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Original Research Article

MWCNTs embedded polyaniline based composites for electrical applications

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ABSTRACT
Multiwalled carbon nanotubes (MWCNTs-8wt.%) embedded polyaniline (PANI)-based nanocomposite in its emeraldine salt form was synthesized through the chemical oxidative polymerization process. Therefore, due to their higher electrical conductivity, it is expected to utilization of this sample in various electrical applications such as supercapacitor, vapors detection and electromagnetic shielding materials. The storage ability of this nanocomposite sample was examined using the cyclic voltammeter at different scan rates. This sample contains the excellent specific capacitance i.e., ~396 F/g at 40 mV/s scan rate. Moreover, this nanocomposite sample also utilized as electromagnetic shielding materials and their electromagnetic shielding interference (EMI) properties were investigated in the X-bands (8.1-12.4 GHz) frequency region. This nanocomposite sample contains the efficient value of total EMI shielding effectiveness i.e., ~49 dB at 12.4 GHz frequency, and this value of total shielding effectiveness is greater than essential value for industrial application i.e., 30 dB. Also, the vapors detection sensor was also fabricated using this nanocomposite sample to the detection of alcoholic vapors of methanol at two different concentrations (50 and 100 ppm levels) at room temperature. This sample reveals the good sensing response (%) i.e., ~42.27% even at 100 ppm of methanol vapors. Therefore, the utilization of PANI/MWCNTs (8wt.%) nanocomposite sample in various electrical application make them suitable candidate for industrial use.

1. Introduction

Since last few decades, the conjugated polymers (especially polyaniline) play an important role at the scientific as well as industrial level due to their utilization in various important applications such as EMI shielding [1], water treatment [2], electrochromic display [3], supercapacitor [4], LEDs [5], batteries [6], antibacterial [7], Sensor [8], etc. Polyaniline can be synthesized in various states i.e., emeraldine salt (high conducting state), emeraldine base (low conducting state), etc. Due to the dual character of polyaniline makes them suitable candidate for the fabrication of various electrical devices. Moreover, the polyaniline has various advantages over other samples such as easy to synthesized, high stability, cost effective, light-weight, etc. Moreover, the above discussed applications are depending upon the conductivity of samples as well as the concentration of charge carriers. Therefore, we have need to synthesized unique sample for the utilization in various applications. Thus, in the present research work, we have synthesized the multiwall carbon nanotubes (MWCNTs) embedded polyaniline (PANI) in emeraldine salt form. After that the synthesized sample was utilized in various electrical applications such as EMI shielding, supercapacitor and vapour detections.

2. Synthesis of PANI/MWCNTs composites

MWCNTs embedded PANI nanocomposite was prepared using the chemical oxidative polymerization synthesis route. For the preparation of desired nanocomposite two identical aqueous solutions of monomer (Aniline hydrochloride: 20 mM) with dopant (8 wt%) and hydrochloric acid and oxidant (ammonium persulphate: 30 mM) were prepared. After that the solutions were cooled using the refrigerator for 1 hour. After the one-hour cooling, the oxidant solution was positioned in ice-bath sustained the temperature below 4^oC. Then pre-cooled oxidant solution added in it drop wise using the fine burette, then immediately polymerization reaction was start and allow for the reaction for over-night. After 24 hours, methanol in sufficient quantity was introduced in final prepared solution to stopover the polymerization. Then, the resultant solution was filtered out using the Whatmann's filter paper, and obtained slurry was treated using methanol and de-ionized water alternatively up to the filtrate turns colour less. The obtained sample was firstly dry in air and then in the vacuum for 24 hours at 55^oC. Al last, the dried yield was trodden out in fine powder.

3. Results and discussion

3.1 EMI shielding investigations

Electromagnetic shielding properties of prepared nanocomposite sample were examined using the Vector Network Analyzer (VNA-Model-PNA-L N5230C Agilent Technologies) in the X-band frequency range (8.1-12.4 GHz) having sample size ~ 22.86 mm × 10.16 mm × 2 mm as rectangular pellet form. EM pollution has a significant impact

on the lifespan and functionality of electronic equipment. Different conducting materials are used to attenuate EMI, where the shielding material interacts with incident EM waves. One part of these EM waves is absorbed, symbolised by the absorption coefficient A; another portion is reflected, given by the reflection coefficient (R); and the remaining is transmitted, described by the transmission coefficient (T). Therefore, attenuation in an EM wave is generally controlled by absorption occurring in the body/bulk of shielding material. Therefore, the operating frequency region [9] and conductive matrix of the shielding material [10] have a significant impact on the strength of attenuation.

The electrical and magnetic characteristics of the shielding materials control the attenuation process because the radiation is electromagnetic (EM) in nature [11]. Under the resonance condition, electric and magnetic dipoles absorb EM radiation. Electric dipoles are found in conducting materials such as conjugated polymers, activated charcoal, CNTs, graphene while magnetic dipoles are present in magnetic materials such as copper, cobalt, nickel, iron [12]. However, compared to magnetic dipoles, electric dipoles interact with EM waves more fluidly, making electrical conductivity one of the most crucial factors in the creation of an EM barrier. As a result, methods to increase electrical conductivity are more advantageous for EMI shielding effectiveness. PANI is being doped with MWCNTs in this instance to enhance its electrical characteristics.

The shielding efficiency through SE_R and SE_A can be computed using the scattering parameters. The shielding efficiencies via reflection, absorption, and cumulative in terms of scattering parameters can be expressed as follow [13, 14]:

$$SE_R = 10 \log \left(\frac{1}{1 - |S_{11}|^2} \right) = 10 \log \left(\frac{1}{1 - R} \right)$$
$$= -10 \log(1 - R) \qquad (1)$$

$$SE_A = 10 \log \left(\frac{1 - |S_{11}|^2}{|S_{12}|^2} \right) = 10 \log \left(\frac{1 - R}{T} \right) \qquad (2)$$

$$SE_T = 10 \log \left(\frac{1}{1 - R} \right) + 10 \log \left(\frac{1 - R}{T} \right) = -10 \log(T) \qquad (3)$$
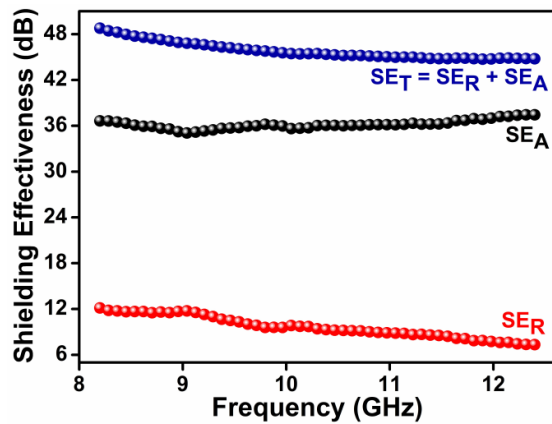

Figure 1: Variation in shielding effectiveness due to reflection (SE_R), absorption (SE_A) and total shielding effectiveness (SE_T) as function of applied frequency.

Figure 1 displays the reflection, absorption, and total components of the shielding efficiency of the PANI/MWCNTs nanocomposite as function of applied frequency. Using the above equations (1-3), the calculated values of shielding effectiveness because of reflection (SE_R) and absorption (SE_A) are ~12 and 37 dB at 8.1 GHz and the total shielding effectiveness (SE_T) are found to be ~ 49 dB [1].

The calculated value of shielding effectiveness due to reflection is almost one-third of shielding effectiveness due to absorption. This indicates that magnetic and electric dipoles present at the surface of the shielding material are less contribute as compared to the electric and magnetic dipoles present at the bulk surface. This also indicates that the incident EM waves interact with these dipoles and transferred their energy to the electric and magnetic dipoles and converted as dissipation of heat. The shielding effectiveness (total) is the combined effect of shielding effectiveness because of absorption and reflection. The shielding effectiveness due to reflection decreases with the enhancement in frequency which can be because of reduction in polarization phenomenon due to frequency dependence characteristics of atomic, dipolar, and electronic polarizations.

3.2 Fabrication of supercapacitor and cyclic-voltametric measurements

In the current work, the synthesized nanocomposite sample was utilized as electrode material for the supercapacitor device. For this experiment, a symmetric parallel electrode design is employed, in which the anode and cathode are constructed of PANI/MWCNTs nanocomposite sample. In contrast, a gel made of polyvinyl alcohol (PVA) and H_2SO_4 served as both an electrolyte and a separator. The electrolytic gel of PVA/H_2SO_4 is made by dissolving 6 g of PVA in 60 ml of de-ionized water, which is then heated at 80°C for two hours during magnetic stirring. After the PVA has completely dissolved in de-ionized water, a pre-determined quantity (6 ml) of H_2SO_4 is added, and the mixture is aggressively agitated for one hour. After cooling, a translucent, homogenous gel is produced [4]. After that, the gel is placed between two polyaniline nanocomposite electrodes (PANI-MWCNTs/PVA-H_2SO_4/ PANI-MWCNTs) and let to dry. To prevent the defect in weight in supercapacitor testing, the electrode pellets are constructed from materials that weight exactly the same. Using the in-house AUTOLAB PGSTAT302N software facility, the produced supercapacitors are tested using the pellet-size aluminium electrode shape.

The characteristic cyclic voltammeter (CV) curves of all the prepared nanocomposite sample are acquired at various values of scan rate i.e., 10, 20, 30 and 40 mV/s, between the applied potential from -0.2 to 0.8 V (Figure 2), to assess the charge storage properties of the fabricated supercapacitor. It has been found that all of the samples' CV curves contain two separate oxidation and reduction peaks, which are consistent with the prepared samples' pseudo-capacitive behaviour. With a rise in scan rate, these peaks become ever more pronounced. The Faradic re-dox characteristics and pseudo-faradic charge propagation interaction control the reduction and oxidation peaks of CV curves, which occur when a semiconducting state of PANI (leucoemeraldine form) changes into the conducting state (polaronic emeraldine form) or vice-versa. During the

redox transition, the conducting polymers typically gather and release the charges through-conjugated polymer chains.

For the CV measurements, the specific capacitance is the most common factor to examine the behaviour of constructed supercapacitor electrode. Using the relation [15], the specific capacitance of the supercapacitor electrode may be determined.

$$C_s = \frac{I\Delta t}{m\Delta V} \tag{4}$$

Where, V, I, Δt, *m* are applied potential, charge-discharge current, charging and discharging time, and mass of electrode, respectively. Using the equation (4), the specific capacitance values were calculated, and are found to be ~ 197, 269, 338 and 396 F/g at 10, 20, 30 and 40 mV/s scan rate, respectively. The specific capacitance of nanocomposite sample is found to rise with the increase in scan rate. The apparent behaviour from CV measurements is strongly supported by the observed behaviour of the fluctuation in specific capacitance with scan rates [16].
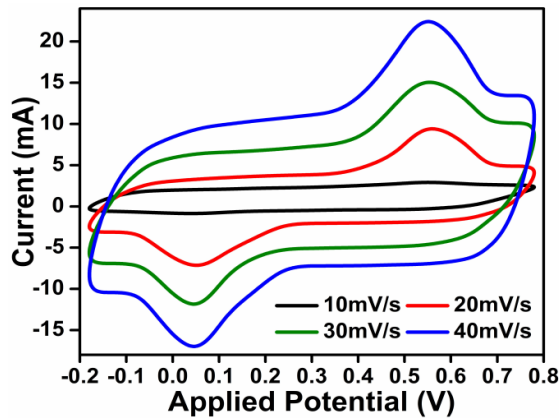

Figure 2: Show CV curves of PANI/MWCNTs nanocomposite sample at scan rates.

3.2 Fabrication of sensor and vapor detection measurements

The prepared nanocomposite sample was further utilized as sensing device for the methanol vapours using Keithley's 6517B electrometer and DNM-121 Nano-ammeter. The sensing device was fabricated using the pellet having two parallel silver electrodes having separation of 1mm on upper surface (Ag/PANI-MWCNTs/Ag). The fabricated sensor was then placed in measuremental chamber containing the low pressure (~500 mbar).The fabricated sensor is subjected to two identical PPM levels of methanol vapours (50 and 100 PPM) to test the behaviour of methanol detection.

On the static voltage of 3 Volt, it is discovered that the electrical current of the prepared samples changes with a change in the environment from air to methanol. Prior to being influenced under the methanol vapours, the fabricated sensor is stabilised to the low pressure. The electric current for all the samples is shown to increase with exposure duration and methanol concentrations (50 and 100 ppm) when exposed to the methanol vapours, reaching saturation in around 200 s. After remove the methanol vapours, the values of current start to decrease and reach to their initial value.

Using the relation [17], the response (%) is estimated utilising the variation in current values of the fabricated sensor with the change in device environment.

$$\text{Response (\%)} = \frac{\Delta I}{I_o} x100 = \frac{I_m - I_o}{I_o} x100 \tag{5}$$

where I_m and I_o are the current under methanol vapours and ambient air, respectively. The variation in response (%) under methanol vapours is plotted as the function of time as shown in Figure 3, and it is examine the response (%) enhances with the enhancement in methanol ppm level. The enhancement in electrical current may be due to enhancement in charge carriers under the methanol vapours after the adsorption of methanol vapours on the active sites of fabricated sensor. That means the p-type character of sensor increases with the increase in methanol vapours [18].
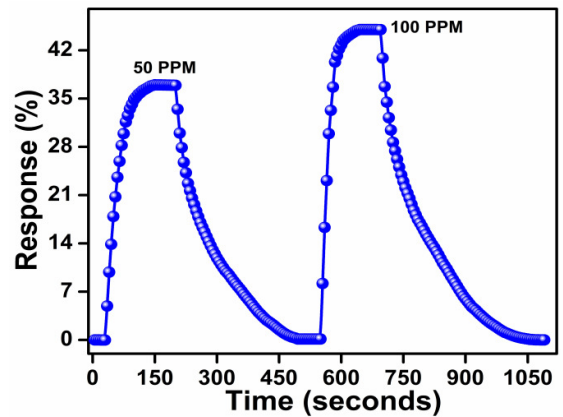

Figure 3: Variation in response (%) as function of time at 50 and 100 PPM levels of methanol.

4. Conclusions

MWCNTs (8wt%) embedded PANI nanocomposite sample has been polymerized through the oxidative polymerization process in its emeraldine salt form. The prepared nanocomposite sample exhibit high value of total shielding effectiveness i.e., 49 dB at 12.4 GHz frequency which is higher than industrial requirement (30 dB).The fabricated nanocomposite sample also contains the excellent charge storage properties. This nanocomposite sample have higher value of specific capacitance ~396 F/g at 40 mV/s scan rate. The methanol detection properties of synthesized nanocomposite sample also investigated at two identical PPM levels. The fabricated sensor reveals the excellent response (%) i.e., ~ 42.27% at 100 PPM level. It is also observed that the response (%) enhances with the enhancement in PPM level.

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