Sensor Functionality of In Situ Synthesised Polyaniline - SnO$_2$Hybrids towards Toluene Vapour

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Abstract

Polyaniline-SnO$_2$ (PANI-SnO$_2$) hybrid materials with varied SnO$_2$ content were prepared by in situ chemical oxidative polymerization method. The prepared materials were characterized by FT-IR, XRD and SEM analyses. Sensitivity of the materials towards toluene was measured at room temperature from their conductivity change. The PANI-SnO$_2$ composite with 40 wt.% SnO$_2$ exhibited highest sensitivity. In situ synthesis enhanced the sensitivity of the materials over their physical mixture. This might be due to the formation of higher number of p-n heterojunctions during in situ synthesis.

Keywords: Composite; Polyaniline-SnO$_2$; Sensor; Toluene analyte.

1. INTRODUCTION

Volatile organic compounds (VOCs) easily evaporate and contribute to the decay of indoor air quality. Most of the VOCs are dangerous and known to cause several kinds of diseases such as allergies, asthma, cancer and emphysema (Godish, 1991). Aromatic hydrocarbons viz. benzene and toluene are widely used in industrial activities, despite being known carcinogens that can easily contaminate air, water and soil. Therefore there is a scientific demand for detection and controlling of such pollutants.

Conducting polymer polyaniline (PANI) has attracted much attention due to its environmental stability, good electrical conductivity and ease of synthesis. It has been studied as a chemo-sensor for a limited range of VOCs (Pang *et al.* 2010). But, aromatics benzene/toluene being weakly interactive are not much studied and hence their sensor works are limited. Metal oxide sensors are effective only at higher temperature. In this context the organic-inorganic hybrid composites are much promising. These hybrids with advantageous physico-chemical properties receive a great deal of attention nowadays. PANI-SnO$_2$ composite has optical (Dutta *et al.* 2007) gas sensing (Geng *et al.* 2007 and Tai *et al.* 2010) and super-capacitor (Hu *et al.* 2009) applications. The sensor study of PANI/SnO$_2$ materials towards polar solvents was reported with varying mass % of SnO$_2$. The dielectric values of PANI-SnO$_2$ composites strongly depend on the wt.% of SnO$_2$ present in the materials and the particle dimension of SnO$_2$ has greater influence on the dielectric values of the composite.

PANI is a p-type semiconductor and SnO$_2$ is a n-type semiconductor and therefore they form p-n hetero

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junctions in the hybrid materials between PANI and SnO_2. The extent of p-n heterojunctions formed in PANI-SnO_2 hybrid can be enhanced via *in situ* polymerization method as compared to the physical grinding and mixture of the individual components. Hence, in the present work, we attempt an *in situ* synthesis of PANI-SnO_2 hybrid materials and investigate the toluene sensor efficiencies of both types of materials.

2. EXPERIMENTAL

2.1 Materials

Aniline (Merck) was purified by distillation over zinc dust. Ammonium peroxodisulfate (APS; Merck), SnO_2 (~325 mesh; Sigma-Aldrich) and other chemicals were used without further purification. Water used in the preparation and washings was doubly distilled unless otherwise mentioned.

2.2 Synthesis of PANI and PANI-SnO_2 composites

PANI was prepared by chemical oxidative polymerization method. In a typical procedure, 20 mmol aniline and calculated quantity of SnO_2 were added to 50 ml 0.2 M H_2SO_4 solution. The solution was stirred at 0-4 ℃ for 30 minutes for the formation of anilinium ion on the surface of SnO_2 particles. Equimolar quantity of APS was added into the above solution and the stirring was continued for further 1 h. The resultant mixture was kept in a refrigerator overnight for the completion of polymerization. The obtained hybrid sample was filtered, washed with 200 ml double distilled water and 50 ml of acetone methanol (1:1) mixture. 100 ml 0.0 1 M H_2SO_4 solution was used for the doping and then the material was dried in an air oven at 120 ℃ for 4h. The dried sample was stored in air-tight polythene cover. The ground materials were pelletized and dried at 120 ℃ for 30 min. in prior to the conductivity measurement. The PANI-SnO_2 hybrids with varied SnO_2 (20-80 wt.%) were prepared by varying the amount of SnO_2.

2.3 Conductivity measurement

Pellets of PANI and its SnO_2 composite were subjected to DC electrical conductivity measurement in a four probe setup. The pellet fitted in a four probe was kept in a sensor chamber provided with inlet and outlet for the flow of gases. Nitrogen was used as a carrier gas for toluene vapour. The flow of N_2 was adjusted to get the required concentration of toluene. The current-voltage measurement of the pellets both in N_2 and toluene atmospheres was taken. The conductivity of each pellet was computed from the slope of *I-V* plot. The normalized conductivity change (NCC) in % was calculated from the conductivity value of each pellet in N_2 (σ_{N2}) and in analyte ($\sigma_{toluene}$ at ~1650 ppm) atmospheres using eqn.(1).

$$\% \ NCC = \frac{\sigma_{Nitrogen} - \sigma_{Toluene}}{\sigma_{Nitrogen}} \ ----- (1)$$

2.4 Characterization of the samples

PANI and its SnO_2 hybrid composites were characterized using fourier transform infrared spectroscopy, X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. IR spectra of the samples were obtained with KBr pellet in JASCO FTIR-410 spectrophotometer provided with computer software. XRD patterns of the samples (2λ =2-80º) were obtained with RigakuMiniflex II desktop X-ray diffractometer using Cu Ka radiation (λ = 1.5418 Å). Scanning electron microscope images of the gold coated samples were observed with JEOL (model 6390) microscope operating at 20 kV.

3. RESULTS & DISCUSSION

3.1 Characterization of the samples

Fig. 1 shows the IR spectra of PANI and its SnO_2 hybrids. The characteristic C=C vibrational band of quinoid(Q) diimine unit appeared at ~1583 cm^{-1}. The

band at 1480 cm^{-1} was attributed to the C=C aromatic ring stretching of benzenoid (B) diamine. The bands at 1300 cm^{-1} was assigned to C-N stretching of the secondary aromatic amine. The above vibrational bands demonstrate that the pristine PANI is in conducting emeraldine salt form.

The quinoid C=C stretching band of the PANI was shifted to lower wavenumber (~1556–1567 cm^{-1}) in the hybrid materials. However benzenoid C=C, secondary amine C–N stretching and aromatic C-H bending vibrational bands were slightly shifted to higher wavenumber (~3–4 cm^{-1}) in the hybrid materials. The characteristic Sn-O stretching of SnO$_2$ appeared as shoulder in the hybrids with the lower % of SnO$_2$; however that was distinctly visible (at 623 cm^{-1}) in the hybrids with higher % of SnO$_2$. The intensity of Sn-O band was found to increase with increase in % of SnO$_2$ loading in the hybrids. The broad band at ~1140 cm^{-1} is attributed to the existence of the positive charge and the distribution of the dihedral angle between the benzenoid (B) and quinoid (Q) rings

$(Q=\overset{+}{N}H\text{-}B \text{ or } B\text{-}\overset{+}{N}H\text{-}B)$.

C-N stretching mode of secondary aromatic amine is observed at ~1300 cm^{-1}. The band due to C-N stretching of the polaron structure BBB (~1245 cm^{-1}) and the band due to C-H in plane vibration of 1,4-substition (~1225cm^{-1}) are merged in PANI and resolved in the hybrid materials. The band ~878 cm^{-1} is assigned to N-H out-of-plane bending vibration of C-N-C backbone.
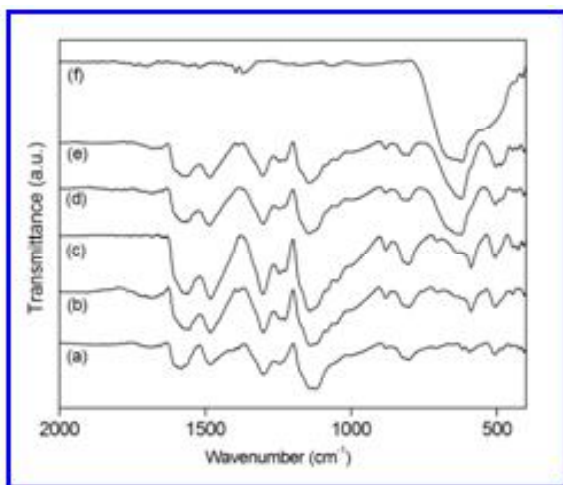

Fig. 1: FT-IR spectra of (a) PANI,(b) PANI-20% SnO$_2$, (c) PANI-40% SnO$_2$, (d) PANI-60% SnO$_2$,(e) PANI-80% SnO$_2$and (f)SnO$_2$.
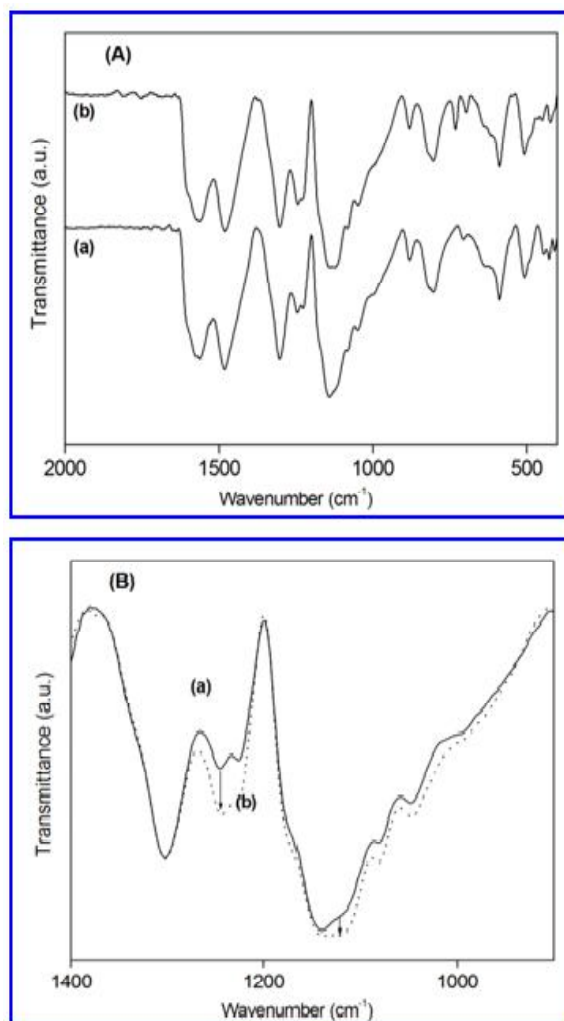
Fig. 2(A): FT-IR spectra of PANI-40% SnO$_2$(a) and its toluene adsorbed form (b); Fig. 2B expanded form

In the toluene vapour adsorbed materials Fig. 2, the intensity of C-N stretching due to the BBB polaron ($\sim$1245 cm^{-1}) and C-H in plane vibration of 1,4-substitution (at 1223 cm^{-1}) is increased. However, the intensity of the band due to the existence of positive charge distribution in the dihedral angle between benzenoid (B) and quinoid (Q) rings ($Q=\overset{+}{N}H\text{-}B$ or $B\text{-}\overset{+}{N}H\text{-}B$) remains unchanged. This suggests the additional overlapping interaction of aromatic ring of toluene to the benzenoid units of the hybrid materials. Adsorption of toluene vapour provides some friction into the polaron sites which are backbones to the conductivity of the polyaniline material.
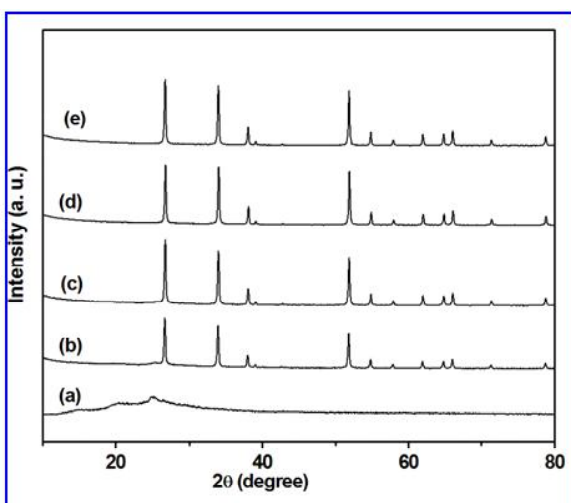
The peak position of SnO_2 ($2\theta = 26.59^\circ$) gets slightly shifted to higher values with maximum for 60% loaded hybrid Table 1. The crystallite size of SnO_2 particle (35.4 nm) is also increased in the hybrid materials with maximum value at 60% loaded hybrid. This enhancement shows the formation of polyaniline coating over the crystals of SnO_2.

Table 1. XRD data of PANI, SnO_2 and their hybrids

Material	2θ (°)	FWHM (°)	d-spacing (Å)	Crystallite size (nm)
PANI	24.88	4.500	3.58	1.9
PANI-20% SnO_2	26.67	0.163	3.39	52.2
PANI-40% SnO_2	26.73	0.163	3.33	52.2
PANI-60% SnO_2	26.78	0.143	3.33	58.1
PANI-80% SnO_2	26.72	0.163	3.33	52.2
SnO_2	26.59	0.241	3.35	35.4

Fig. 3: XRD spectra of (a) PANI, (b) PANI-20% SnO_2, (c) PANI-40% SnO_2, (d) PANI-60% SnO_2, (e) PANI-80% SnO_2

Powder diffraction pattern of the hybrid materials Fig. 3 clearly demonstrate the presence of SnO_2 with 2è values 26.6, 33.9, 38.0 and 51.8° corresponding respectively to the planes of (110), (101), (200) and (211). This pattern certainly reveals the existence of tetragonal SnO_2 (JCPDS file No. 01-088-0287) in the hybrid materials.

Table 2. Change in conductivity of PANI and its SnO_2 hybrids in toluene vapour

Sample	Wt. % of SnO_2	NCC (%)	
		In situ	Physical mixture
PANI	-	1.57	1.57
PANI-20% SnO_2	20	5.39	2.79
PANI-30% SnO_2	30	15.49	6.30
PANI-40% SnO_2	40	19.53	10.41
PANI-50% SnO_2	50	14.79	5.17
PANI-60% SnO_2	60	13.15	4.50
PANI-70% SnO_2	70	7.72	ND
PANI-80% SnO_2	80	3.55	---
SnO_2	100	---	---

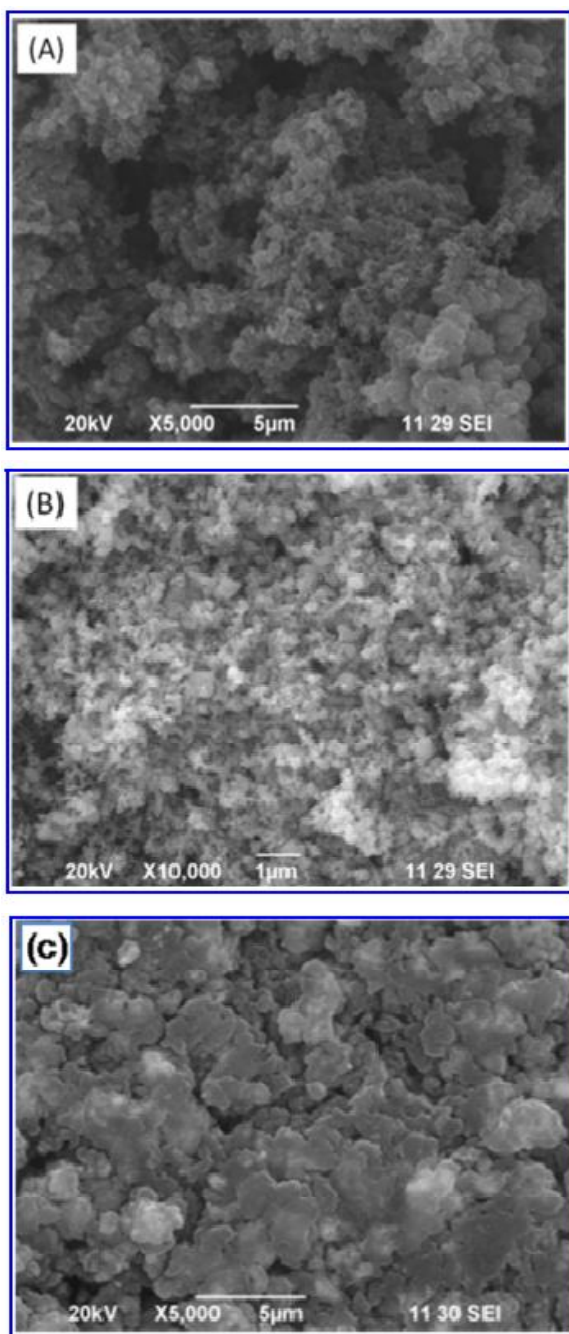[Toluene] = $\sim$1650 ppm. NCC represents normalized conductivity change.

Fig. 4: SEM images of (A) PANI, (B) SnO$_2$, and (C) PANI-40 % SnO$_2$

3.2 Vapour sensing behaviour

Fig. 4 displays the SEM images of PANI, SnO$_2$ and their composites. PANI exhibits uniform spherical agglomerated particles in the range of ~0.5 ìm whereas SnO$_2$ has uniform particles of the range 100 nm. The degree of surface distribution of SnO$_2$ particles increases in the composite materials with increase in wt.% of SnO$_2$.

Table 2 displays the sensor functionality of PANI-SnO$_2$ hybrids synthesized via both physical mixing and *in situ* polymerization towards toluene vapour. In all the samples, the presence of toluene atmosphere resulted in a decrease in conductivity of each material in comparison to nitrogen atmosphere. NCC values increased with SnO$_2$ content in the hybrids upto 40% of SnO$_2$ and decreased beyond 40 wt.%. In the composite physical mixture with higher SnO$_2$ content ($\leq$ 60% SnO$_2$) the pellet become brittle and therefore the NCC values could not be found. *In situ* synthesized hybrid materials exhibit good physical strength even with 80% SnO$_2$ content. These materials exhibit nearly two times higher sensitivity than the composites obtained from physical mixture. This might be due to the formation of larger number of p-n heterojunctions in the hybrid materials. Greater the number of p-n heterojunctions, greater is the interaction between active sites and analytetoluene resulting in higher sensitivity.

3.3 Sensor mechanism

The absorbed analyte gas changes the surface property of the hybrid/composite rendering friction to the flow of charge which in turn reduces the conductivity of the materials. The composite material with 40 wt.% SnO$_2$ exhibits maximum sensor efficiency providing maximum accessible grain surfaces for the adsorption of non-polar toluene via forming optimized number of p-n heterojunctions and dielectric values.

4. CONCLUSION

Polyaniline-SnO$_2$ hybrid materials with various wt.% of SnO$_2$ were prepared and investigated for toluene vapour sensor. SnO$_2$ does not show sensitivity while pristine PANI has very feeble value in N$_2$ atmosphere. However, the hybrid materials exhibit enhanced sensitivities and the sensor efficiency becomes maximal at 40 wt.% loading of SnO$_2$. The *in situ* synthesised materials have nearly two-times higher sensitivity than those of physical mixtures. The intimate contact and strong interaction between PANI and SnO$_2$ in former as revealed in characterization techniques lead to the enhanced sensitivity.

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