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The present work derives motivation from the so called surface/interfacial magnetism in core shell structures and commercial samples of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ with sizes ranging from 20 to 30 nm were coated with polyaniline using plasma polymerization and studied. The High Resolution Transmission Electron Microscopy images indicate a core shell structure after polyaniline coating and exhibited an increase in saturation magnetization by 2 emu/g. For confirmation, plasma polymerization was performed on maghemite nanoparticles which also exhibited an increase in saturation magnetization. This enhanced magnetization is rather surprising and the reason is found to be an interfacial phenomenon resulting from a contact potential. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4826459>]

With the advent of nanoscience and nanotechnology, nanoparticles are in great demand for a variety of applications. They exhibit size effects and by virtue of which they display superlative physical and chemical properties. Among nanoparticles magnetic nanoparticles occupy a unique position because of their wide application potential in a horde of devices like bearings and dampers in automobiles, nanoparticle based catalysis, magnetic particle imaging, optical filters, and magnetoresistive devices.¹ Magnetic iron oxides, namely, magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) are well known for their usefulness as a magnetic storage medium and was extensively used in audio/video tapes.² They also find end uses in making ferrofluids which can function as liquid sealants and in data storage devices like hard disks and floppy diskettes. Magnetic iron oxides enjoy a unique position because below a critical particle size, they transform from ferromagnetic to superparamagnetic. Superparamagnetic iron oxide nanoparticles (SPIONs) are in great demand and they find innumerable applications in the area of biomedicines in the form of drug delivery agents, contrast enhancing agents in Magnetic Resonance Imaging (MRI), *in-vivo* applications such as magnetic hyperthermia, tissue repair, and immunomagnetic methods in cell separation and cell biology.³⁻⁶

Magnetite and maghemite occupy an important place among magnetic oxides. From a fundamental perspective magnetite (Fe_3O_4) is an inverse cubic spinel where both Fe^{3+} and Fe^{2+} ions are distributed among the tetrahedral(A) and octahedral(B) sites and can be written in the form $\text{Fe}^{3+}_A[\text{Fe}^{3+}\text{Fe}^{2+}]_B\text{O}_4^{2-}$ while maghemite belongs to the class of inverse spinels wherein vacancies are exclusively

concentrated on the octahedral sites and can be represented by $\text{Fe}^{3+}_A[\text{Fe}^{3+}_\Delta]_B\text{O}_4^{2-}$. They are widely used as a magnetic recording media. Magnetic oxides are sought after because they are biocompatible, non toxic, and inexpensive. Since magnetic nanoparticles have large surface to volume ratio and are highly reactive, they tend to agglomerate as clusters to reduce the surface energy. In free state, they get oxidized easily which adversely affects their magnetic properties. So the surface of these materials needs to be guarded suitably for achieving stable properties. Surface passivation of magnetic nanoparticles are resorted to inhibit further oxidation as well as to enable functionalization especially for biomedical applications. To enhance biocompatibility and to enable functionalization, these oxides are protected with a thin coating of organics like polyethylene glycol/polyaniline/polyvinyl alcohol (PEG/PANI/PVA). Passivation of nanoparticles is thus important from an application perspective. On passivation they take the form of a core-shell architecture having a core of the magnetic iron oxide and the shell that of the organic coating. The magnetism exhibited by core-shell structures have been a subject of intense study.^{7,8} Most of the researchers have reported decrease in magnetization in core shell structures.⁹ Magnetic studies in nickel ferrite nanoparticles revealed a decrease in saturation magnetization than the corresponding bulk counterpart and the decreased magnetization have been attributed to spin canting effects^{10,11} as well as to magnetic dead layer formation on the surface.^{12,13}

Recently, researchers have reported enhanced magnetization on surface modified Pd with a thin coating of polymer,^{14,15} whereas Banerjee *et al.*¹⁶ reported that iron oxide nanoparticles (IONs) when surface modified with gold displayed increased magnetization. Similar results were also observed for aluminium coated IONs¹⁷ and thiol capped

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gold nanoparticles.¹⁸ The phenomenon of enhanced magnetization is interesting as well as intriguing and a proper explanation for the display of enhanced magnetization is rather elusive. This type of magnetic behavior is attributed to an interfacial phenomenon and the magnetization is assumed to be originating from orbital contribution¹⁹ while there are also reports suggesting the role of bosons in the magnetic behavior of organic monolayers.²⁰ Thus the study of surface modified magnetic properties of nanoparticles and specifically, surface modified iron oxide particles assume significance both from an applied perspective as well as from a fundamental point of view.

Surface modification is an easy and effective method by which surface of a material is coated by organic layers, polymers or inorganic layers such as silica which provide a shell like protection to the inner core material.²¹ Surface modification protects the core material from chemical reaction and prevents agglomeration. It can also be viewed as a prime step pointing towards the biocompatibility since most of the nanomaterials with appropriate magnetic properties interact less with the environment which shows that they are not fully biocompatible. Hence the need for the modification of the surface of the cores of these materials so as to bind their surface to drugs, enzymes, proteins, and other molecular targets. The binding material alters the surface characteristics and thereby the whole nature of the core material. There are several methods ranging from wet chemical methods to solgel preparative techniques to provide a thin layer of an organic coating. Plasma polymerization offers effective pin hole free coating on surfaces and thickness of coating can be controlled by deposition time and pressure. Polymerization can be categorized into three forms namely ac/dc, radiofrequency (RF), and plasma. Each one of them has its own strength and weakness. The advantage of employing plasma polymerization is that this is a single step process and requires bare minimum sophistication. The twin objective of this particular investigation is to employ a rather inexpensive method of plasma polymerization to passivate the nanoparticle as well as for functionalization and to experimentally verify the veracity of earlier experiments conducted using various techniques and different materials. In this study RF plasma polymerization is employed to passivate IONs. Thus the primary motive of the present study is to passivate iron oxide nanoparticles and to observe whether there is any change in magnetization with respect to uncoated samples and to propose a tentative mechanism for the observed increase/decrease in magnetization.

Commercial samples of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ with sizes ranging from 20 to 30 nm were procured for the present analysis. A thin film of PANI is deposited on the surface of nanoparticles using plasma polymerization of the monomer vapours of aniline under an RF voltage. The structural characterization of the samples was carried out using X-ray diffraction (XRD) and magnetic studies at 300 K were performed using Vibrating Sample Magnetometer (VSM). The surface analysis of core shell structure of iron oxide-PANI was carried out using Transmission Electron Microscope and High resolution Transmission Electron Microscope.

An homemade experimental set up is employed for surface modification and is shown in Figure 1. The set up

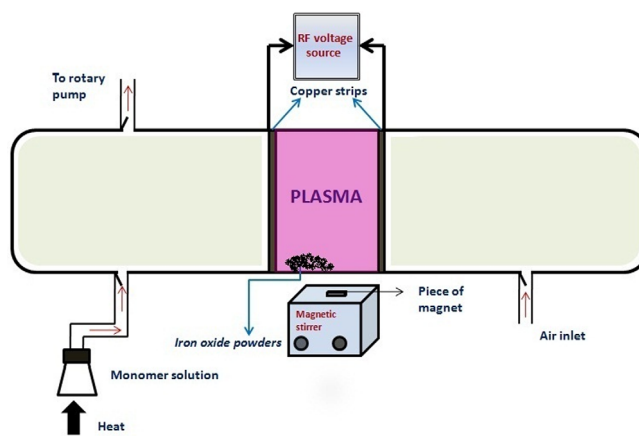


FIG. 1. Plasma polymerization experiment set up.

consists of a long glass tube of about 50 cm in length and a diameter of 8 cm with provisions for evacuation and deposition of monomer. Two copper strips plates (as electrodes) are wrapped around the glass tube at a distance of about 5 cm apart and are connected to the RF voltage source. The iron oxide powder to be coated is placed inside the glass tube and the tube is evacuated to a pressure of the order of 10^{-2} millibars and aniline vapours are allowed to pass onto oxide nanoparticles which are stirred by means of a magnetic stirrer. A glow discharge or plasma appears in between the electrodes at a high frequency (7–13 MHz), current range of 60–80 mA and plasma power of 20 W. Monomer units of aniline in the region of plasma undergo polymerization and get deposited on the surface of nanoparticles.²²

Prior to plasma polymerization, standard samples of IONs were structurally characterized using XRD [Rigaku D Max-C (30 kV, 20 mA)] with an incident Cu $K\alpha$ radiation of 1.54 Å. Plasma Polymerization was carried out and finally PANI was coated on the surface of IONs. X-ray diffraction of the coated samples were carried out and later magnetization measurements were performed using vibrating sample magnetometer [PAR EG & G 4500]. For microstructural analysis of the core-shell particles at high resolution, Transmission Electron Microscopy (TEM) [JEOL 2010 Transmission Electron Microscope] was conducted on these samples. Particle size distribution was also estimated from TEM measurements and High Resolution Transmission Electron Microscope (HRTEM) [JEOL 1230 High Contrast Transmission Electron Microscope] was carried out for observing the core shell structure with greater precision.

X-ray diffraction patterns of PANI coated and uncoated iron oxide nanoparticles are analyzed and a representative XRD pattern is shown in Figure 2. They correspond to an Fd3m space group and the d values are in agreement with the corresponding values for inverse spinel ferrite in the ICDD [ICDD No. 85-1436]. Particle size evaluated from XRD patterns using Scherrer formula is about 30 nm for uncoated Fe_3O_4 samples. The TEM images of PANI coated Fe_3O_4 nanoparticles are shown in Figures 3 and 4. The particle size distribution from Figure 4 shows that the average size of particles is about 35–40 nm.

HRTEM images 5(a) and 5(b) confirm the core-shell structure of Fe_3O_4 -PANI structure. The particle size of a single core shell structure of Fe_3O_4 is 30 nm with PANI

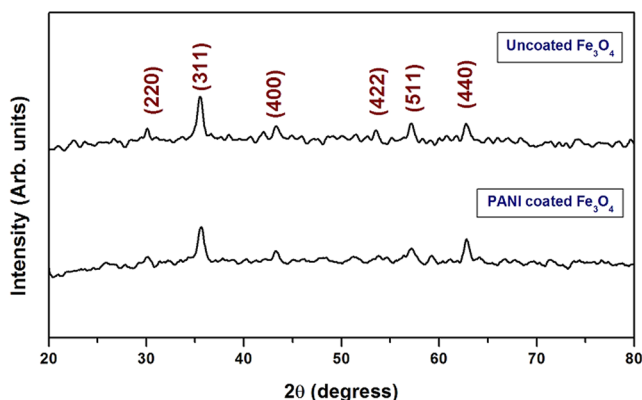


FIG. 2. XRD pattern of PANI coated and uncoated magnetite (Fe_3O_4) nanoparticles.

coating of about 4 nm. This is in good agreement with size distribution from the histogram. The interplanar spacing (d) estimated from the image corresponds to the lattice plane (400) which is indexed in Figure 5(a) and the PANI coating uniformly covers the Fe_3O_4 nanoparticle as evident from Figure 5(b).

Magnetic measurements were carried out using VSM on pristine (uncoated) samples. The hysteresis loops are depicted in Figures 6 and 7. The hysteresis is typical of a ferromagnet. The saturation magnetization of magnetite was found to be 71 emu/g which is less than the actual value of 84 emu/g. The reduced magnetization (M_s) of as purchased iron oxides can be attributed to the non contribution of the surface to the magnetic property. Kim and Shima²³ have proposed that reduced magnetization can be clearly explained using the relation $M_s = M_{sb} \left(\frac{D_{av} - 2a}{D_{av}} \right)^3$, where M_{sb} is the theoretical M_s of magnetite ($M_{sb} = 84$ emu/g) and D_{av} is the average particle size of the sample, a is the lattice constant of magnetite ($a = 0.832$ nm). The average particle size of magnetite sample before PANI coating as estimated from XRD pattern using Debye Scherrer formula is 30 nm. It is interesting to note here that uncoated Fe_3O_4 particles recorded a saturation magnetization of 71 emu/g while PANI coated nanoparticles displayed a saturation magnetization of

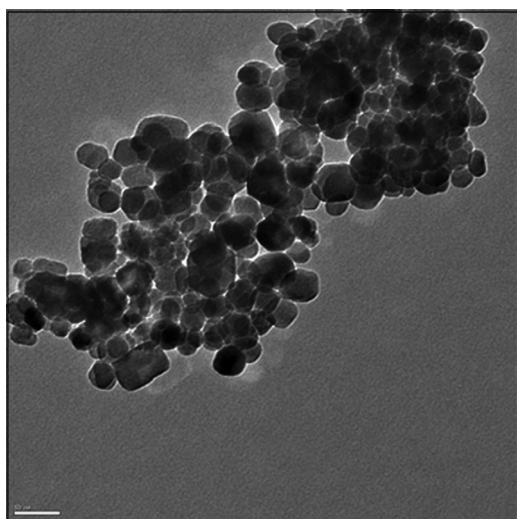


FIG. 3. TEM image of PANI coated Fe_3O_4 nanoparticles.

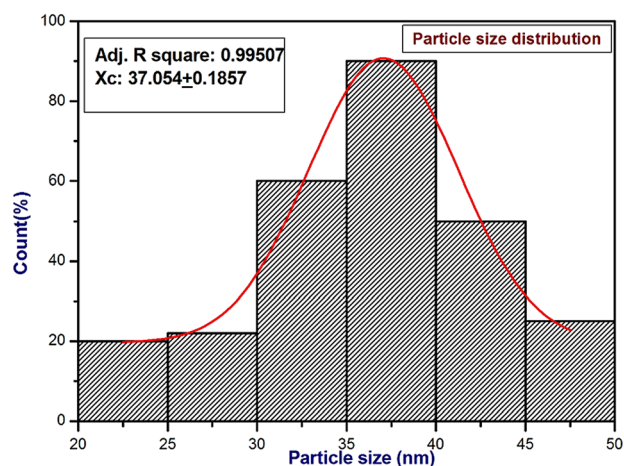


FIG. 4. Histogram showing particle size distribution from TEM image of Fe_3O_4 nanoparticles.

73 emu/g, an enhancement of magnetization by 2 emu/g. Similar measurements carried out on γ Fe_2O_3 nanoparticles also registered an increase in magnetization of 5 emu/g on PANI coating. As far as coercivity is concerned Fe_3O_4 showed a coercive field (H_c) of 80 Oe (uncoated) while γ Fe_2O_3 has a coercivity of 150 Oe. In both cases PANI coated samples did not exhibit any marked increase in H_c .

The observed magnetic behavior of IONs on PANI coating is unique and cannot be considered to be originating from the unfilled state of d or f orbitals which end up in exchange interactions. According to the exchange theory of magnetism, when surface of metallic nanoparticles is coated with an organic layer orderly arrangement of surface moments will be disrupted and will lead to a reduced magnetization. Thus the enhanced magnetism exhibited by the PANI coated IONs can be considered to be orbital in origin and in tune with the results observed in Au coated IONs and thiol capped Au nanoparticles by Banerjee *et al.*¹⁶ and Garitaonandia *et al.*,¹⁸ respectively. IONs on gold coating exhibited an enhancement of magnetization close to 1 or 2 emu/g while core shell Au-IONS exhibited a drastic change in magnetization by a factor of six and in the case of thiol capped Au nanoparticles a saturation magnetization of 5 emu/g was also observed. Moreover, going by simple mixture equations a coating of a non-magnetic component on a magnetic core ought to have reduced the saturation magnetization instead of an enhancement.

Earlier, Clogston²⁴ has studied the theoretical aspects of spin polarization of conduction electrons of a nonmagnetic metal, Palladium in contact with ferromagnets like iron later experimentally verified by Hauser.²⁵ But such spin polarization of moments was explained in the case of a nonmagnetic metal (Pd) in contact with a magnetic metal (Fe) and later Taniyama *et al.*²⁶ proposed that bare Pd also possess ferromagnetic moments. But spin polarization cannot be attributed to the observed enhanced magnetization in Fe_3O_4 -PANI core shell structure even though PANI can be argued to be a conducting polymer but in bare state PANI does not possess any magnetic moment. Monomer aniline used for the present analysis was double distilled prior to plasma polymerization and pristine films of PANI were subjected to magnetization studies and was found to be non

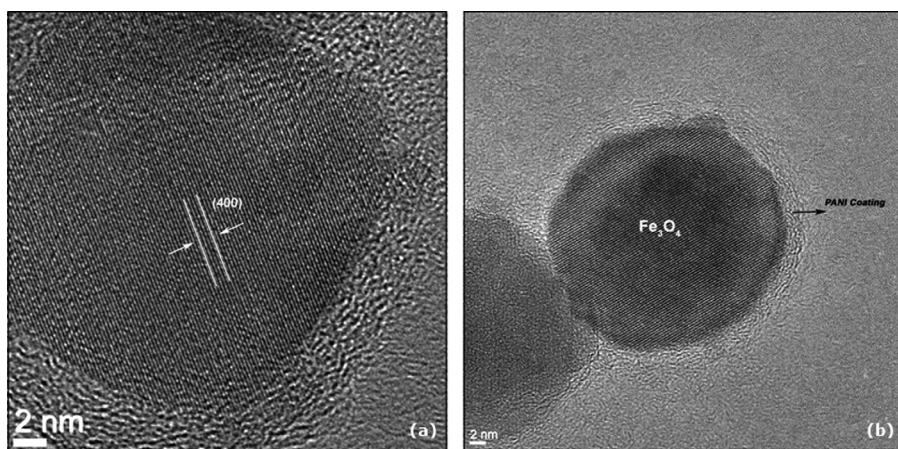


FIG. 5. HRTEM images of (a) PANI coated Fe_3O_4 nanoparticles (b) single Fe_3O_4 particle with core-shell structure on PANI coating.

magnetic. Moreover spin polarization could extend only up to length scales less than 2 nm.

Hernando *et al.*¹⁹ put forth a theory to explain the origin of ferromagnetism in thiol capped gold nanoparticles by assuming contact potential induced at the interface of gold and polymer. The contact potential arises from the transfer of electrons from the gold nanoparticles to organic material. Such contact potential evokes an electrostatic interaction between trapped electrons leading to a spin alignment which in turn through spin orbit coupling induces orbital moment alignment. This mechanism was invoked to explain the enhancement of saturation magnetization in gold coated iron oxide nanoparticles. In our case, the core shell structure of ION-PANI offers an interface which allows charge transfer and thereby increases magnetic moment and the saturation magnetization. This establishes that the origin of magnetization in core shell of ION-PANI structure is an interfacial phenomenon and is observed in both types of magnetic oxides illustrating that the enhanced magnetism in both iron oxides has the same origin from the orbital moment formation from an interfacial/surface effect while $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions have no significant role in the enhancement of magnetization. This type of magnetic moment formation is confined to the nano range, since increase in particle size decreases the rate of surface atom contribution and in effect will have the

magnetic characteristic of the core material alone. This mechanism appears more plausible in our case. However, confirmatory experiments are to be conducted on the nature of bonding, effect of thickness, etc. These experiments are on.

Magnetic oxide nanoparticles of magnetite and maghemite were surface passivated by polyaniline using RF plasma polymerization. The core shell architecture of iron oxide—PANI was identified from the HRTEM images. Saturation magnetization of Fe_3O_4 —PANI core shell structure is enhanced by 3 emu/g in comparison with uncoated Fe_3O_4 nanoparticles. Similar magnetic moment increase was found in the case of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on coating with PANI. The enhanced magnetization have been explained due to magnetic moment formation at the magnetic material—polymer interface induced by a contact potential created by charge transfer to the polymer layer from magnetic material. This type of magnetism is characteristic of nanomaterials since the surface contribution is less for larger sized particles. More experiments are necessary to firmly establish the dependence of contact potential induced magnetic moments on thickness of the polymer or organic layer coating to find out the critical thickness of deposition for best magnetization results.

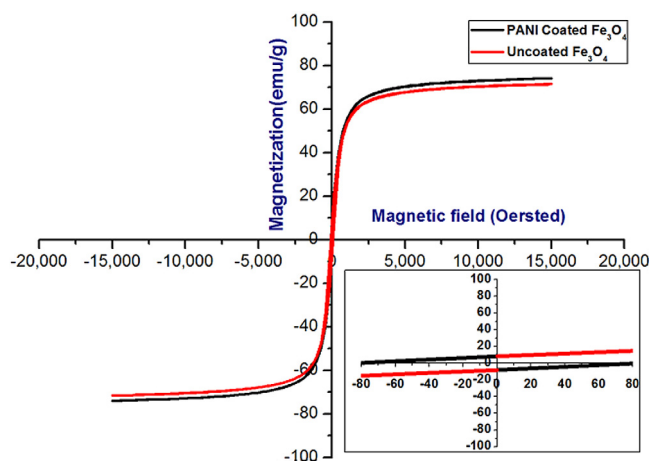


FIG. 6. Magnetization vs magnetic field for PANI coated and uncoated magnetite (Fe_3O_4) nanoparticles.

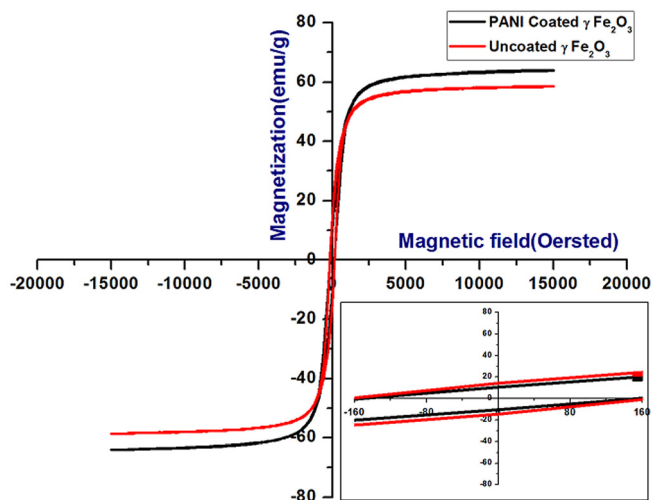


FIG. 7. Magnetization vs magnetic field for PANI coated and uncoated maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles.

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