Iron-Polyvinylpyrrolidone (Fe-PVP) nanocomposite coated Inductive Proximity Sensor

M. Savitha, N. R. Dhineshbabu, G. Sriram, V. Rajendran* and Karan V. I. S. Kaler

Centre for Nanoscience and Technology, K. S. Rangasamy College of Technology, Tiruchengode – 637215, Tamil Nadu, India

1Schulich School of Engineering, Department of Electrical and Computer Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB, Canada

(REceived 27 March, 2015; accepted 20 April 2015; published 01 July, 2015)

INTRODUCTION

Nanomagnetism is a research field that deals with the magnetic properties of matter that has at least one dimension in the nanoscale range [1-3]. Such materials have numerous practical applications, ranging from geology to magnetic recordings. Example utility of such materials include ferrofluids in medicine, either for drug delivery or targeted to specific biological tissues [2-4]. The size, surface and interfacial region of such nanoscale particles have a profound effect on electronic structure and moreover their intrinsic magnetic properties [1-4]. Magnetic nanoparticles in ferrofluids are governed by the number of neighboring atoms and furthermore also influenced by chemi-adsorption of magnetic particles [3]. Magnetic iron (Fe) nanoparticles, with high surface area, exhibit ferromagnetic properties which are utilized in MRI imaging and used in the purification of contaminated water [5-7]. More recently Fe nanoparticles, have been used in clinical applications such as medical imaging, targeted drug delivery and treatments of certain disorders [6-12]. Magnetic nanoparticles have furthermore been used to coat bulk iron cores as in inductive proximity sensors [3]. An inductive proximity sensor leverages change in the coil impedance and quality factor due to eddy current losses to detect target objects in a noninvasive fashion. Other modes operations of such sensors are based on changes in the capacitance, or photo electric properties to detect other class of targets [13]. In a conventional proximity sensor, the sensing distances are very small and hence, may result in damage to the sensor by the target object. Hence, there is need to enhance the sensitivity of such sensors in order to increase their operating distance [14]. In this present study, we have explored the utility of Fe nanoparticles in order to achieve this goal. Furthermore, we have utilized magnetic iron nanoparticles coating on a pot core (magnetic iron nanoparticles coated inductive proximity sensor - MINDIPS) as the sensing coil to extend the sensor operating range. Additionally, we have incorporated magnetic Fe nanoparticles in polyvinylpyrrolidone (PVP), used as a thin layer on the pot core of the proximity sensor. Here PVP was chosen due to its desirable physicalchemical properties, such as mechanical stability, chemically inert, good optical transparency, as well as providing good protective, binding and adhesive characteristics when used in colloidal suspension [15-17]. In the present work, the nano Fe/PVP composite coatings are prepared using a sol-gel preparation method. The colloidal PVP/Fe nanocomposites were used to coat the ferrite pot core of the sensor, which was subsequently utilized in an industrial setting for process automation.

EXPERIMENTAL
Ferric chloride (FeCl₂, 4H₂O), Sodium borohydride (NaBH₄), Ethanol (EtOH), poly (vinylpyrrolidone) (PVP: MW = 29,000) were purchased from Merck with 99% of purity and De-ionized water was used without any further purification.

The Fe nanoparticles were synthesized using a chemical reduction process and carried out in 4/1 (v/v) ethanol/water solution. In this solution, 0.5 g of FeCl₃·6H₂O was dissolved and suitably stirred. After this step, 0.1 M of sodium borohydride (NaBH₄) was dissolved in 100 ml of deionized water and then poured in a burette and added to the ferric chloride solution in a drop by drop fashion under vigorous stirring condition until a black colloidal Fe nanoparticles suspension was formed. Following the remaining sodium borohydride was added to accelerate the reduction reaction. The Fe nanoparticles suspension was washed four times with 25 ml of ethanol to remove any impurity utilizing a centrifugation process carried out 10⁴ rpm. This washing process is considered to be essential since it prevents the rapid oxidation of Fe nanoparticles. Following the washing procedure the synthesized Fe nanoparticles dried in a hot air oven at 80 °C over a 12 hour time period.

After the preparation of the Fe nanoparticles, PVP/Fe nanocomposites were synthesised using a sol-gel preparation method, where 0.2 g of PVP was dissolved in 15 ml ethanol to make a PVP solution, which was mechanically stirred and maintained at 50°C. After this step, colloidal Fe nanoparticles (0.2 g) were added to the PVP solution and vigorously stirred for a period of 30 mins, at room temperature, resulting in the formation of PVP coated Fe nanoparticles (PVP/Fe) as shown in Figure 1. This PVP/Fe nanocomposite is referred to as “PFe”.

The nanoparticles coated pot core surface was used in the fabrication of the automated sensor, which was subsequently employed in an industrial setting for sensing applications. The sensing distance of the fabricated MINIDIPS was experimentally verified, as detailed in the following section. Furthermore, the coated PFe thin film was peeled off the pot core surface and the thickness of the thin film as 12 mm which was measured by Digitmetric Screw Thread Micrometer and Further, experimentally analyzed The structural properties of Fe nanoparticles was characterized by X-Ray diffractometer (XRD, X’Pert Pro, PANalytical, Netherland) at a diffraction angle (2θ) ranging from 20 to 60°, using a CuKα (λ=0.154 nm) radiation source, operated at 40 kV and 30 mA. The functional groups of Fe nanoparticles were determined in the wave number region from 4000 to 400 cm⁻¹, using a fourier transform infrared spectrometer (FTIR, PerkinElmer, Spectra 100, USA). In addition, the surface morphology and elemental analysis of Fe nanoparticles were carried out using high resolution scanning electron microscopy and a energy-dispersive X-ray spectroscopy (HRSEM-EDS, Quanta 200 FEG) respectively. The particle size analysis of the prepared Fe nanoparticles were performed by high resolution scanning electron microscopy (HRTEM, JEOL, JEM 2100, USA) while the magnetic moment measurements of compounds were conducted with vibrating sample magnetometer (Lakeshore, VSM 7410, OH, USA), at room temperature.

RESULTS AND DISCUSSION

Figure 2a shows the structural analysis of Fe nanoparticles. It clearly reveals the amorphous nature of the sample due to the absence of any sharp diffraction peaks in the XRD pattern [18], however a broad peak, was observed at a diffraction angle (20 – 29°). The functional groups of Fe nanoparticles are shown in Figure 2b.
The vibrational bands at 3413 cm⁻¹ and 2938 cm⁻¹ are considered to be due to O-H and C-H stretching respectively, while the vibrational band peak at 1626 cm⁻¹ can be attributed to the stretching of H₂O. The additional vibrational bands at 1438 cm⁻¹ and 1285 cm⁻¹ are assigned respectively to the stretching of C-N and C-O bonds. The peaks at 666 cm⁻¹ and 473 cm⁻¹ are indicative of the presence of metal (Fe) nanoparticles. The FTIR spectral observation furthermore confirmed the presence of water molecules surrounded by Fe nanoparticles. Figure 2c shows the surface morphology of Fe nanoparticles, which reveals the agglomerated nature of the particles with an average size of about 80-160 nm. The purity of the iron nanoparticles as 100 wt %, was confirmed by the absence of any elemental peaks in the EDS spectral data (Figure 2d). The primary size of Fe nanoparticles is shown in Figure 2e. The size and shape of particles are quite dissimilar to the 100-130 nm size range of agglomerated particles. The selected area electron diffraction pattern (inset in Figure 2e) shows the amorphous nature of Fe nanoparticles which again confirms the observation made from XRD pattern (Fig. 2a).

The colloidal PFe nanocomposites imaged using a TEM are shown in Figure 3a. Figure 3a clearly shows the presence of a thin PVP layer deposited on the surface of Fe nanoparticles with amorphous nature (insert Figure 3a). The agglomerated particle size determined from the TEM images yield an average particle size of 130-160 nm. The composite of PFe particle size is larger than Fe nanoparticle which is due to the capping PVP agent. Basically, PVP has the polar group of polyvinyl frame donates the lone-pair electrons forming a coordinative interface between metal (Fe & Cu) ions and PVP complex in the solution [19, 20]. However, Fe nanoparticles are strongly absorbed in the surface with coordination bonds by PVP hinders the nuclei of the polar groups [21]. Figure 3b shows the PFe composite thin film vibrational spectrum. PVP adsorption is evident based on the presence of the vibrational bands at 2461 and 1629 cm⁻¹ which are considered to be due to the presence of O-H and C-O stretching vibrations respectively. The most striking evidence, obtained from the FTIR spectrum of the PVP stabilized Fe nanoparticles, which corresponds to the interaction between metal (Fe) nanoparticle stretching motion and carbonyl oxygen groups in PVP respectively [22-24]. The narrow absorption peak centered at 1469 cm⁻¹ and 2461 cm⁻¹, as shown in Figure 3b, is ascribed to the C–H bonding due to the presence of PVP. From the above observation of FTIR spectra of PVP/Fe composite reveals that Fe nanoparticles are the encapsulation by PVP.

| Table 1 Quantitative analysis of coated and un-coated pot core surface. |
|------------------|---|---|---|---|---|---|
| S.No. | Samples | C | O | Fe | Zn | Mn | Cu |
| 1. | Un-coated | -- | -- | 99.08 | 0.41 | 0.43 | 0.06 |
| 2. | Coated | 31.7 | 12.88 | 54.68 | 0.34 | 0.35 | 0.05 |

| Table 2 Evaluation of sensing distance for commercial and Iron nanoparticle coated Inductive proximity sensor |
|----------------------------------------------------|---|---|---|
| Distance (mm) | Hysteresis (mm) | Distance (mm) | Hysteresis (mm) |
| 9.78 | 0.14 | 10.55 | 0.13 |
| 9.78 | 0.14 | 11.31 | 0.16 |
| 9.78 | 0.14 | 11.91 | 0.52 |
| 9.78 | 0.14 | 11.64 | 0.54 |
| 9.78 | 0.14 | 12.64 | 0.64 |
| 9.78 | 0.14 | 12.95 | 0.70 |
| 9.78 | 0.14 | 14.4 | 0.79 |
| 9.78 | 0.14 | 20.21 | 0.85 |

Figure 3. Characterisation of PVP/Fe nanocomposites
RESEARCH ARTICLE

Iron-Polyvinylpyrrolidone (Fe-PVP) Inductive Proximity Sensor

The surface morphology of coated and uncoated pot core surface is shown in Figure 4. Figure 4a and 4b reveals the respectively irregular morphology of uncoated surface compared to the smooth morphology of Fe/PVP coated surface of the pot core. A quantitative EDS analysis of the coated and un-coated pot core samples results, showing the presence of the various elements are identified in Table 1.

The magnetic characteristics (Hysteresis loops) of Fe nanoparticles and PFe composite thin films as shown in Figure 5 over the applied range of -15 kOe to 15 kOe. This plot reveals that the magnetic Fe nanoparticles (Figure 5a) exhibit a high magnetization saturation (36 emu/g), with a relative high magnetic field (Hs) of 6000 Oe and coercivity (Hc) value of 394.61 Oe. The PFe composite thin film exhibits ferromagnetic behaviour at room temperature, as shown in Figure 5b. The magnetization saturation of PFe is 1.6 emu/g, saturation magnetic field (Hs) is 2400 Oe and a coercivity (Hc) of 559.12 Oe. A decrease in magnetization value of PFe nanocomposite thin film, is considered to be due (i) the oxidation of the sample during polymerization and (ii) possibly due to the presence of the polymer shell decreasing the dipole – dipole interaction [25,26].

The physical phenomenon of PFe leads to an increase (between 394.61 and 559.12 Oe) of coercivities compared with the pure Fe nanoparticles. The magnetic moments of Fe nanoparticles are covered by the polymer (PVP) matrix, so that a single domain nanoparticles required for aligning in the field direction by higher magnetic field [27,28]. The PFe composite has a smaller magnetization value is correlated to pure Fe nanoparticle. The reduction in magnetization is possibly due to the coulomb interaction of Fe nanoparticle with the non-magnetic PVP, resulting in a decrease the aggregation of Fe nanoparticles. The low magnetization saturation value of Fe nanoparticle, as compared that...
of PFe composite thin film, is due to the addition of PVP polymer. At the same time, the coercivity is high for the PVP/Fe nanocomposites when compared to that of the Fe nanoparticle. The above observation is confirmed that the increased coercivity of PVP/Fe nanocomposite attained hard ferromagnetic properties. Table 2 shows the comparison studies of the commercial and PVP/Fe nanoparticle coated inductive proximity sensor. The uncoated inductive proximity sensor can detect the presence of metallic objects when they are located at distances of 10mm (± 10% tolerance) or lower. However, the magnetic nanoparticles coated on the inductive proximity sensor is capable of detecting similar such objects up to twice the distance values, compared as that of the uncoated sensor.

CONCLUSION

The Fe nanoparticles were finely synthesized by reduction method and the composite PVP/Fe nanoparticle confirmation of particles size, shape, amorphous structure, magnetic properties and functional group was identified through characterization studies. The PVP/Fe nanoparticle coated ferrite pot core, when employed in an industrial application setting, was capable of detecting the magnetic nanoparticles coated on the inductive proximity sensor is capable of detecting similar such objects up to twice the distance values, compared as that of the uncoated sensor. The composite PVP/Fe nanoparticle confirmation of particles size, shape, amorphous structure, magnetic properties and functional group was identified through characterization studies. The PVP/Fe nanoparticle coated ferrite pot core, when employed in an industrial application setting, was capable of detecting the presence of metallic objects when they are located at distances of 10mm (± 10% tolerance) or lower. However, the magnetic nanoparticles coated on the inductive proximity sensor is capable of detecting similar such objects up to twice the distance values, compared as that of the uncoated sensor.

REFERENCES


BIography

Savitha M received her degree B.E. in Electronic and Communication Engineering and M.Tech Nanoscience and Technology from Anna University, India in 2010 and 2013, respectively. Her research interest include synthesis of Nano particles (metal, metal oxides) and its applications.

Rajendran Venkatachalap completed his M.Tech. in Nanotechnology from Anna University of Technology, Coimbatore, and Ph.D. in Ultrasonics from Annamalai University, Chidambaram, India, in 2009 and 1993, respectively. He is currently working as Director, Research and Development, Centre for Nanoscience and Technology, K.S. Rangasamy College of Technology, Tiruchengode, India. His current research interest

RESEARCH ARTICLE

of PFe composite thin film, is due to the addition of PVP polymer. At the same time, the coercivity is high for the PVP/Fe nanocomposites when compared to that of the Fe nanoparticle. The above observation is confirmed that the increased coercivity of PVP/Fe nanocomposite attained hard ferromagnetic properties. Table 2 shows the comparison studies of the commercial and PVP/Fe nanoparticle coated inductive proximity sensor. The uncoated inductive proximity sensor can detect the presence of metallic objects when they are located at distances of 10mm (± 10% tolerance) or lower. However, the magnetic nanoparticles coated on the inductive proximity sensor is capable of detecting similar such objects up to twice the distance values, compared as that of the uncoated sensor.

CONCLUSION

The Fe nanoparticles were finely synthesized by reduction method and the composite PVP/Fe nanoparticle confirmation of particles size, shape, amorphous structure, magnetic properties and functional group was identified through characterization studies. The PVP/Fe nanoparticle coated ferrite pot core, when employed in an industrial application setting, was capable of detecting the presence of metallic objects with increase sensitivity and at twice the distance compared to a commercial pot core. The nanocomposite coated pot core, with its improved sensitivity may be usefully applied in other situations requiring the sensing/detection of objects.

*Corresponding author: veerajendran@gmail.com
Tel: +91-4288-274741-4, 274860; Fax: 91 -4288-274880 (direct), 274860

REFERENCES


BIography

Savitha M received her degree B.E. in Electronic and Communication Engineering and M.Tech Nanoscience and Technology from Anna University, India in 2010 and 2013, respectively. Her research interest include synthesis of Nano particles (metal, metal oxides) and its applications.

Rajendran Venkatachalap completed his M.Tech. in Nanotechnology from Anna University of Technology, Coimbatore, and Ph.D. in Ultrasonics from Annamalai University, Chidambaram, India, in 2009 and 1993, respectively. He is currently working as Director, Research and Development, Centre for Nanoscience and Technology, K.S. Rangasamy College of Technology, Tiruchengode, India. His current research interest
includes nanomaterial oxides, biomaterials, nano-herbal, sensors, and magnetic materials. He has published more than 185 research articles in various peer-reviewed international journals and filed more than 14 patents. He is on editorial board of many international journals namely Green Nanotechnology; Nanosystems: Physics, Chemistry, Mathematics; Soft Nanoscience Letters, Advances in Nano Research; and Journal of Acoustical Society of India.