

Synthesis and characterization of oleic acid stabilized magnetic - Polypyrrole (PPy) Core-Shell nanoparticles via emulsion polymerization

D.Prabu^{1*}, R. Parthiban²

¹Department of Chemical Engineering, Sathyabama University Chennai-600119, India

²Department of Chemical Engineering, Sri Venkateswara College of Engineering, Chennai – 602117, India

Abstract: In this research paper oleic acid stabilized Fe_3O_4 particles are successfully entrapped inside polypyrrole (PPy) through emulsion polymerization using polyvinyl alcohol as a surfactant. The oleic acid stabilized PPy- Fe_3O_4 nanoparticles have structural, electrical and good superparamagnetic properties. Electronically conducting polymer (ECP) has been used for optical devices, batteries, and anti-static coatings. The resulting functionalized (PPy- Fe_3O_4) nanoparticles can also be utilized for cancer cell targeting. The nanoparticles are characterized by SEM, HR-TEM. Morphology studies confirms that the prepared (PPy- Fe_3O_4) nanoparticles in the size range of 100nm. Superparamagnetism were studied by using a permanent Ferro bar magnet.

Keywords: PPy- Fe_3O_4 nanoparticles, electronically conducting polymers, core- shell structure.

1.Introduction

Electronically conducting polymers (ECP) s plays a prominent role as smart materials for electronic and optical devices, batteries, anti-static coatings.[1]. Polypyrrole is a frequently studied conducting polymer due to its application in sensing and catalysis. Polypyrrole is considered among the most promising conductive polymers due to its stability and ease of conversion between conducting and insulating forms. There is currently immense interest in the materials having both electrical and magnetic properties for the potential application as batteries, non-linear optics, and electrochemical display devices, molecular electronic, electrical and magnetic shields, and microwave absorbing materials. [2-4]. Among ECPs, polythiophene and polypyrrole are versatile since they are air-stable and can be easily prepared by chemical or electrochemical oxidative polymerization. Polypyrrole (PPy) [5, 6], polyaniline (PANI) [7] and more recently polyethylenedioxythiophene (PEDOT) [8] or polyparaphenylene (PP) [9] were used as the ECP in these nanocomposites. Electronically conducting polymers have great potential for use in batteries, electronics, bio- and chemical sensors. PPy, a highly conducting polymer, has been studied for the immobilization of enzymes, antibodies and nucleic acids. It is also suitable as a substrate for cell attachment and proliferation and possesses excellent biocompatibility. [10]

In this paper, we describe the emulsion polymerization method to synthesize PPy nanoparticles of 100 nm with entrapped oleic acid stabilized Fe_3O_4 particles, using polyvinyl alcohol (PVA) as the surfactant. The obtained PPy- oleic acid stabilized Fe_3O_4 nanoparticles are well defined and display high levels of magnetization, good electrical conductivity. In addition, the Fe_3O_4 content of the nanoparticles can be varied over a wide range by using different starting Fe_3O_4 pyrrole monomer mass ratios. Our results helps in future studies that the oleic acid functionalized PPy- Fe_3O_4 nanoparticles with their high magnetization and as well as cancer cell targeting capability, would have great advantages for use in intracellular hyperthermia treatment of cancer tumors.

2. Experimental

2.1 Materials

Pyrrole, polyvinyl alcohol (average molecular weight 13000–23000), oleic acid were purchased from Aldrich Chemical Co. Iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate and ammonia solution were from Merck Co. Sodium dodecylbenzene sulfonate (NaDS) was purchased from Sigma Chemical. The other solvents and reagents were of analytical grade.

2.2 Synthesis of magnetite particles

The magnetite (Fe_3O_4) particles were prepared using a co-precipitation method. To prepare oleic acid stabilized magnetic particles, 11.6 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4.3 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 400 ml of deionized (DI) water under argon gas protection with vigorous stirring at 60 °C. 15 ml of 25% ammonia solution was then added to the solution, followed by immediate addition of 9 ml of oleic acid drop wise. After a few minutes, the magnetite particles were isolated from the solvent by centrifugation at 6000 rpm for 10 min. The particles were washed with DI water twice to remove the excess oleic acid, redispersed in hexane and precipitated with ethanol. The precipitated particles were then washed twice with ethanol and dried under room temperature.

2.3 Synthesis of PPy- Fe_3O_4 nanoparticles

The oleic-acid stabilized Fe_3O_4 particles (0.75 g) were dispersed in 5 ml of hexane to form the ferrofluid. The ferrofluid was then added to 8 ml of DI water containing 0.28 g NaDS. The mixture was stirred for 1 hour to form a stable water-based dispersion of magnetite particles, and subjected to sonication for 10 min in an ice-cooled bath. NaDS coats the magnetite particles and allows for their dispersion in water.[11] Hexane was then evaporated from the mixture at 80 °C. 1 ml of pyrrole monomer was added after complete evaporation of hexane, and the mixture was stirred for 1 hour to form the magnetite monomer dispersion. This dispersion was then added drop wise to 12 ml of the oxidant ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) solution containing 12 mg ml^{-1} of PVA in an ice-cooled bath with continual stirring.

3. Results & Discussion:

3.1 Synthesis of magnetic particles and magnetic properties

Table: 1 Properties and quantities of PPy- Fe_3O_4 nanoparticles

S No.	Fe_3O_4 (g)	Pyrrole (μl)
1.	0.2	10
2.	0.2	20
3.	0.2	50
4.	0.2	100
5.	0.2	200

To obtain the nanocomposites, two methods have been followed. The first method involve the preparation of oleic-acid stabilized Fe_3O_4 particles and the second one polymerizing polypyrrole at the outer surface of Fe_3O_4 particles, by a emulsion polymerization process using PVA as a surfactant successively [11]. As shown in the Table: 1 Fe_3O_4 particles and PPy monomer mass ratios were synthesized.

3.2 Structure Characterization

Morphological study of oleic acid stabilized PPy- Fe_3O_4 nanocomposites were studied by SEM. Fig: 1 (a) shows the PPy- Fe_3O_4 nanocomposites were spherical and uniform in shape. By varying the concentration of Fe_3O_4 aggregation were promoted (Fig: 1 (b)). Core shell structure and particle-size distributions were measured by a High resolution transmission electron microscope (HR-TEM) Fig: 2(a) and (b). Fig: 2(a) shows the Fe_3O_4 nanoparticles were encapsulated inside the polypyrrole and shows a core-shell structure. [11]. Fig: 2(b) shows the synthesized oleic acid stabilized Fe_3O_4 particles are roughly spherical in shape, with average diameters of 100 nm and they can be spontaneously dispersed in hexane. The magnetic behaviour of synthesized PPy- Fe_3O_4 nanocomposites was shown in (Fig.3). After exposure to magnetic field, the obtained

PPy- Fe_3O_4 nanoparticles were aggregated and attracted to the magnet within 30 seconds, left behind a clear solution which shows that the particles possess super paramagnetic behaviour. This prominent method of magnetic separation finds the way in drug delivery system.

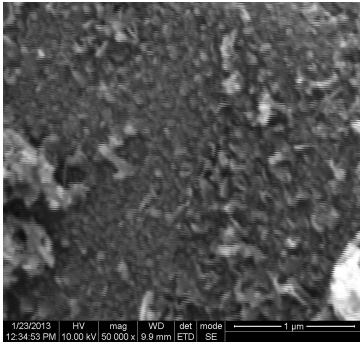


Fig: 1 (a) SEM images of PPy- Fe_3O_4 nanoparticles

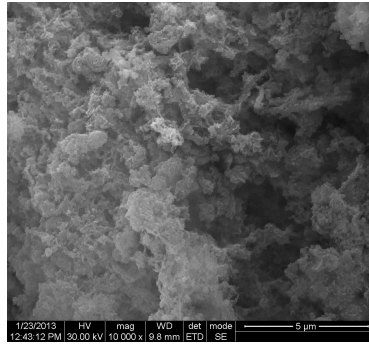


Fig: 1(b) SEM images of PPy- Fe_3O_4 nanoparticles

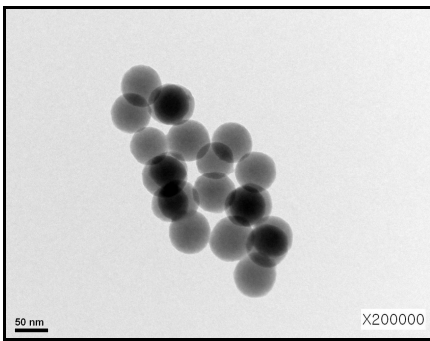


Fig: 2 (a) HR-TEM image of core-shell structure PPy- Fe_3O_4 nanoparticles

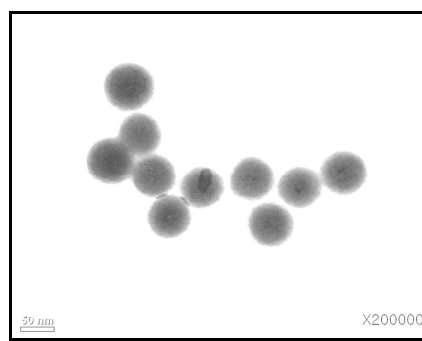


Fig: 2 (b) HR- TEM image of core-shell structure PPy- Fe_3O_4 nanoparticles



Fig: 3 Photograph showing super paramagnetic behaviour of PPy- Fe_3O_4 nanoparticles

4. Conclusion

Core-shell oleic acid stabilized PPy- Fe_3O_4 nanocomposites were successfully synthesized by an emulsion polymerization via PVA as a surfactant. The prepared Nano composites exhibit well defined in size of 100nm, spherical in shape, and super paramagnetism property. Accordingly, it provides an easy way to control the ferromagnetic and electric properties by modifying ratios of starting materials. Morphology studies were carried out by HR-TEM, SEM. However aggregation was observed with increasing iron oxide content. The resulting composites have both ferromagnetic and electric properties.

References

1. Miomandre F, Audebert P, Bonnet J.P, Brosseau A, Perriat P, Weisbuch C, Wen W, and Sheng P, "Silica-Polypyrrole Core-Shell Nanocomposites as Active Materials for Dielectrophoretic Displays", *Journal of Nanoscience and Nanotechnology*, 2003, 8, pp.4353–4359.

2. Ateh DD, Navsaria H.H and Vadgama P, “ Polypyrrole-based conducting polymers and interactions with biological tissues”, J. R. Soc. Interface, 2006, 3, pp.741-752.
3. Jiang X, Marois Y, Traore A, Tessier D, Dao LH, Guidoin R and Zhang Z, “Tissue reaction to polypyrrole-coated polyester fabrics”, Tissue Eng, 2002,8,pp. 635– 647.
4. Zhelikin AN, Lynn DM, Farhadi J, Martin I, V. Shastri V and Langer R, “Erodible Conducting Polymers for Potential Biomedical Applications”, Angew. Chem., Int. Ed., 2002, 41, pp.141-144.
5. Sufen Ai, Qiang He, Cheng Tao, Suping Zheng, Junbai L, “Conductive Polypyrrole and Poly(allylaminehydrochloride) Nanotubes Fabricated with Layer-by-Layer Assembly”, Macromol. Rapid Commun, 2005, 26, pp.1965–1969.
6. Azioune, A, Ben Slimane, Hamou L A, .Pleuvy A , Chehimi M.M, Perruchot C, and Armes S P, “Synthesis and Characterization of Active Ester-Functionalized Polypyrrole–Silica Nanoparticles: Application to the Covalent Attachment of Proteins”, Langmuir, 2004, 20,pp. 3350-3356.
7. Gill M, Baines F L, and Armes S P, “Some observations on the preparation of colloidal polyaniline - silica composites”, Synth Metals, 1993, 55, pp.1029-1033.
8. Moon G H, Stephen and Foulger H Chem.Commun 2004, 20, pp. 2150-2155.
9. Ravindranath R, Ajikumar PK , Hanafiah N B M, Knoll W, and Valiyaveetil S Chem. Mater, 2006, 18,pp.1213-1219.
10. MacDiarmid, A. G, Kanner, R. B,“In Handbook of Conducting Polymers; Skotheim, T. A., Ed.; Marcel Dekker: New York,1986, 1, pp. 687.
11. Wuang S C, Neoh KG, Kang ET, Daniel Pack W and Deborah E Leckband,synthesis and functionalization of polypyrrole-Fe₃O₄ nanopartilcles for applications in biomedicine”, J. Mater. Chem 2007; 17:pp.3354–3362.
