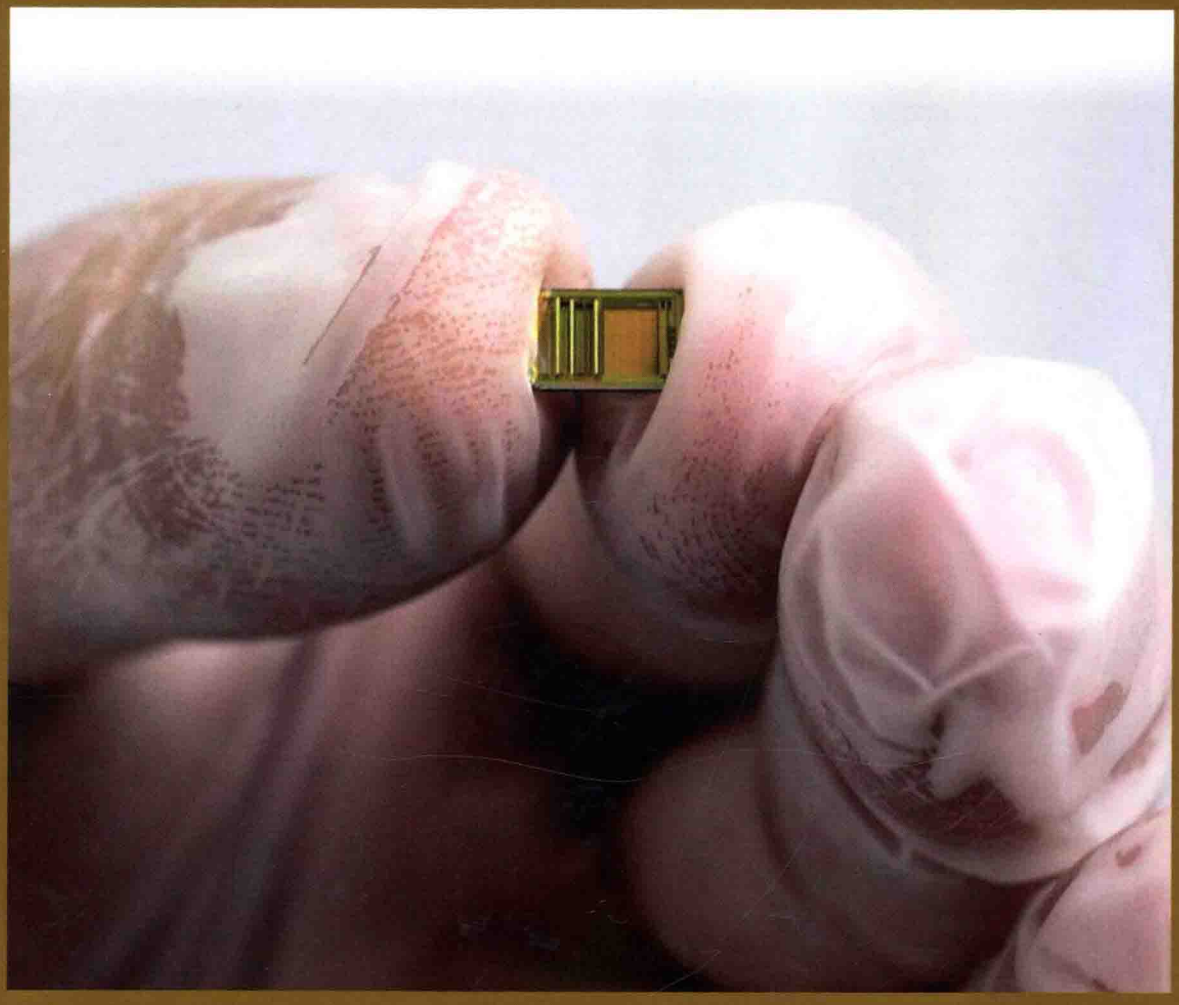
Smart Nanomaterials
Synthesis, Properties and Applications

Rich Falcon



Smart Nanomaterials: Synthesis, Properties and Applications

About the Book

Comprehensive insights into the emerging field of smart nanomaterials have been provided in this book. It discusses the synthesis, properties and applications of smart nanomaterials. Smart nanomaterials use nano-scale engineering and superior system integration of existing materials to continuously develop better materials and better products. Defense, automobile industries etc. benefit from the development of these materials. This book unfolds the innovative aspects of developing smart nanomaterials, helping the reader to explore the unexplored. As this field is emerging at a fast pace, this book will help the readers to better understand the concepts of synthesizing smart nanomaterials.

About the Editor

Rich Falcon received his masters in Nanomaterials and Nanocomposites from the University of Bristol, United Kingdom. He is a professor and an adjunct researcher of nanofabrication and nanomaterials in United States. His current research work is based on developing novel synthetic methods based on microfluidic reactors for multifunctional nanomaterials. Falcon is involved in the development of innovative useful and analytical tools based on nanotechnology and has eight years of industrial R&D experience.

ISBN 978-1-63238-556-7

NY RESEARCH PRESS

www.nyresearchpress.com

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NY RESEARCH
PRESS
New York

Published by NY Research Press
118-35 Queens Blvd., Suite 400,
Forest Hills, NY 11375, USA
www.nyresearchpress.com

Smart Nanomaterials: Synthesis, Properties and Applications
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International Standard Book Number: 978-1-63238-556-7 (Hardback)

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Cataloging-in-Publication Data

Smart nanomaterials : synthesis, properties and applications / edited by Rich Falcon.
p. cm.
Includes bibliographical references and index.
ISBN 978-1-63238-556-7
1. Nanostructured materials. 2. Nanostructured materials--Analysis.
3. Nanocomposites (Materials). I. Falcon, Rich.
TA418.9.N35 S63 2017
620.5--dc23

Printed in China.

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Preface

Comprehensive insights into the emerging field of smart nanomaterials have been provided in this book. It discusses the synthesis, properties and applications of smart nanomaterials. Smart nanomaterials use nano-scale engineering and superior system integration of existing materials to continuously develop better materials and better products. Defense, automobile industries etc. benefit from the development of these materials. This book unfolds the innovative aspects of developing smart nanomaterials, helping the reader to explore the unexplored. As this field is emerging at a fast pace, this book will help the readers to better understand the concepts of synthesizing smart nanomaterials.

This book is the end result of constructive efforts and intensive research done by experts in this field. The aim of this book is to enlighten the readers with recent information in this area of research. The information provided in this profound book would serve as a valuable reference to students and researchers in this field.

At the end, I would like to thank all the authors for devoting their precious time and providing their valuable contributions to this book. I would also like to express my gratitude to my fellow colleagues who encouraged me throughout the process.

Editor

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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 insolubility 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 ($-SO_3H$) 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 hybrid nanostructures [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 hybrid 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 HNO_3/H_2SO_4 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 60°C 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 diffractometry (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 $2\theta = 25^0$, 43.5^0, and 51^0. No crystalline peak of SPANI was observed as SPANI is amorphous. In SWCNT, the peaks are at 26^0, 42.5^0, 44^0, 51^0, and 53.5^0 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.

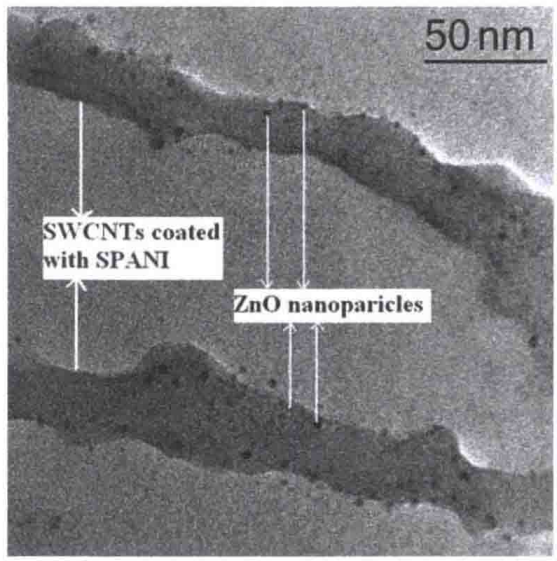

Figure 1. HRTEM micrograph of SPANI/SWCNT/ZnO nanocomposite.

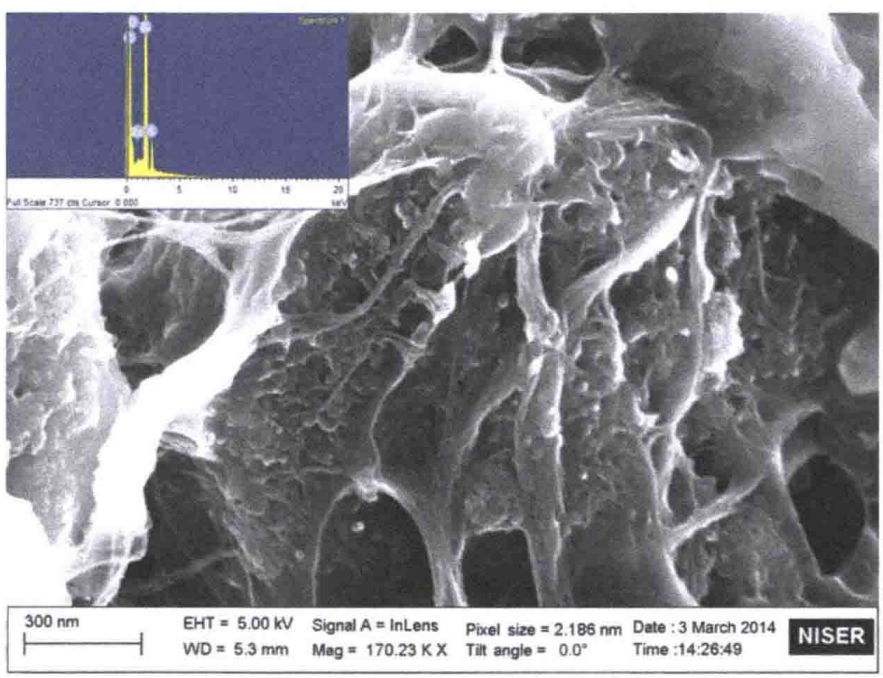

Figure 2. FESEM image with EDAX spectrum of SPANI/SWCNT/ZnO composite.

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

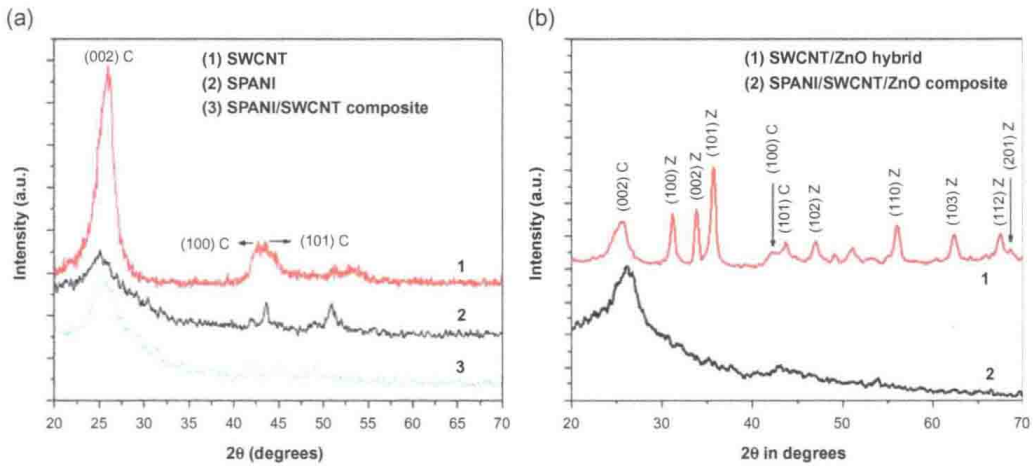

Figure 3. (a) XRD patterns of SWCNT, SPANI, and SPANI/SWCNT composite. (b) XRD patterns of SWCNT/ZnO hybrid and SPANI/SWCNT/ZnO composite captioned C (CNT) and Z (ZnO).

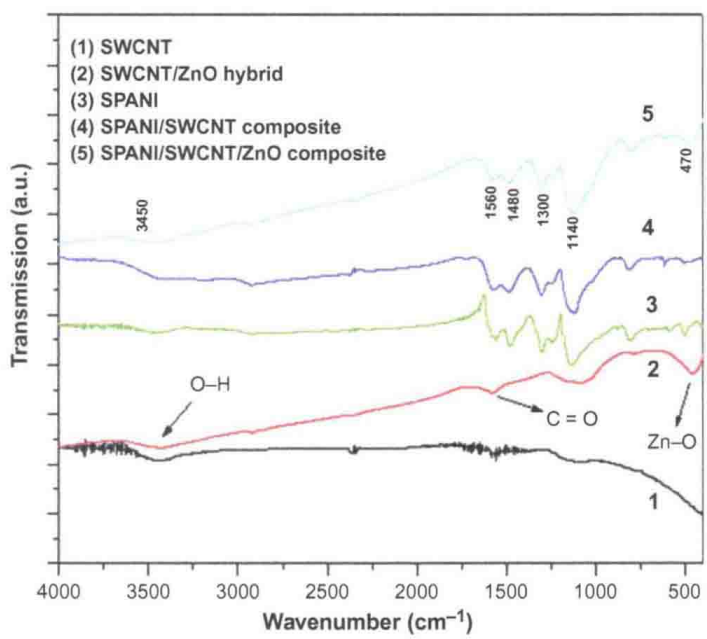

Figure 4. FTIR spectra of SWCNT, SWCNT/ZnO hybrid, SPANI, SPANI/SWCNT composite, and SPANI/SWCNT/ZnO composite.

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/

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