



# Field emission enhancement of polypyrrole due to band bending induced tunnelling in polypyrrole-carbon nanotubes nanocomposite



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## ABSTRACT

Polypyrrole–multiwalled carbon nanotubes (PPy–MWCNT) nanocomposites with high field emission characteristics have been fabricated by a very simple and effective in situ chemical polymerization technique that bypasses the need of de-agglomerating the MWCNT. Based on structural characterization, we have proposed formation of a three tier structure of PPy–MWCNTs composite with granular PPy on the top. Field emission studies, explained on the basis of band bending at the PPy–MWCNT interface, show drastic increase of field enhancement factor ( $\sim 4664$ ) and low turn on field ( $1.7 \text{ V}/\mu\text{m}$ ), opening new possibilities of improvement of PPy/PPy–MWCNT composites.

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## 1. Introduction

Conducting polymers have attracted a lot of attention in the past decade. Due to their inherent properties like high electrical conductivity in doped states, easy synthesis, low material cost, high specific capacitance, and so on, they have found application in various electronic devices such as transistors, sensors and actuators, memory devices, photovoltaic devices, batteries and supercapacitors [1,2]. However conducting polymers (CP) also have certain drawbacks which seriously encumber their applications. They possess low mechanical strength and have to be doped to be electrically conducting, their electronic property depending on the extent of doping. One of the techniques to increase the mechanical strength but at the cost of conductivity is to form composites with other copolymers. Moreover, for supercapacitor applications, CP possess poor cycle life due to the volume change during doping and dedoping process, which lead to degradation of the polymer electrode during cycling [3]. As field emission devices, conducting polymer nanostructures give relatively high turn on field and low field enhancement factor [4–7]. These drawbacks can be overcome by forming composites with a mechanically strong and conducting material. In this respect, carbon nanotube (CNT) is a very viable option. They also possess other properties like high surface area, low mass density, chemical and mechanical stability,

which are all desirable for various electronic device application [8,9].

CNT–CP composites represent a new class of multifunctional advanced materials and as such have been the subject of active research in recent years [8,10,11]. However, in spite of a lot of work being done on CNT–CP composites, their synthesis still remains a challenge. The main obstacle for CNT–CP composite formation is that CNT tend to exist as bundles or aggregates due to their hydrophobic nature and strong Van der Waals interaction between them [10–13]. Therefore it is very difficult to isolate them so as to obtain uniform CNT–CP composite. Moreover weak CNT–polymer interactions result in poor interfacial adherence resulting in agglomeration of CP [14–16]. The polymer chain tends to form deposits of irregular nanoparticles or clusters instead of uniform coating on CNT surface.

The conventional processes of preparation of CNT–CP composite include methods such as solvent mixing, melt blending, electrochemical and in situ polymerization [10,17–19]. Of these different processes, in situ polymerization is very effective to significantly improve dispersion of CNT and interaction between CNT and polymer matrix. CNT are generally isolated using surface treatments such as functionalization, use of surfactants, organic solvents and/or sonication, mixed with monomers and then polymerized to obtain CNT–polymer composites [10–12,17,20]. However surface treatments can prove to be detrimental for electronic properties of CNT. For example, functionalization involves attachment of functional groups on CNT surface. This process leads to creation of  $sp^3$  hybridized carbon defects. Use of

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surfactants means physically coating the CNT by the surfactant which can thereby decrease the conductive property of CNT/CNT-polymer composite. Sonication treatment can also result in damage to the CNT walls [10,11,21,22]. Thus all these treatments can adversely affect the electrical properties of CNT and hence the overall conductivity of the composite.

Prior works done on CNT-CP composites have mainly been done by incorporating functionalised CNT into polymer matrix. In this work, we synthesized a layered polypyrrole(PPy)/PPy-CNT/CNT nanocomposite using a very simple technique that circumvents the need of surface treatment of multiwalled carbon nanotube (MWCNT). The simplicity of the synthesis process of these nanocomposites has been explored and justified from thermodynamic consideration. Structural and electronic characterisations show the formation of dense PPy-MWCNT composites with improved electronic properties. Significant improvement of field emission (FE) properties of PPy/MWCNT composites is observed and explained on the basis of tunnelling of charge carriers across the PPy-MWCNT interface due to band bending of the polymer under bias.

## 2. Experimental

Synthesis of PPy on MWCNT films were carried out using in situ chemical polymerization of pyrrole (Py) (Spectrochem) monomers. Pristine MWCNT have been synthesized in our home made chemical vapour deposition (CVD) setup on iron seeded silicon substrate using acetylene ( $C_2H_2$ ) gas at  $700^\circ C$  at a base pressure  $2 \times 10^2$  mbar. As synthesized MWCNT films were then dipped in Py for a given interval of time. Subsequently, the monomer was polymerised by drop casting 0.1 M ammonium persulphate (APS) (Merck, India) solution on to the substrate. Doping of some of the samples was achieved by adding Hydrochloric acid (35%) to APS solution before drop casting. For comparison, PPy (Cl doped) films were also synthesised on silicon substrate, which were made hydrophobic by dipping in 10% hydrofluoric acid solution for 3 min, by following the same procedure. The excess oxidant was then rinsed with excess of deionised water and alcohol and allowed to dry at room temperature. The films were characterised using X-ray diffraction (Rigaku ultima III X-ray diffractometer) of  $CuK\alpha$  radiation of wavelength  $\lambda = 1.54 \text{ \AA}$ , Field emission scanning electron microscopy (FESEM, Hitachi S-4800) and High resolution transmission electron microscopy (HRTEM) (JEOL-JEM 2100). The field emission properties of PPy-MWCNT films have been studied (using a setup designed indigenously in our laboratory) and compared with CNT film and PPy film (prepared in the same way). Details of synthesis condition are given in Table 1.

## 3. Results and discussion

### 3.1. XRD analysis

X-ray diffraction pattern of the PPy-MWCNT composite is shown in Fig. 1. The inset shows the X-ray diffraction pattern of the pristine MWCNT and PPy, synthesized separately, using the

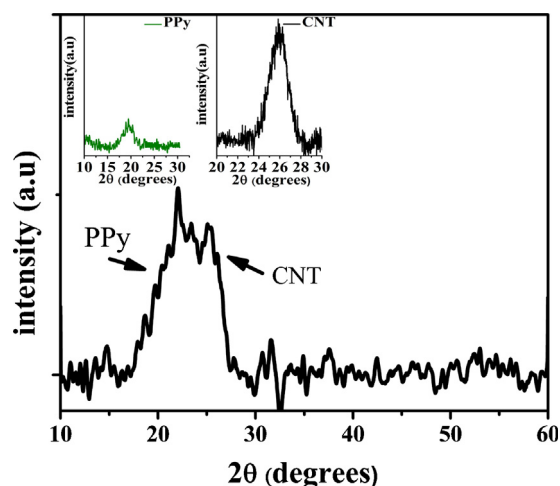


Fig. 1. XRD spectra of PPy-MWCNT composite [inset XRD pattern of MWCNT and PPy].

process mentioned in Section 2. The XRD signature of amorphous PPy is observed to be a broad peak around  $2\theta \sim 19^\circ$ , while MWCNT shows a relatively sharper peak around  $2\theta \sim 25.8^\circ$ . Similar reports of XRD signature of amorphous PPy and MWCNT are also reported in literature [18,23]. The XRD pattern of the composite on the other hand shows a wide peak between  $2\theta \sim 16^\circ$ – $28^\circ$ . Comparing the XRD pattern of the composite with the graphs shown in the insets, the signatures of both amorphous polypyrrole and MWCNT can be identified in the peak between  $2\theta \sim 16^\circ$ – $28^\circ$ . XRD pattern indicates that the amorphous nature of PPy is not changed due to the presence of MWCNT.

### 3.2. HRTEM study

HRTEM images of MWCNT and PPy-MWCNT nanocomposite are shown in Fig. 2a and b, respectively. The insets of the figures show higher magnification HRTEM images. PPy is seen to exist in two different morphologies (Fig. 2b), as a sheet like structure overlaying the nanotubes and also as coating on the MWCNT (inset of Fig. 2b), resulting in thicker nanotubes. The increase in thickness of the nanotubes is more clearly seen from the insets. The diameter of MWCNT is  $\sim 15$  nm while those of the PPy-MWCNT structure are  $\sim 30$  nm. PPy, therefore, are uniformly coated on the crystalline MWCNT to form a core shell structure, where PPy forms the outer shell and MWCNT form the inner core. The multiwalls of CNT are clearly seen in Fig. 2a, but are difficult to identify in Fig. 2b because of PPy coating.

### 3.3. FESEM study

FESEM image of MWCNT film and PPy-MWCNT composite synthesized on the MWCNT layer are shown in Fig. 3a and b, respectively. Instead of uniform coating of CNT with PPy, as reported in some articles [24], we observe a dense growth of PPy, having granular morphology, on MWCNT films. The average grain size is  $\sim 100$  nm.

The growth of PPy layer is, however, subject to synthesis conditions like dipping time and polymerization temperature. The FESEM images, shown in Fig. 4a–d compares the morphology of PPy-MWCNT and PPy films, synthesised under different conditions. As seen from the Fig. 4, though the morphology remains the same, the growth of PPy on MWCNT films increase when either the dipping time or polymerization temperature is increased. In the former case, it probably due to higher adsorption of Py monomers while in the latter case, polymerization rate increases.

Table 1

Deposition conditions of PPy-MWCNT and PPy films.

Sample name	Sample type	Dipping time (CNT film in monomer pyrrole) (s)	Polymerization temperature ( $^\circ C$ )
a	PPy(doped)-MWCNT	15	4
b	PPy-MWCNT	15	4
c	PPy-MWCNT	1	4
d	PPy-MWCNT	1	27
e	PPy	15	4
f	PPy	1	27

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