Synthesis of Pyrrole-*N*-vinylcarbazole Neat Copolymer and ZnO Nanocomposite

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The present work focused on the synthesis of neat copolymer (Py-NVK) and ZnO nanocomposite from their pyrrole (Py) and N-vinylcarbazole (NVK) host monomers and creating new conducting materials (Py-NVK and Py-NVK_ZnO). The choice of neat copolymer and ZnO nanocomposite was motivated by the unique properties of their host monomers (Py and NVK). The neat and ZnO nanocomposite copolymer was prepared by the sol-gel method using FeCl$_3$ as initiator. The structural analyses were performed using field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

Keywords: Pyrrole, N-vinylcarbazole, ZnO nanocomposite, Copolymer.

INTRODUCTION

Conducting polymers (CPs) exploit the delocalization of π-electrons to transfer charge. They exhibit conductivity in metallic to semiconductor ranges [1,2]. Chemical, optical and biosensor applications of CPs, immensely explored for their electrical and optical traits are reversibly transformed *via* doping or dedoping regimes [3-7]. The CPs have evoked much interest for biosensors as they furnish brilliant resources to immobilize biomolecules by rapid electron transfer [8]. Gas sensing device materials are important for biomedical industry, food processing, ecological monitoring, *etc.* [9-13].

Polypyrrole (PPy) is an organic polymer resulting from the polymerization of pyrrole monomer. Its characteristics were testified long back in 1968 for superior redox properties, conductance and simple synthetic routes [14]. Appreciable conductivity, stable oxidized form, commercial accessibility, water-solubility and valuable optoelectrical properties render it a material of choice for advance research [15]. Phenomenal interest has been evoked in electrically-conducting heterocyclic polymers of which PPy furnishes excellent candidature. Polypyrrole (PPy) is easily accessible through electropolymerization nevertheless polymerization using oxidizing metal salts has also been reported [16]. Attempts to copolymerize pyrrole with other heterocyclic monomers to enhance the product's conduction and mechanical qualities have been reported [17].

Poly(*N*-vinylcarbazole) (PNVK) is the key photoconductive polymer employed as organic photorefractive material for LED and photovoltaic applications. Subsequent to the first efficacious use of PNVK in electro-photographics [18,19] polymers bearing the carbazole linkage have been studied progressively. N-vinylcarbazole (NVK) behaves as an excellent reactive monomer in cationic, radical and charge-transfer polymerization routes [20]. Moreover, NVK is prominently acknowledged for its thermal steadiness and interesting photo physical performance [20,21].

Various linkages between the pyrrole and NVK are possible *viz.* 2- and/or 5-position of pyrrole and 3- and/or 6-position of NVK. Pattern of substitution on NVK influences the conductivity of the consequential copolymer. Polymers with an extended π-electrons system facilitate electron mobility along the polymer web. These π-electrons exhibit very high flexibility, exploitable for their electrical properties by employing appropriate synthetic techniques and modeling to develop conducting

polymers (CPs) [22-24]. Exclusive characteristics of CPs have applica-tions in diverse fields *viz.* anti-static coating [25], design of light-emitting diodes [26], solar cells [27], electrochromic instru-ments [28], anti-corrosion coatings [29], drug-release systems [30] along with chemical sensors and biosensors [31]. To date, several CPs such as polypyrrole (PPy), poly(acetylene), poly(terthiophene), polythiophene (PTh), poly(fluorine), poly-aniline (PANI), poly(tetrathiafulvalene), poly(3-alkylthio-phene), poly(*p*-phenylene sulfide), poly(naphthalene) and poly-(*para*-phenylene vinylene) are used in sensing technologies [32].

Polypyrrole (PPy) has prominent use in drug transport and delivery [33], sensors [34] and weathering fortification for materials [35]. Semiconductor properties of PPy have been exploited for the electronic components in photo electrochemical devices [36], OLEDs [37] and self-repairing devices [38], *etc.* PPy possesses properties apposite for use in sensors [39], actuators [40] and immunosensor [41] applications. Poly-(N-vinylcarbazole) (PNVK) is important for electronic applic-ations owing to easy processability, environmental steadiness and virtuous electro-optical properties with operational stability [42].

Semiconducting metal oxide nanoparticles have been used in resistive switching applications *viz.* NiO [43], ZnO [44], MnO_2 [45] and HfO_2 [46]. ZnO commands attraction for excep-tional exciton binding energies, exploitable physical characte-ristics, chemical steadiness, eco-compatibility, low cost and varied crystal defects [47]. Nano-ZnO partakes a wide range of appli-cations *viz.* nano-laser, LED, gas sensing and heterogeneous catalysis [48-50]. Additionally, appreciable compatibility to biological systems and pro-environmental nature of ZnO renders it a material of choice for electrochemical sensors [51]. Nano ZnO morphologies include nanorods [52], nanowires [53], nanotubes [54], nanoflowers [55], nanoneedles [56] and hollow spheres [57] as reported. ZnO-nanosheet based graded structures exhibit appreciable electrocatalysis owing to large surface area exposing diverse crystal facets [58-60]. Nowadays, the demand for miniaturization in the design of microelectronic nano-devices has evoked interest in ZnO nano forms. Nanoparticle composites with polymers prominently appear in the literature, such as polyaniline-metal oxide nanoparticle fusions [61], PPy-Ti [62], $PPy-TiO_2$ [63], PPy-Au [64], PPy-Pt [65], PPy-Ag [66] and PPy-Pd [67].

In this research, an effort has been made to synthesize a neat copolymer and ZnO nanocomposite (Py-NVK and Py-NVK_ZnO) from the host monomers (Py and NVK) using diethyl ether solvent and $FeCl_3$ initiator by sol-gel method [68].

The consequence of copolymerization on the electrical, electr-onic and structural properties of neat copolymer and ZnO nano-composite has been investigated.

EXPERIMENTAL

ZnO nanopowder from Sigma Aldrich (assay 97%), pyrrole from Spectrochem (assay 99%) and N-vinylcarbazole from Alfa Aesar, diethyl ether from Fischer-Scientific with stated purity of 98% were used to prepare the neat copolymer and the ZnO nanocomposite. The synthesized neat copolymer and ZnO nanocomposite was washed using HCl and methanol from Fischer-Scientific with stated purity of 38% and 99%, respec-tively. Toluene was from Fischer-Scientific (assay 99%) used for refluxing of synthesized neat copolymer and ZnO nano-composite. Ferric chloride used was from Fischer-Scientific with stated purity of 96%. All chemicals were used without further purification.

Preparation of neat copolymer: Two-necked 250 mL round bottom flask provided with a stirrer and inlet for nitrogen gas constituted and thermometer the reaction setup. A 0.029 mol of pyrrole, 0.004 mol of $FeCl_3$ and 0.029 mol of N-vinyl-carbazole (NVK) were dissolved in 100 mL diethyl ether solvent. The reaction was conducted with continuous stirring for 24 h under nitrogen atmosphere at 28 ºC (**Scheme-I**). The insoluble black mass of the neat copolymer (Py-NVK) obtained was first washed with 10% HCl followed by water and boiling methanol. The copolymer was finally extracted free of PNVK homopoly-mer, by refluxing with toluene for 1 h. The obtained product was vacuum dried at 100 ºC for 6-8 h.

Preparation of ZnO nanocomposite: The synthetic reac-tion scheme of ZnO nanocomposite (Py-NVK_ZnO) from their host monomers (Py and NVK) is shown in **Scheme-II**. ZnO nanocomposite was synthesized by the host monomers with nano-ZnO and $FeCl_3$ as initiator by the sol-gel reaction method [69]. A 250 mL round bottom flask with stirrer and nitrogen inlet was used to react nano-ZnO (0.01 mol), pyrrole (0.029 mol), ferric chloride (0.004 mol) and N-vinylcarbazole (0.029 mol) dissolved in 100 mL diethyl ether with continuous stirring under nitrogen atmosphere for 24 h at 28 ºC. Insoluble black mass of ZnO nanocomposite produced was first washed with 10% HCl, then water, followed by boiling methanol and finally extracted, free of PNVK homopolymers, by refluxing with toluene for 1 h. Finally, ZnO nanocomposite was dried under vacuum for 6-8 h at 100 ºC.

Characterization: To assess the surface morphology, structure and functional group orientation, the synthesized neat copolymer and ZnO nanocomposite was characterized using

Scheme-I: Preparation of neat copolymer

Scheme-II: Preparation of ZnO nanocomposite
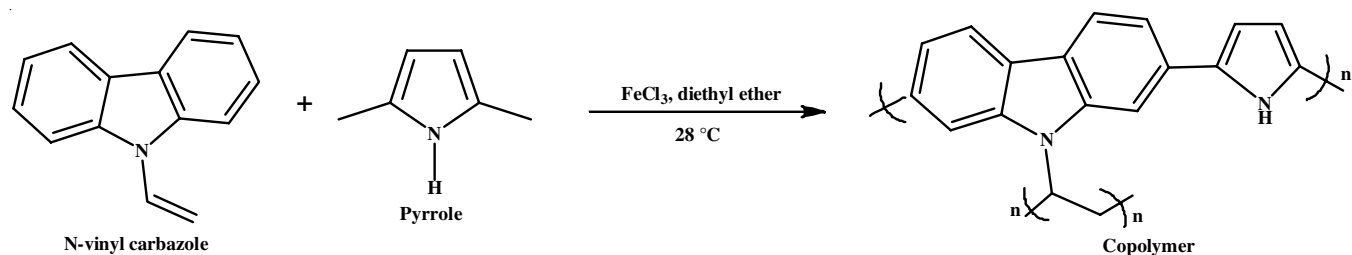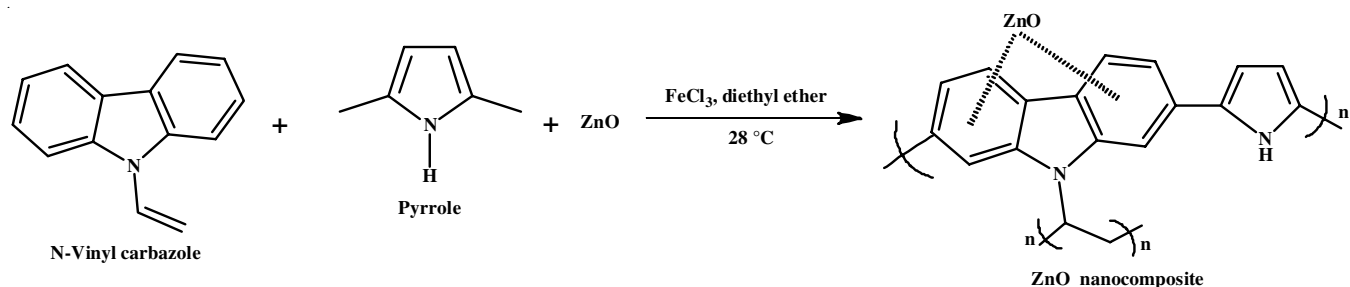
FESEM, HRTEM, XRD and FTIR. FESEM was performed on Nova nano FE-SEM 450 (FEI), while the HRTEM was performed using Tecnai G2 S-TWIN (FEI) with 200 mesh copper grids used for sample preparation. X-ray diffractometer panalytical-X-Pert-Pro was used to record X-ray diffractograms. FTIR was performed using Perkin-Elmer (in KBr pellets) and cyclic voltammograms were recorded on Potentiostat-Versastat EG & G II Princeton Applied Research Model 273.

RESULTS AND DISCUSSION

FESEM analysis of neat copolymer: Fig. 1(a-f) shows the surface characteristics of the neat copolymer (Py-NVK) studied by FESEM at various magnifications. The FESEM of pyrrole demonstrate close-packed agglomerates of irregular size, shapes and the presence of small spherical beads distributed uniformly throughout the surface [70]. The morphology of N-vinylcarbazole (NVK) as layered, homogenous, forming discrete pieces of irregular shape and size [71]. The FESEM study of Py and NVK shows many irregularities (voids, microholes and joints), while, the FESEM images of the synthesized neat copolymer are distinct from host monomers (Py and NVK) and showed distinctly formed spherical particles. Spherical particles at various magnifications confirmed the formation of copolymer *i.e.*, Py-NVK.

FESEM analysis of ZnO nanocomposite: Emission scanning electron micrographs pertaining to ZnO nanocomposite (Py-NVK_ ZnO) was studied by FESEM at different magnifications. The FESEM images of the ZnO nanocomposite polypyrrole (PPy_ ZnO) clearly depict the even dispersal of ZnO nanoparticles around the PPy matrix with regular grain size [Fig. 2(a-d)]. This is also supported by literature reports that ZnO nanoparticles relate with PPy [72,73]. Similarly, literature also mentioned that ZnO nanocomposite *N*-vinylcarbazole (NVK_ZnO) micro-structure shows nanotubular formations possessing micrometer length with regular diameter. The shady portions represent ZnO nanoparticles and the lighter portion depicts NVK, inferred so, for the electron movement through the organic and inorganic constituent parts varies markedly [42]. The porous spherical particles of ZnO entrenching the polymer matrix enhance the interface interaction. The FESEM images of the synthesized ZnO nanocomposite (Py-NVK_ ZnO) clearly formed spherical particles, confirmed the synthesis of ZnO nanocomposite in compared to the ZnO nanocomposite host monomers (PPy_ ZnO and PNVK_ZnO).

HRTEM analysis of neat copolymer: To obtain more information on the morphology of neat copolymer (Py-NVK), HRTEM analysis was performed using copper grid at different magnifications. As per reported literature, HRTEM analysis
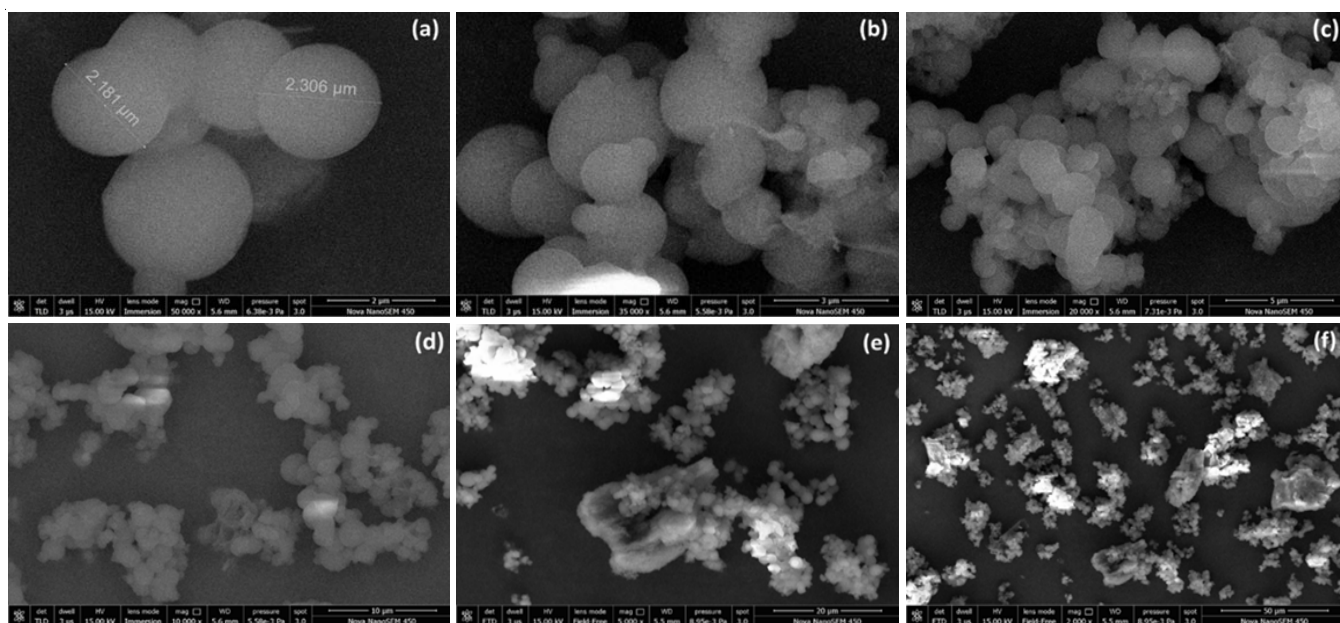

Fig. 1. FESEM micrographs of neat copolymer at different magnification (a) 2 μm, (b) 3 μm, (c) 5 μm, (d) 10 μm, (e) 20 μm and (f) 50 μm
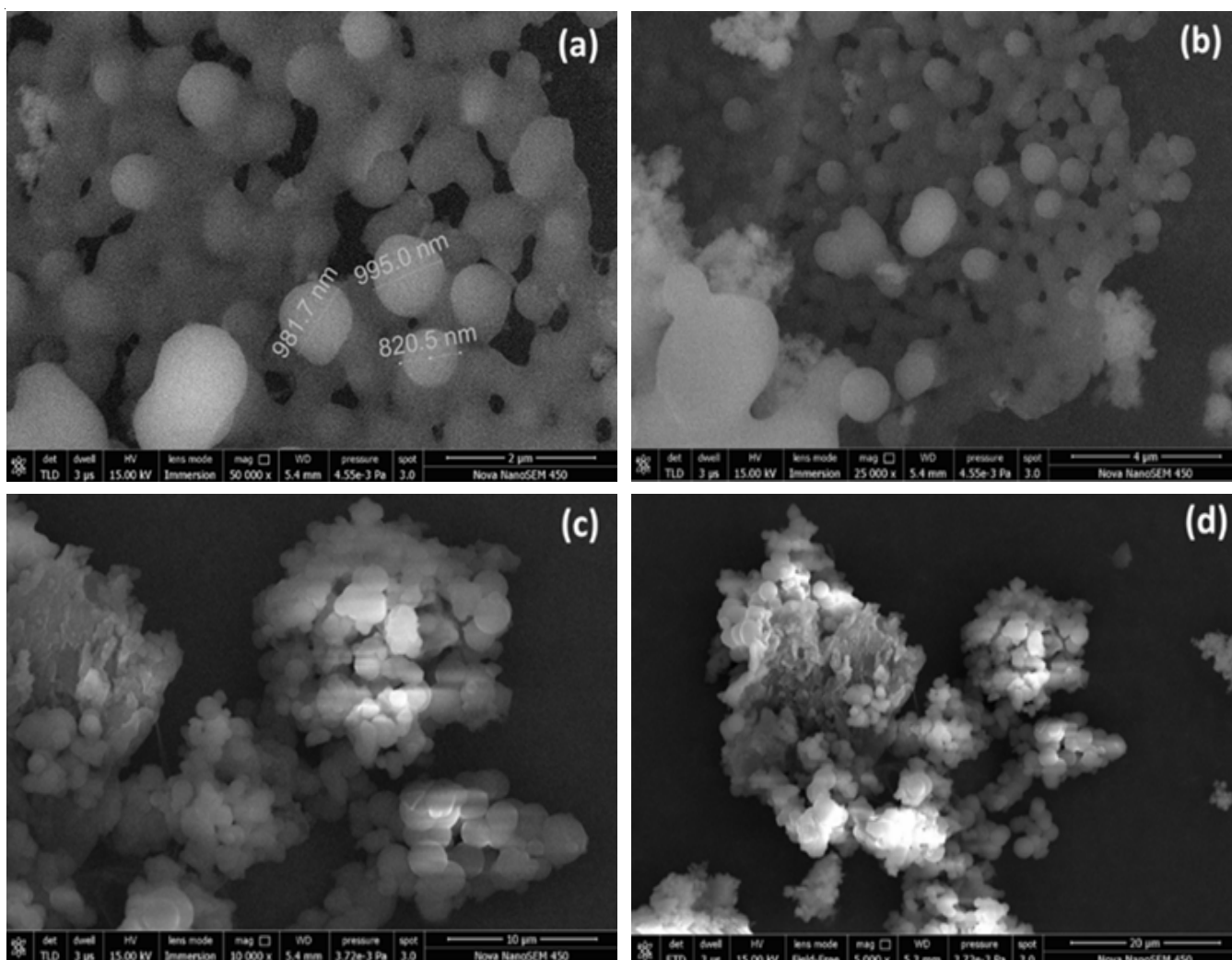
Fig. 2. FESEM micrographs of ZnO nanocomposite at different magnifications (a) 2 μm, (b) 4 μm, (c) 10 μm and (d) 20 μm

of pyrrole indicates most of the particles (about 80%) prevailed as round platelets of size 40-75 nm with some longer particles of the range 120-220 nm [74] (Fig. 3a-d). Literature also reported that NVK exhibits an irregular and spherical structure, which appears to be interconnected, forming a network [71]. The HRTEM images of the neat copolymer show completely different structures compared to the host monomers (Py and NVK) and show spherical ball-like structures. The HRTEM findings support the SEM results by providing the evidence for the existence of the spherical particles.

HRTEM analysis of ZnO nanocomposite: The HRTEM micrographs pertaining to ZnO nanocomposite at different magnifications are presented in Fig. 4a-d. The images are the indicative of spherical morphology for copolymer furnished with ZnO nanoparticles, which clearly visibly specifies the ZnO nanoparticles as the ones with dark colour and those around the oxide core as copolymer which is about several nanometers thick. The HRTEM analysis of ZnO nanocomposite indicates the average size, which complements the FESEM analysis results.

XRD studies of neat copolymer: Fig. 5 illustrates the XRD spectrum pertaining to the synthesized neat copolymer (Py-

NVK) as a function of 2θ. Literature reports the XRD diffractograms of pyrrole showing broad diffraction peak at 2θ = 20.10º portraying the intermolecular spacing and indicative of amorphous structure of pyrrole. Likewise, the literature on XRD spectra of N-vinylcarbazole (NVK) report partially crystalline structure with a peak at 20.8º [75], whereas, the XRD pattern of the synthesized neat copolymer shows amorphous nature and the diffraction signal of 2θ value was observed at 20.18º. Formation of the copolymer was indicated by peak shift towards 20.18º in comparison to the XRD peaks of Py and NVK at 20.10º and 20.80º respectively.

XRD studies of of ZnO nanocomposite: Fig. 6 depicts the XRD diffractogram of ZnO nanocomposite (Py-NVK_ZnO) as a function of 2θ. As reported in literature [76,77], the main peaks of pure ZnO nanoparticles at 2θ values of 32º (100), 34.5º (002), 36.0º (102), 47.5º (102), 56.5º (110), 63.0º (103), 66.5º (200), 68.0º (112) and 69.0º (201). In literature, the XRD diffractogram of pyrrole (Py) has been reported to exhibit broad peak around 2θ = 20.1º indicative of amorphous structure of pyrrole. The XRD spectrum of NVK revealed a discrete peak at 20.8º [75]. Similar to it, the XRD spectra of the synthesized ZnO nanocomposite suggest the amorphous nature with short
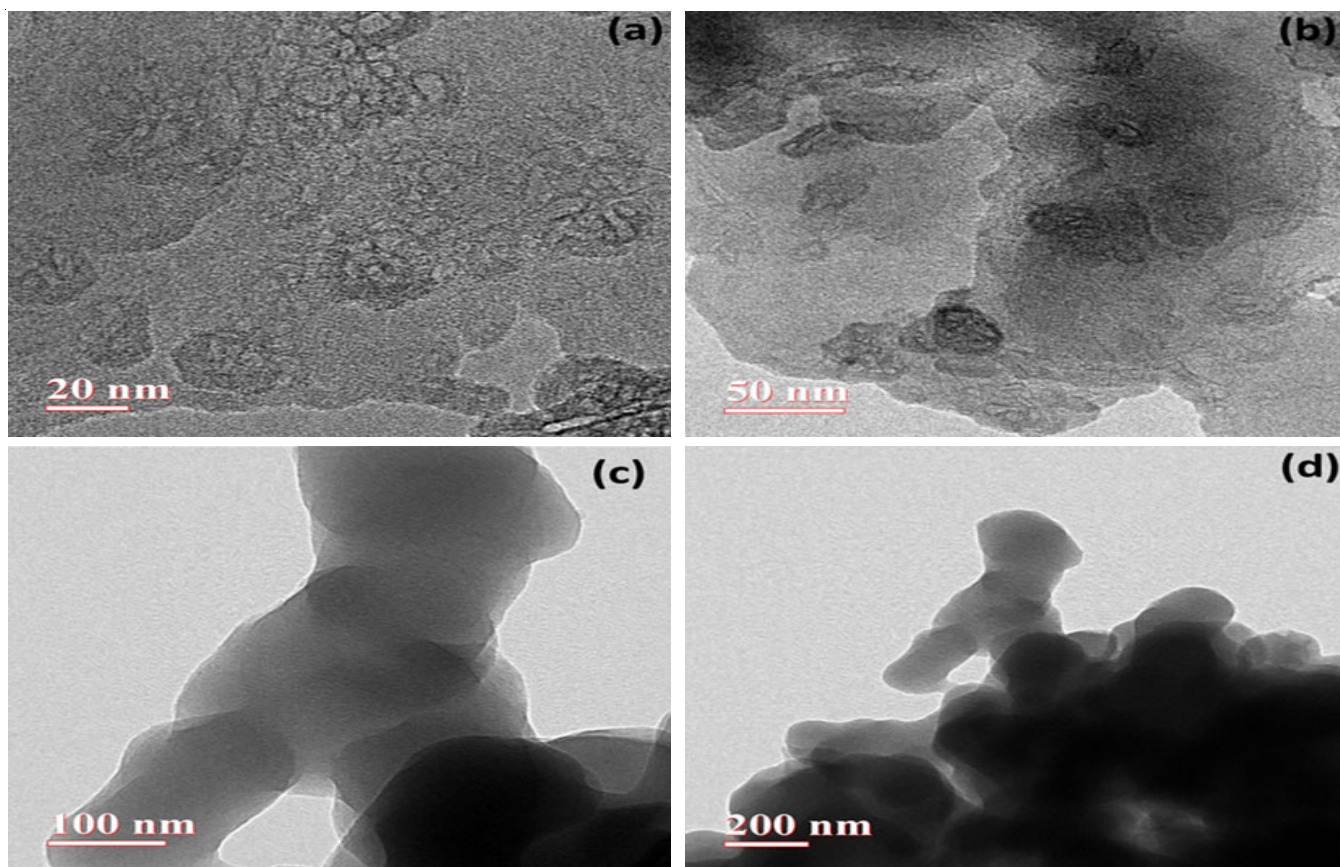
Fig. 3. HRTEM micrographs of neat copolymer at different magnifications (a) 20 nm, (b) 50 nm, (c) 100 nm and (d) 200 nm
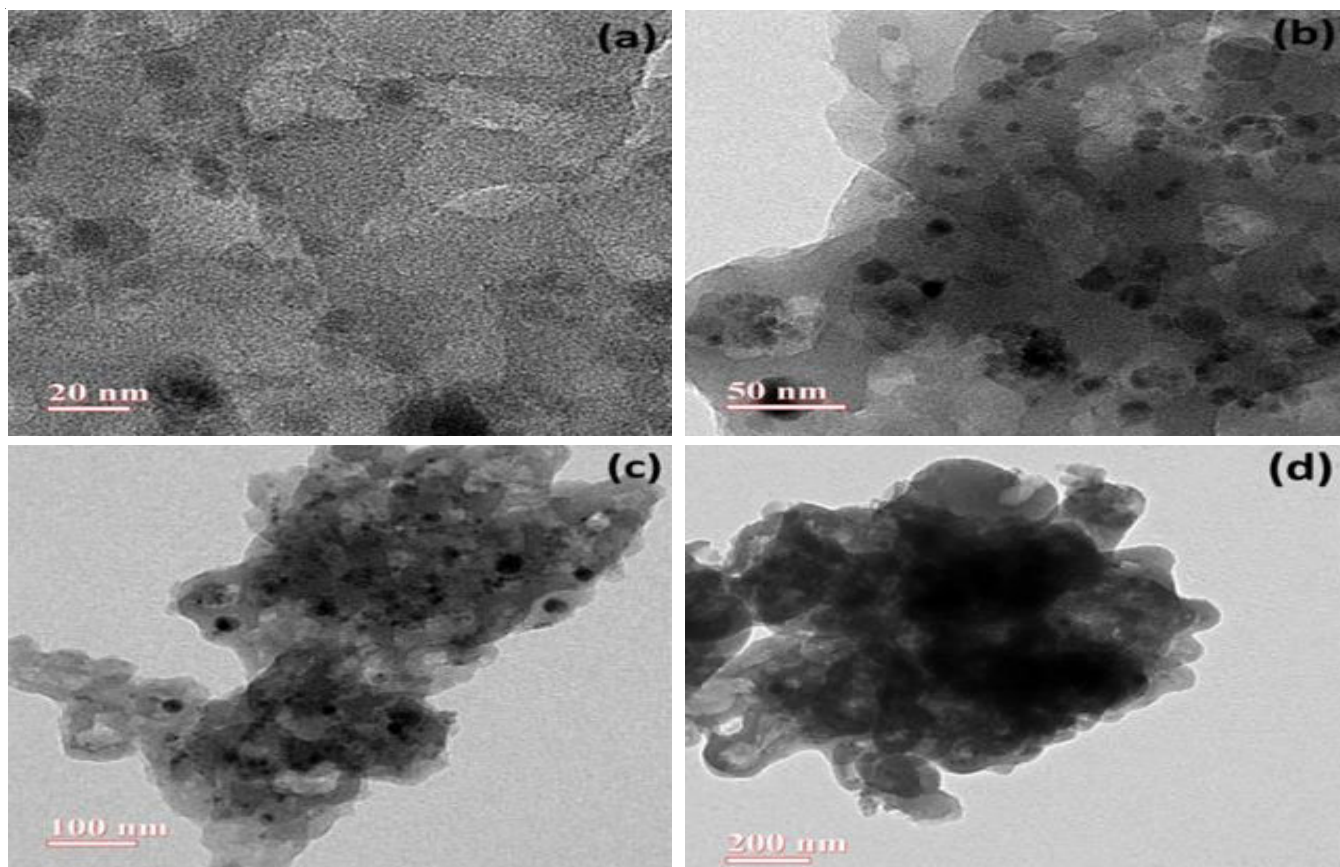

Fig. 4. HRTEM micrographs of ZnO nanocomposite at different magnifications (a) 20 nm, (b) 50 nm, (c) 100 nm and (d) 200 nm
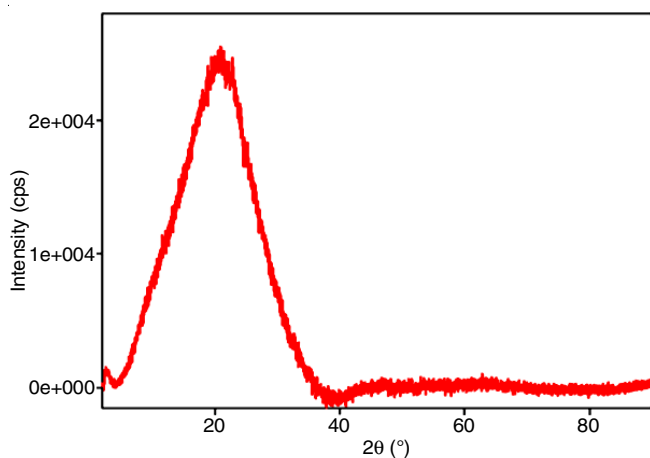
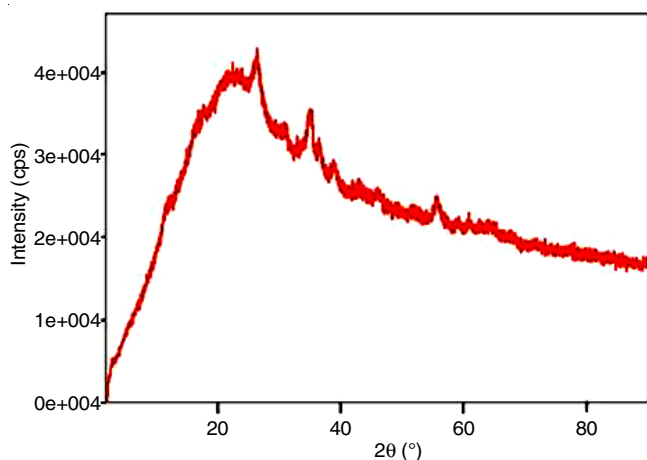Fig. 5. X-ray diffractogram of the synthesized neat copolymer

Fig. 6. X-ray diffractogram of the ZnO nanocomposite

range order as the diffraction signals were observed at 16.80°, 26.60°, 32.53°, 35.31°, 39.16°, 42.98°, 46.16°, 55.57° and 64.78° value of 2θ. These data are in close agreement with the reported literature and confirmed by peak shifts of Py, NVK and ZnO nanoparticles due to mutual interactions in copolymerization. The results also revealed the formation of ZnO nanocomposite (Py-NVK_ZnO) as amorphous material with intermittent crystalline nano ZnO characteristics.

FTIR studies of neat copolymer: The FTIR spectrum pertaining to neat copolymer (Py-NVK) in the wavelength of 4000 to 500 cm^{-1} depicting the distinctive peaks are shown in Fig. 7. The major peaks for synthesized neat copolymer can be seen at 3419.21, 1624.22, 1451.84 and 1383.50 cm^{-1}, corresponding to C-H asymmetric stretching of aromatic structure, C=C stretching of vinylidene group, C-N stretching vibration and =C-N planar vibrations, respectively. The observed FTIR spectrum of the synthesized neat copolymer is closely similar to the reported literature [75,78] with the additional appearance of some distinctive peaks, which confirms the copolymerization of pyrrole and N-vinylcarbazole.

FTIR studies of ZnO nanocomposite: To ascertain the chemical structure of the synthesized ZnO nanocomposite (Py-NVK_ZnO), FTIR spectrum was obtained for 4000-500 cm^{-1} spectral range (Fig. 8). As reported in literature, in 3443 cm^{-1}
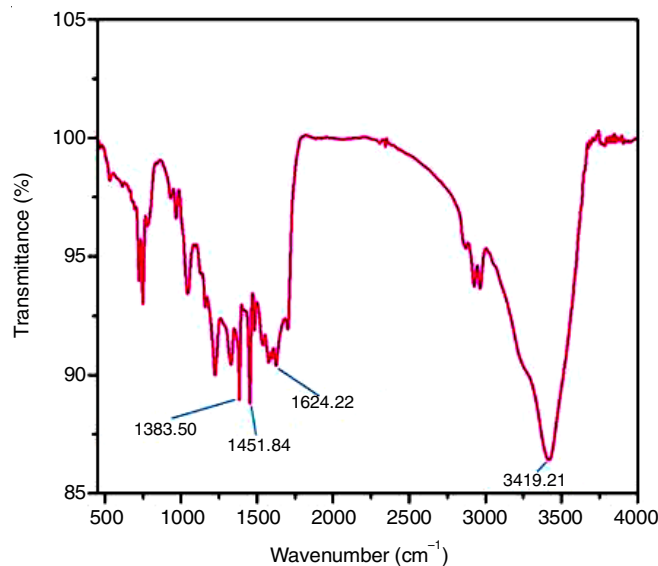

Fig. 7. FTIR spectrum of the synthesized neat copolymer

region, ZnO nanoparticles exhibit a broad peak pertaining to the hydroxyl groups [76]. While in the synthesized ZnO nanocomposite, a strong absorption observed at 3404.64 cm^{-1} and was attributed to the hydroxyl group associated with the polymer matrix. Shifting of this peak in the spectrum of modified ZnO nanocomposite (Py-NVK_ZnO) is suggestive that the hydroxyl group of ZnO interacts with the composite copolymer matrix. The absorption bands are observed at 2966.16, 1578.42, 1482.96, 1452.09, 1382.39 and 1326.97 cm^{-1} relate to the C-H asymmetric stretching for aromatic C-H group, asymmetric deformation of N-H and C=C, ring vibration of NVK moiety, stretching vibration of C-N, =CH$_2$ deformation of vinylidene group and C-H in plane deformation of vinylidene group, respectively. The FT-IR peaks identified in the synthesized ZnO nanocomposite are consistent with those described in the existing literature [70,78], while the formation of the ZnO nanocomposite was confirmed by the shifting of Py, NVK and ZnO nanoparticles peaks due to copolymerization and interaction of ZnO nanoparticles with copolymer and host monomers.
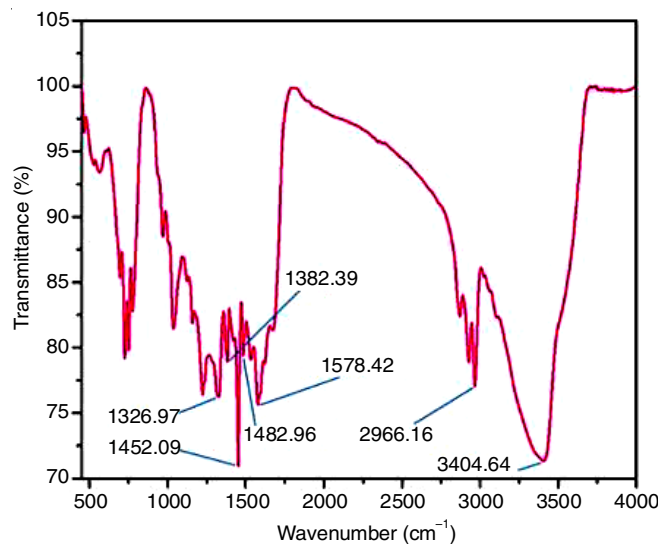

Fig. 8. FTIR spectrum of the synthesized ZnO nanocomposite

Conclusion

The neat copolymer (Py-NVK) and ZnO nanocomposite (Py-NVK_ZnO) was synthesized using the host monomers (Py and NVK) using $FeCl_3$ as initiator by the sol-gel reaction process. Effective synthesis of the neat copolymer and ZnO nanocomposite has been confirmed by FESEM, HRTEM, XRD and FTIR analyses. The FESEM and HRTEM images confirmed the morphology of synthesized neat copolymer and ZnO nanocomposite depicting the formation of spherical agglomerates. The XRD and FTIR analyses confirmed the formation of the neat copolymer and ZnO nanocomposite, compared with their host monomers, while the synthesized neat copolymer and ZnO nanocomposite has an amorphous structure with short range order.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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