Synthesis, Characterization of Polypyrrole/Cr_2O_3 Nanocomposites (NCs) for their Structural, Morphological and electrical studies

Hajeebaba K Inamdar[1], M.Sasikala[3], M.V.N. Ambika Prasad[1*]
[1] *Department of PG Studies and Research in Physics, Gulbarga University Gulbarga-585105, India*
[2]*Department of E&CE, Godutai Engineering College for Women, Gulbarga-585104, India*
* Corresponding author. Tel.: +91 9448405817.
*E-mail address:*prasad1_amb@rediffmail.com

ABSTRACT
This study information the synthesis of polypyrrole/Cr2O3 doped nanocomposites (NCs) as a shielding pigment in organic coatings. Polypyrrole/Cr2O3 doped NCs were prepared by in situ chemical oxidative polymerization of pyrrole monomer. Here dopant Cr2O3 nanoparticles (NPs) were synthesized by solution combustion method using Aloe-vera gel as fuel with ammonium per sulphate (APS) as oxidant. Different concentrations of Cr2O3 (10-50 wt %) NPs were incorporated into the polypyrrole. The synthesized nanocomposites were characterized by means of powder X-ray diffraction (PXRD) and Scanning electron microscopy (SEM). The size of the NPs were calculated by Scherer method, and found to be around 20 nm. TEM results are in consistent with the XRD results. The morphology of the obtained composites shows the porous and agglomerated particles which are due to large amount of gas evolution during NPs synthesis by solution combustion method and electrical properties were studied.
Keywords: Polypyrole (PPy), Cr2O3, Nanocomposites, SEM, XRD.

1.INTRODUCTION

Conducting electroactive polymers (CEP) still remain a subject of intense investigation of many research groups worldwide. During the past decade, there have been many reports concerning fruitful investigations. Conductive polymers such as Polypyrrole (PPY), polypyrrole (PPy), and their composites are widely uses as sensors [2], energy storage materials, due to the facile synthesis and flexibility in processing [3]. Conducting polymers including polypyrrole (PPy), Polypyrrole (PPY), polyethylene di-oxythiophene (PEDOT), and polythiophene (PT) have both electrochemical double layer capacitance and pseudo-capacitance arising from the fast and reversible oxidation and reduction processes related to their p-conjugated polymer chains [1-3]. Among these conducting polymers, PPy is outstanding as a promising electrode material for supercapacitors, because it has various significant advantages such as high specific capacitance, good conductivity, bio-compatibility and outstanding mechanical properties [4]. However, like other electronically conducting polymers, PPy suffers from volumetric shrinkage during discharge process which can lead to decrease in cyclic stability [6-9]. Nanocomposites are a class of composites in which the reinforcing phase dimensions are in the order of nanometers [4]. Because of their nanometer size characteristics nanocomposites possess superior properties than the conventional , micro composites due to maximize the interfacial adhesion. Such improved properties can be attained in nanocomposites in which the building blocks are dispersed in a polymer matrix. Of conducting polymers, polypyrrole (PPy) is generally recognized to be one of promising conducting polymers for commercial application due to its high electrical conductivity, good environmental stability and ease of synthesis [4]. To improve the cyclic stability of the conducting polymer, researchers have recently synthesized various PPy-based composites with hierarchical structured materials to hinder the volume change of the conducting polymer during the charge–discharge processes [10-12]. As is known to all, transition metal oxides have been massively

reported as electrode materials for pseudo-capacitors because of their large capacitance and fast redox kinetics [3]. In this paper we report the synthesis of Cr2O3 nanoparticles using Aloe-vera gel, synthesis of polypyrrole/Cr2O3 nanocomposites and their structural, morphological and electrical studies in detail.

2. Materials and methods

2 Experimental

2.1 Synthesis of Polymer

The synthesis Polypyrrole (PPY) was based on mixing aqueous solution of aniline hydrochloride and ammonium persulphate at room temperature, followed by the separation of PPY hydrochloride precipitate by filtration and drying. An equi-molar volume of aniline and hydrochloride acid was dissolved in distilled water in a volumetric flask to obtain 100 ml of solution. Similarly, ammoniumpersulphate (0.6M) was dissolved in 100 ml water. Both solutions were kept for 1 hour at room temperature and then mixed in a beaker, stirred with a mechanical stirrer and allowed to polymerizing. After a day, the PPY precipitate was collected on a filter, washed with 0.3 M HCL and acetone repeatedly. The Polypyrrole hydrochloride powder was then dried in air in vacuum at 60 ^{o}C for 24 hour.

Bio-Mediated Synthesis of Cr_2O_3 Nanoparticles:

The chromiumoxide nanoparticles were synthesized by 'self-propagating low temperature combustion method', employing chromium nitrate (Cr $(NO_3)_2.6H_2O$)) as precursor and *Aloe-Vera* gel as a fuel. In fact 2.14 g of chromiumnitrate was taken in 300 ml petri-dish and 10 ml of *Aloe-Vera* gel was added to the petri-dish and kept on a magnetic stirrer for ~10 min. The uniform mixture of both oxidizer as well as the fuel was then introduced into the pre-heated muffle furnace kept at 450 ^{0}C. The mixture boils with froth yielding finally a black powder of NiO nanoparticles. The average particle size of the NiO was calculated by Debye-Scherrer and it was found to be ~15 nm **[12-16]**.

Fig 1 Flow Chart for Preparation of Cr_2O_3 NPs

2.3 Synthesis of Polypyrrole/Cr2O3 nanocomposites

Synthesis of Polypyrrole–Copper oxide composites were carried out by *in-situ* polymerization method. Aniline (0.3 M) was mixed in 0.3 M HCl and stirred for 15 min to form aniline hydrochloride. Copper oxide powder were added in the mass fraction to the above solution with vigorous stirring in order to keep the copper oxide homogeneously suspended in the solution. To this

solution, 0.6 M of ammonium per-sulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at ice temperature for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water and acetone, and finally dried in an oven for 24 h to achieve a constant mass. The Polypyrrole - copper oxide composites were thus obtained containing various weight percentage of chromium oxide (*i.e.*10, 20, 30, 40, & 50%)

3. Results and Discussions

3.1. XRD Analysis

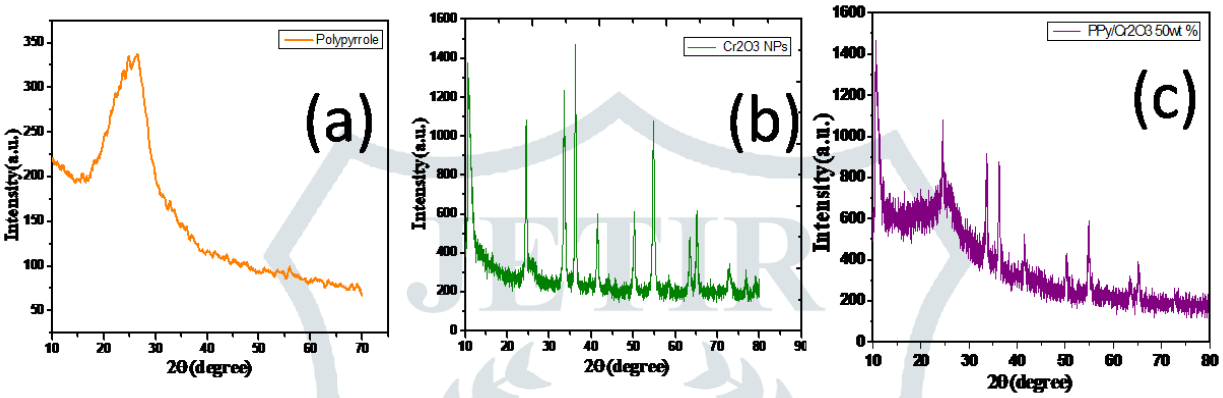

Fig2. XRD Pattern of (a) PPy (b)PPy/ Cr2O3, (50 wt %).

X-Ray Diffraction studies were performed using Shimadzu-7000 diffractometer with Cu as the target (1.54 Å) and chromiumas the filter. Fig.2 shows X-ray diffraction pattern of Polypyrrole. A broad peak centered at $2\theta = 25.53^0$ may be assigned to the scattering from the Pyrrole chains at interplanar spacing which clearly implies the amorphous nature of Polypyrrole and it corresponds to diffraction planes (200) of pure Polypyrrole and PPy/Cr2O3 nanocomposites. It was clearly observed from the PXRD graph that pure PPy was in amorphous nature and as the Cr2O3 concentration increases from 30wt % the amorphous nature partially disappear and crystallinity in the NCs

were observed. It was evident that the Cr2O3 nanoparticles were completely interlocked between the polypyrrole chains. There were no additional impurity peaks were observed in XRD spectrum. The average crystallite size (D) was designed by using Scherrer's formula[5],

$$D = \frac{0.89\lambda}{\beta \cos\theta} \qquad (1)$$

Where D, the average crystallite size, λ ; the wavelength of the X-rays (0.15405 nm). The deliberate average crystalline size (D) of PPy/Cr2O3 30 wt % NCs were establish to be 28-36 nm.

3.2. Morphology studies

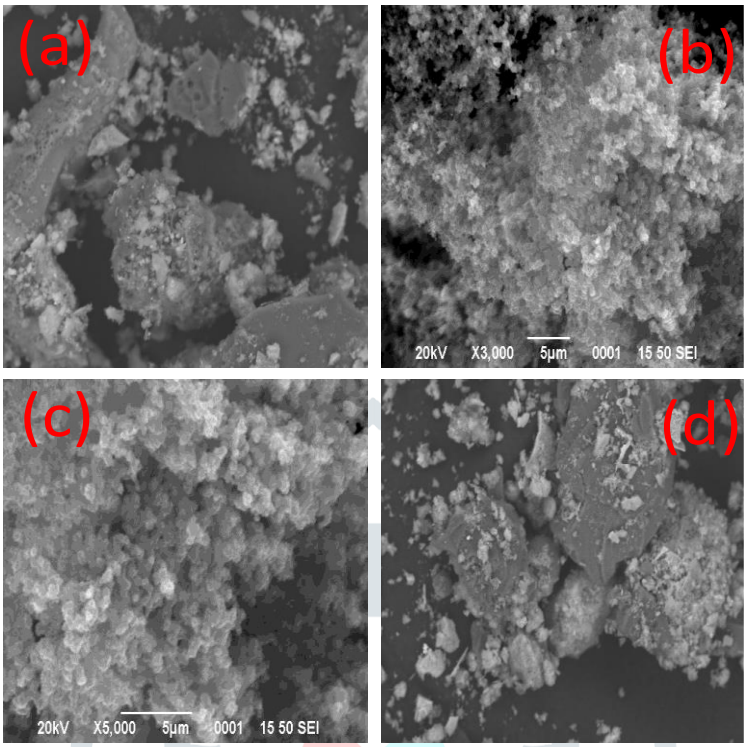

Fig3. SEM Images Of a) Cr_2O_3 b)Ppy c) & d) 10wt% &50wt% of Ppy/Cr_2O_3 NCs

The Fig.3 shows surface morphology of the composites were studied by means of SEM and the results showed agglomeration of particles. From micrographs of TEM, particles size was around 25nm. Since it is exposed that the nanocomposite is accomppyed by much micrometric and nanometric irregularity[12-14].

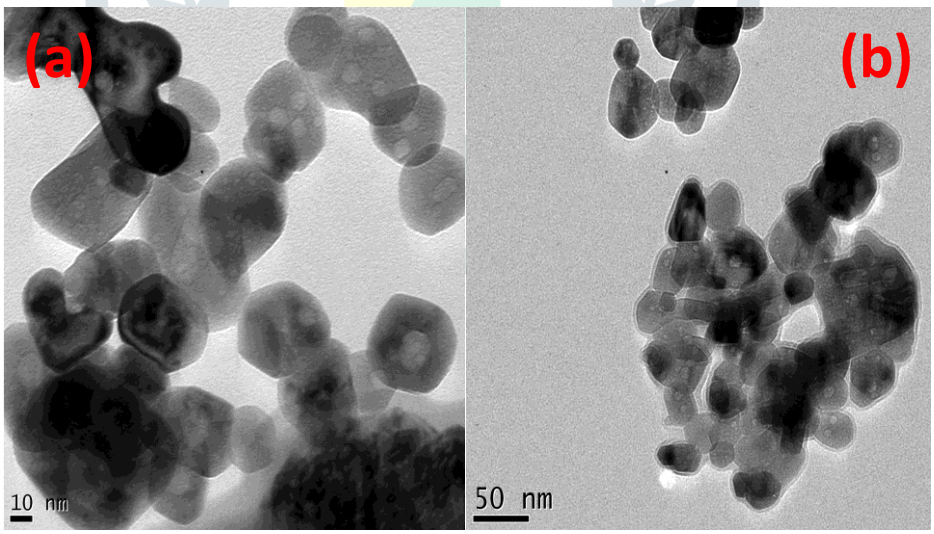

Fig4. TEM Images of Polypyrrole/Cr_2O_3 50wt% NCs

Fig (a) and (b)Shows TEM image of **Polypyrrole/Cr_2O_3 50wt% NCs** (50 wt %) nanocomposites. TEM image with interplanar spacing d value equal to 0.28 nm. These results are in consistent with the PXRD.

4. DC Conductivity Studies

The dc conductivity of the nano-composites were studied by using Keithley 6514 electrometer. The plot of surface dc conductivity of PPy and its composites with temperature are shown in Fig. The conductively is found to increase with increase in temperature. This increase in conductivity with temperature is the characteristic of "thermal activated behavior". The increase in conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with enhancement in temperature. The thermal curing affects of the alignment of polymer chain, which leads to the increase of conjugation length possibly also brings about increase in the conductivity of the composites.

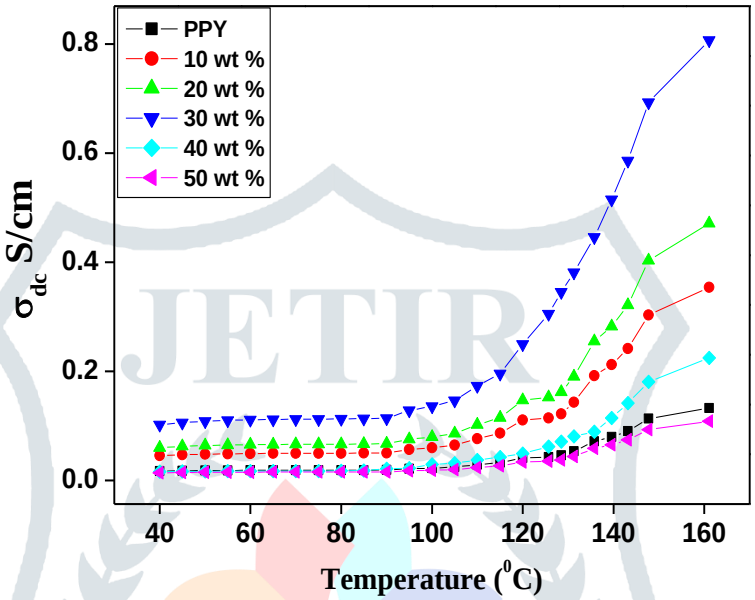

Fig5. DC Conductivity Study of Ppy/Cr_2O_3 NC

5.CONCLUSIONS

Pure and PPy/Cr2O3 NCs were successfully prepared by in-situ polymerization technique. The nanocomposites showed high crystalline nature with no impurity peaks. The surface morphology of the composites were studied by means of SEM and the results showed agglomeration of particles. From micrographs of TEM, particles size was around 25 nm which was in good agreement with that of the particle size calculated from Scherer equation. The increase in conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with enhancement in temperature. All these results together reveal that the synthesized composites can be used in the field of optical applications.

5.REFERENCES

[1]. Hajeebaba K Inamdar, H. Nagabhushana, Basavaraja Sannakki, R.D. Mathad , DC Conductivity Study of Polypyrrole/Cr2O3 Nanocomposites prepared through Green Synthesis Materials Today: Proceedings 3 (2016), pp3850–3854.

[2]. R. L. N. Chandrakanthi,M. A. Careem, Preparation and characterization of CdS and Cu2S nanoparticle/Polypyrrole composite films, Thin Solid Films, 417(2002), pp- 51-56.

[3]. Sharanabasamma M Ambalagi*, Hajeebaba K Inamdar and Basavaraja Sannakki,Materials Mechanism of DC Conductivity Measurement of Zinc Oxide Doped Polypyrrole Nanocomposites Today: Proceedings 3 (2016), pp3945–3950.

[4]. Ali Fakhri a,⋆, Sajjad Behrouz b, Mohammad Asif c, Inderjeet Tyagi d, Shilpi Agarwal d,e, Vinod Kumar Gupta d,e,⋆⋆, "Synthesis, structural and morphological characteristics of Cr2O3 nanoparticles Co-doped with boron and nitrogen" , Journal of Molecular Liquids 213 (2016) 326–331.

[5]. Y. He, Synthesis of Polypyrrole/nano-CeO2composite microspheres via a solid – stabilized emulsion route, Mater. Chem. Phys, 92, (2005), pp134- 137.

[6]. A. G. MacDiarmid, L. S. Yang, W. S. Huang, B. D. Humphrey, Polyaniline: electrochemistry and application to rechargeable batteries, Synth. Met.,18,(1987), PP- 393- 398.

[7]. D. Verma, V. Datta, Role of novel microstructure of polyaniline-CSA thin film in ammonia sensing at room temperature, Sens. Actuat. B,134,(2008) PP-373-376.

[8]. S Farheen, F Jahan, HK Inamdar, RD Mathad, "Effect of polymer blending on mechanical and thermal properties",Modern Applied Science, (2015),12 (1), pp 520-22

[9]. SM Ambalgi, HK Inamdar, VT Manjula, SG Sannakki Nagaraja," Synthesis, Characterization and Electrical Properties of Polypyrrole/ChromiumOxide Nanocomposites", International Journal of Engineering Research (2016), 5 (2), pp 119-122

[10]. M. P. Pileni, "Magnetic fluids: fabrication, magnetic properties, and organization of nanocrystals," Advanced Funtional Materials", Vol.11, (2001), pp-323–336.

[11]. S.C. Chen ⋆, T.Y. Kuo, T.H. Sun, "Microstructures, electrical and optical properties of non-stoichiometric p-type chromiumoxide films by radio frequency reactive sputtering", Surface & Coatings Technology 205 (2010) S236–S240.

[12]. J. Sort, J. Nogues. X.Amils, S.Surinach. J.S.Munoz, and M.D.Baro, "Room temperature magnetic hardening in mechanically milled ferromagnetic-antiferromagnetic. composites,"Journal of Magnetism and Magnetic Materials,Vol.219, (2000) pp-53–57.

[13]. I. Hotovy, J. Huran, P. Siciliano, S. Capone, L. Spiess, and V.Rehacek "The influences of preparation parameters on Cr2O3thin film properties for gas-sensing application," Sen and Act, B, (2001) pp-126– 132.

[14]. V. Ponnarasan and A. Krishnan, " Studies on Pure and Divalent Metal Doped Copper Oxide Nanoparticles", *Adv. Studies Theory Phys*.,vol.8, no. 6, 251-258, 2014.

[15]. Wei Chen, Gary C. Lickfield and Charles Q. (2004). Yang polymer 45(3), 2004, P 1063-1071.

[16]. S. A. Chen, K. R. Chuang, C. I. Chao, H. T.Lee, White light emission from electroluminescence diode with polyaniline as the emitting layer, Synth. Met.,82,(1996)PP-207-210.