

In-situ chemical synthesis of PANI dodecylbenzene sulfonic acid doped vanadium pentoxide: Optical and electrical properties

Niranjana M, Sharanappa Chapi, Yesappa L, Archana K, Raghu S, Devendrappa H*

Department of Physics, Mangalore University, Mangalagangothri, Karnataka 574199, India

*Corresponding author, E-mail: dehu2010@gmail.com; Tel: (+91) 08-242888707; Fax: (+91) 08-242287289

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Abstract

Polyaniline (PANI) composites doped with Vanadium pentoxide (V_2O_5) of different weight percentage using dodecylbenzene sulfonic acid (DBSA) as surfactant was prepared by in-situ chemical oxidation reaction method. Here ammonium persulphate was used as an oxidizing agent. The formation of composite (PANI/DBSA/ V_2O_5) was confirmed with the help of analytical studies like scanning electron microscopy (SEM) and UV/Vis spectroscopy. SEM images show a substantial change in PANI morphology after incorporation of vanadium pentoxide. The optical characterizations by UV-Vis absorption spectroscopy show the increased absorption with addition of V_2O_5 . The electrical conductivity has been studied in the frequency range of 20 Hz to 1MHz and it is found that PANI/DBSA:2%(V_2O_5) shows high electrical conductivity compared to pure PANI and other composites. It is observed that the dielectric constant and dielectric loss increase with concentration of V_2O_5 . PANI/DBSA/ V_2O_5 composites are most promising material for many electrical and potential applications. This semiconducting polymer combination of PANI and Vanadium pentoxide (V_2O_5) which produce hybrid material, behaves as semiconductor at low temperatures; this behavior is predicted by results of dielectric properties studied. Copyright © 2017 VBRI Press.

Keywords: Conducting polymer, polyaniline, V_2O_5 , morphology, electrical conductivity.

Introduction

Conducting polymers have been widely studied because of its fascinating electrical and optical properties which are derived from conjugated electron system [1, 2]. The PANI based composite has occupied prime priority for extensive applications in making devices like polymer photovoltaic cells, sensors, batteries and super capacitors [3]. Huang and Kaner's excellent work on PANI nanofibers preparation has received tremendous development [4, 5]. PANI has depends on concentration of monomer, catalyst and temperature during polymerization, hence it gained more attraction due to simple and cost effective method of synthesis. The important characteristics of PANI is that, it exhibits two forms one as good insulator which is PANI base and other is a high conducting form i.e. PANI salt. PANI emeraldine salt formed because of protonation by acid doping, this process is reversible with presence of imine group basic sites along the conducting polymer backbone. The distortions created by the addition of H^+ ions to the basic groups of quinone and benzoine creates modification of the polymer chains. These distortions play a key role in the electrical properties of the conducting polymer

and even affect the morphology of the material; sometimes the sterical hindrance generated by "too close" substituent to the aromatic ring is responsible of the spontaneous undoping process [6]. Vanadium pentoxide (V_2O_5) is a wide band gap n-type semiconductor material [8] and is a typical intercalation compound and due to its special layer structure and the weak van der Waals forces that hold the layers together, it can accept multi-Li ion reversibly [7]. The properties that charge transport is performed by means of polarons and the amorphous V_2O_5 layers [10, 11]. The V_2O_5 thin films candidates for many practical uses, such as a catalyst material in gas sensors [12, 13] as a high capacity storage medium in Li-ion batteries as a dielectric constituent material in super capacitors [14] as cathode in these batteries [15]. The unions of PANI-CuO hybrid nanocomposites with various blends of two materials have pulled in more consideration, since they have fascinating physical properties and potential applications. These particles not just consolidate the favorable properties of CuO and PANI [16] but also have its interesting physical and chemical properties and it can be utilized as a part of the combination of superconducting materials to manufacture diodes, solar cells, gas sensors, etc. With all these

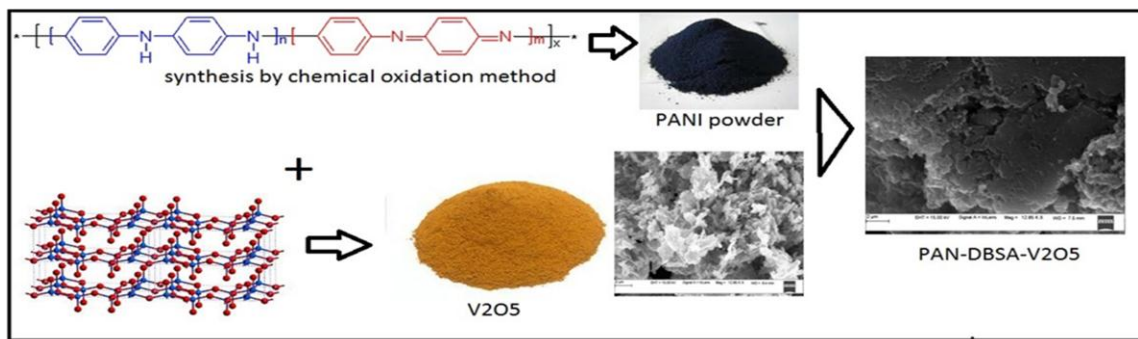


Fig. 1. Graphical Representation of synthesis procedure carried out.

considerations and need for a better semiconducting composite, have made us to investigate a better PANI based composite. In this study, efforts have been made to synthesize composites by in-situ chemical polymerization method to correlate aniline oxidation mechanisms. Study explains the synthesis of PANI-DBSA- V_2O_5 composite and characterizations by SEM, UV-Visible Spectroscopy, conductivity and Dielectric measurements. The dielectric and electrical properties differ from basic materials when taken in composite form [17, 18], such improvements in the physical properties may make composites suitable for super capacitor applications.

Experimental

Materials

Aniline monomer procured from Sigma-Aldrich USA, (99.5% purity) is distilled under reduced pressure before use, Dodecylbenzene sulfonic acid (mol wt.348.48 g/mol) Vanadium pentoxide (V_2O_5) (mol wt.181.88 g/mol) were purchased from Sigma-Aldrich USA, Ammonium persulfate ($(NH_4)_2S_2O_8$) (mol Wt, 228.20 g/mol) and Hydrochloric acid were purchased from Merck, India and used as received.

Synthesis of polyaniline

PANI was synthesized using familiar and cost-effective in-situ chemical reaction method reported earlier [19]. The double distillation of aniline monomer was done before use, 4.6ml of aniline monomer was dissolved in 100 ml 1 M HCl and 2.8 gm of $(NH_4)_2S_2O_8$ (APS) was dissolved in 100ml 1M HCl solution. The APS solution was added to aniline solution drop wise with constant stirring and freezing temperature of 0-3°C is maintained using ice bath, final product thus obtained is the dark green residue mixture. The mixture was continuously stirred for 24 hours and later filtered with Whatman 100 paper, resultant product is dark green powdered PANI and was exhaustively washed with distilled water in order to eliminate the unwanted content and powder was dried in hot air oven at 45°C for about 24 hours to eliminate the moisture.

Synthesis of PANI-DBSA- V_2O_5 composite

The same procedure as above is followed, the surfactant Dodecylbenzene sulphonic acid (DBSA)

and the dopant Vanadium pentoxide (V_2O_5) particles of desired amount were added to aniline prior to addition of APS to it. Subsequently addition of APS was followed according to the procedure described earlier to prepare PANI. Further the procedure was repeated to get all other compositions of composites and composite PANI/DBSA, PANI/DBSA:1% (V_2O_5) PANI/DBSA:2% (V_2O_5) and PANI/DBSA:5% (V_2O_5) were coded as PANI, PD, PDV1, PDV2 and PDV5 respectively for usage ease.

Characterization methods

The PANI and PANI-DBSA- V_2O_5 were characterized by SEM, UV Vis and Dielectric Properties. The study of surface morphology with the help of Sigma Zeiss Scanning Electron Microscope (SEM) images were acquired using an operating voltage of 15 kV. Ultraviolet-Visible absorption spectroscopy (Computer aided double beam spectrometer Perkin-Elmer LAMBDA-35) and dielectric Properties and electrical conductivity studies by Wayne Kerr Precision Impedance Analyzer model 6500B.

Results and discussion

SEM analysis

SEM unveils the images of PANI, PD, PDV1, PDV2 and PDV5 composites shown in Fig. 2(a-e). The SEM image of PANI (Fig. 2a) shows the spherical granular morphology with highly agglomerated granules. The Fig. 2(b) reveals that the surface morphology too differs from PANI and shows small granular closed structural arrangement. In case of Fig. 2(c) reveals the agglomerated granular with more porosity shows the effect due to vanadium pentoxide through surfactant. In case of PDV2 it is seen that uniform agglomeration of granules as shown in Fig. 2(d) this signifies the formation of polarons. For PDV5 analysis in Fig. 2(e) shows that grains appear clearly with improper dispersion which leads to decrease the electrical conductivity of composite which signifies the formation of bipolarons.

There is quite difference in the SEM of PDV2 from PDV1, PDV5 because of the increase in the amount of the vanadium pentoxide and here the particles are agglomerated at one side and it indicates the composite formation. It can be concluding the size of

the granules decrease and change in morphology helps to improve the charge transportation PANI composite [20].

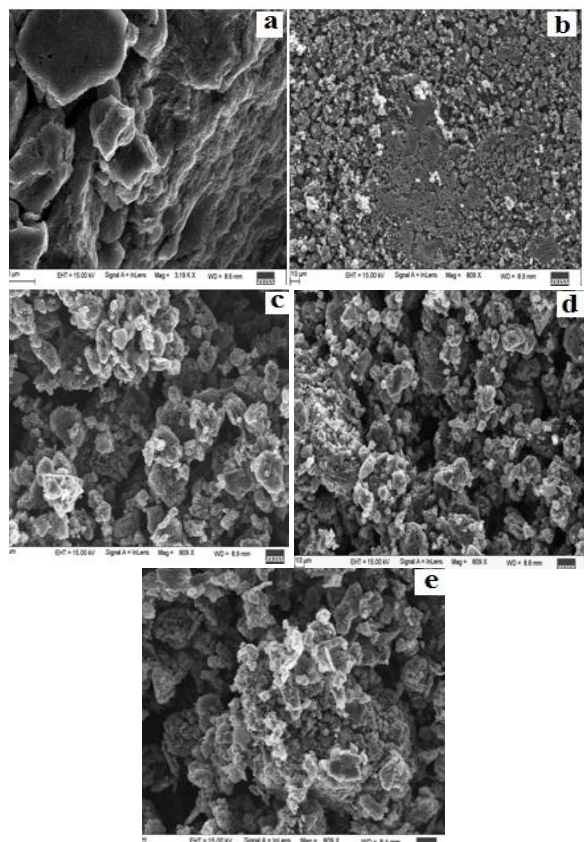


Fig. 2. SEM images of a) PANI, b) PD, c) PDV1 d) PDV2 and d) PDV5 composites.

UV-visible studies

UV-Visible study gives the material information in terms of absorption spectra which helps to understand the electronic transition in the PDV composites. The UV-Visible absorption spectra of PANI, PD, PDV1, PDV2 and PDV5 composites are shown in Fig. 3. From the figure observed that the absorbance increases with increasing dopant concentration. It shows a hypochromic shift due to the successful interaction of vanadium pentoxide particle through surfactant. It is observed that the PDV composites show two distinctive peaks in the range 370-390, 530-676 nm. In visible region the absorption peak of PANI occurred at 386nm has shifted to 378 nm for PDC2 correspond shift represent the interaction of vanadium pentoxide particles with amine and imine units of PANI via surfactant as a result it changes in the inter-intra electronic band transition. It can also interpret that the absorption shift is blue shift, due to the band gap created by a sub energy level within existing gap, hence charges move faster in PDV composites. Spectra shows two peaks, the first one being in the range of 370 to 390 nm attributed to the excitation transition from the benzenoid to quinoid rings ($\pi-\pi^*$) transition and the second peak being observed in the range of 530 to 650 nm due to

polaron/bipolaron transition [21, 22]. The absorption peaks of the composites are slightly shifted to higher wavelength with increased vanadium pentoxide concentration through surfactant. This can be attributed to energy confinement produced from surface which exactly correlates with SEM images, mainly in terms of change in size grains as well as porosity. These changes increase the absorption cross section of the PANI composite [23-25].

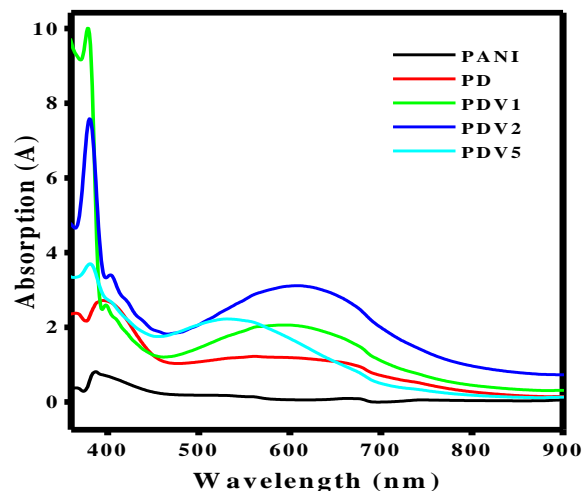


Fig. 3. Absorbance spectra of a) PANI, b) PD, c) PDV1, d) PDV2, and e) PDV5 composites.

Dielectric property

Dielectric constant can be calculated using equation: $\epsilon^* = \epsilon' - i\epsilon''$, where ϵ' and ϵ'' indicates real and imaginary parts respectively. The real and imaginary parts were calculated using equations: $\epsilon' = C_p d / \epsilon_0 A$ and $\epsilon'' = \epsilon' \tan \delta$. The ac conductivity σ_{ac} was calculated from $\sigma_{ac} = \omega C_p \tan \delta / A$, where d is the thickness of the sample, A is the electrode area, ϵ_0 is the dielectric permittivity in vacuum ($8.85 \times 10^{-12} \text{ Fm}^{-1}$) and ω is the angular frequency [19]. Dielectric Constant variation with frequency plot is shown in Fig. 4. There is sharp rise in dielectric in low frequency region which is attributed to interfacial polarization.

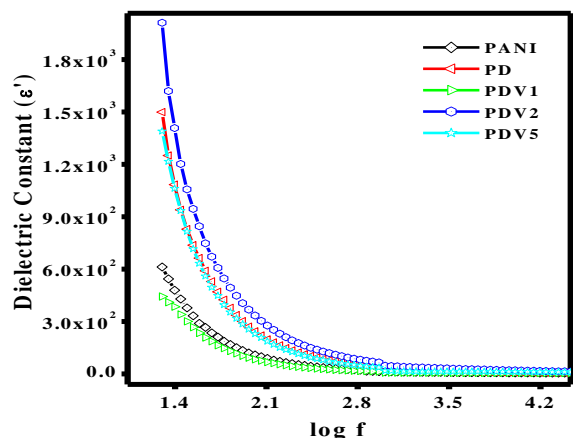


Fig. 4. Variation of ϵ' as a function of frequency of PANI and different wt% of V_2O_5 at room temperature.

The charge carriers may be blocked at an electrode-dielectric interface when migrated under the influence of an electric field, which results in the interfacial polarization [26]. With the increase in frequency the dielectric constant and dielectric loss (Fig. 5) values decrease after the onset frequency of ac conductivity which falls off rapidly.

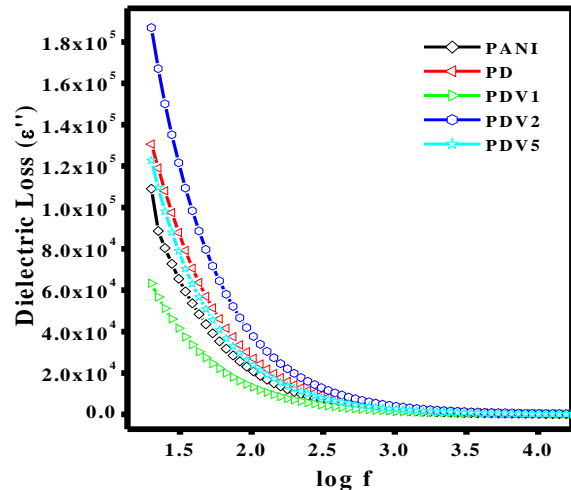


Fig. 5. Variation of ϵ'' as a function of frequency of PANI and different wt% of V_2O_5 at room temperature.

The increasing frequency of applied field results in the decrease of dielectric constant and loss which attributes to mismatch of interfacial polarization at higher frequencies [27]. The electrical property of Vanadium pentoxide varies to larger extent at threshold, in the environment of this threshold it is effective to know the electrical transport behavior of V_2O_5 . Such results can be explained in light of such dielectric polarization results.

Transport property

From Fig. 6 it can be demonstrated that PDV forms conducting path and makes maximum hopping of electrons at low frequencies.

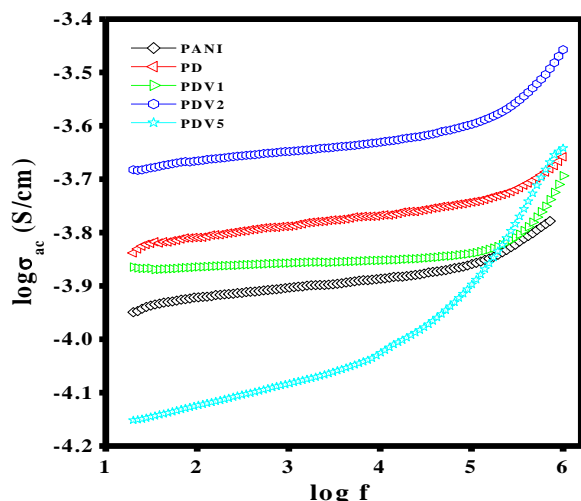


Fig. 6. Variation of $\log ac$ as a function of $\log f$ for all the composites.

At lower frequency (upto 1kHz) region ac conductivity shows that it is almost independent of frequency attributed to the long-range translational motion of ions contributing to dc conductivity. This kind of dc conductivity was explained by Funke et al [28], it shows a greater dependence at higher frequencies (above 1kHz).

In the lower frequency the ac conductivity of the PANI could be ascribed to low level of protonation of the PANI chains. There is maximum improvement in the ac conductivity for PDV2 composite due to effects of V_2O_5 particles in the PANI matrix and clearly evidenced from the SEM image (Fig. 2(d)), which is in favor for strong hopping. It can also interpret that there may be charge carriers which easily transports by hopping through the defect sites along the polymer chain through surfactant, observed result is well agreed with reported result [29].

Conclusion

A facile method to prepare Vanadium pentoxide doped PANI composites have been proposed by an *in-situ* chemical oxidation reaction method. The results of the analytical characterization carried out show that the composition PDV2 have shown better results and found to be best composition. This composite can be further used as alternative for other conducting polymer possessing the conductivity and dielectric property of same order. These results suggest that PDV composites can be used for various storage devices like battery, optical and super capacitor applications.

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Author's contributions

Conceived the plan: Niranjana M; Devendrappa H; Performed the experiments: Niranjana M; Devendrappa H; Data analysis: Niranjana M; Sharanappa Chapi; Yesappa L; Devendrappa H; Wrote the paper: Niranjana M; Yesappa L; Archana K; Raghu S; Devendrappa H (xx, xy, yz are the initials of authors). Authors have no competing financial interests.

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