

Properties of Functionally Graded Vanadium Doped Polyaniline with Copper Phthalocyanine

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Abstract:

Vanadium doped Polyaniline (VPAni) and Copperphthalocyanine (CuPc) were synthesized by chemical route. These synthesized materials were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Keithley electrometer. Vanadium doped Polyaniline (VPAni) was mixed with Copperphthalocyanine (CuPc) with different concentrations on volume to volume basis. An electrical behavior such as resistivity was checked with different combinations of above material. An effective decremented variation in resistances had been occurred when it was measured with electrometer. This may be happening due to strong oxidation state of doped vanadium which causes variation in grain sizes or resistances of charge electrode, semi charge electrode and insulator combination in parallel fashion.

Keywords: Vanadium, Polyaniline, Copperphthalocyanine, Resistivity.

Introduction:

Polymers were seen as good electrical insulators and most of their applications had valid on their insulating properties. Early studies showed that out of the group of polymers some of them exhibit signs of conductivity such as Polypyrroles, Polyaniline, Polythiophene etc. Since this discovery reported by Shirakawa et.al, conducting polymers (CPs) received much attention in the field of science. [1-3] Out of the other conducting polymers, Polyaniline is widely used one due to its ease of preparation, highly physical and chemical stabilities. It acts as a semiconductor or a conductor. It has π electron delocalization along its polymer backbone; hence it shows unique optical and electrical properties.[4-6]

Conducting polymers (CPs) are extensively conjugated molecules; they have alternating single and double bonds. In these molecules, electrons are able to move from one end of the polymer to the other through the extended p-orbital system. Hence CP's are known to be either semiconductors or conductors, which are related to how bands and shells of electrons form within a compound.[7-11]

There is another class of organic semiconductors such as metallophthalocyanines, which shows interesting and valuable

potentialities for conducting applications. Phthalocyanine is a beautifully symmetrical 18- π electron containing aromatic macrocyclic, structurally similar to porphyrin system. Unlike porphyrin, this can be found, in the nature such as hemoglobin, chlorophyll and vitamin - 12. Their physicochemical properties confirm them as most important; small molecular weight organic material ever used. The properties such as high thermal and chemical stability compared with other similar organic materials, a rich substitution chemistry and very practical processability to build devices, leads this material to use as conducting and sensing of various materials and gases respectively. [12-14]

Present paper expresses a phenomenon of combinations of Vanadium doped Polyaniline (VPAni) with Copperphthalocyanine (CuPc). In this, VPAni is conducting material and that of CuPc is semiconducting one. The fusion of VPAni with CuPc shows remarkable results. Both VPAni and CuPc were synthesized by chemical rout. The synthesized powders of VPAni and CuPc were characterized by FT-IR techniques. Their resistivity was measured by Keithley electrometer. The comparative study of VPAni, CuPc and fusion of VPAni with CuPc were shows remarkable evidences; which will give notable sensing properties in the future.

Experimental Details:

Synthesis of Vanadium doped Polyaniline (VPAni):

Vanadium doped Polyaniline was synthesized by chemical route by using aniline (monomer), oxidizing agent (potassium persulphate) and sulphuric acid (H_2SO_4). The reaction is mainly carried out in acidic medium at pH between 0 - 2. The chemical oxidative polymerization of aniline has been carried out in aqueous solution at $0^\circ C$ in ice bath by dissolving aniline in a strong acidic solution of 1M H_2SO_4 . The polymerization is initiated by drop wise adding of aqueous potassium persulphate solution [15-17]. A 10 % to 50% concentration of vanadium pentoxide (V_2O_5) added in this solvent. The reaction is exothermic. When chemical oxidant was added to aniline in a reaction vessel and left for a certain period of time under stirring, the solution gradually becomes coloured and greenish black precipitate appears. The colouration of the solvent was possible due to the formation of soluble oligomers. The polymer synthesized by chemical method was then isolated from the reaction medium by filtration. The precipitate was then washed and conditioned using an appropriate solvent depending on the nature of the studies that has to be carried out.

Synthesis of Copperphthalocyanine (CuPc):

Copperphthalocyanine (CuPc) was synthesized by using Phthalic anhydride, urea and as copper sulphate in 4:4:1 ratio. Phthalic anhydride, urea and metal salt were mixed together and crushed using mortar and pestle into the form of fine powder. The mixture was then slowly heated in the evaporating dish with continuous stirring, the reaction takes place at about $250^\circ C$ to $300^\circ C$ and sufficient heat was generated to maintain the reaction temperature. After completion of the reaction, the residue was washed with distilled water and methyl alcohol many times for purification. The powder form then dried under IR lamps for about half an hour and then crushed rigorously in mortar and pestle to make fine grains. In the process of synthesis of CuPc, the cyclotramerization reaction takes

place at about temperature 250° to $300^\circ C$. If this temperature is not achieved, the reaction could not be completed and no expected color of the material will be found. While washing with methyl alcohol and distilled water, all the precursors washed out till product will yield. After number of trials, the parameters were settled and the material was properly synthesized.[18-25]

Pellet Making:

The powder is compacted in the form of pellet using press technique. The samples in the form of pellets were prepared by using low cost equipment's such as hydraulic press and a die set. The sample preparation parameters can be easily optimized. The synthesized VPAni and CuPc material were compacted into the pellet form of 11mm diameter under optimized pressure and time using press technique for different concentrations. These pellets were then used for studying the electrical behavior by measuring their resistivity. While making such pellets, three parameters viz. pressure, time and weight of sample material were optimized.

Characterization:

Resistivity measurement:

Resistivity response:

The resistance of each pellet was measured by making an electrode contact on the surface of 11mm diameter pellet with the help of Keithly Electrometer of 2401 series. The resistance of the pellets gets varied in decreasing manner as the concentration of the VPAni in CuPc has been changed, shown by the electrometer. Hence, it was seen that the number of charge carriers were increased with VPAni concentration.

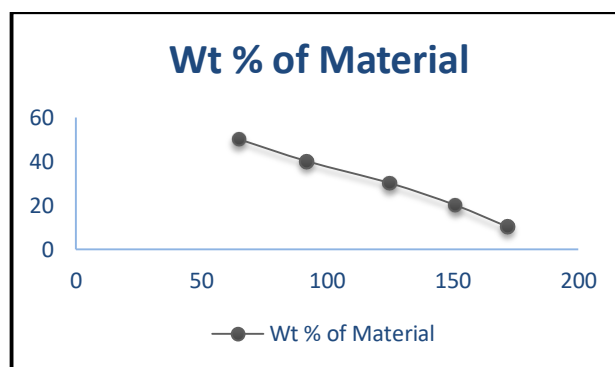


Fig. 1.1 Variation of resistance with concentration of VPAni

FT-IR: The synthesized Polyaniline was characterized by using UV-Vis spectroscopy and FT-IR spectroscopy. FT-IR spectra were recorded using Thermo Nicolet iS5, iD1 transmission FT-IR spectrometer by KBr pellet method as well as ATR facility in the region 500-4000 cm^{-1} .

Result and Discussions:

a) FT-IR of PANi:

Figure 1.1 below shows FT-IR spectrum of chemically synthesized PANi. The peak observed at 3440.18 cm^{-1} is attributed to N-H stretching vibrations. The characteristic bands at 2928.27 cm^{-1} is corresponding to C-H stretching. The peak observed at 1559.83 is mainly due to C=N & C=C stretching vibrations of the quinoiddiamine unit. The band around 1475-1479 cm^{-1} is attributed to the C=C ring stretching of the benzoiddiamine unit. The bands around 1298 & 798 cm^{-1} can be assigned to C-N stretching of the secondary aromatic amine and aromatic C-H out of plane bending modes respectively.

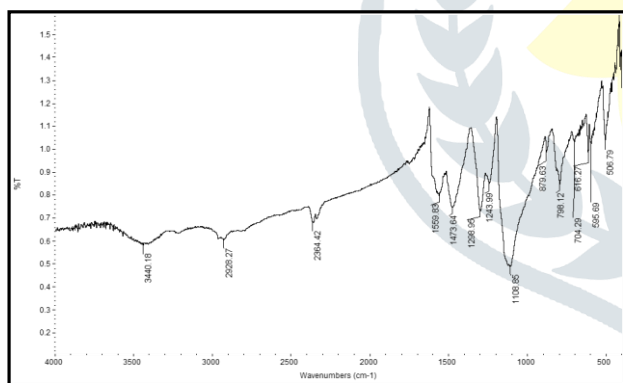


Fig. 1.2 FT-IR of PANi

b) FT-IR of CuPc:

Figure 1.2 shows FT-IR spectra of chemically synthesized CuPc. The region between 500 cm^{-1} to 1800 cm^{-1} corresponds to the skeleton of metallophthalocyanine. The change in spectral range from 1800 cm^{-1} to 3500 cm^{-1} was due to the Cu metal incorporated centrally in the phthalocyanine. A series of weak absorption was observed between 3000 cm^{-1} to 3500 cm^{-1} . The bands appearing at 1183 cm^{-1} , 1252 cm^{-1} , 1287 cm^{-1} , and 1307 cm^{-1} are assigned due to the C-N

in isoindole and in plane band stretching vibration. The band corresponding to C-C stretching (isoindole) was observed at 1387 cm^{-1} . The bands appearing at 817 cm^{-1} and 745 cm^{-1} were assigned to the C-H bending out of plane deformations. The peaks observed in the range 700 cm^{-1} to 500 cm^{-1} interval originates from the vibrations in the benzene ring interaction with the pyrrole ring. The peak at 793 cm^{-1} was due to C-N stretching vibration and that of peak at 715 cm^{-1} indicates the macrocycle ring deformation.

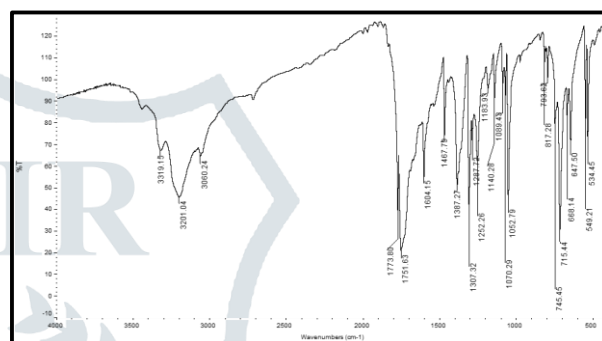


Fig. 1.3 FT-IR of CuPc

c) FT-IR of Fusion of VPAni and CuPc:

The figure 1.3 below shows the FT-IR of fusion of VPAni with CuPc. It was observed that many peaks of both PANi and CuPc material were disappeared. Some of them get modified and remaining gets shifted corresponding to their absorbed wavenumbers. The peak observed at 3626.61 cm^{-1} to 3897.18 cm^{-1} was due to the N-H and O-H stretching. The peaks between 843.47 cm^{-1} to 2972.25 cm^{-1} was due to C-H stretching. The wavenumbers 1651.44 cm^{-1} and 1682.63 cm^{-1} shows C=O ring stretching band. The wavenumbers 1538.30 cm^{-1} to 1567.73 cm^{-1} indicates C=C stretching mode of quinoid. 1454.83 cm^{-1} shows strong CH₂ bending. The wavenumbers 1306.16 cm^{-1} to 1345.58 cm^{-1} indicates weak stretching band of aromatic amine. The wave numbers 1012.45 cm^{-1} to 1054.11 cm^{-1} are due to strong absorption sulfonic acid, S=O stretching.

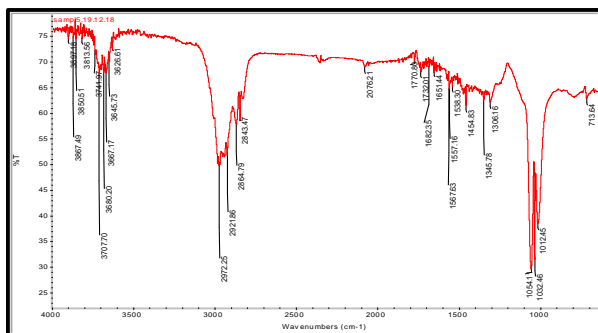


Fig. 1.4 FT-IR of fusion of VPAni with CuPc

Conclusion:

The electrical properties of composites of PANi with CuPc have been studied by analyzing FT-IR, UV and Resistivity response. The composite FT-IR spectrum has recorded some modified as well as shifted peaks. The composite UV spectra assign to average bandwidth than that of individual PANi and CuPc. There may be increment in charge carriers as the PANi composites with CuPc as above mentioned manner. All this may happen due to variation in grain sizes or resistances of conducting, semiconducting, insulating combinations in parallel fashion.

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References:

1. T. Ito, H. Shirakawa, and S. Ikeda, "Simultaneous polymerization and formation of polyacetylene film on surface of concentrated soluble Ziegler-type catalyst solution," *J. Polym. Sci. Pol. Chem.*, vol. 12, no. 1, pp. 11–20, 1974.
2. H. Shirakawa, E. J. Louis, A. G. Macdiarmid, C. K. Chiang, and A. J. Heeger, "Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)_x," *J. Chem. Soc.-Chem. Commun.*, no. 16, pp. 578–580, 1977.
3. F. Faridbod, M. R. Ganjali, R. Dinarvand, and P. Norouzi, "Developments in the field of conducting and non-conducting polymer based potentiometric membrane sensors for ions over the past decade," *Sensors*, vol. 8, no. 4, pp. 2331–2412, 2008.
4. S. Radhakrishnan, Sanjay Chakane, P.N. Shelke "High Piezoresistivity in conducting polymer composites", *Mater. Lett.* 18 (1994) 358.
5. R.D. Kankaria, S.D. Gaikawad, Sanjay Chakane, P.R.Sagar, B.A. Kulkarni "Antimicrobial activity of some phthicolates and plumbaginates" *Environmental Chem.* (2001).
6. M. Naddaf, Sanjay Chakane, S. Jain, S.V. Bhoraskar, A.B. Mandle "Modification of sensing properties of metallophthalocyanine by an ECR plasma" *NIM-B 194 (1) PP 54-60 (2002)*.
7. M. V. Murugendrappa and M. Prasad, "Chemical synthesis, characterization, and direct-current conductivity studies of polypyrrole/ gamma-Fe O composites," *J. Appl. Polym. Sci.*, vol. 103, no. 5, pp. 2797–2801, 2007.
8. A. Ramanavicius, A. Ramanaviciene, and A. Malinauskas, "Electrochemical sensors based on conducting polymer—polypyrrole," *Electrochim.Acta.*, vol. 51, no. 27, pp. 6025–6037, 2006.
9. T Skotheim. *Handbook of Conducting Polymers Vol I & II*. Marcel Dekker. New York, 1986.
10. W R Salaneck, D T Clark and E J Samuelsen. *Science and Applications of Conducting Polymers*. Published by Adam Hilger. Bristol, 1991.
11. Gerard, M., Chaubey, A. & Malhotra, B. D. Application of conducting polymers to

- biosensors. *Biosens. Bioelectron.* 17, 345–359 (2002).
12. Sanjay Chakane, S. V. Bhoraskar, Arun Adsool “Blends of camphorated polyaniline with styrene butyl acrylate as ammonia sensors” communicated to *Sensors and Actuators* (2010).
 13. P. N. Shelke, A. M. Datir, S. D. Chakane, A. D. Adsool “Use of cobalt oxide in an ammonia gas sensor operating at room temperature” *Environment Enrich* (2008).
 14. Datir A.M. Ghole V.S., Koinkar P., Chakane S. D. “Nitrogen dioxide gas sensor based on cobalt and nickel phthalocyanine working at room temperature” *International Journal of modern physics B* 25 (31), PP. 4190-4193 (2011).
 15. Leising, G., Tasch, S. & Graupner, W. in *Handbook of Conducting Polymers 2nd edn* (eds Skotheim, T. A. Elsenbaumer, R. L. & Reynolds, J. R.) 854 (Marcel Dekker, New York, 1998).
 16. Abdiryim, T., Xiao-Gang, Z. and Jamal, R. 2005. Comparative studies of solid-state synthesized polyaniline doped with inorganic acids. *Mater. Chem. Phys.*, 90: 367-372.
 17. Silverstein, M.S; Tai, H.W.; Sergienko, A.; Lumelsky, Y.L.; Pavlosky, S. PolyHIPE: IPNs, hybrids, nanoscale porosity, silica monoliths and ICP-based sensors. *Polymer* 2005, 46, 6682-6694.
 18. Sanjay Chakane, Priyamvada Likhite, Shilpa Jain, S.V. Bhoraskar “Synthesis and characterization of conducting Polyaniline in presence of cuprous ions” *Transactions of the SEAST* 37 (1) PP 35-38 (2002).
 19. Chakane S., Gokarana A., Bhoraskar S.V. “Metallophthalocyanine coated porous silicon gas sensor selective to NO_2 ” *Sensors and Actuators B* 92 (1-2) PP 1-5.
 20. Sanjay Chakane, S. Jain, S.V. Bhoraskar, A.B. Samui, V.N. Krishnamurthy “Sensitive and selective based ammonia gas sensor” *Sensors and Actuators B* (2002).
 21. Jain S., Chakane S., Samui A.B., Krishnamurthy V.N., Bhoraskar S.V. “Humidity sensing with weak acid doped polyaniline and its composites” *Sensors and Actuators B* 96(1-2), PP 124-129 (2003).
 22. Jain S., Chakane S., Samui A.B., Krishnamurthy V.N. Bhoraskar S.V. “Humidity sensing with weak acid doped polyaniline and its composites” *Sensors and Actuators B* 96 (1-2), PP. 114-123 (2003).
 23. A.M. Datir, Sanjay Chakane, A. D. Adsool “Humidity sensing application of Metallophthalocyanines” *Environment Enrich* (2009).
 24. V. K. Gade, D. J. Shirale, P. D. Gaikwad, P. A. Savale, K. P. Kakde, H. J. Kharat and M. D. Shirsat, *Reactive & Functional Polymers* (2006) Available online (www.sciencedirect.com)
 25. Yonezawa, S., Kanamura, K. and Takehara, Z. 1993. Discharge and Charge Characteristics of Polyaniline Prepared by Electropolymerization of Aniline in Nonaqueous Solvent. *J Electrochem. Soc.*, 140:629-634.
 26. Rohit Londhe, Sanjay Chakane, Ashok Datir *Electrical Properties of Functionally Upgraded Conducting Polyaniline with Copper Phthalocyanine* *International Multidisciplinary Research Journal*, pp 128-136, Volume III Issue IV: August 2016
 27. Ashok Datir Sanjay Satale, Sanjay Chakane, Rohit Londhe, Nilesh Kadam, *Characterization Study of SnO_2 Blended with Polyaniline* *International Multidisciplinary Research journal* Volume IV Issue II: March 2016