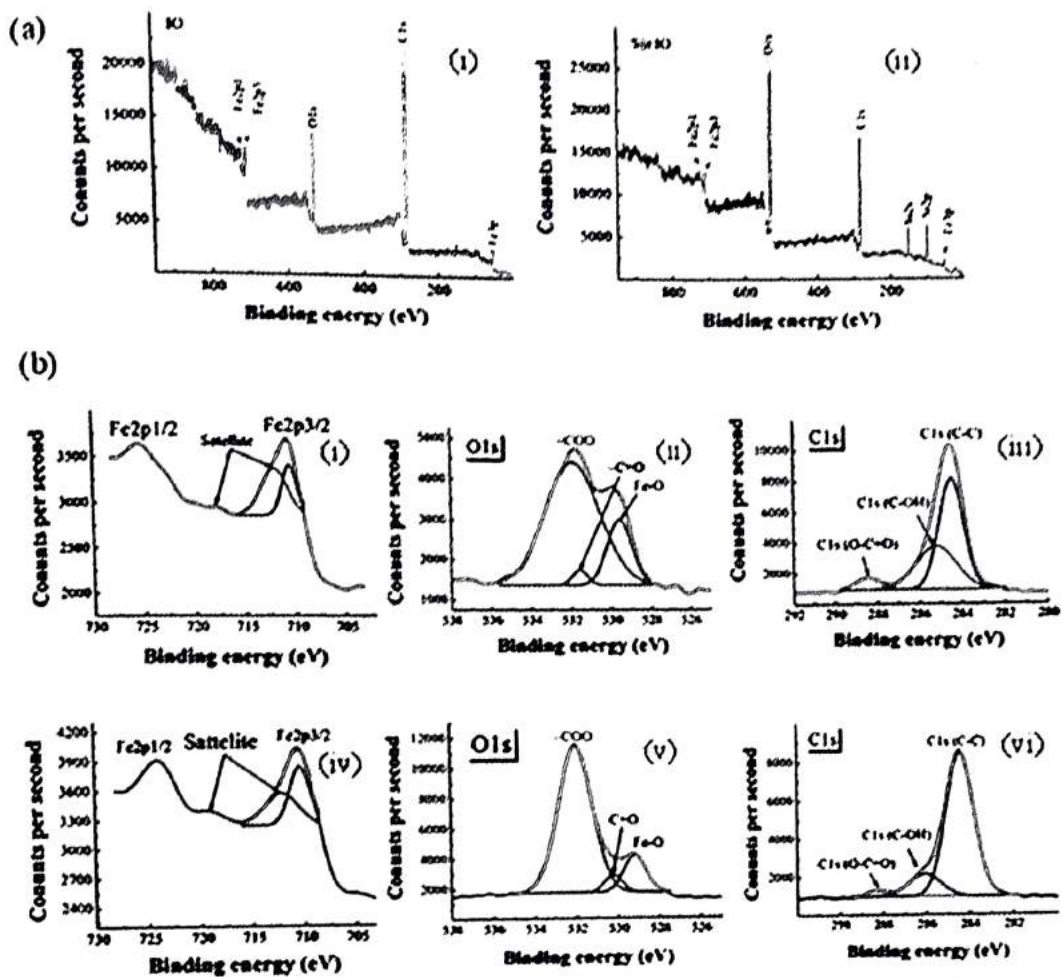


Figure 5: (a) XPS spectra of iron oxide NPs (i) and iron oxide NPs loaded silica spheres (ii); (b) High resolution XPS spectra of Fe^{2p} (i & iv), O^{1s} (ii & v) and C^{1s} (iii & vi) of iron oxide nanoparticles and nanoparticles loaded silica spheres respectively

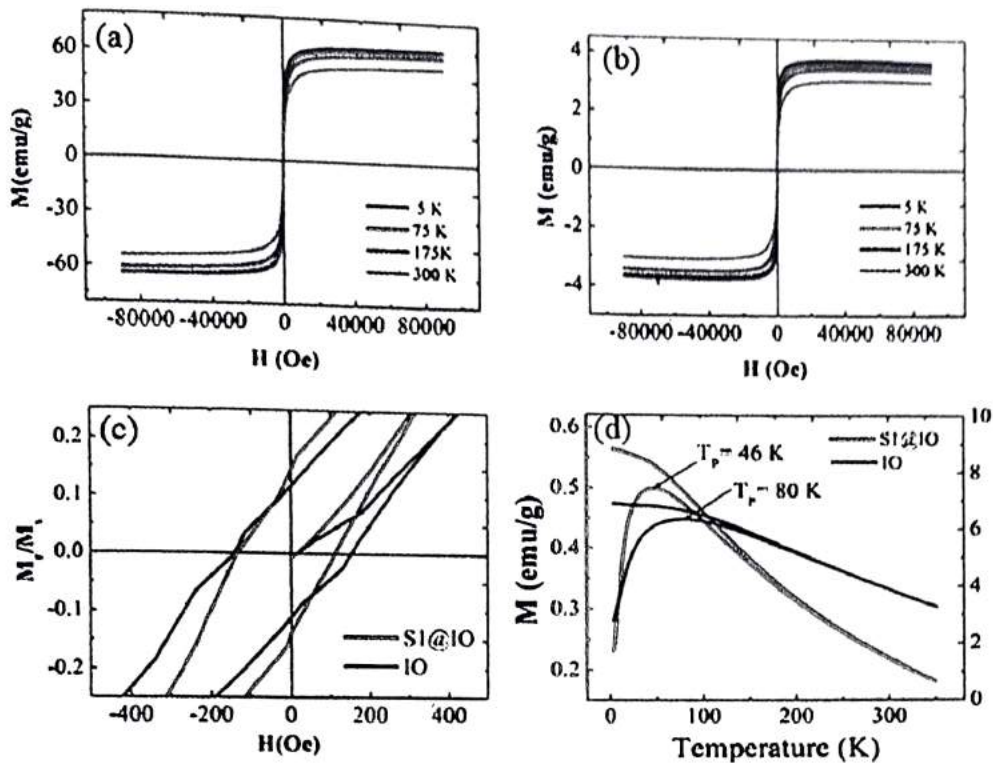


Figure 6: M-H plots of iron oxide nanoparticles (a) and nanoparticles loaded silica spheres (b) at the mentioned temperatures; Fig. c shows the comparative M-H plots (normalized plots) of the two systems at 5 K and; Fig. d shows the comparative ZFC and FC plots of the two systems in double y plot

3.1 Controlled secondary growth of CoFe_2O_4 nanoparticles for the formation of their mesoscale assemblies

In this work, hierarchical assemblies of cobalt ferrite nanoparticles have been developed by modified co-precipitation route using unsaturated oleic acid acting as a structure directing agent. The stability of the primary nanoparticles is controlled by the unsaturated oleic acid concentration leading to the mesoscale assembly structure formation. The stability of the primary particles and growth of secondary nanoparticles give their different ordered structures. The microstructural investigations and crystalline phase of the prepared powder sample with oleic acid has been characterized by Transmission electron microscopy (TEM) and X-ray diffraction (XRD) technique respectively shown in figure 1. From the TEM images, it is seen that primary particles are not spherically uniform, and the adjacent particles form unified structures by sharing their edges. The cubic spinel structure of CoFe_2O_4 is confirmed by the diffraction pattern of the assembly system shown in figure 1(d).

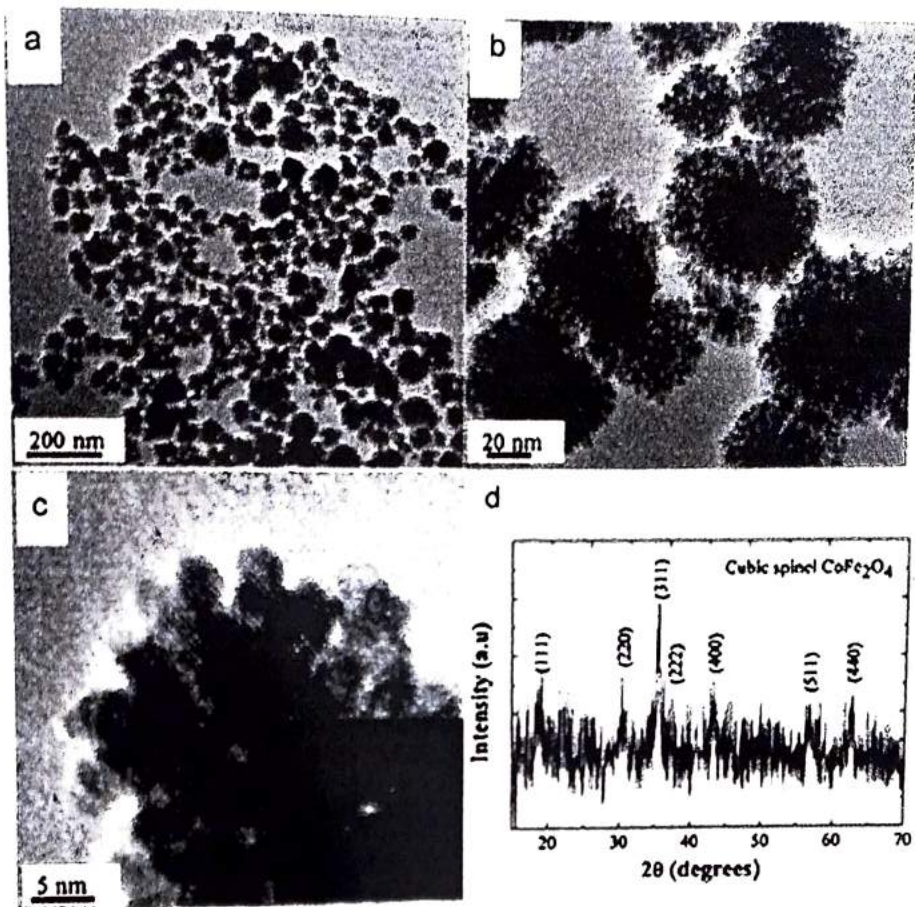


Figure 7: CoFe_2O_4 hierarchical assemblies obtained with 0.14M of oleic acid: (a) TEM image (scale is 200nm), (b&c) HRTEM (scales are 20nm and 5 nm respectively) and (d) shows the XRD pattern (Red lines show the FFT filter smoothing)

3.2 Effect of oleic acid concentration on the secondary growth of CoFe_2O_4 nanoparticles:

In this work, the three systems of CoFe_2O_4 nanoparticles have been developed by oxidative precipitation method where DMSO is used as an oxidizing agent and using the three concentration of oleic acid. Here, the samples namely, CF1, CF2 and CF3 are prepared with oleic acid having concentrations as 0.07 M, 0.14 M and 0.21 M respectively. It can be observed that the developed nanoparticles at a critical concentration of oleic acid boost a secondary growth assembly instead of their individual growth. This is due to the domination of hydrophobic interaction over steric repulsion among the primary particles, which is the driving force to build a spherical aggregation of particles resulting spherical hierarchical assemblies. Raman spectroscopy shows the cation distribution factor and the five Raman active bands present in these three systems namely, A_{1g} , E_g and three F_{2g} shown in figure 8. The comparative M-H plots for all the three systems namely, CF1, CF2 and CF3 at room temperature has been plotted in figure 9. From the hysteresis behaviour it is observed that, the CF1 sample signifies long-range magnetic ordering and the other two samples (CF2 and CF3) show superparamagnetic behaviour where the coercivity values are not vanished. The coercivity and remanence

values for these three systems decrease as the oleic acid concentration increases at the room temperature which reflect the stronger inter-particle interaction in the assembly system (CF1 and CF2). Comparative M-T plots has been conducted with ZFC and FC conditions for the three systems shown in figure 10 which implies the effect of strong interparticle interaction among the primary particles in the assembly system and the FC curve shows the higher magnetic moments in the hierarchical system at low magnetic field.

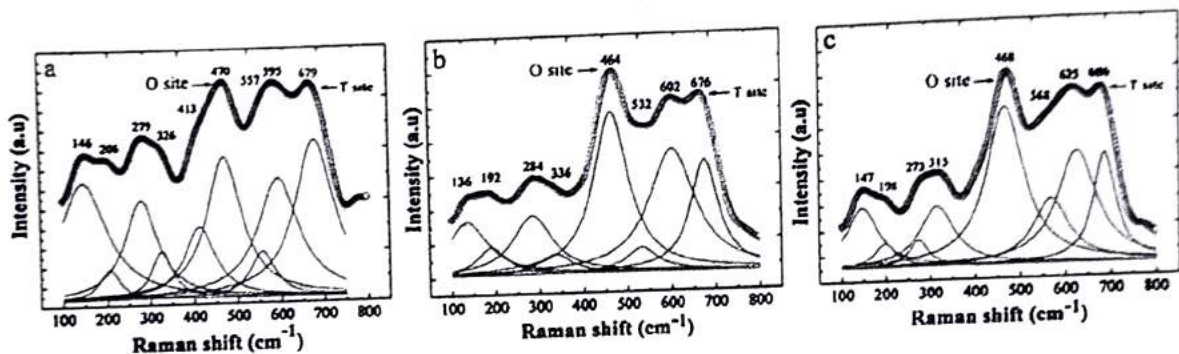


Figure 8: Raman spectra of the samples CF1(a), CF2(b) and CF3(c)

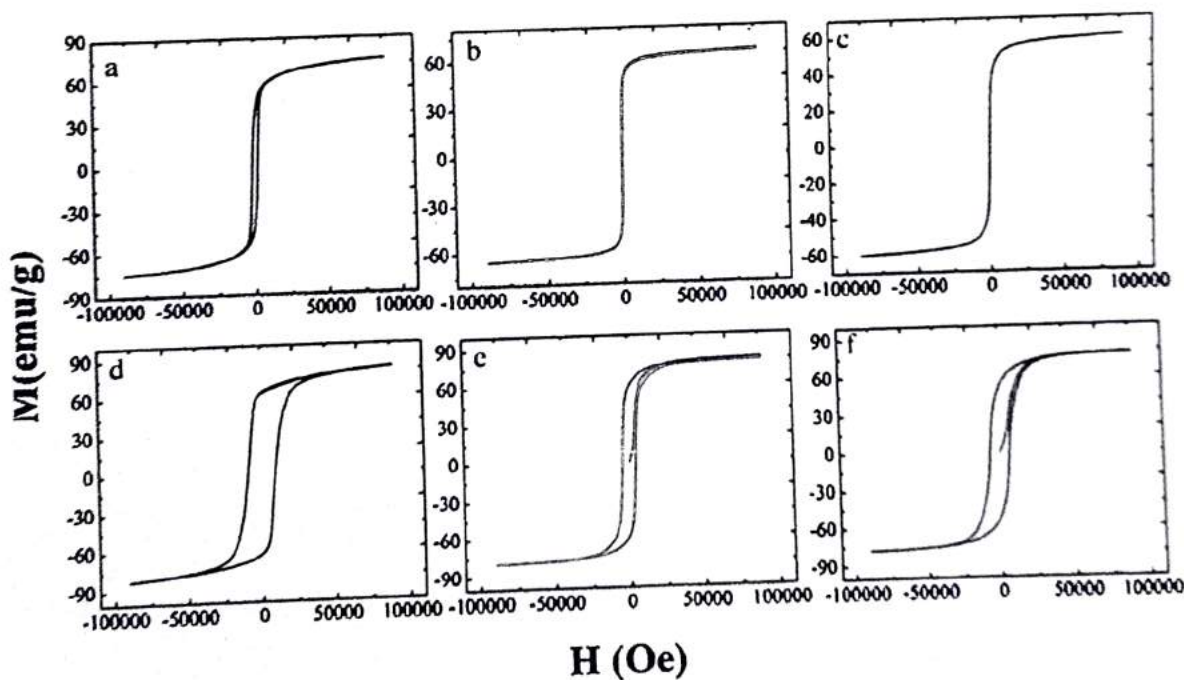


Figure 9: Room temperature and low temperature M-H plots of CF1, CF2, CF3

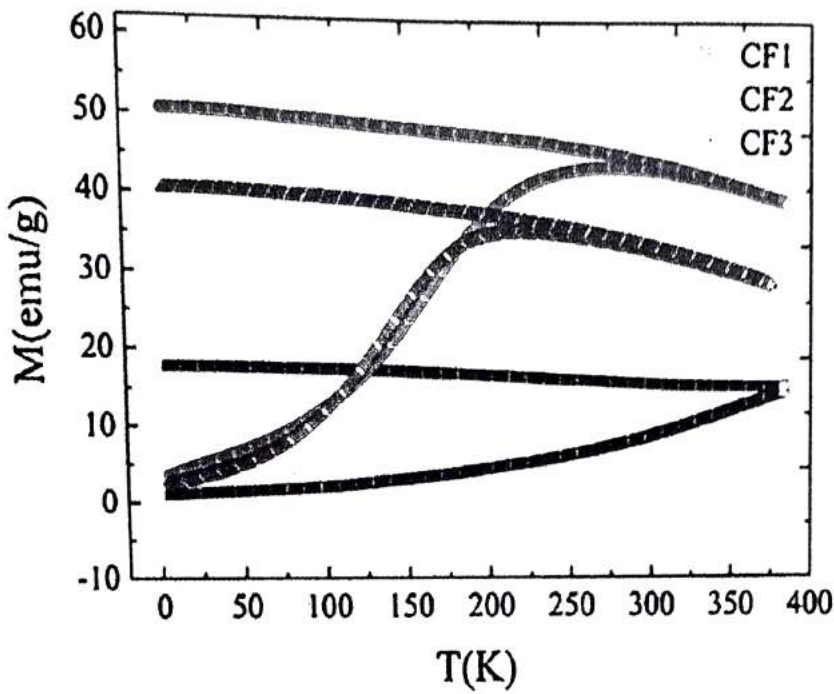


Figure 10: Comparative M-T plots of the three systems with applied probe field 1000 Oe

New Leads obtained

We have proposed a model which explains the dependency of spatial ordering and easy axes orientation on the dipolar interaction to modulate the collective magnetic property of the systems. The trend of coercivity and remanence is affected by the respective broadening in the distribution of anisotropy energy barrier. The fastest relaxation in spins compelled by the strong interparticle interaction results lowering in blocking temperature even with higher strength of demagnetization interaction. The field cooling (FC) memory effect in the superparamagnetic secondary nanosystems is considered as an independent feature of magnetizing or demagnetizing effect but depends only on the relative arrangement of the magnetic easy axes which regulates the resultant dipolar strength.

We have also developed a series of new generation 2-dimensional systems as a promising candidate in the field of technology such as efficient crude oil removal, flexible planar micro-supercapacitor, etc. A theoretical approach for understanding of inherent physical property of 2-D heterostructure has been performed by considering the Density Functional Theory (DFT) simulation.

Publications from this award

Seven papers have been published in peer-reviewed journal from this award

1. M. Talukdar, S. K. Behera, K. Bhattacharya and **P. Deb**, Surface modified mesoporous $g\text{-C}_3\text{N}_4@FeNi_3$ as prompt and proficient magnetic adsorbent for crude oil recovery. *Applied Surface Science* 473 (2018) 275.
2. K. Saikia, K. Bhattacharya, D. Sen, S. D. Kaushik, J. Biswas, S. Lodha, B. Gogoi, A. K. Buragohain, W. Kockenberger and **P. Deb**, Solvent evaporation driven entrapment of magnetic nanoparticles in mesoporous frame for designing a highly efficient MRI contrast probe. *Applied Surface Science* 464 (2019) 567.
3. M. Talukdar, S. K. Behera, K. Bhattacharya and **P. Deb**, Surface modified mesoporous $g\text{-C}_3\text{N}_4@FeNi_3$ as prompt and proficient magnetic adsorbent for crude oil recovery. *Applied Surface Science* 473 (2018) 275.
4. S. K. Behera and **P. Deb**, Controlling the bandgap in graphene/h-BN heterostructures to realize electron mobility for high performing FETs. *RSC Advances* 7 (2017) 31393
5. K. Bhattacharya, V. Dupuis, D.L. Roy, **P. Deb**, Progressive freezing of interacting spins in isolated finite magnetic ensembles. *Journal of Physics: Condensed Matter* 29 (2016) 045002.
6. K. Saikia, S. D. Kaushik, D. Sen, S. Mazumder and **P. Deb**, Fatty acid as structure directing agent for controlled secondary growth of $CoFe_2O_4$ nanoparticles to achieve mesoscale assemblies: A facile approach for developing hierarchical structures. *Applied Surface Science* 379 (2016) 530.
7. K. Saikia, D. D. Sarma and **P. Deb**, Organization dependent collective magnetic properties of secondary nanostructures with differential spatial ordering and magnetic easy axis orientation. *Journal of Magnetism and Magnetic Materials* 408 (2016) 127.

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