Surface Structure-Dependent Low Turn-On Electron Field Emission from Polypyrrole/Tin Oxide Hybrid Cathodes

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ABSTRACT: We present a new surface structure-dependent cold cathode material capable of sustaining high electron emission current suitable for next-generation low turn-on field-emission devices. The low turn-on electric field for electron emission in the cathode materials is critical, which facilitates the low-power room-temperature operation, a key factor required by the industrial sector. We demonstrate the facile synthesis of polypyrrole (PPy)/tin oxide (SnO2)-based core−shell hybrid cold cathode materials for large area applications. The technique used here is based on a simple and economical method of surfactant-mediated polymerization. The coupled investigation of X-ray diffraction along with electron microscopy reveals the formation of rutile phase SnO2 nanoparticles of size ∼15 nm. These SnO2 nanoparticles act as nucleation sites for the growth of PPy nanofibers, resulting in encapsulated SnO2 nanoparticles in the PPy amorphous matrix. The coupling of spherical-shaped core−shell structures of PPy/SnO2 resulted into the particle train-like nanostructured form of the hybrid material. These core−shell structures formed the local p−n junction between the n-type SnO2 (core) and p-type PPy (shell). The long chains of these p−n junctions in nanofibers result in the modification of the electronic band structure of PPy, leading to a reduction in the work function of the electrons. The significant surface structural modification in PPy/SnO2 causes a prominent reduction in the turn-on electric field for electron emission in PPy/SnO2 nanocomposite (∼1.5 V/µm) as compared to the pure PPy (∼3.3 V/µm) without significant loss in current density (∼1 mA/cm2). The mechanism of improved field-emission behavior and advantages of using such hybrid nanomaterials as compared to other composite nanomaterials have also been discussed in detail.

1. INTRODUCTION

In the recent times, we have witnessed a colossal interest in the research and development activity aimed at realization of the cold cathode emitters. The widely used traditional thermionic cathode emitters operate at very high temperature, leading to the high power consumption. To counter this problem, it would be desirable to develop the cathode emitter operating at room temperature. The cold cathode emitters found potential applications in microwave electronics, vacuum microelectronic devices, power switches, cathode ray tubes for bright lights, applications in microwave electronics, vacuum microelectronic devices, power switches, cathode ray tubes for bright lights, and so forth.1−7 The field-emission process is governed by a quantum tunneling through the cathode surface under the influence of applied electric field. It is well-established that the field-emission characteristics strongly depend on the surface geometry (i.e., the aspect ratio and the surface structure or the apex size and shape) and the spatial distribution of the emitters (i.e., alignment and their density). The nanomaterials with sharp geometrical features (i.e., grainy or sharp edges) provide high local field, resulting in better field emission and are considered as ideal candidates for such applications.8−12 Furthermore, one-dimensional structures are considered to be the perfect configurations for cathode emitters attributed to their concomitant properties such as improved aspect ratios, low work functions, linearity to the charge transportation leading to high conductivities, and high mechanical stabilities.15−17 As field-emission characteristics depend strongly on the surface structure, a variety of organic or inorganic materials in different structural forms are extensively investigated at nanoscale, including single/multiwalled carbon nanotubes (MWCNTs),8 silicon nanowires,9 GaS nanohorns,10 CdS nanowires11 and multipoles,12 TiO2 nanotip array,13 ZnS nanobelts,14 graphene sheets (GS),15 ZnO nanowires,16 nanonails,17 nanopencils,17 diamond films,18 and ultrananoc-
rystalline diamond (UNCD) decorated silicon nanowires for the advanced electron field emitters. These nanostructure forms have exhibited an excellent field-emission current density; however, most of these materials have limitations like high turn-on field because of their large electrical band gap, high self-degradation rate like in CNTs via oxidation, and so forth which have exhibited an excellent field-emission properties for electron-transporting materials.27,28 And the work function of the cathode emitters are the key parameters for electron-emission.27 The emission current density from any cathode surface can be determined by three rate-limiting processes described as follows: (i) availability of high concentration of free electrons in the emitting materials or injection of electrons from another source into the emitting material, which may be a back electrode or a substrate such as silicon or any dopant material in the interior of emitter, and the mechanism is the so-called injection-controlled emission process, (ii) transport of free electrons to the emitting surface of the emitter that primarily depends on the conductive islands (such as sp2-hybridized grains/clusters in carbon allotropes) or doping states, and the process is known to transport controlled electron emission, and (iii) final emission of electrons through the cathode–vacuum interface, which is defined as the front surface-controlled emission process and is strongly dependent on the surface structure of the emitters, which determines the probability of electron tunneling across the emitter–vacuum interface.50 Thus, according to Fowler–Nordheim (F–N) hypothesis, the surface structure (i.e., field-enhancement factor) and work function of the cathode emitters are the key parameters for electron-field emitters. However, the work function is an intrinsic characteristic of the given materials under study and may be invariable. On the other hand, the field-enhancement factor is defined as the ratio of the local field to the applied field and is dependent on the surface structure. The field-enhancement factor can be altered by varying parameters such as aspect ratio and tip diameter and synthesizing nanocomposites based on low work function materials such as SnO2 (4.3 eV).10,31 Pure SnO2-based nanomaterials are well-known for cathode materials, but the relatively high turn-on field and low current density limited their practical applicability for device fabrications. However, the hybrid nanostructural forms of SnO2 with an intrinsically conducting polymer (PPy) having an sp2-hybridized carbon structure could be a good alternative comprising the properties of both types of organic and inorganic nanomaterials. This combination can behave like a core–shell structure where SnO2 nanocrystalline acts as a core, placed at the interior of the structure while PPy acts as a shell structure, wrapped over the SnO2 nanoparticles. Thus, SnO2 may play the role of an electron source to inject the electrons into the PPy matrix while the PPy layer acts as a cathode surface for the tunneling of electrons to the vacuum. In the present study, we have prepared one-dimensional nanofibers of PPy and its nanocomposite (PPy/SnO2) with hexagonal SnO2 nanoparticles. The prepared samples are analyzed for the structural, morphology conformations and tested for the electron field emission under the simplified F–N model.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of SnO2 Nanoparticles. Hexagonal-shaped SnO2 nanoparticles were synthesized by a simple hydrothermal process. In this process, the salt solution of SnCl4·5H2O (50 mM) was prepared in 100 mL of methanol and refluxed at 150 °C for 2 h. The solution was continuously stirred and refluxed to avoid the loss of the solvent. It was followed by the addition of 30 mM oley amine as a capping agent and 1 M NH4 to increase the pH of the solution. A separately prepared solution of 50 mM KOH was added to it dropwise, and the reaction was further carried out at the same temperature for 2 h. After that, the solution was allowed to cool down naturally to room temperature, and SnO2 nanoparticles were collected by the filtration. The collected nanoparticles were then washed with a copious amount of water and dried at 80 °C. The synthesized SnO2 nanoparticles were further annealed at 300 °C for the removal of traces of the solvent and to improve the crystallinity of the nanoparticles. The following is the reaction mechanism of the synthesis of the SnO2 nanoparticles

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{Sn}^{4+} + 4\text{OH}^- \rightarrow \text{Sn(OH)}_4^{2-} \\
\text{Sn(OH)}_4^{2-} \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O}
\]
labeled as PPy/SnO2. A similar route has also been used for the synthesis of pure PPy nanofibers.

2.3. Sample Characterization. The morphology of the PPy/SnO2 hybrid nanomaterials was investigated by the scanning electron microscopy (SEM), using an LEO 440 electron microscope, whereas the crystallinity of the SnO2 nanoparticles was analyzed by high-resolution transmission electron microscopy (HRTEM), using an FEI Tecnai G2 F30 S-TWIN microscope. The structural investigation of the pure SnO2 nanoparticles and PPy/SnO2 hybrid nanostructures was done through X-ray diffraction, using a D8 DISCOVER (ASX-Bruker) instrument and an X-ray diffractometer employing Cu Kα radiation. The molecular structural transformation of PPy due to the incorporation of SnO2 nanoparticles in the amorphous polymeric matrix and the formation of PPy/SnO2 nanocomposite were further confirmed by Fourier transform infrared (FTIR) spectroscopy, using the PerkinElmer-RX1 spectrum. The field-emission measurements were carried out in a high vacuum (3 × 10⁻⁷ mbar) condition created by a high-efficiency turbo-molecular pump backed with the rotary pump. The electron emission current was recorded by a Keithley 2410 source measure unit in the two-electrode geometry at different applied voltages in a sandwich structure [indium tin oxide (ITO)/Teflon spacer/sample/silver] as shown in Figure 1. The ITO-coated glass was used as an anode, whereas a Teflon spacer (150 μm thickness) was used to produce the vacuum gap between the sample and the anode. The emission of the electron took place from the sample surface area of ~0.0708 cm² through a hole (dia. 3 mm) in the Teflon spacer used to produce vacuum gap. To scale up the reproducibility and stability of the samples, the applied field was cycled 15 times up to a current density of about 1 mA/cm². The turn-on field, which is defined as the applied electric field at the electron emission current density of ~1.7 × 10⁻⁷ A/cm², successively reduced in each cycle. Such successive reduction in the turn-on field with each cycle of the applied field is generally referred to the conditioning and very often for the cathode materials, used for the cleaning of the emitter surface.

3. RESULTS AND DISCUSSION

3.1. Surface Morphological Investigations. Figure 2a shows the TEM image of hexagonal-shaped SnO2 nanoparticles having a particle size of ~15 nm. The nanoparticles are highly crystalline, as exhibited by the clear lattice planes and the formation of PPy/SnO2 nanocomposite were further confirmed by Fourier transform infrared (FTIR) spectroscopy, using the PerkinElmer-RX1 spectrum. The field-emission measurements were carried out in a high vacuum (3 × 10⁻⁷ mbar) condition created by a high-efficiency turbo-molecular pump backed with the rotary pump. The electron emission current was recorded by a Keithley 2410 source measure unit in the two-electrode geometry at different applied voltages in a sandwich structure [indium tin oxide (ITO)/Teflon spacer/sample/silver] as shown in Figure 1. The ITO-coated glass was used as an anode, whereas a Teflon spacer (150 μm thickness) was used to produce the vacuum gap between the sample and the anode. The emission of the electron took place from the sample surface area of ~0.0708 cm² through a hole (dia. 3 mm) in the Teflon spacer used to produce vacuum gap. To scale up the reproducibility and stability of the samples, the applied field was cycled 15 times up to a current density of about 1 mA/cm². The turn-on field, which is defined as the applied electric field at the electron emission current density of ~1.7 × 10⁻⁷ A/cm², successively reduced in each cycle. Such successive reduction in the turn-on field with each cycle of the applied field is generally referred to the conditioning and very often for the cathode materials, used for the cleaning of the emitter surface.
SnO₂ nanocomposite consisting of long chains of core−shell structures in the form of particles’ nanotrain-like features. A single core−shell structure has a diameter of about ~150 nm; however, the diameter of the prepared nanostructures is slightly higher because of the side-by-side overlapping of core−shell structures. However, the presence of the granule structure with fine pores between side layers may provide a larger surface area for improved field-emission characteristics. The length of these particle trains is very large (5–6 μm) as compared to the pure PPy nanoclips, which is further increased because of the knot-like heads. This is because particle-like core−shell nanostructures are formed because of the wrapping of PPy chains (p-type) over the SnO₂ (n-type) nanoparticles. Thus, these elongated nanostructures with increased length are presumed to be the long chains of a large number of p−n junctions formed between the p-type PPy and n-type SnO₂. The presence of these nodule-like structures and the improved length significantly increase the electron-emitting surface area and surface roughness, that is, electron-emitting sites at the surface, which are backed with an electron source and SnO₂ (i.e., the surface roughness, that is, electron-emitting sites at the surface, oxygen vacancies present in SnO₂ nanoparticles) and may be responsible for good field emission.

The growth mechanism of core−shell structures (p−n junctions) in the surfactant-mediated approach used for the synthesis of PPy/SnO₂ hybrid nanostructures can be understood as follows (Figure 2d). CTAB is a cationic surfactant, whose molecule has a hydrophilic head and hydrophobic tail; thus, in the aqueous solution at the lower concentration, these molecules form a monolayer at the water/air interface, pointing the tails in the air. On increasing the concentration, the agglomeration of surfactant molecules starts in the bulk of the solution and takes the spherical shape throughout the solution as soon as the critical micelle concentration (0.89 mM for CTAB\(^{35}\)) is reached. With the addition of SnO₂ nanoparticles, they are trapped inside the cages of micelles and on the addition of APS solution, the self-assembling of surfactant micelles takes place in the form of a (CTA)\(_2\)S\(_2\)O\(_8\) crystal into fibular shapes embedded with SnO₂ nanoparticles. While the polymerization proceeds, these crystals are wrapped by uniform layers of PPy chains, resulting in the train-like nanostructural features. The synthesis of pure PPy was also done by the same method, following the similar mechanism of nanofiber formation without SnO₂ doping.

### 3.2. Structural and Chemical Bonding Analysis

Figure 3a illustrates the XRD patterns of SnO₂ nanoparticles and the PPy/SnO₂ nanocomposite. It is observed that the XRD pattern of SnO₂ nanoparticles comprises four broad peaks located at ~26, 31, 39, and 51° corresponding to (hkl) planes (110), (101), (200), and (211), respectively, and well-matched with the rutile phase of SnO₂ (JCPDS 41-1145).\(^{32,34,35}\) The observed peaks of SnO₂ are used to evaluate the crystallite size by the standard Scherrer’s formula and are found to be ~10–12 nm. The average crystallite size observed by XRD study is very close to the average particle size evaluated through the HRTEM study. The XRD pattern of the PPy/SnO₂ nanocomposite also contains peaks similar to those observed in pure SnO₂ nanoparticles, indicating the formation of the PPy/SnO₂ nanocomposite.

The chemical structure of pure PPy, SnO₂ nanoparticles, and their nanocomposites (PPy/SnO₂) has been analyzed through the FTIR spectroscopic studies (Figure 3b). The FTIR spectrum of SnO₂ consists of an intense broad band located at ~566 cm\(^{-1}\) with a satellite band observed around 648 cm\(^{-1}\), which are ascribed to Sn−O−Sn stretching vibration and O−Sn−O bending vibrations in SnO₂, respectively. Apart from these fundamental bands of SnO₂, some more bands are also observed at ~1678, 3054, and 3476 cm\(^{-1}\) because of the O−H group owing to the precursor materials and environmental exposure.\(^{36}\) While the FTIR spectrum of pure PPy consisting of an intense broad band at ~3422 cm\(^{-1}\) associated with the N−H stretching vibration of PPy, related with the bonding state of heteroatom (−N−) present in the pyrrole monomer, with hydrogen. The position and the intensity of this band are very crucial because a decrease in the intensity of this band is directly related with the deficiency of the hydrogen atom at the heteroatom and hence the change in the conducting state of PPy. The doublet present at ~2854 and 2922 cm\(^{-1}\) can be attributed to the C−H stretching vibration of methyl and methylene and generally arises because of the trace of organic precursor materials in the form of traces of surfactant molecules and so forth. In the mid-frequency region of the spectrum, two fundamental bands of PPy are present at ~1558 and 1456 cm\(^{-1}\), which are attributed to the asymmetric (C=C) and symmetric (C≡N) ring stretching vibrations, respectively. These bands are very crucial in understanding the conducting state of PPy and the order of conjugation (i.e., conjugation length). The intensity ratio of the symmetric (1456 cm\(^{-1}\)) to asymmetric (1558 cm\(^{-1}\)) bands is associated with the conjugation length, that is, the higher intensity ratio (I\(_{1456}/I_{1558}\)) means the higher conjugation and the high conducting state of PPy. Besides the fundamental bands of PPy, these bands arise because of the doping states of PPy are also present in both the PPy and PPy/SnO₂ samples at ~1314, 1188, 1050, 924, and 796 cm\(^{-1}\) and can be attributed to the C−N stretching.
because of the doping of SnO₂. The decrease in the intensity of layers associated with the O decreases significantly along with the presence of the band associated with the O–H group at ∼3120 cm⁻¹ and arises because of the doping of SnO₂. The decrease in the intensity of the N–H stretching vibration band can be attributed to the deficiency of the hydrogen atom at the heteroatom (–N–) in the presence of surface (on SnO₂ surface)-adsorbed oxygen ions (O²⁻ or O¹⁻). The deficiency of the hydrogen atom at the heteroatom can be ascribed to the transfer of one proton (H⁺) to the oxygen ion to form O–H, and a charge compensation process takes place. Such a charge compensation process can be understood via the chemical reactions as follows

\[ H^+ + O^-(\text{ads}) \leftrightarrow O-H \]  
(4)

\[ 2H^+ + O^2-(\text{ads}) \leftrightarrow 2(OH) \]  
(5)

\[ H^+ + O^3-(\text{ads}) \leftrightarrow (O-H)^- \]  
(6)

or

\[ \text{PPy}^+(p\text{-type}) + O^-\text{(ads)} \leftrightarrow [\text{PPy}−1H]^0 + O-H \]  
(7)

Apart from this, a doublet was observed at ∼622 and 682 cm⁻¹ in the PPy/SnO₂ nanocomposite (encircled with dots), which can be attributed to the p–n junction bands obtained by the overlapping of n-type SnO₂ nanoparticles by p-type PPy layers.

### 3.3. Field-Emission Properties of PPy and PPy/SnO₂ Hybrid Cathodes

The electron field-emission behavior of the pure PPy and PPy/SnO₂ hybrid samples is analyzed in terms of the simplified F–N relation of emission current density, and the applied electric field is given by

\[ J = \frac{A\beta^2E^2}{\Phi} \exp \left( -\frac{B\Phi^{3/2}}{\beta E} \right) \]  
(8)

where J is the emission current density, Φ is the work function of the emitter material which is ∼5.1 eV for PPy and ∼4.3 eV for SnO₂ nanoparticles, E is the strength of the electric applied field, and β is the field-enhancement factor which generally depends upon the geometry of the emitter, crystal structure, vacuum gaps, and spatial distribution of electron-emitting centers. A and B are the F–N constants given by

\[ A = \frac{\epsilon e^2}{8\pi\hbar^2} = 1.54 \times 10^{-6} \text{ A V}^{-2} \text{ eV and } B = \frac{8e}{3\hbar c}(2m_e)^{1/2} \approx 6.83 \times 10^5 \text{ eV}^{-3/2} \text{ V m}^{-1} \]

where \( \epsilon \), \( h \), and \( m_e \) are the elementary positive charge, Planck constant, and the electron mass, respectively. The field-emission current density \( J \) as a function of the applied electric field \( E \) is measured repeatedly (about 15 runs) on both the PPy and PPy/SnO₂ samples (Figure 4a,b), and it is observed that in the successive run, the turn-on field decreases from 4.1 to 3.3 V/μm in PPy nanofibers and from 2.0 to 1.5 V/μm in PPy/SnO₂ p–n junctions. This type of electronic roughing or preconditioning is an important step for the field emitter to neutralize the defective site and clean the cathode surface. Such electronic conditioning made the emitter surface clean which leads to the stable high emission current at low field. However, it is an interestingly striking feature of the prepared PPy nanofibers and the PPy/SnO₂ hybrid sample that the emission current density remains almost constant during all cycles. Moreover, such electronic conditioning of the samples determines the reusability of the sample for the same applied electric field. It has been observed that beyond the 10th run, the field-emission current and turn-on fields are not changed significantly, which indicates that the sample becomes stable against the electronic roughing/
conditioning and suggests the potential applicability for practical purposes. Moreover, it is observed that the decrease in the turn-on field is very small for the PPy/SnO₂ hybrid sample (∼0.4 V/μm) as compared to the pure PPy (∼0.8 V/μm), indicating the high stability of the PPy/SnO₂ sample in terms of both the turn-on field and the emission current. However, both samples are stable electron emitters for cold cathode devices.

After ensuring the stability of the samples, J–E characteristics of both samples have been recorded and plotted in Figure 4c as the comparative curves. It is revealed from Figure 4c that the turn-on field decreased from ∼3.3 V/μm in the PPy nanofibers to 1.5 V/μm in the PPy/SnO₂ hybrid at the same current density, which indicates that the p–n junctions of PPy/SnO₂ exhibit the same current density at a very low (at about one third) applied electric field. The turn-on field is defined as the electric field required for drawing the current from the cathode surface and observed that the turn-on field for both the PPy nanofibers and PPy/SnO₂ samples is comparable or less than the nanostructures of different materials used for field emission. For example, the turn-on field for the GaS nanohorns is 4.2 V/μm,[10] for the aligned CdS nanowires, it is 7.8 V/μm,[11] for the multipods, it is 7.2 V/μm,[12] for the TiO₂ nanopit array, it is 9.4 V/μm,[13] for the nanotube, it is 34 V/μm,[14] for the ZnS nanobelts, it is 3.8 V/μm,[15] for the ZnO nanowires, it is 5 V/μm,[16] for the nanonails, it is 7.9 V/μm,[17] and for the nanopenicils, it is 7.2 V/μm.[18] The turn-on field ∼1.3 V/μm for the PPy/SnO₂ p–n junctions is also less than the electric field observed in different carbon nanostructures such as UNCD (5.6 V/μm),[19] CNTs (2.3 V/μm),[20] UNCD/CNTs (4.9 V/μm),[21] CNT/ZnO films (1.3 and 2.5 V/μm),[22] UNCD-decorated silicon nanowires (3.7 V/μm),[23] GS (4.4 V/μm),[24] GS/CS (2.5 V/μm), MWCNTs/CS (3.2 V/μm),[25] and various other nanostructures of carbon.[26]–[29] The turn-on field of the prepared p–n junction in PPy is also less than or equal to the MWCNT/PPy nanocomposite (1.4 V/μm)[30] and PPy/tetrabutylammonium-hexafluorophosphate (PPy/TBAPF₆) nanowires (3.5 V/μm).[31] The electron density is strongly dependent upon the work function (Φ) and the field-enhancement factor (β), and the value of β can be obtained from the F–N plots of ln(J/E²) versus 1/E as shown in Figure 4d by considering that Φ is known. The straight lines between the ln(J/E²) and 1/E curves suggest that the electrons are emitted via the cold cathode emission process determined by the barrier tunneling and quantum mechanical processes.[32]–[35] The field-enhancement factors (β) have been evaluated for both samples from the slopes of F–N plots by using the relation

$$\beta = \frac{Bd^{3/2}}{\text{slope}}$$

where d is the thickness of spacer. The value of the field-enhancement factor has been calculated from the slope of F–N plots for both the pure and doped PPy samples and are found to be 2142.24 and 5665.45, respectively, which indicates that the PPy/SnO₂ p–n junctions have the higher field-enhancement factor as compared to the PPy and can be attributed to the emission of electrons from the sp²-hybridized conjugated structure of PPy assisted with SnO₂ doping and the emission directly from PPy via the higher local electric field. The value of β for PPy/SnO₂ p–n junctions is found to be greater than the reported values for MWCNT/PPy (5480),[36] PPy/TBAPF₆ nanowires (∼700),[37] and MWCNTs (1980).[38] The field emission is strongly determined by the geometric shape of the emitters because the geometric field-enhancement factor gives the major contribution in the total field-enhanced factor. In the case of the PPy/SnO₂ nanocomposite, the field-enhancement factor can be given by the product of three components of the field-enhancement factor such as the geometric factor (βgs), that is, the granule structures distributed throughout the one-dimensional feature of nanofibers responsible for the enhanced surface area and surface roughness, the sp²-hybridized conjugated carbon structure/clusters (βsp²), and the doping of n-type SnO₂ nanoparticles (βp) in the p-type polymer matrix responsible for the distribution of a large number of p–n junctions throughout the sample and expressed as

$$\beta = \beta_{gs} \beta_{sp²} \beta_p$$

This is because the parameter β is related with the local induced field and generally expressed in terms of the ratio of
local \((E_{\text{local}})\) to applied \((E_{\text{applied}})\) electric field.\(^{35}\) Thus, the higher value of \(\beta\) of PPy/SnO\(_2\) via the above-discussed mechanism suggests the generation of the high local field \((E_{\text{local}} = \beta E_{\text{applied}})\) at the lower applied electric field that is required for good field-emission property of the material and also confirms the lower value of the turn-on field for the PPy/SnO\(_2\) sample.

3.4. Mechanism of Electron Emission in PPy/SnO\(_2\) p–n Junctions. The observation of electron emission in these organic materials at the low turn-on field can be understood via the three types of mechanisms. First, the higher value of emission current at the low turn-on field in PPy/SnO\(_2\) over the pure PPy may be due to the injection of electrons from SnO\(_2\) crystals to PPy layer due to the band bending at the PPy/SnO\(_2\) interfaces. To explore the mechanism of the flow of electrons across the PPy/SnO\(_2\) p–n junctions, the energy-level diagram of PPy/SnO\(_2\) has been shown in Figure 5a. Figure 5a represents the energy-level diagrams of p-type and n-type materials that represent the location of the Fermi and vacuum levels. The formation of p–n junctions between the PPy and SnO\(_2\) modifies the band gap of PPy and reduces the work function of the electron that can be defined as the difference between the Fermi level \((E_F)\) and the vacuum energy level \((E_{\text{vac}})\) and having values 5.1 and 4.3 eV for PPy and SnO\(_2\), respectively. In the equilibrium condition of the PPy/SnO\(_2\) p–n junction, the Fermi levels of both the organic and inorganic materials are aligned (Figure 5b). This interfacial interaction between PPy and SnO\(_2\) promotes the tunneling of electrons across the PPy/SnO\(_2\) interface and emission through the PPy layers. The modification in the electronic structure of PPy causes a synergetic effect in the field emission. The mechanism of band bending in different interfaces such as CNT−dielectric material interface, CNT−diamond interface, CNT−aC interface, and other materials is available in the literature.\(^{6,7,58}\)

The second mechanism that may strongly contribute in the electron emission is the change in the work function and the potential barrier height due to the change in geometrical structure factors. The electron affinity (\(\chi\)) and the work function (\(\Phi\)) are also strongly dependent on the geometrical structure of the surface and can vary with the spatial distance on the surface. In the case of granular surfaces with patches as in the present case of PPy/SnO\(_2\), the values of these parameters change with the location on the surface because in the equilibrium, the Fermi level remains constant throughout the material, but the vacuum level can change with the location. On the other hand, for the smoother surface as in the case of pure PPy nanofibers, we can ignore the effect of the surface structure and image forces on the work function, but the work function depends on the position of the Fermi level with respect to the conduction band edge that can be affected by the doping. Moreover, in the case of smoother surfaces, the band bending takes place under the influence of the applied field for which the electron affinity may remain constant, but the work function may change because of the downward band bending in the case of the strong field and referred to as the operative work function. On the other hand, for the rough (granule) surfaces with surface states, the upward bending will take place and cause the change in the work function. Thus, the extent of bending and sign depends on the strength of the field and the presence of surface states which determines the value of the work function. Moreover, when the image forces are taken into consideration and the external field is present, because of the Schottky lowering or other related effects, the barrier height due to the electron at the Fermi level is less than the work function and defined as the apparent work function or reduced barrier height,\(^{38}\) and thus the electron emission takes place at the lower applied field.

Apart from the contribution of local p–n junctions in the band bending and surface structures on work function and barrier height for electron emission, field-emission characteristics of the present samples strongly depend on the surface morphology-arbitrated geometrical structure factor. The incorporation of hexagonal-shaped SnO\(_2\) nanoparticles with the six sharp edges results in the granule-like surface morphology of the prepared hybrid sample, where these granules act as an individual electron emitter. The sharp edges of SnO\(_2\) nanoparticles act as an electron source because of the high oxygen vacancies in SnO\(_2\), whereas the PPy layer over these crystals acts as a tunneling layer for electron transport.

The electron emission in PPy/SnO\(_2\) may be caused by the decrease in the work function of PPy nanofibers as discussed previously because of the incorporation of SnO\(_2\) nanoparticles and the change in the surface structure of the sample. It is believed here that the surface morphology of the emitter made profound impact on the reduction of the turn-on fields as compared to the work function due to the major contribution of geometrical field-enhancement factor in the induced field. It is well-reported in the literature that the whisker-like tips emit at significant lower field as compared to the planar morphology of the same material.\(^{56,59}\) Moreover, materials with the high surface-to-volume ratios and/or the geometrical/morphological disorderness (rough surfaces) will experience high local electric field because such surfaces have high field-enhancement factor \(\beta\), which determines the strength of emission current occurring from electron tunneling through the emitter−vacuum potential barrier. The relatively high value of \(\beta\) parameter in the present case is responsible for significant electron emission current at the low turn-on field in these samples. The development of the high local field at the interface of dielectric/semiconducting (SnO\(_2\)) and highly conducting sp\(^2\)-hybridized PPy can be understood via the mechanism demonstrated in Figure 5d because SnO\(_2\) crystals are thoroughly distributed into the sp\(^2\)-hybridized polymer matrix, that is, the conducting sp\(^2\)-bonded grain boundaries surround the dielectric crystalline grains and under the action of external applied field, a strong local field will develop around the SnO\(_2\) crystal at the PPy/SnO\(_2\) interface. This results in the high value of the field-enhancement factor \((\beta)\) and hence in the low-threshold field-emission behavior of the PPy/SnO\(_2\) p–n junctions. It is reported in the literature that the presence of sp\(^2\) clusters (size as well as the density) may play an important role in determining the field-emission properties of the carbon films. It is believed that the rapid hopping or exchange of electrons between the sp\(^2\)-hybridized clusters results in improved field emission. The high sp\(^3\) content results in the overlapping of the clusters, which plausibly improves the effective connectivity between the clusters and hence enhanced electron delocalization or hopping between the clusters.\(^{55,56}\)

Thus, the conjugated structure of PPy may be one of the reasons for high emission current at low field in these samples. Under the influence of the external field, the electrons are extracted from the surface of the sample, and replenishment of the emitted electron of the surface layer is fulfilled because of the good conductivity between the clusters. The electron emission in such sp\(^3\)-hybridized samples can be expressed as a “front face”-type emission, which exhibit a lower threshold field.\(^{55,60,61}\) The size of the cluster can be a crucial parameter for field emission; the pure PPy sample may have
small-sized clusters separated by a larger gap, whereas SnO2 doping may act as a catalyst which results in the clustering of the sp²-hybridized carbon and hence lower turn-on and threshold voltage in the PPy/SnO2 nanocomposite. The schematic representation of the field-emission model for such materials is depicted in Figure 5d, in which dielectric regions (SnO2) or crystals are surrounded by sp²-hybridized conducting (PPy) grain boundaries. These conducting grain boundaries provided the easy pathway for the transport of electrons and hence the improved field-emission properties. Thus, the field emission of these samples can be explained in terms of size and number of the sp³ clusters lying at or near the Fermi level, and the size of clusters must be large enough for the effective connectivity between them. Ilie et al.61 demonstrated the effect of clusters’ size on the field threshold of different amorphous carbon films and suggested that the optimal size of the clusters is found to be 1.5 to 2 nm for emission depending upon the type of the film. In summary, the enhanced field emission in these samples can be governed by the band-bending process under the influence of surface geometrical structures and applied field, change in the work function of the material due to the surface states, and the improved field-enhancement factor via the change in the surface morphology due to the incorporation of SnO2 crystals. A continuous supply of electrons from the SnO2 to the sp²-hybridized conjugated structure of PPy provides an easy pathway for the tunneling of electron and hence electron emission through the vacuum gap.

4. CONCLUSIONS

Hexagonal-shaped SnO2 nanoparticles were synthesized by the surfactant-directed hydrothermal process, whereas the pure PPy and PPy/SnO2 nanocomposite have been prepared by the surfactant-assisted chemical oxidation polymerization method. The SEM studies reveal that pure PPy has nanodip-like nanofibers with a diameter of about 72 nm that changes into a nanoribbon-like morphology of PPy nanoparticles in the SnO2-doped PPy (PPy/SnO2) sample. The change in surface morphology in the PPy/SnO2 nanocomposite may be due to the wrapping of PPy chains over the SnO2 crystals. The presence of SnO2 nanoparticles may play an important role in the nucleation of the PPy, resulting in the formation of particle train-like nanostructured form of the hybrid material, encapsulated with SnO2 nanoparticles in the PPy amorphous matrix. The coupling of spherical-shaped core–shell structures of PPy/SnO2 resulted in the localized p–n junctions between the n-type SnO2 (cores) and p-type PPy (shells). The presence of chains of these p–n junctions in nanofibers causes a reduction in the work function for electrons via the modification of the electronic band structure of PPy. The significant surface structural modification in PPy/SnO2 leads to a prominent reduction in the turn-on electric field for electron emission in the PPy/SnO2 nanocomposite (~1.5 V/µm) as compared to the pure PPy (~3.3 V/µm) without a significant loss in current density (~1 mA/cm²).

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