A facile synthesis of a novel optoelectric material: a nanocomposite of SWCNT/ZnO nanostructures embedded in sulfonated polyaniline

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Functionalized single-walled carbon nanotubes (f-SWCNTs) hybridized with freshly prepared zinc oxide (ZnO) nanocrystals have been found to be good luminescent material with tuned emission properties. A three-phase nanocomposite of sulfonated polyaniline embedded with such SWCNT/ZnO nanostructures has been prepared by a simple solution mixing chemical process and characterized by using high-resolution transmission electron microscopy, X-ray diffractometry, Raman spectroscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis. The study of UV-visible absorption and photoluminescence spectroscopies reveal that the ternary polymer nanocomposite is a luminescent material with enhanced emission intensity. Also an increase in DC conductivity indicates that the nanocomposite is also a good conductive material, satisfying Mott’s variable range hopping model for a two-dimensional conduction. Such a three-phase nanocomposite may find extensive application in dye-sensitized solar cells, sensors, and supercapacitors.

Keywords: SPANI; SWCNT/ZnO hybrid; polymer nanocomposite

1. Introduction

Polyaniline (PANI) is the most studied conducting polymer in recent years due to its numerous potential applications. Carbon nanotubes (CNTs) possess remarkable physical properties and have been extensively used as reinforcing fibers in PANI matrix to improve the characteristic properties of the polymer. However, a major drawback of PANI is its insolvency in water and common organic solvents. Water solubility is essential for many electrical applications. Sulfonation is one of the common methods to improve the solubility and processability of PANI in water. The prepared sulfonated PANI (SPANI) becomes water-soluble at all pH values. The various copolymers of PANI nanoparticles with sulfonic acid (−SO₃H) groups have been synthesized [1–5]. Such polymeric materials possess many interesting features such as sensing [1] and toxic ion removal [2–4] characteristics. However, the presence of the strong electron-withdrawing sulfonic group significantly reduces the conductivity of SPANI compared to that of pure PANI, limiting its electrical applications. Therefore, an improvement in the electrical conductivity of the water-soluble SPANI is very much necessary. Researchers have combined CNTs with PANI [6–10] and SPANI [11,12] to form composites in which the idea was to exploit

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excellent electrical properties of CNTs to increase the conductivity of the nanocomposite thus produced. The PANI/CNT composite has improved electrical, optical, and thermal properties. It finds application in biosensors [9], supercapacitors [13], metal–semiconductor devices [14], and actuators [15].

Zinc oxide (ZnO) is one of the hardest materials in the II–VI semiconductor family and it does not suffer from any dislocation degradation [16]. It is a wide band gap compound semiconductor possessing strong luminescence properties and has various applications as a luminescent material [17–19]. Kondawar et al. [20] reinforced ZnO nanoparticles in PANI matrix and measured the electrical conductivity of the composite. They observed higher conductivity for the composite when the PANI–ZnO ratio was 1:2, compared with other ratios. A polaron band was observed in the UV-visible spectra of PANI/ZnO nanocomposite owing to ZnO nanostructures [21]. Dhingra et al. [22] prepared PANI/ZnO composite by direct solid-state mixing of doped PANI powder and ZnO nanoparticles and observed an enhancement in the UV emission for the obtained nanocomposite. ZnO has also been combined with CNTs by different physical as well as chemical methods to obtain CNT/ZnO hybrids [23–26]. Paul et al. [25] synthesized the single-walled carbon nanotubes (SWCNT)/ZnO nanohybrid by simple wet chemical method and investigated its photoluminescence (PL) characteristics.

While there are published reports on CNT-based PANI or SPANI composites [6–15], ZnO-based PANI composites [20–22], and CNT/ZnO hybrids [23–25]; to the best of our knowledge, there is hardly any published work till date on ternary polymer composites containing SPANI, SWCNT, and ZnO nanoparticles. We report here a simple chemical synthesis of polymer nanocomposite containing SPANI and SWCNT/ZnO nanostructures by a solution mixing process. The SPANI was prepared by sulfonation of emeraldine salt of PANI through treatment with chlorosulfonic acid in an inert solvent. The SWCNT/ZnO nanohybrid was prepared by a simple wet chemical process. The synthesized SPANI/SWCNT/ZnO nanocomposite is a promising optical as well as conducting material and may find applications in sensors, optoelectronics, display devices, and supercapacitors.

A major area of application of polymer/CNT composites is in photovoltaic cells, particularly as counter electrodes in dye-sensitized solar cells [27–30]. In organic solar cells, CNTs have been used as electron acceptors in the photoactive layer, and the hybrid nanostructure of SWCNT/ZnO could be a better material for the purpose, in conjunction with SPANI.

2. Materials and methods

2.1. Materials

The SWCNTs used in our work were supplied by Chengdu Organic Chemicals Co. Ltd, China with average diameter, length, and purity, as stated by the manufacturer being 1–2 nm, 1–3 µm, and 95 wt.%, respectively. Aniline, 1,2-dichloroethane (DCE) and ammonium persulfate were supplied by Merck Specialties Pvt. Ltd., Mumbai. The chlorosulfonic acid was supplied by LOBA Chemie Pvt. Ltd., Mumbai. Except SWCNTs, all other chemicals were used as received without further purification.

2.2. Purification and functionalization of SWCNTs

The as-received SWCNTs were purified by heating in a muffle furnace at 350°C in air for 6 h followed by soaking and stirring in 6 M HCl for 12 h. The acid-treated SWCNTs were
filtered using vacuum filtration system (Millipore, pore size ~ 0.22 µm) and washed thoroughly with deionized water. The purified SWCNTs were further treated in a mixture of concentrated HNO3/H2SO4 in 1:3 volume proportion for 4 h followed by washing with dilute NaOH aqueous solution and filtration with Millipore filtration apparatus until the pH became neutral, thereby attaching carboxylic acid (-COOH) groups to obtain the functionalized single-walled carbon nanotubes (f-SWCNT).

2.3. Synthesis of SWCNT/ZnO hybrid nanostructures
We mixed 0.779 gm potassium hydroxide (KOH) pellets in 60 ml of deionized water and ultrasonicated using 250 W Piezo-U-Sonic ultrasonic apparatus at 50°C for 30 min. This was followed by mixing of 0.8475 gm of zinc nitrate hexahydrate in 40 ml of deionized water and subsequent stirring. Subsequently, we mixed 0.358 gm of f-SWCNTs in the zinc nitrate solution and the solution was stirred for 2 h at room temperature in magnetic stirrer (REMI 2 MLH). The KOH solution was added dropwise to this solution till the pH became 7. The grey viscous precipitate was filtered using Whatman filter paper followed by drying under IR lamp to obtain SWCNT/ZnO hybrid nanostructures.

2.4. Synthesis of sulfonated polyaniline (SPANI)
We mixed 0.2 M aniline hydrochloride and 0.25 M ammonium persulfate solutions in equal volumes and left overnight for polymerization to take place. The salt precipitate (PANI) was collected by filtration using a Whatman filter paper. It was then mixed with 1,2-DCE and heated to 80°C under stirring using the magnetic stirrer. Chlorosulfonic acid diluted with DCE was added dropwise to the reaction mixture and stirred at 80°C for 1 h. The semi-solid precipitate of SPANI obtained by filtration was then mixed with 400 ml of deionized water and heated to 60°C and stirred for 2 h to promote hydrolysis. The solution was further diluted with deionized water and filtered through a cellulose membrane using a vacuum filtration system (Millipore). The sample of SPANI collected over the filter membrane was dried in air at room temperature.

2.5. Synthesis of SPANI/SWCNT and SPANI/SWCNT/ZnO composites
Aqueous dispersion of SWCNTs was prepared by sonication in the ultrasonicator. The dispersion was mixed with SPANI aqueous solution with stirring at 60ºC for 3 h. The resulting solution was cooled and filtered using vacuum filtration system (Millipore). The sample collected by filtration was dried in air at room temperature to get SPANI/SWCNT composite with 6 wt.% of SWCNTs. The whole process of solution mixing was repeated with SWCNT/ZnO nanohybrids in place of SWCNTs, to obtain SPANI/SWCNT/ZnO three-phase nanocomposite. We added 0.045 gm of SWCNT/ZnO nanohybrid into deionized water followed by mixing with SPANI solution to obtain the desired nanocomposite. The SPANI/SWCNT/ZnO nanocomposite contains 15 wt.% of SWCNT/ZnO nanohybrids. The weight percentage of SWCNTs and SWCNT/ZnO nanohybrids in the respective composites were estimated by weighing the composite powder samples obtained after drying.
2.6. Characterization of the samples

The micrographs of the sample were obtained using high-resolution transmission electron microscope (HRTEM model JEOL JEM-2010; operating acceleration voltage 200 kV) as well as field-emission scanning electron microscope (FESEM model Zeiss Sigma VP, operating accelerating voltage 5 kV). The X-ray diffraclorometry (XRD) patterns were obtained using Philips PANalytical X-Pert Pro diffractometer. The molecular structures of the samples were characterized by a Perkin–Elmer Spectrum RX I Fourier transform infrared (FTIR) Spectrometer. The laser source used in the spectrometer was a He–Ne laser (633 nm). Raman spectroscopy was performed using EZ-Raman – M field portable Raman analyzer (Enwave Optronics, Inc.). A diode laser of wavelength 785 nm was used as excitation source. The thermogravimetric analysis (TGA) was carried out with PerkinElmer Pyris 1 TGA thermogravimetric analyzer at the heating rate of 10°C/min in nitrogen atmosphere. The optical absorbance spectra were recorded using a HITACHI U-3010 UV-visible absorption spectrophotometer. PL spectra of the samples were acquired using a PerkinElmer LS 55 Fluorescence spectrophotometer. The electrical conductivity of the samples was measured by a Four-Probe set-up (DFP-02, Scientific Equipment).

3. Results and discussions

3.1. HRTEM and FESEM microscopy

The HRTEM micrograph of SPANI/SWCNT/ZnO nanocomposite is shown in Figure 1 and its FESEM images with energy dispersive X-ray analysis (EDAX) are shown in Figure 2. We observe that SWCNT bundles are decorated with ZnO nanoparticles and are also coated by SPANI to form SPANI/SWCNT/ZnO ternary composite. The average size of the ZnO nanoparticles is found to be 3–5 nm by direct measurement in the HRTEM micrograph. The presence of ZnO in the composite is confirmed by EDAX analysis. The ‘carbon’ comes from the polymer and SWCNT, while ‘sulfur’ comes from sulfonation of the polymer. ‘Silicon’ is present as the sample was put on a silicon substrate.

3.2. XRD study

The structural characteristics of SPANI, SWCNT, SPANI/SWCNT binary composite, SWCNT/ZnO hybrid and SPANI/SWCNT/ZnO ternary composite have been analyzed by X-ray diffractograms shown in Figure 3(a) and (b). In the XRD pattern of SPANI, there are three prominent humps at 2θ = 25°, 43.5°, and 51°. No crystalline peak of SPANI was observed as SPANI is amorphous. In SWCNT, the peaks are at 26°, 42.5°, 44°, 51°, and 53.5° and these correspond to (002), (100), (101), (102), and (004) reflections of the graphitic planes of the nanotubes, respectively (JCPDS card no. 75-1621). The pattern of SPANI/SWCNT composite is dominated by the features of SWCNTs. The peaks for SWCNT/ZnO hybrid as well as SPANI/SWCNT/ZnO composite are obtained at the positions which correspond to (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of hexagonal ZnO crystallites (JCPDS card no. 80-0075) as well as (002), (100), (101), (102), and (004) reflections of the graphitic planes of SWCNTs [25]. However, the sharp peaks of ZnO nanocrystallites are suppressed in the diffractogram of the ternary nanocomposite.
3.3. FTIR Spectra

In FTIR spectra, in Figure 4, the stretches at different points indicate the absorption bands. The stretch near 3450 cm\(^{-1}\) indicates O–H stretching vibration arising from the absorption of water by KBr used for analysis. The spectrum of pristine SWCNT has stretches near 1600 cm\(^{-1}\) due to C = O vibration formed due to acid treatment. In SWCNT/ZnO hybrid, the stretch at 460 cm\(^{-1}\) arises due to Zn–O vibration. SPANI shows the characteristic
stretches at 1560 cm$^{-1}$, 1480 cm$^{-1}$, 1300 cm$^{-1}$, and 1140 cm$^{-1}$. The stretches at 1560 cm$^{-1}$ and 1480 cm$^{-1}$ arise due to the stretching vibrations of quinoid ring (–N = quinoid = N–) and the benzenoid ring (–N–benzenoid-N–), respectively. The stretches at 1300 cm$^{-1}$ and 1140 cm$^{-1}$ are due to C–N stretching and C = N stretching, respectively. The prominent stretch at 1140 cm$^{-1}$ represents the characteristic stretch of conductivity of SPANI and it measures the degree of delocalization of electrons [31]. The FTIR spectra of SPANI/SWCNT and SPANI/SWCNT/ZnO composites almost match with that of SPANI, which indicates good coating of SWCNTs and SWCNT/ZnO hybrid with SPANI. But an increase in the characteristic conductivity stretch, i.e., C = N stretching intensity is observed for SPANI/SWCNT composite and it further increases for SPANI/SWCNT/ZnO composite.

Figure 3. (a) XRD patterns of SWCNT, SPANI, and SPANI/SWCNT composite. (b) XRD patterns of SWCNT/ZnO hybrid and SPANI/SWCNT/ZnO composite captioned C (CNT) and Z (ZnO).

Figure 4. FTIR spectra of SWCNT, SWCNT/ZnO hybrid, SPANI, SPANI/SWCNT composite, and SPANI/SWCNT/ZnO composite.
ZnO composite. This indicates gradual enhancement in the delocalization of electrons due to charge transfer between SPANI and SWCNTs or hybrids. This is also supported by enhanced electrical conductivity of the composites. We have not observed any shift in the stretches of the polymer on reinforcing nanotubes or hybrids, so no conclusions on chemical bonding between the components can be drawn on this basis. Earlier, some researchers reported an interaction between the nanotubes and the polymer from the shifts in FTIR spectra [8], while some reported no significant interaction between them [10].

3.4. Raman spectra

The Figure 5 shows the Raman spectra of SWCNT, SWCNT/ZnO hybrid, and SPANI/SWCNT/ZnO composite. The Raman spectrum of SWCNTs shows the normal characteristic peaks, the G-band at 1589 cm\(^{-1}\), the D-band at 1314 cm\(^{-1}\), and the Radial Breathing Mode (RBM) band at 265 cm\(^{-1}\). The G-band originates from in-plane vibrations of the graphitic wall and the D-band originates from defects in the graphitic structure. The position of G-band of pristine SWCNT is red shifted from 1589 to 1579 cm\(^{-1}\) on decorating ZnO nanoparticles, which indicates charge transfer from ZnO to SWCNTs [25]. Further the I\(_D\)/I\(_G\) factor decreases on decorating SWCNT with the ZnO nanoparticles, which indicates bonding of ZnO nanoparticles with SWCNT surfaces and transfer of charge. For pristine SWCNT, the ratio between the intensity of D-band and that of G-band i.e., I\(_D\)/I\(_G\) is 0.51, while for SWCNT/ZnO hybrid, it has been found to be 0.47. After coating of the SWCNT/ZnO hybrid with SPANI, the spectrum of the polymer dominates. For SPANI/SWCNT/ZnO, the peak at 1617 cm\(^{-1}\) arises from C–C stretching of the benzenoid ring and the peak at 1516 cm\(^{-1}\) comes from C=N stretching of the quinonoid ring. The peak at 1350 cm\(^{-1}\) arises from the C–N\(^{+}\) stretching and that of 1185 cm\(^{-1}\) arises from C–H bending of the quinoid/benzenoid ring. This observation indicates that a good coating of the hybrid nanostructure has been achieved. This is also supported by images of HRTEM and FESEM. No chemical interaction between the polymer and the nanotubes could be proved on the basis of Raman spectra [8].

![Figure 5. Raman spectra of SWCNT, SWCNT/ZnO hybrid, and SPANI/SWCNT/ZnO composite.](image-url)
3.5. Thermogravimetric analysis

TGA was done to investigate the thermal stability of the samples. The Figure 6 shows the TGA thermograms of SWCNT, SPANI, SPANI/SWCNT composite, and SPANI/SWCNT/ZnO composite. The SWCNT has a higher thermal stability than other samples and it shows no appreciable mass loss up to about 550°C. The thermograms of SPANI, SPANI/SWCNT, and SPANI/SWCNT/ZnO composites are almost similar. However, the mass loss for SPANI/SWCNT/ZnO composite is slightly less than that of SPANI/SWCNT till 550°C, which indicates higher thermal stability for SPANI/SWCNT/ZnO composite in this temperature region.

3.6. UV-visible absorbance spectra

The UV-visible absorption spectra of SPANI, SPANI/SWCNT, and SPANI/SWCNT/ZnO are compared and shown in Figure 7. The spectrum of SPANI consists of humps at 360 nm corresponding to π–π* transition as well as at 445 nm and 750 nm corresponding to polaron transitions. For SPANI/SWCNT composite, a red shift of π–π* transition from 360 to 365 nm and polaron transition from 445 to 450 nm is observed. A further red shift in these transitions is observed in the spectrum of SPANI/SWCNT/ZnO composite, where we observe transition bands with peak emissions at 370 nm, 455 nm, and 750 nm. An additional peak at 340 nm is also observed for this composite, which is the characteristic absorption peak of ZnO nanoparticles.

Calculation of optical band gap:

The optical band gap $E_g$ is related to the absorption coefficient $\alpha$ by the relation

$$\alpha = \frac{B(h\nu - E_g)^{1/2}}{h\nu}$$  \hspace{1cm} (1)
where \( B \) is the absorption constant for a direct transition. We have plotted \((\alpha h \nu)^2\) versus \(h \nu\) for SPANI, SPANI/SWCNT, and SPANI/SWCNT/ZnO in Figure 8 and extrapolated the linear portion of each to \(\alpha = 0\) value and obtained the corresponding band gaps. The optical band gap of pure SPANI and SPANI/SWCNT composite was estimated to be 3.75 eV and 3.6 eV, respectively. For SPANI/SWCNT/ZnO nanocomposite, there is a further decrease in the band gap energy, the value being 3.5 eV. We observe that the
decrease in band gap is more when the polymer is reinforced with SWCNT/ZnO nanohybrid rather with SWCNTs, the direct band gap of ZnO nanoparticles being 3.3 eV. These observations indicate creation of new exciton energy levels below the regular band edge due to charge transfer from ZnO to SWCNT, and subsequently from SWCNT to SPANI.

### 3.7. Photoluminescence spectra

Figure 9 shows the PL spectra of SPANI/SWCNT/ZnO nanocomposite obtained at different excitation wavelengths from 220 nm to 300 nm. We obtained emission in the UV-visible region with maxima at 365 nm, 380 nm, and 385 nm for excitation wavelengths 220 nm, 240 nm, and 300 nm, respectively. We observed a red shift in the emission maxima with increase in excitation wavelength from 220 to 300 nm. When SPANI/SWCNT/ZnO composite is excited by radiation of wavelengths 220–300 nm, the higher energy photons of smaller wavelength cause emission with enhanced intensity.

### 3.8. Electrical conductivity

The Figure 10 shows the DC electrical conductivity of SPANI and the two composites (SPANI/SWCNT and SPANI/SWCNT/ZnO) at temperatures ranging from 317 to 353 K. We observe an increase in the conductivity with increase in temperature for all the samples, thus showing semiconductor like behavior. The addition of SWCNTs or SWCNT/ZnO hybrids to SPANI increases the conductivity of the polymer. The SPANI has conductivity of 0.042 S/m at 323 K, whereas the SPANI/SWCNT and SPANI/SWCNT/ZnO composite samples show the conductivity values of 0.23 S/m and 0.88 S/m, respectively, at that temperature. The value for SPANI/SWCNT/ZnO nanocomposite is 20.8 times and 3.7 times higher than SPANI and SPANI/SWCNT composite, respectively. At 353 K, the conductivity values for SPANI, SPANI/SWCNT and SPANI/SWCNT/ZnO samples are 0.082 S/m, 0.58 S/m, and 1.54 S/m, respectively. For the
sample SPANI/SWCNT/ZnO, the value increases 18.7 times compared to SPANI and 2.6 times compared to SPANI/SWCNT composite.

The Mott’s variable range hopping (VRH) model is suitable for explaining the temperature dependence of conductivity. The variation of conductivity as per this theory is given by the relation

$$\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^\gamma$$

where $\gamma = 1/(1 + d)$, where $d = 1$, 2, and 3 for one-, two, and three-dimensional conduction, respectively, and $\sigma_0$ is the conductivity when $T$ tends to infinity. $T_0$ is the characteristic Mott temperature, which depends on the electronic structure and the energy distribution of the localized states as follows

$$T_0 = \frac{16}{k_B N(E_F) L_{loc}^3}$$

where $k_B$ is Boltzmann constant, $N(E_F)$ is the density of states at the Fermi level, and $L_{loc}$ is the localization length.

We find that the log of DC conductivity of SPANI/SWCNT/ZnO composite sample satisfies Mott’s VRH model for $\gamma = 1/3$, indicating a two-dimensional conduction, as shown in Figure 11.

We obtained the values of $T_0$ for the three samples (SPANI, SPANI/SWCNT composite, and SPANI/SWCNT/ZnO composite) from the slopes of the linear variation of log $\sigma$ with $T^{-1/3}$. The estimated values of $T_0$ were 180,362 K, 926,859 K, and 112,329 K for SPANI, SPANI/SWCNT composite, and SPANI/SWCNT/ZnO composite, respectively. We see that $T_0$ for SPANI/SWCNT/ZnO composite is much lower than that for other samples.
4. Conclusions

We reported the synthesis of a novel luminescent and conductive material containing SPANI and SWCNT/ZnO hybrid nanostructures by a simple chemical process. A good coating of the hybrid by the polymer is observed, but a chemical bonding between them is not confirmed. Characterization established the desired nanostructure of the composite. The optical band gap energy of 3.75 eV for pure SPANI was found to decrease to 3.6 eV for the SPANI/SWCNT two-phase composite, which was further reduced to 3.5 eV for the SPANI/SWCNT/ZnO three-phase composite. This was supported by electrical conductivity measurement. The SPANI/SWCNT/ZnO nanocomposite showed strong absorbance peaks in the UV-visible region, including the characteristic peak of ZnO nanocrystals at 340 nm. The PL study showed a broad emission range in the UV-visible region between 340 and 420 nm. Such a ternary polymer nanocomposite may find application as a tailored conducting luminescent material in different electro-optical and energy devices, particularly as a photovoltaic material in dye-sensitized solar cells.

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