Band-gap Engineering of Polyaniline-VanadiumOxide Nanocomposites

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In this attricle we reported microwave assisted processing of Vanadium oxide – polyaniline nanocomposite (V_2O_5 -PANI). Firstly, Polyaniline (PANI) nanotubes created by oxidative polymerization method and in the second step depostion of V_2O_5 on synthesized PANI nanotubes is carried out in microwave at 200^oC for 30 minutes in teflon crucibles. The processed materials show requires morphology and outstanding electrochemical properties. The band gap of the Nanocomposites (NC's) found to be 2.6 eV which is the requirment of field emission. The XRD exhibit a set of well defined peak support the crystal nature of the NC's. The peaks obtained by cyclic voltammetry (CV) shows marginal seperation between anodic peaks at 3.6 and 3.7 V for PANI and shifted to higher potential for V2O5-PANI NC's. Also, the electrical conductivity is found to be 10^o S cm⁻¹ for PANI and higher electrical conductivity, 10⁻⁴ S cm⁻¹ for NC's.

Keywords: V2O5-PANI, nanocomposites, electrochemical properties, CV, etc.

Introduction

The amalgamation of conducting nanoparticles and conducting polymers is a novelarea of research.¹Due to unusual properties such as tunability, electrical conductivity, decentecofriendlysteadiness etc. make thisNanocomposites(NC's) as prospectiveentrant for extensiveassortment of solicitations such as gas sensors², light emitting diodes(LEDs)³, photovoltaic devices⁴, corrosion inhibitors⁵, storage devices⁴ etc. By modifyingmorphology of the nanostructures their new set physicochemical properties can be developed. In this lieu many prominent researchers tried to synthesis one dimensional (1-D) nanostructure of conducting polymers.⁶One dimensional (1-D) nanostructure of conducting polymers a unique advantage for field emission (FE) practicalapplication due to high aspect ratio.8Several scientific group have carried out FE investigation of various conducting polymers and NC's.7-¹¹Amongother conducting polymers PANIhas been extensively used in the energy storage and conversion devices due to high specific capacitance, processability and cost-effectiveness.¹² It alone can be used in fabricating an electrode. However, the unstable nature PANIrestrict its application.PANI-NC's can be used in super capacitors, sensing platforms, fuel cells, electrochemical devices, solar cells, lithium ion batteries etc.¹ Polyaniline nanofibril synthesised and its FE investigation is reported and observed threshold field of $5-6V/\mu m$ corresponding to emission current density of 0.01 mA/cm² by Wang et al.⁷Kim and his co-worker reported electrical conductivity studies of nanowire and nanotubes of doped and de-doped PANI, Polypyrrole etc.⁸⁻⁹Electrochemical properties of carbon nanotube-polyaniline composites have been reported by many researchers.¹³It has been perceive that, the functionality of the conducting polymers NC's also improve their emission characteristics. In this perspective Rakhi et al and Nair et al. have investigate the electrochemical properties studies of different conducting polymers.¹³⁻¹⁴ Sandip S Patil and his co-worker reported the FE investigation of CdS-PANI NC's.15

 $V_2O_5 in$ arrears to its small band gap of 2.6 eV make it more convincing promise with stately photoemission and optical properties. 16 If we doped $V_2O_5 with conducting materials which$

effectively increase electrons density give rise to change in Fermi energy from the top of the valence band to the bottom the conduction band. The band gapwas almost identical to the bulk structure band gap with a value of 1.66 eV.¹⁷ Optical properties of this oxide is reported by Karolina Sieradzka and his co-worker.¹⁸The V₂O₅ nanowires shows morphology dependent optical properties and conductivity measurments display a minor turn-on field voltage ~8.3 V/µm, at 1.8 mA/cm^{2.19}V₂O₅·nH₂O nanotube array a novel material for energy storage reported by Chiwei Zhou his co-worker.²⁰Due to structure stability amalgam of inorganic semiconductorsconducting polymers and favourable low band gap make this materials as promising candidates for diversifiedapplications in vacuum microelectronics²¹, biosensors²², photovoltaicand light emitting diodes.²³

Our main aim focused on simple synthesis and characterization of V_2O_5 nanotubes and Polyaniline-Vanadium Oxide (PANI-V2O5) Nanocomposites by microwave assisted chemical synthesis. This method of synthesis is fast, simple and ecofriendly in which microwave radiation was employed as a heating source for nanoparticle synthesizing. Compare to conventional method of synthesis, microwaves directly react to the material by means of numerous possible mechanisms and the chemical react quickly.^{24,33} Also we report conductivity ofV₂O₅-PANI nanocomposite. The obtained value is higher than the individual counterparts' i.e. V_2O_5 and PANI nanostructures. The results obtained are encouraging with excellent morphological stability and outstanding physicochemical properties.

Result and Discussion

Experimental

Synthesis methods

Materials

The precursors, aniline monomer $(C_6H_5NH_2)$, acetic acid (CH_3COOH) , ammonium persulphate $((NH_4)_2S_2O_8)$, Ammonium Metavanadate (NH_4VO_3) and nitric acid (HNO_3) were procured from Sigma Aldrich (Merck) and use as received.

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Synthesis of PANI

The polyaniline was synthesis by oxidative polymerization method. 0.2 M ammonium persulphate($(NH_4)_2S_2O_8$) was slowly added in the homogenous mixture of0.1Maniline monomer and0.5 M acetic acid.The reaction is proceed with constant stirring for 5 minutes by the appearance of dark brown colourwhich turn green and finally into dark green. Themixture was kept undisturbed for next 24 h followed by filtration and washing 2 to 3 times with distilled water and ethanol and drying in air by using IR lamp.²⁵⁻²⁷

Synthesis of V₂O₅hollow Nanotubes

Vanadium oxide hollownanotubes was synthesis using 0.1 M solution of Ammonium Meta vanadate (NH₄VO₃) mixed in 0.1 M nitric acid (HNO₃) with constant stirring for half an hour in acidic environment. The solution appear to dark red colour. The solution was kept at rest for 45 minutes to form the precipitate. The Precipitate was collected and repeatedly washed by double distil water. The precipitate was then taken into Teflon crucible and placed microwave oven for 30 minutes. After that the product is kept in muffle furnace at 400^o C for 4 hours for drying.²⁸⁻³¹

Synthesis of PANI-V₂O₅Nanocomposites

Polyaniline- vanadium oxide nanocompositewas synthesis by mixing synthesized PANI powder with small amount vanadium oxide nanotubes. The amalgam is then placed in microwave oven for 30 minutes at 200^oC. After that the product was kept undisturbed for next 24 hours. The procedure is further proceed with filtration, washing serval times with double distilledwater and ethanol and drying by IR lamp.³²⁻³⁶ The proposed route for the growth of Polyaniline- vanadium oxide nanocomposite is shown by Fig.-1.

AnilineMonomer Aniline + Acetic Acid+ APSPANI+V2O5 (Microwave)

Fig. 1Proposed route for the growth of Polyaniline- Vanadium Oxide Nanocomposite

Material characterizations

The characterization of synthesized materialsis carried out at UGC-DAE Consortium for scientific research, Indore.X-ray diffraction scattering (XRD) study is carried out by using Bruker D8 Advance XRDdiffractometer.This diffractometer is equipped with a sealed tube of Cu-K x-ray source. Scanning electron microscopy (SEM) images were captured using F model-JEOL JSM 5600.CV study is carried on CH Instruments (USA), CHI620DDAVV, Indore. FTIR study is also carried out to reveal the presence of PANI.



Growth of the NC's and their morphology is revealed by the SEM (Fig.-2 a) and TEM (Fig.-2 b). The aggregation PANI Nano particle of 5-10 nanometres in size over 1-DhollowNanotubes of V_2O_5 of micron in length.



Fig. 2 (a&b) SEM imag and 2 (c&d) TEM image of V₂O₅-PANI nanocomposite

A set of well-defined peaks observed which is in good agreement for the crystallinity of the V_2O_5 -PANI nanocomposite. The diffraction peaks observed at 2 θ values 34.9°, 39.3°, 47.4, 62.3° and 72.4° are indexed to (134), (685), (205), (735), (248), and (101) planes of crystalline V_2O_5 phase, respectively.





Apparently change in CV curve is observed indicating there is no change in the structure of bayer V_2O_5 and remarkable shift is observed when the deposition of V_2O_5 on the surface of PANI is taken place Fig.-4.



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Potential (V, $V_2O_5Vs V_2O_5$ -PANI)

Fig. 4 Cyclic volttamettry curve of V₂O₅-PANI nanocomposite The electrical conductivity is found to be 10^{-6} for PANI which get enhance for V₂O₅-PANI nanocomposite. Tupper peak at 4.13 V indicate oxidation of V⁴⁺ to V⁺⁵.



Fig. 5 FTIR graph of PANI and Its composites with V₂O₅

The bands at 1617, 1597, 1571, 1492, 1311, 1279, 1131-1173 cm⁻¹ are assigned as the characteristics bands of PANI in turn also confirming the presence of PANI within the composite. The corresponding bands of V_2O_5 have been obtained in the region 500-1000 cm⁻¹.

There are some small shifts in the band positions in the assynthesized PANI/VO2 composite with that from PANI and VO2 individually, indicating some interaction between PANI and VO2 in the composite.

Conclusions

The PANI nanoparticle is successfully synthesised by oxidative polymerization method. Also we carried out successful microwave assisted synthesis of V_2O_5 -PANI nanocomposite at $200^{\circ}C$ The XRD peaks is in good agreement of the crystlanity of NC's. Electrode reaction reversibility get enhanced for NC's which is supported by the obtained CV curve. The reported result in this paper support that the synthesised material are the promising material for various application in the field of energy storage.

Conflicts of interest

There is no conflict of interest.

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Notes and references

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