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Controlling the sensing performance of rGO filled PVDF nanocomposite with the addition of secondary nanofillers

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ABSTRACT

This study reports the synthesis and characterization of polyvinylidene fluoride (PVDF) nanocomposites containing binary filler combination of reduced graphene oxide and titanium dioxide (TiO_2) nanotubes. The PVDF nanocomposite films prepared by simple solution mixing process showed enhanced thermal and dielectric properties. Sensing performance for the nanocomposites was analyzed in presence of a few industrially significant solvent vapors such as benzene, ethanol, chloroform, acetone, SO_2 and liquefied petroleum gas. The variation in sensing properties illustrates the possibility of using this material in detecting a range of solvent vapors. Maximum sensing ability was noticed for the nanocomposite containing 2.5 wt.% of graphene-titania hybrid filler by the formation of p-n heterojunctions. The sensing performance is explained on the basis of synergistic effect of nanoarchitectures-nanosheets and nanotubes.

1. Introduction

Titanium dioxide (TiO_2) is a common semiconductor used in photochemical, biomedical and electronic applications [1]. Its wide band gap (≈3 eV) and appropriate band edges make it a promising material in fabricating photocatalysts, solar cells and sensors. TiO_2 in one dimensional structural form (TiO_2 nanotubes or TNT) is particularly notable due to the high specific surface area, controlled properties and maximum efficiency and quantum confinements [2]. Many synthetic methods including template assisted techniques [3], electrochemical methods [4], sol gel approach [5] and hydro/solvo thermal methods [6,7] are employed to prepare one dimensional TiO_2 nanostructures. The TNT reported a room temperature hydrogen gas sensitivity of 10^4 along with self-cleaning nature [8]. With 1000 ppm H_2 gas, about 1,75,000% reversible change in electrical resistance was noticed. In addition, the sensing properties were fully recovered by UV irradiation. Majority of the gas sensors based on TiO_2 works by Schottky barrier modulation [9].

Hydrothermal growth of TiO_2 nanotubes on graphene oxide (GO) sheets was utilized for many applications. Perera et al. achieved a three times higher photocatalytic efficiency for the hybrid TNT-reduced graphene oxide (rGO) composite compared to the pure TNTs [10]. Another report by Huang et. al. suggests the TiO_2 nanotubes/graphene hybrid structure with improved electrochemical properties having suitable applications in lithium ion batteries [11]. Graphene/TNT nanoarchitecture synthesized by the hydrothermal method was found to be suitable for supercapacitors by our research group [7]. Zheng et. al. observed excellent capacity (263 $mAhg^{-1}$), cycle stability (even after 500 cycles) and rate performance (102 and 151 $mAhg^{-1}$ respectively at 5 and 2 Ag^{-1}) for the rGO/TNT synthesized by electrostatic coating [12].

Graphene is a p-type sensing material and so capable of introducing pn-hetero junctions in semiconductors like ZnO [13–15]. The low cost, high density electronic states, low Johnson noise, high theoretical surface area etc. allow graphene to provide extra ordinary sensing sites for gas molecules [13,16–18]. The microwave irradiated ZnO/graphene hybrid composite material showed excellent NO_2 gas sensing behavior in a very recently reported article [13]. Another report showed promising room temperature methanol vapor sensitivity with ~18 s response time and ~61 s recovery time for the TNT/rGO hybrid device [19]. Though huge varieties of sensors are developed with promising applications in agriculture, industry and medicine, still efforts are going on to improve the 3S properties (response, selectivity and stability) [20].

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Sensors provide remarkable technological impacts as they detect the chemical, physical and biological environments [21]. Numerous reports have come up with the sensing properties of polyvinylidene fluoride (PVDF) and its copolymer based nanocomposites [21–23]. The semi-crystalline polymer, PVDF possesses a lamellar structure of 50% crystallinity. PVDF consists of the electroactive β-phase and stable α-phase, both of which contribute towards its high thermal stability, dielectric constant, mechanical properties, impact resistance, piezoelectric behavior and enhanced electroactivity [21,24,25]. For the nanocomposites, these properties are further enhanced due to the incorporation of outstanding filler particles [26,27]. Electrically conducting nanoparticles such as metallic and metal oxide particles, carbon nanotubes, graphene etc. enormously add to the sensing properties of PVDF and its copolymers [22,23,28]. Many sensors developed using piezoelectric polymer nanocomposites are used in automobiles, microphones, microscopes and biomedical devices [29,30]. Eswaraiah et al. reported the strain sensing application of PVDF containing functionalized as well as reduced GO in their subsequent studies [31,32]. One of the most important advantage of PVDF flexible sensors is the possible attachment, directly to the materials without affecting its mechanical motion [22,33].

Superior chemical interaction and electronic functionality for the graphene-TiO_2 hybrid combination were well reported by various research groups [34–36]. This particular synergistic combination finds efficient applications in Li-ion batteries [34], supercapacitors [7], photocatalysis [37], and in intelligent electronics [38]. A combination of GO and TiO_2 nanolayers were added to PVDF to fabricate thin films useful in pressure sensing [39]. However chemical interaction was not ensured by this simple method of mixing [39]. Lee et al. used sol-gel method to decorate TiO_2 on graphene sheets through the formation of a Ti−C bond [40]. Similar bond formation was observed in our case of hydrothermal reaction as well [7]. We have also reported the vapor sensing for a similar hydrothermally synthesized carbon-TiO_2 filler combination embedded in PVDF. MWCNT was used as the carbon based filler part in order to synthesize those nanocomposite films [41]. In short, the unique combination of graphene-TiO_2 hybrid filler can induce good sensing properties to polymers useful in flexible devices.

Since such flexible composite films can have many applications in smart electronics and biomedical fields, here we design vapor sensors from PVDF fluoro polymer nanocomposites. The hydrothermally synthesized TNT/rGO hybrid nanostructures were uniformly dispersed in PVDF by solvent mixing, and sensing elements were made on electrodes by drop casting. The facile and efficient strategy of hybrid nanocomposite fabrication ensures the synergistic influence of fillers in showing good response towards various organic vapors. The selectivity and sensitivity were compared with the PVDF/TNT and PVDF/rGO sensors. Highly sensitive flexible films propose its applicability in smart textiles useful in drastic chemical environments.

2. Experimental details

Reduced graphene oxide-TiO_2 (G-TNT) nanostructure and TNTs were synthesized by hydrothermal method. Reagents such as TiO_2 nanopowder, NaOH, graphite etc. and solvents like DMF and Acetone were purchased from Sigma Aldrich. First the GO was synthesized by the improved graphene oxide synthesis method and the TNT was hydrothermally grown in presence of GO. The whole production process was according to the reported methodology [7]. Pure rGO sheets were also made under the same experimental conditions of TNT and G-TNT.

PVDF pellets of molecular weight ~1,80,000, used for the nanocomposite preparation were also obtained from Aldrich. Solution mixing method was employed for the sample preparation. For this, about 2 g PVDF was dissolved in 15 ml solvent mixture (1:1) of DMF and Acetone by magnetic stirring at 70 °C for a few hours. To this PVDF dissolution, ultrasonically mixed G-TNT, TNT, and rGO nanoparticles (in the same solvent mixture of 5 ml each) were added again by magnetic stirring at room temperature, overnight. After mixing, the samples were casted in petri dishes for drying and the sample films of uniform dimension was made by hot pressing at 170 °C for 4 min. Sample details provided in Table 1 show the filler concentrations adopted for this study.

Table 1
Sample details and their contact angle values.

Sample	Composition	Contact Angle
Neat	Pure PVDF	87.83 ± 1.87
PT	PVDF with 2.5 wt.% TNT	78.28 ± 3.32
PG	PVDF with 2.5 wt.% rGO	90.79 ± 0.79
PGT1	PVDF with 1 wt.% G-TNT	88.38 ± 1.41
PGT2.5	PVDF with 2.5 wt.% G-TNT	89.14 ± 0.82
PGT5	PVDF with 5 wt.% G-TNT	92.48 ± 2.52

Detailed characterization of the nanocomposites were done by the following methods. Sample morphology was analyzed by SEM and TEM techniques. The SEM studies were conducted by scanning electron microscope SEM, XL-30E Philips Co., Holland and TEM by Transmission Electron Microscope FEI TECNAI G^2. FTIR spectra of the samples were recorded with PerkinElmer Spectrum 400 spectrophotometer in the range 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. X-ray diffraction studies were performed by XRD diffractometer (Mini Flex 2, Rigaku). Nickel filtered CuKα radiation (λ = 0.1564 nm) operated at 30 V and 15 mA served as the source. The patterns were recorded in the 2θ range of 5–80° at a scanning speed of 1.8°/min. The surface contact angle was measured on a drop shape analysis system (OCA 35-Dataphysics) using deionized water to study the hydrophobic effect of the surface. Differential scanning calorimeter (DSC 8500 Perkin Elmer) was used to measure the melting point and the glass transition at a temperature range of 20–200 °C at 10 °C/min. The viscoelastic properties of the samples were measured using a dynamic mechanical analyzer TA-RSA-G2, at 25 °C/min temperature and a change in stress frequency from 0.01 to 100 Hz. Dielectric properties of samples (circular disks of 2 cm diameter) as function of frequency were obtained using broadband dielectric spectroscope GmbH Concept 40 (Novocontrol Technologies, Germany) under room temperature. The dielectric constant, dielectric loss, tan δ and conductivity values of the samples were checked during the frequency range from 10^{-2} to 10^6 Hz.

Sensing experiments were done after carefully making composite sample substrates. For this a typical silicon substrate was cleaned with acetone and distilled water and sample suspensions in DMF/Acetone was coated as thin layer on its surface. Electrical contacts were made on both sides of the sensing film and is connected to a Keithley multimeter through which the resistance change upon passing the vapors is detected.

3. Results and discussion

3.1. Morphology and composition

The PVDF hybrid nanocomposite was obtained using a solution casting method as schematically shown in Fig. 1. Hydrothermal method was employed to synthesize the G-TNT nanoarchitecture [7] and later uniformly dispersed in the PVDF polymer. During the hydrothermal synthesis of TiO_2 nanotubes, the GO sheets get reduced and mix well up with the TNTs. This ensures good interactions between the component fillers of one dimension and two dimension and leads to efficient nanosynergy. The PVDF nanocomposite films of 0.2 mm thicknesses were obtained following the casting and hot pressing methods.

Fig. 2 shows the TEM images for the rGO, TNT and GTNT nanomaterials at 50 nm resolution. Sheet like morphology of rGO and tubular TNTs are clearly notable from the figure. During hydrothermal reaction the GOs undergo thermal reduction and becomes rGOs. The thickness of the obtained rGO was ~2 nm. The TiO_2 spherical particle