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# Synthesis and Characterization of Fe<sub>3</sub>O<sub>4</sub>: Porous Carbon Nanocomposites for Biosensor Application

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**Abstract.** Fe<sub>3</sub>O<sub>4</sub>:Porous carbon (Fe<sub>3</sub>O<sub>4</sub>:PC) nano-magnetic composites were prepared by using different weight fractions of acid treated PC by the chemical co-precipitation route and annealed at 573 K, 773 K and 973 K temperatures in inert N<sub>2</sub> gas atmosphere for 2 hrs to obtain desired stoichiometry of nanocomposites. The structural, morphological and magnetic properties of these composites were characterized by powder XRD, TEM, EPR and VSM analytical techniques. The crystallinity of the composites, g-value and spin concentration increases with increasing annealing temperature. TEM images confirmed the formation of nanosized ferrite nanoparticles whose size increases from 23 nm to 54 nm on increasing annealing temperature. Porous carbon increases porosity, coercivity and reduces saturation magnetization of these prepared nanocomposites.

## INTRODUCTION

Porous carbon (PC) has been extensively studied for their potential applications from nanotechnology to biomedicine. The preparation of magnetic:PC (M:PC) opens new avenues in nanobiotechnology and biomedical applications [1-6] due to the combination multiple physical and chemical properties. Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) are biocompatible with optimal magnetic properties [4] can be used for in-vivo or in-vitro application and found to be promising suitable materials for the fabrication of biosensors. The nanostructured Fe<sub>3</sub>O<sub>4</sub>:PCs composites belong to the class of magnetoelectric materials and successfully used in magnetic stirrers, fluidics and magnetic valves etc. This sensing material encourages physical as well as chemical adsorption of organic and ionic species through pore structure and ionic network. The simple and easy preparation of ferrite: porous carbon nanocomposites (NCs) matrices are one of the attractive options for covalent immobilization of heme proteins for the fabrication of biosensor device. The sensitivity of the biosensors depends on the synthesis parameters of NC and proteins immobilization procedure on the conducting electrode.

Fe<sub>3</sub>O<sub>4</sub>:PC NCs have been prepared using different weight fractions of acid treated PC (i.e. 0.1 0.3 and 0.5 g PCs) by the chemical co-precipitation route. The functionalized PC produces carboxylic and hydroxyl functional group at the surface and in the pores structure which interacts with Fe<sub>3</sub>O<sub>4</sub> NPs to form NC. These composites were annealed from 573 K to 973K in inert N<sub>2</sub> atmosphere for 2 hrs to reveal the effect temperature to get desired stoichiometric NC. The paramagnetic resonance and magnetic properties of these NCs are also measured to reveal interaction between PCs and Fe<sub>3</sub>O<sub>4</sub> NPs and their effect on the magnetic and adsorption properties for sensing application.

## EXPERIMENTAL MEASUREMENTS

### Synthesis of Functionalized PC and Fe<sub>3</sub>O<sub>4</sub> nanoparticles

PC in the form of activated charcoal (AR grade) was procured from Sigma Aldrich and functionalized by treating with concentrated HNO<sub>3</sub> (69%) acid. Ferrite NPs were synthesized by chemical co-precipitation route in two steps, (i) the metal ions form respective hydroxides during the co-precipitation and (ii) hydroxides are converted into ferrite particles on heating at ~ 353 K during ferritization reaction. Fe<sub>3</sub>O<sub>4</sub> magnetic NPs were synthesized by using the Aldrich AR grade of FeCl<sub>2</sub>.4H<sub>2</sub>O and FeCl<sub>3</sub> (anhydrous) salts. The aqueous and the transparent reddish solution with 125 mM FeCl<sub>2</sub>.4H<sub>2</sub>O and 250 mM FeCl<sub>3</sub> concentrations were prepared by continuous mixing and stirring at 323K. The complex ferrous hydroxide-ferric hydroxide [Fe(OH)<sub>2</sub>. Fe(OH)<sub>3</sub>] particles were precipitated from solution by adding 15 ml of ammonia solution drop by drop till pH reaches to ~ 10. The chemical reaction is represented by the following chemical equation 1.



During the synthesis process, the homogenization was frequently done to prevent the agglomeration of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. These complex Fe(OH)<sub>2</sub>. Fe(OH)<sub>3</sub> particles were heated at 353K to form Fe<sub>3</sub>O<sub>4</sub> formed.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>:PC composites

The synthesis of Fe<sub>3</sub>O<sub>4</sub>:PC NCs has been carried out by the chemical attachment of ferrite NPs with acid treated PC. The aqueous solution consisting of 125 mM FeCl<sub>2</sub>.4H<sub>2</sub>O, 250 mM FeCl<sub>3</sub> (anhydrous) and acid treated PC in different weight fraction (i.e. 0.1 gm, 0.3 gm and 0.5 gm) was prepared by continuously mixing and stirring at 333K. The complexes of ferrous hydroxide-ferric hydroxide [Fe(OH)<sub>2</sub>. Fe(OH)<sub>3</sub>] were precipitated out by adding 15 ml of NH<sub>4</sub>OH drop by drop till pH of solution is ~ 10-11. In this process, ferrite NPs may be attached or inserted in the pores of PC. The composites were washed with doubled distilled water several times and dried by keeping at the 353 K. Finally different sets of the composite were prepared by annealed them in inert atmosphere at 573K, 773K and 973 K for 2 hr.

### Characterization

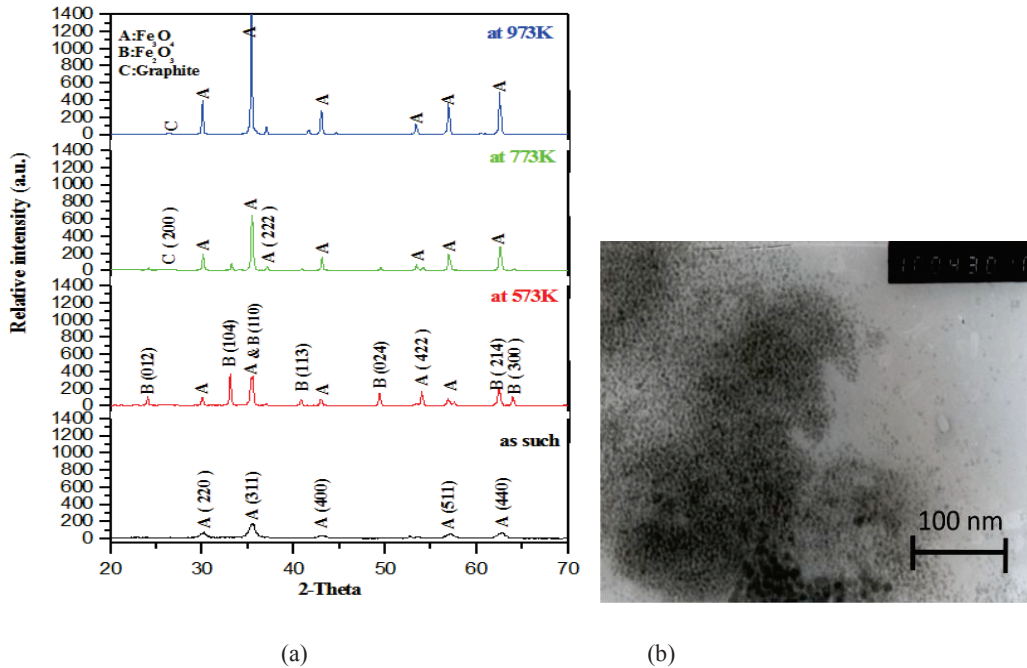
The crystalline phase formation and crystallite size of all samples were characterized from their XRD patterns. The XRD patterns were recorded by Rigaku powder X-ray diffractometer in the 2θ range from 20° to 70° using Cu K<sub>α</sub> radiation (λ=1.54059Å). The concentration of paramagnetic spins, g-value, nature of interactions and peak-to-peak line width of the composites were calculated from EPR spectra measured at ambient temperature on Bruker Biospin make X-band EPR spectrometer. Hysteresis loops were recorded on VSM at ambient temperature.

## RESULTS AND DISCUSSION

### X-ray diffraction and TEM Investigation

X-ray diffraction patterns of pure and (573 K and 773 K) temperature annealed Fe<sub>3</sub>O<sub>4</sub>:PC (0.1 g) , Fe<sub>3</sub>O<sub>4</sub>:PC (0.3 g) and Fe<sub>3</sub>O<sub>4</sub>:PC (0.5 g) were recorded and shown in Fig. 1(a) for Fe<sub>3</sub>O<sub>4</sub>:PC (0.5 g) compositions respectively. The characteristic diffraction peaks (012), (104), (110), (113), (024), (116), (214) and (300) are corresponds to hexagonal Fe<sub>2</sub>O<sub>3</sub> phase (JCPDS Card No-080-2377), while the peaks (220), (311), (400), (422), (511) and (440) corresponds to cubic phase of Fe<sub>3</sub>O<sub>4</sub> (JCPDS Card No-019-0629). It has been observed, in all the samples annealed at 573K, Fe<sub>2</sub>O<sub>3</sub> is dominating phase which exist, while at 973K the dominating phase is Fe<sub>3</sub>O<sub>4</sub>. It has been observed that in higher PC concentration NCs, PC restricts reduction of Fe<sub>3</sub>O<sub>4</sub> to Fe<sub>2</sub>O<sub>3</sub> phase. It means, the places where the presence of both conducting and magnetic phases is required, these Fe<sub>3</sub>O<sub>4</sub>-PC composites materials will be very useful. As prepared magnetic phase is Fe<sub>3</sub>O<sub>4</sub>, while the Fe<sub>3</sub>O<sub>4</sub> annealed at 573 K consists of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> phases. At 973K only Fe<sub>3</sub>O<sub>4</sub> phase is present. The different parameters calculated from the XRD pattern are *d*-values,

crystallite size (nm) ( $P$ ), distortion parameter (lattice strain) and lattice parameter of the (311) peak and listed in Table 1



**Figure 1.** (a) XRD patterns of  $\text{Fe}_3\text{O}_4\text{:PC}$  (0.5 g) NCs as such and annealed at different temperatures and (b) TEM image of  $\text{Fe}_3\text{O}_4$  NPs

**Table 1.** Structural parameters calculated from XRD patterns

Nanoparticles/ Nanocomposites	$d$ - value ( $\text{\AA}$ )	Crystallite size (nm)	Lattice Strain	Lattice parameter ( $\text{\AA}$ )
$\text{Fe}_3\text{O}_4$	2.540	9.44	0.0482	8.4243
$\text{Fe}_3\text{O}_4\text{:PC}$ (0.5 g)	2.532	12.17	0.0373	8.3965
$\text{Fe}_3\text{O}_4\text{:PC}$ (0.5 g) 573K	2.531	26.43	0.0175	8.3923
$\text{Fe}_3\text{O}_4\text{:PC}$ (0.5 g) 773K	2.533	41.52	0.0108	8.4080
$\text{Fe}_3\text{O}_4\text{:PC}$ (0.5 g) 973K	2.535	41.54	0.0110	8.4082

Figure 1(b) presented the TEM image of ferrite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles annealed at 973 K. This image clearly indicates the formation of ultrafine particles with some agglomerated particles. Their size varies from 23 - 54 nm.

## Magnetic Measurement of the Composites

### EPR spectroscopy and VSM studies

Figure 2 shows EPR spectra of  $\text{Fe}_3\text{O}_4\text{:PC}$  (0.5g) sample as such and annealed at different temperatures. The broad resonance signal exhibits the ferromagnetic nature of these NCs due to strong dipole-dipole interactions. The spectra were analyzed by using Lorentzian distribution function to evaluate  $g$ -value, peak-to-peak linewidth ( $\Delta H_{pp}$ ) and spins concentration ( $N_S$ ) of these composites increases with increasing PC concentration and annealing temperatures due to the variation in particle size and the composites formation. The  $g$ -value of these samples is  $\sim 2.0358$  for  $\text{Fe}_3\text{O}_4$  NPs which increases to 2.1345 on increasing PC concentration to 0.5 g. While spin concentration

increases from  $1.425 \times 10^{21}$  spins/g to  $3.825 \times 10^{21}$  spins/g. Magnetic properties of the  $\text{Fe}_3\text{O}_4$ , PC and  $\text{Fe}_3\text{O}_4:\text{PC}$  (0.5 g) were measured in the field of  $\pm 6000$  G at room temperature and hysteresis loops are presented in Figure 3. The saturation magnetization ( $M_s$ ) is less than  $M_s$  value of  $\text{Fe}_3\text{O}_4$  due to non-magnetic PC. The saturated magnetization of  $\text{Fe}_3\text{O}_4$  varies from 44.7 emu/g to 32.75 emu/g with the increase in PC wt %.

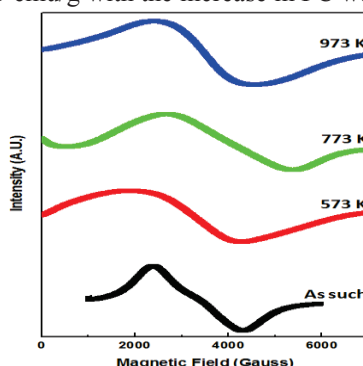


Figure 2: EPR spectra of  $\text{Fe}_3\text{O}_4:\text{PC}$  (0.5 g) NCs as such and annealed at different temperatures

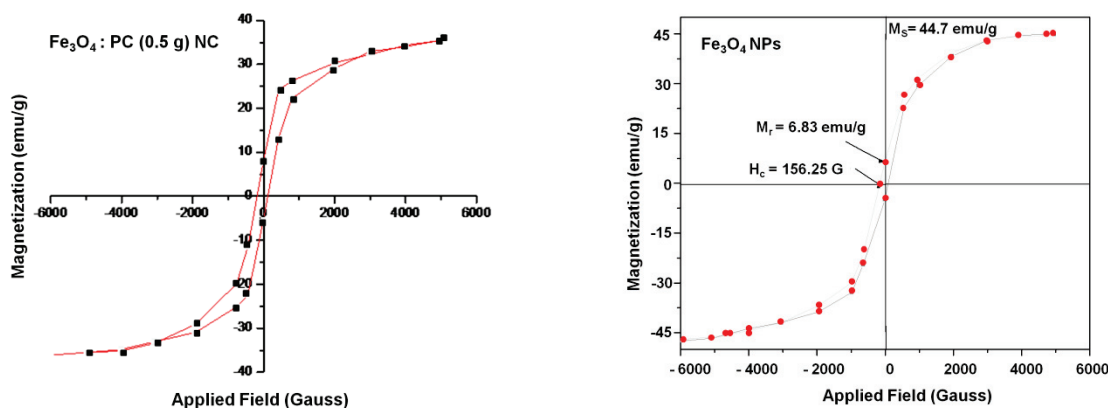


Figure 3: Hysteresis loops  $\text{Fe}_3\text{O}_4:\text{PC}$  (0.5 g) and  $\text{Fe}_2\text{O}_3$

## CONCLUSION

The size of particles play significant role on the magnetic properties and loss in the magnetization from the movement of the domain walls in the ferrite porous carbon NCs. The addition of porous carbon enhances porosity, increases surface to volume ratio and adsorption capacity of NCs markedly. The crystallite size of the composites is increased on increasing PC concentration and annealing temperature as observed from XRD and TEM studies. These results are further supported by magnetic properties investigations by EPR spectroscopy and VSM studies of these NCs. These materials are found to be suitable candidate for biosensor application.

## REFERENCES

1. Y. G. Alfaro, P. Aranda, F.M. Fernandes, B. Wicklein, M. Darder and E. R. Hitzky, *Adv. Mater.* **23**, 5224-5228 (2011).
2. R. Kumar, Somvir, S. Singh and Kulwant, *Int. J. Engn. Res.* **3**, 279 (2014).
3. O. ur Rahman, S. C. Mohapatra and S. Ahmad, *Mater. Chem. Phys.* **132**, 19-285 (2014).
4. X. Zhang, Q. Guo and D. Cui, *Sensors* **9**, 1033-1053 (2009).
5. J. Wan, H. Deng, J. Shi, L. Zhou and T. Su, *CLEAN – Soil, Air, Water*, **42**, 1199-1207 (2014).
6. I. Safarik, K. Horska, K. Pospiskova and M. Safarikova, *Int. Rev. Chem. Engg.* **4**, 346-352 (2012).