Chapter 3

Synthesis and characterization of PANI nanostructures and PANI nanocomposites

In this chapter, the synthesis and characterization of polyaniline nanostructures, metal oxide - polyaniline, metal sulfide-polyaniline, reduced graphene oxide-polyaniline and metal-metal oxide nanocomposites are discussed.

3.1 Synthesis and characterization of polyaniline nanostructures

In this section, we have demonstrated the behavior of polyaniline nanofibers (PANI NFs) as silver -PANI NFs nanocomposites (NC) with new physical insights. The synthesis of PANI NFs and PANI nanospheres (NSs) was carried out for different polymerization period and studied their effect on the structure, morphology and electrochemical performance. The HCl doped PANI NFs shows similar properties of silver-PANI NFs NCs. Structural information obtained from X-Ray diffraction (XRD) along with Ultraviolet- Visible (UV-Vis.), Fourier Transform Infrared Red (FTIR), Raman and Nuclear Magnetic Resonance (NMR) spectroscopy. Morphological study was carried out by Field Emission Scanning Electron Microscopy (FESEM) and High Resolution Transmission Electron (HRTEM) Microscopy.

Among the various existing conducting polymers, PANI NFs shows very wide range of applications.\(^1\) The most commonly observed well-defined morphology of PANI NFs was firstly reported in 1986.\(^2\) A variety of approaches have been employed to synthesize NFs of PANI including template-assisted, interfacial, seeding polymerization etc.\(^3\) The doping of different acids during synthesis of PANI NFs contain different type of counter-ions which are key factors responsible for the worth significance of this class of conducting polymers.\(^3-5\) However, such techniques require relatively large amount of surfactants and it is tedious to recycle the surfactants after polymerization \(^6\), which ultimately make PANI NFs difficult to
attach to the substrate without involving large contact resistance.\[7\] The factors like temperature, post polymerization, monomer and acid concentration, mechanical disturbances, seeding strategy and type of dopant can affect the morphology of PANI.\[8-11\] The formation of PANI–NFs is related to the homogeneous nucleation, while heterogeneous nucleation leads to PANI nanogranular particles (PANI-NGPs).\[12,13\] By this motivation, significant research efforts have been directed in the past few years towards the improvement of solution and thermal processing of PANI-NFs.\[5\]

It is proven that, in all reported methods, use of the template is common to control the growth and morphology of PANI which ultimately becomes uneconomical. However, small enlargement in the NFs may act as active sites for further growth of nanorods (NRs) at the later stage of the polymerization. Thus, the growth of PANI NFs favors the active species which eventually initiates the secondary growth of PANI NFs, resulting in relatively thinner PANI NFs. This agrees with the recent report on PANI NFs prepared with ammonium per sulfate (APS) as an oxidant, suggested that the anisotropic growth of polymer could be attributed to a depletion region along with the growth of PANI NFs and the fresh polymer growth occurred predominantly at the ends of the NFs.\[6,7\] In recent few years researchers have focused their work to prepare different kinds of metal-polymer NC to improve the activity and stability of polymers.

Herein, we presented the PANI NFs synthesized by a template free, post polymerization method which behaved like silver–PANI NFs NC (similar properties like silver NCs) and reported its suitability for energy storage devices (ESD’s). However, the synthesis of mixed morphology (NFs, NTs, NGPs etc.) of PANI using template with rapid polymerization and at high temperature was reported by Du et. al.\[11\], Tran et. al.\[12\], Quiet et. al.\[13\], Ma et. al.\[14\], and Pan et. al.\[15\] Sapurina et. al.\[16\] suggested nanostructures of PANI can act as NC of PANI-metal by changing the synthesis technique. Accordingly, we have tuned the reported methods and synthesized HCl doped PANI NFs at room temperature which behaved (similar properties) like a silver–PANI NFs NC.\[17,18\] We have performed the spectroscopic characterization and electrochemical characterization of the HCl doped PANI NFs.
3.2 Characterization

X-ray diffraction (XRD) patterns of HCl and HNO₃ doped PANI NFs synthesized at room temperature were recorded on. morphology was examined by Field emission scanning electron microscopy (FESEM, Hitachi S-4800) and Transmission electron microscopy (TEM, JEOL, JEM 2100). For detection of functional groups, measurement of order and disorder in the PANI, Fourier Transform Infra-Red (FTIR, Perkin Elmer) techniques have been used. Ultraviolet-visible (UV-Vis.) spectroscopy measurement was recorded by using Perkin Elmer Lambda 950 in the range of 200–1000 nm in aqueous medium. The thermal behavior was studied by (TGA, SETRAM) in the range of 50-650°C. Raman spectroscopy study of the samples was also performed. The NMR study was performed by using DMSO-d₆ as a solvent.

3.2.1 X-ray diffraction analysis (XRD)

Fig.1 reveals the X-ray diffraction (XRD) patterns of HCl, HNO₃ doped PANI NFs and ST-PANI NSs. XRD patterns of HCl and HNO₃ doped PANI NFs shows the characteristic peaks centered at 2θ = 9.76 (001), 14.71 (011), 21.53 (100) and 25.96° (110). All peaks are in good agreement with the report of Pouget et. al. The sharp peak appears in HCl doped PANI NFs at 6.34° specified by (*) corresponds to the organization of lamellae of PANI –NFs as well as formation of silver-PANI NFs NC. The XRD peak of silver is obtained at 19.1° corresponds to JCPDS- 011164. The two peaks appeared around 6.34 and 19.1°are the indication of silverious behaviour of the PANI NFs. The simultaneous appearance of the two peaks at 2θ = 19.1 and 21.53° are not yet reported, indicates the formation of a new phase of PANI NFs synthesized by HCl doping and post polymerization method. The presence of XRD peaks around 2θ = 21.53 and 25.53° are the characteristic peaks of silver-PANI NF NC observed in HCl doped PANI NFs i.e. silver-PANI NFs NCs. Park et. al. presented each XRD pattern gives individual components of PANI NFs. The peak at (110) decreases from HCl doped PANI NFs, HNO₃ doped PANI NFs and ST-PANI NCs. These results indicate that the structural change is taking place on successive exposure to HCl which is confirmed by NMR study.
In ST-PANI NSs, the conductive phase is formed but it is difficult to recognize other phases (Fig. 1), since the spectrum is very broad and peak resolution is poor. The similarity of XRD patterns of PANI prepared by using different dopant indicates the presence of emeraldine salt form of the product. All these results confirm that the products with good crystallinity can be synthesized at room temperature with same morphologies instead of the system at high temperatures and by rapid polymerization. [11,12]

Fig. 1 XRD patterns of the HCl, HNO$_3$ doped PANI NFs and ST-PANI NSs,

3.2.2 UV-Vis. Spectroscopy

Fig. 2 reveals the UV-Visible spectra of (a) ST-PANI NSs (b) HNO$_3$ and (c) HCl doped PANI NFs. The characteristic band of ST-PANI NSs and PANI NFs appears at 357, 428 and 812 nm with a free carrying tail extending to the near-infrared region. These bands are attributed to $\pi$-$\pi^*$ transition of benzeniod rings, polaron-$\pi^*$ transition and $\pi$-polaron transition respectively (Fig. 2a). However, in Fig. 2b and c the characteristic peaks at 357 and 428 nm are absent but at 408 nm and 369 nm bands
obtained which is quite similar to the absorption due to silver in HCl doped PANI NFs. The absorption band of the silver usually appears at around 400 nm, which is caused by surface Plasmon resonance. It is difficult to differentiate these bands due to the overlapping of two bands. [23,24]

Fig. 2 UV-Vis spectra of (a) ST-PANI NSs (b) HNO$_3$ and (c) HCl doped PANI NFs

3.2.3 Fourier transforms infrared spectroscopy (FTIR)

The FTIR spectrums of PANI NFs and PANI NSs are shown in Fig.3. The characteristic peaks at ~1477 and 1558 cm$^{-1}$ belongs to the C=C stretching vibration mode of benzenoid and quinonoid rings, respectively. The absorption bands at ~ 1282,
1100 and 1230 cm⁻¹ correspond to the C-N stretching modes and the C-H in-plane bending and the protonated C-N group, respectively. The characteristic bands at about 1601 and 1494 cm⁻¹ is the sign of the PANI NFs backbone due to the stretching modes of the protonated quinonoid ring and the benzeniod ring. The band at ~1277 cm⁻¹ can be assigned to the C-N stretching mode in a secondary aromatic amine. Therefore, the results of FTIR spectrum demonstrated that the PANI NFs and ST-PANI NSs existing in the conducting emeraldine form. However, these spectrums exhibited difference in their intensities. The integrated band intensities are minimum in HCl doped PANI NFs (Fig.3a) due to different structures as observed in XRD.\textsuperscript{[23]} However, slightly higher intensity bands are observed in HNO₃ doped PANI NFs and ST-PANI NSs (Fig.3b, c).

Fig. 3 FTIR spectrums of (a) HCl (b) HNO₃ doped PANI NFs and (c) ST-PANI NSs.
FTIR spectroscopic studies clarify more insight on the behavior of PANI-NFs as a silver-PANI NFs NCs. The information about resulting structure of PANI NFs as a silver-PANI NFs NC is shown in Fig.3a. The FTIR spectrum of the HCl doped PANI NF’s NC and other two nanostructures of PANI (NFs and NSs) are quite similar (irrespective of band intensities) indicates the formation of PANI backbone. However, it is found that the integrated peak intensity of benzeniod rings against quinoid rings of the HCl doped PANI NFs NC is significantly different than that of NFs and NSs of PANI. It suggests that, HCl doped PANI NFs showing higher conjugation. [24,25]

All these results indicate that HCl doped PANI NFs is similar to silver-PANI NFs NC.

3.2.4 Morphological study

Fig.4 show the morphology of HCl (a,b) and HNO$_3$(c,d) doped PANI NFs at different magnifications. The ST-PANI morphology is presented in Fig. 4e,f. The use of different monobasic acid is seen to be significantly affected the morphology of PANI NFs. The growth of PANI NFs is in one dimensional (1D) (Fig.4b) instead of two dimensional (2D). [26]

![Fig.4 FESEM images of the (a, b) HCl, (c, d) HNO$_3$ doped PANI NFs and (e, f) ST-PANI](image-url)
In Fig. 4a, bulk quantity of PANI in the form of entangled chains appearing as worms like nanofibers (NFs). The diameter of the nanofibers is ~ 50 nm with length up to few microns and most of the NFs show the aspect ratio ~ 1: 4. In Fig.4b, the PANI- NFs are in the form of bunch with the aspect ratio ~ 1:2. In Fig.4c, the PANI NFs are in the form of bunch forming network of NFs shows the aspect ratio ~ 1:8 and same was also observed in Fig.4d. The morphology of ST-PANI observed in the form of agglomeration / nanospheres (Fig.4e, f), because super saturation is not achieved and heterogeneous nucleation dominates, which can form PANI NFs by post polymerization.\cite{8}

Overall, the HCl doped PANI NFs gives a higher aspect ratio than HNO\textsubscript{3} doped PANI NFs. The HCl doped PANI NFs are quite thicker \cite{13} and distinct (Fig. 4b), however, in case of HNO\textsubscript{3} doped PANI, close network of PANI NFs is observed. This is quite similar to the report of Stejskal’s group \cite{27}. In order to obtain isolated NFs of PANI; it is observed that the use of HCl is preferable. The FESEM image of PANI NFs is more distinct than reported elsewhere \cite{28} and exactly similar to the reports of Khanna \textit{et al}. \cite{24} Such structures of PANI NFs can be obtained only by fast reaction \cite{29-31} but we could fabricate the same by slow reaction and post polymerization. Moreover, the morphology of PANI NFs looks similar to the morphology of silver -PANI NFs NC (Fig. 4a). \cite{24}

The PANI NFs do not have a uniform cylindrical or tubular structure rather they form a random, interconnected, nearly flat web like structure of diameter ~ 30-70 nm and 0.4-3 µm in length. This highly interconnected microstructure is the identity of the formation of silver -PANI NFs NC.\cite{32} From the morphological evolution of HCl doped PANI NFs (Fig. 4a) it is clearly seen that the structure is more porous and uniform (Fig. 4b) due to behavior of silver-PANI NFs NC. \cite{33}

\textbf{3.2.5 Transmission electron microscopy (TEM)}

Fig. 5a, b represents the TEM images of HCl doped PANI -NFs. NFs are found to be thinner, broader in size which is in accordance with the FESEM investigations (Fig. 4a,b) supported by Du \textit{et.al} \cite{17} synthesized at 60\textdegree C. Fig. 5c, d reveals TEM images of HNO\textsubscript{3} doped PANI NFs. NFs are in bunches forming tubular like network. The thickness of HNO\textsubscript{3} doped PANI NFs is observed to be higher than HCl doped PANI NFs. Additionally, the TEM image indicates that the PANI NFs has a coarse surface.
The coarse surface has a positive effect on the specific surface area of PANI NFs. All these factors should be considered in designing of PANI NFs supercapacitor with higher capacitance. [9,26]

Fig. 5 TEM images (a, b) HCl and (c, d) HNO₃ doped PANI NFs

Morphological study shows that the experimental conditions affect the morphology of PANI. By increasing the reaction temperature the formation of smoother, thinner (Fig. 5b) and longer PANI NFs are possible. [17] Here, predominantly achieved the same at room temperature by post polymerization and by template free method. Along with this, randomly oriented network structures are also observed in TEM micrographs. A white circle indicates one of cross-linked point between each PANI NF within a network structure which is very common in metal-polymer NC and to enhance the conductivity. [32,34]
3.2.6 Thermal Study

Fig. 6 shows the thermo-gravimetric study of the HCl and HNO₃ doped PANI NFs. In Fig. 6a and b, the major similarity is the presence of three step decomposition patterns. The first step of decomposition is observed at 50-100°C in both the samples which is due to the loss of absorbed water molecules present in the PANI NFs.

![Thermogravimetric analysis (TGA) of (a) HCl and (b) HNO₃ doped PANI NFs](image)

In Fig. 6a and 6b, the second step decomposition starts at ~ 140°C and continued up to 240°C followed by the third step of decomposition pattern. The second step weight loss is mainly due to the loss of dopant ion (thermal dedoping of the polymer) from the polymer chains. There is not much variation in to 1st and 2nd step of the decomposition in HCl and HNO₃ doped PANI NFs. However, the 3rd step of decomposition is found to be varied in both polymers. In HNO₃ (Fig. 6b) doped PANI NFs the 100% loss is observed at ~ 550°C while it is extended up to 600°C in HCl doped PANI NFs indicating the more thermal stability of HCl doped material than that doped with HNO₃. This is due to the similar silver –PANI NFs NC’s structural behavior of HCl doped PANI NFs. [35]
Bober et al. [36] presented the Raman study of silver-PANI NC. Fig. 7 reveals the Raman study of (a) HCl doped PANI NFs and (b) HNO₃ doped PANI NFs. The intensity of several sharp peaks in HCl doped PANI NFs is found to be higher than that of HNO₃ doped PANI NFs, it indicates the surface enhanced with laser excitation due to the behavior of metal–PANI NFs NCs.

### 3.2.7 NMR study of HCl, HNO₃ doped PANI NFs and ST-PANI NCs

Nuclear Magnetic resonance spectroscopy is useful to know the behavior of certain atomic nuclei, namely those which have magnetic moments arising from their spin in the presence of applied magnetic fields. The applied field is responsible for the splitting up of nuclear energy levels between which transitions may be caused by absorption of suitable electromagnetic radiation. The sensitivity of NMR method depends primarily upon the strength of nuclear magnet. It is also affected by certain experimental variables. It is observed that only aromatic ring protons around 7-7.5 ppm appeared & NH protons disappeared which are involved in the polymerization. The crystallinity and orientation of conducting polymers are of much interest, because the more highly ordered system could display a silver conductive state. [35,37-45]

In Fig. 8a, major peaks of the HCl doped PANI NFs have chemical shifts at 8.5-7.58 ppm (m 10H) for aromatic rings, 7.6-7.1 (4H) for delocalized conjugate aromatic ring,
6.27 (1H), and 5.72 ppm (1H). The 1H signals with chemical shifts at 7.0-8.5 ppm (14H) are associated with protons directly bonded to aromatic rings. Since, the observed chemical shifts are all < 5.9 ppm; each aromatic ring may be directly bonded to amines. The sharp peaks at 6.27 and 5.72 ppm are characteristic of HCl doped PANI NFs. It is not certain that these peaks can be readily assigned to N-H. The primary amine groups (-NH$_2$) easily form hydrogen bonding thus usually have broad peaks. The secondary amine groups (-NH-), when connected to two aromatic rings, usually have a high chemical shift (>8 ppm). However, in spectrum $^1$H-NMR of HCl doped PANI NFs the signal at 8.7 ppm was assigned to hydrogen of hydrochloric acid groups. The integrals of hydrogen of hydrochloric acid and methyl signals are in the ratio HCl/HCH$_3$ = 8.2/8.83 = 0.92 indicating that 92 % of hydrochloric acid was used in the reaction.[37]

Fig.8 describes the liquid $^1$H NMR and $^{13}$C NMR of HCl, HNO$_3$ doped PANI NFs and (e-f) ST-PANI NSs in dimethyl sulfoxide (DMSO-d$_6$) with very small amount of tetramethylsilane (TMS) as an internal standard.[47]
In Fig. 8d, $^{13}$C NMR spectra are surprisingly clean, considering that the HCl doped PANI NFs is a mixture of different oxidation states of PANI NFs. The simplicity of the carbon lines suggests that the major components (tetramers) have symmetric structures. The $^{13}$C lines at 80.2-80.4 ppm correspond to carbons connected to the protons with chemical shifts of 5.72 and 6.27 ppm, respectively.$^{[38]}$ High intensity peak at 45.5 ppm indicates PANI NFs in presence of acidic medium. The two peaks with very high chemical shifts may correspond to carbon atoms connected to the phenazinium nitrogen.

In Fig. 8b, signals appear at 0.5 ppm and 2.00 ppm are attributed to hydrogen resonances of DMSO –d6 (solvent) and water molecules respectively, which are difficult to eliminate from the PANI NFs.

In Fig. 8e, the signals centered at 3.5 ppm and 7.25 ppm was assigned to the resonances of the hydrogen amine and aromatic hydrogen, respectively. The integral signals of hydrogen methyl and aromatics are in the ratio of $\text{HNO}_3 / \text{H aromatic} = 25.52/ 29.03 = 0.87$ indicating that 87% of nitric acid were used in the reaction supported by Wolteret et al. $^{[39]}$

The ST-PANI NSs product obtained at the early stages of aniline polymerization by the oxidation of aniline with APS was also analyzed by NMR. Relevant parts of $^1$H NMR spectra of the products collected. The spectra does not contain the very broad signals of NH protons, which appear in the range 8.0-6.5 ppm (as shown in Fig. 8c) and could not give much information about the same. As clearly seen, the spectra are virtually the same, differing only in the width of the signals and in some cases the broadening being probably observed by some higher-molecular-weight components. The major parts of the NMR detectable products are identical or at least closely analogous in accordance with the results of the earlier FTIR spectroscopic characterization. This was explained by the easy oxidation of neutral aniline molecules to oligomers $^{[40]}$ which preferentially takes place even in acidic media where the concentration of aniline molecules is low. The similar oxidation of anilinium cations is much more difficult and proceeds only later during the subsequent polymerization.
In conclusion, using various $^1$H, $^{13}$C, NMR spectra of PANI NFs and ST-PANI NSs, we have shown that the products of early stages of oxidative aniline polymerization have quite analogous structures irrespective of the polymerization time, kind and concentration of the added acid. In addition to the expected oligomeric chains with intermittent diamine and quinoneimine moieties, which are only partly detected by NMR with broad signals, a markedly populated and hitherto not described oxygen-containing quinoneimine group was also detected. It destroys the chain conjugation needed for the conductivity of product.

It is clear from $^1$H NMR and $^{13}$C NMR study of the HCl; HNO$_3$ doped PANI NFs that, the hydrochloric acid is more preferable for polymerization of aniline as well as enhancement of conductivity which is ultimately responsible for behaviour of silver-PANI nanocomposite synthesized by post polymerization.

3.3 Synthesis and characterization silver vanadium oxide (SVO) – polyaniline Nanocomposite

We have successfully designed and synthesized nanocomposites (NCs) of silver vanadium oxide nanospheres dispersed in different ultrathin layers of polyaniline (PANI-$\beta$-AgVO$_3$) at different temperatures (60 and 80$^\circ$C) by in situ chemical oxidative polymerization for the first time. X-ray diffraction (XRD) shows a monoclinic crystallographic form of silver vanadium oxide (SVO) to be dispersed in ultrathin layers of PANI. Morphological studies were performed by field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM). The NCs synthesized at 60 and 80$^\circ$C temperatures show approximately 4 and 2 nm ultra thin layers of PANI grown on SVO nanospheres, respectively. The sizes of the SVO nanospheres dispersed in the ultra thin PANI layers are in the range of 10–40 nm. Fourier transformed infrared (FTIR) spectroscopic and energy dispersive X-ray (EDAX) spectroscopic investigations indicate the existence of SVO in the PANI layer. The NCs are further characterized by ultraviolet-visible (UV-Vis) spectroscopy. Layers of PANI on SVO are studied for the first time and correlated by XRD, Raman spectroscopy, AFM and HRTEM studies.
Chapter 3

The conducting polymer nanocomposites (NCs) and their applications has seen significant surge in research in modern era.\textsuperscript{48} Polyaniline (PANI) has been extensively investigated by various research groups, mainly for the exploitation of its interesting physico-chemical properties, such as high conductivity, humidity and other gas sensing, redox, ion-exchange, excellent environmental stability along with ease of preparation from common chemicals.\textsuperscript{49} Recently, PANI in the form of different nanostructured has attracted more attention as an excellent material for supercapacitor irrespective of its stability.\textsuperscript{50} However, the stability and activity of PANI is very low, which needs further attention. In order to overcome these difficulties, transition metal oxide based PANI NCs were developed.

Owing to the issue of stability and activity of PANI, several other materials have been investigated for supercapacitor, particularly transition metal oxides used for the synthesis of PANI-metal oxide NCs which are more suitable material for supercapacitors.\textsuperscript{51,52} PANI NCs can be prepared by simply blending of polymer and metal oxides. Dzenis \textsuperscript{53} reported that the NCs show significant achievement in all types of applications, if the deficiencies in processing of nanocomposite are successfully overcome. PANI-silver vanadium oxide (SVO, $\beta$-AgVO$_3$) nanospheres NCs will display new and improved mechanical, catalytic, electronic, magnetic and optical properties which are not exhibited by the individual phases.\textsuperscript{54}

As mentioned earlier, PANI is an excellent material for supercapacitor but the PANI-metal oxides NCs is still in embryonic stage. Some transition metal oxides, such as RuO$_2$ and IrO$_2$ exhibit excellent properties as pseudocapacitive electrode materials.\textsuperscript{50} However, despite of remarkable performance of this material, its prohibitively high cost restricts it from wider applications. Cost effective metal oxides (such as MnO$_2$ or NiO) also exhibit electrochemical capacitance behavior to some extent but their performance is much lower than RuO$_2$.\textsuperscript{50} Further, recently, SnO$_2$, $\gamma$-Fe$_2$O$_3$, CuO, WO$_3$ as well as silica have been reported as a cathode materials for supercapacitor.\textsuperscript{55}

In association of above metal oxides, vanadium pentoxide (V$_2$O$_5$) has versatile redox properties because of the multiple valence state of vanadium and layered structure which is leading to good capacitive performance in neutral solutions.\textsuperscript{56} It produces a ordered organic–inorganic nanocomposite with synergistic properties like enhanced electrical property.\textsuperscript{57,58,59} The PANI- V$_2$O$_5$ NCs was reported by Kanatzidis \textit{et.al}
[60] and Liu et al. [61] with good electrical conductivity. Nazar and co-workers demonstrated the feasibility of these materials for energy storage devices. Few research groups reported the potential application of PANI-TiO$_2$ [61-64] conducting polymer-V$_2$O$_5$, [65,66,67] PANI-clay composite also exhibits improved conductivity [68] as well as PANI accumulated metal/metal oxide NCs for supercapacitor. [69,70] Various morphologies of PANI-V$_2$O$_5$ nanocomposite have also been reported such as tremella and nanosheets. [71]

Akin to the different phase forms of V$_2$O$_5$, SVO also exhibits different forms of phases. Much of the attention has been given to the $\beta$ phase of AgVO$_3$ because it shows excellent properties for electrochromic devices (ECDs). [71,72] The use of solids containing redox ions in their structure is the common strategy to avoid the use of additional redox reagents to promote polymerization of any monomer. However, several methods have been reported predominantly with the use of ex-situ polymerization for the synthesis of NCs. Very recently, we have presented the capacitance of SVO containing lithium NTs. [73] Zang et al. [74] recently reported the hybrid materials used for the supercapacitor. Further, there is assortment of various reports where SVO testimony in the form of nanorods, nanorings, nanowires are synthesized at very high temperature. [74-77] Mai et al. [78] presented the same nanocomposite in the form of nanowire. In the present investigation, we have demonstrated the synthesis of SVO dispersed in ultrathin layers of PANI NCs by in-situ polymerization for the first time at different temperatures (60 and 80 $^\circ$C). To the best of our knowledge, the work presented in this article is novel because the role of SVO in comparison with V$_2$O$_5$ or other metal oxides are desirable. We obtained exclusively SVO nanospheres rather than nanorods, nanorings or nanowires reported earlier in the SVO dispersed in ultrathin layers of PANI NCs synthesized by ex-situ polymerization. We have characterized the NCs and studied its electrochemical and sensing properties. Moreover, the ultrathin layers of PANI on SVO were first time correlated by XRD, AFM and Raman spectroscopic results. The layered materials have the potential to be used in next generation nanoelectronic devices because of their enhanced performance and unusual physics of transport and related properties.

Synthesis of SVO and SVO-polyaniline nanocomposites is described in section 2.1.6, 2.3.2 and 2.3.4 characterization of the same is discussed below.
3.3.1 Characterization

XRD patterns of SVO nanospheres covered ultrathin layers of PANI NCs (Synthesized at 60 °C and 80 °C), PANI NFs and SVO nanorods, were recorded at room temperature in 20-60° 2θ range by using radiation source of Cu Kα (λ=1.5418 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech ESCA 3000 instrument. The morphology was examined by FESEM (Hitachi S-4800) and elemental composition by EDAX. HR-TEM analysis was performed on the instrument JEOL, JEM 2100. AFM images were taken with NTEGRA aura model (NT MDT) SPM instrument with semi contact mode by NSG 01 Silicon nitride probe. For detection of functional groups, Fourier Transform Infrared (FTIR) (SHIMADZU 8300) spectroscopy was used. UV-Vis. spectroscopy measurements were recorded by using Perkin Elmer Lambda 950 in the range of 300–800 nm in aqueous medium making the green suspension by sonication. The thermal behavior was studied by SETARAM thermogravimetric (TG) instruments in the range 50-800°C.

3.3.2 Morphological study

Fig. 9 represents the HRTEM image SVO nanospheres growth in ultrathin layer of PANI, NCs synthesized at 60°C. Fig. 9a clearly shows the SVO nanoparticles having the particle size ~10-15 nm, are dispersed in ultrathin layer of PANI during in-situ polymerization. Interestingly, very few nanospheres (Black spots) of SVO are partially embedded in ultrathin layer of PANI. Fig. 9b indicates the ultrathin layer having thickness ~ 4 nm of PANI on SVO nanospheres which is also supported by further study of XRD, AFM and Raman analysis.
Fig. 9 (a) HR-TEM image of NC consist of ultrathin layer of PANI with SVO nanospheres (b) SVO nanospheres is fixed in layer (~ 4nm) of PANI to form PANI- SVO NC synthesized at 60°C

Fig. 10 represents FESEM image of thin layer of PANI anchored SVO NC synthesized at 80°C with different magnification. The image clearly shows that the SVO nanospheres are dispersed in thin PANI layer and the size of SVO nanospheres are in the range of 30-40 nm (Fig. 10a, b). The EDAX (Fig. 10c) pattern clearly shows the composition of PANI -SVO NCs. The spectra clearly indicates the presence of C, Ag, V, O elements which confirms the existence of SVO and PANI in NC.

Fig. 10 (a-c) FESEM of thin layer of PANI on SVO nanospheres NCs synthesized at 80°C with magnification (a) 80K (b) 350K with (c) corresponding EDAX
The HRTEM image in Fig. 11 shows the thin layer of PANI dispersed SVO NC synthesized at 80°C. The size of SVO nanospheres are about 20-40 nm (Fig. 11a-c). Clear fringes perpendicular to the longitudinal direction of the nanospheres with an interplanar spacing of 0.27 nm (Fig.11f ) were observed, which corresponds to the (404) lattice plane of SVO. The selected area electron diffraction (SAED) pattern shows crystalline nature of the SVO nanospheres embedded in PANI. The d spacing given in Fig.12 values are in good agreement with the XRD.

![HRTEM of thin layer of PANI dispersed SVO nanospheres NCs synthesized at 80°C with different magnification and (f) is the SAED pattern](image_url)

It is well known that the crystal growth is temperature dependent and hence larger particle size is observed at 80°C. The nanofibers of PANI forms at 80°C are shown in Fig. 11a and b. Fig. 11d reveals the layer of PANI having thickness ~2 nm developed on SVO nanospheres. The results are similar to PANI-NFs (Fig.13) synthesized at 60°C which is unique.
Fig. 12 d-spacing of SVO-PANI nanocomposites

Fig. 13 Polyaniline nanofibers

FESEM image of PANI synthesized at 60°C clearly shows the formation of PANI-NFs with diameter in the range of 40-45 nm and few micrometers (μm) in length. TEM image of PANI reveals network of PANI-NFs. Formation of layer of PANI-NFs on SVO is also supported by the formation of PANI-NFs (Fig. 11a and b). Morphological study of SVO dispersed in ultrathin layer of PANI NCs synthesized at 80°C and PANI synthesized at 60°C indicates that the formation of nanofiber is predominant in both cases.\textsuperscript{[3]} (Fig. 11a,b Fig.14) Formation of NFs is favorable at high
temperature due to homogeneous nucleation. Whereas in case of ultrathin layer of PANI on SVO NCs there is formation of PANI-NFs at 80°C (Fig. 11a and b) indicating of homogeneous nucleation. Moreover, the formation of SVO nanowires/nanorods/nanorings are expected from our experimental condition but we obtained the nanospheres embedded in PANI.\textsuperscript{[72,75]} The one dimensional growth (nanowires/ nanorods as shown in Fig.15) may be restricted due to layered structure of PANI during \textit{in-situ} polymerization.

Fig.14 FESEM/ TEM images clearly show the formation of PANI- NF’s at 60°C.

Fig.15 Micro/Nanorods of SVO

The atomic force microscopy (AFM) image of layer of PANI on SVO nanospheres synthesized at 80 °C is shown in Fig. 16. Fig. 16a and b indicates 2D (two
dimensional) and 3D (three dimensional) images, respectively. The surface morphology of the 2D image clearly shows SVO nanospheres (white color spots in images) of size 40-45 nm and they are dispersed in layer of PANI (brown color). The 3D image also shows surface roughness and height of the SVO nanospheres. Most of the nanospheres with their height are around 40-45 nm and there are very few particles with their height to be in the range of 50-100 nm and grown in PANI. The surface morphology obtained using AFM is in good agreement with FESEM (Fig. 10) and HR-TEM results (Fig. 11). FESEM morphology of SVO nano/micro rods are shown in Fig.15.

![AFM image of layer of PANI anchored SVO nanospheres NC synthesized at 80 ºC](image)

**Fig. 16 (a-b) AFM image of layer of PANI anchored SVO nanospheres NC synthesized at 80 ºC**

### 3.3.3 Structural Characterization

X-ray diffraction (XRD) peaks obtained (Fig. 17) at 2θ value of 32.23, 46.20, 54.81 and 57.55° are the characteristics of β-AgVO₃ with space group: 12/m (No. 12),
(JCPDS 29-1154) suggesting that there is formation of monoclinic phase of silver vanadium oxide. These peaks can be assigned to (411), (404), (401), (712) and (105) lattice planes, respectively.

Fig. 17 XRD patterns of ultrathin layers of PANI on SVO nanospheres NCs, synthesized at (a) 60°C and (b) 80°C

All the diffraction peaks of as-prepared AgVO₃ nanospheres dispersed in the layer of PANI can be readily indexed to pure phase of β-AgVO₃ peaks in both samples. The peaks of NCs have no shift and hence indicate that the PANI did not intercalate into the interlayers of β-AgVO₃ but dispersed. The intensity of XRD peaks of NCs synthesized at 60°C (Fig. 17a) is slightly lower than synthesized at 80°C (Fig. 17b). SVO synthesized at 60 °C has lower particle size and dispersed in PANI and hence the low intensity peaks with broadness as compared to SVO synthesized at 80°C is desirable. However, the intensity, broadness of XRD peaks depend on number of nanoparticles grown in matrix as well as synthesis temperature. Mai et al. [78] reported that intensity of XRD peak depends on growth of PANI on SVO. The growth of SVO nanospheres are more, size of particle is less at 60°C so that the thickness of the layer (∼ 4 nm) of PANI eventually becomes more and intensity of XRD peaks are less (Fig.
17(a)) which is exactly apposite for the case of 80ºC (Fig. 17 b). The intensity of XRD peaks of SVO\textsuperscript{[78,79]} nanorods / micro rods are very high as shown in Fig.18 which is an evidence of the effect of ultrathin layer of PANI on SVO.

Fig.18 XRD of SVO microrods

Fig. 18 shows the XRD patterns of the SVO micro rods. It can be seen that the characteristic peaks of PANI-NFs are centered at 9.76, 14.71, 20.53 and 25.96 º as shown in Fig 19. All the peaks are in good agreement with the reported results of Pouget et al.\textsuperscript{[3]} Pouget et al demonstrated that the peaks observed at 20.53 and 25.96º can be ascribed to the periodicity parallel and perpendicular to the PANI-NFs, respectively. An interesting additional sharp peak appears in HNO\textsubscript{3} doped PANI-NFs at ~ 6.5º corresponds to the organization of lamellae of PANI –NFs which is absent in the case of other nanostructures of PANI indicated by (*).\textsuperscript{[80-89]}
3.3.4 Raman spectroscopy

Raman spectroscopy is an well known technique, widely used to distinguish order and disorder in the crystal structure of polymeric materials (carbonaceous). The typical features for polymeric materials in Raman spectra are the G and D peaks. It is well known that the G band arises from the first-order scattering of the $E_{2g}$ mode that corresponds to sp$^2$ carbon atoms of polymer and that the D band is associated with disordered structural defects due to the SVO. The intensity ratio of D band to G band shows the carbon ratio of sp$^2$/sp$^3$ which is a measure of the extent of disorder.$^{[79,89,90]}$ Fig. 20 shows the Raman spectra of PANI - SVO NC. The peak intensity ratio I (D)/I (G) is high for SVO- PANI NCs indicates the thick layer of PANI anchored SVO nanospheres. This change indicates that the average density of in-plane sp$^2$ domains anchored the ordered crystal structure of SVO during in-situ polymerization. It suggests that the concentration of defect can be reduced slightly by hydrothermal treatment as well as by in-situ polymerization.
3.3.5 Correlation of XRD, AFM and Raman study with respect to growth of Ultrathin layers of PANI on SVO

The physical property of polymer nanocomposites involves the lattice which is very sensitive to all the planar defects and appears as complementary of structural and morphological techniques. Indeed this approach allows to study the ultrathin layers of PANI, using Raman spectroscopy and AFM. The band gap of SVO is 2.5 eV \[79\] and therefore does not exhibit the complexities associated with non adiabatic electron – phonon coupling which is prominent in PANI. The intensity of XRD peaks in SVO-PANI NC depends upon the quantity of PANI layer on SVO\[78\]. Late et al\[91\] recently reported that the intensity, broadness and shifting of D and G peaks depend on the layered structure of the chalcogenide on substrate. The similar phenomenon is observed in case of ultrathin layers of PANI on SVO in PANI-SVO NCs. The intensity of sharp peak of G band in Fig. 20 indicates the thick layer (~4nm, Fig. 9 (b)) of PANI synthesized at 60 °C. The same is supported by AFM study, where the height profile of PANI layer on SVO is ~200 nm (Fig. 16b) and 20 nm (synthesized at 80 °C). High intensity peaks of XRD (in Fig. 17 (b)) indicate the thin layer (~2 nm,
Fig. 9(d)) of PANI on SVO.\cite{78,80}

### 3.3.6 X-ray photoelectron spectroscopy (XPS)

XPS spectrum of the PANI - SVO nanospheres NC is depicted in Fig. 21. In Fig. 21a, the peak at 286.9 eV suggests the presence of the C 1s.\cite{90} The two nitrogen peaks at 401.5 and 402.5 eV corresponds to positively charged nitrogen (Fig. 21c).\cite{79} The doublet peaks of vanadium with binding energy \( \sim 516.8 \) and 522.4 eV can be attributed to the \( V^{5+} \). In addition, broad peak with high intensity at 529.6eV indicate the presence of oxygen (Fig. 21b). The electrons located at \( 3d_{5/2} \) and \( 3d_{3/2} \) (Fig. 21d) indicating the presence of different valences of silver i.e. \( Ag^+ \) and \( Ag^0 \). There are two distinct spectra of both silver and vanadium that is only obtained in \( \beta \)-AgVO\(_3\). These two spectrums (Fig. 21d) suggest that during the electrochemical reactions, there may be the probability of reductions of \( Ag^+ \) to \( Ag^0 \) and \( V^{5+} \) to \( V^{4+} \).\cite{76,90} Thus, these results indicate the confirmation of SVO which are effectively embedded in ultrathin layer of PANI. All data are carbon corrected.

![XPS spectra of layer of PANI- SVO NC](image)

A FT-IR spectrum of PANI- SVO NCs is shown in Fig.22. The role of silverious material in PANI anchored in SVO nanospheres are important where the interaction of inorganic and organic phase elucidated with the help of FTIR shown by (*). The characteristic absorption peaks of SVO are mainly in the range from 400 to 1000 cm\(^{-1}\), including the symmetric and asymmetric stretching vibration peaks of the V-O band.
and the stretching vibration mode of the V=O band. The ultrathin layers of PANI-SVO NC shows four characteristic peaks at ~1150, 1325, 1505, and 1589 cm$^{-1}$ (♯) can be assigned as C-H plane-bending vibration, C-N stretching vibration, benzenoid ring stretching mode and quinoid ring stretching mode, respectively. The band at 1040 cm$^{-1}$ (*) can be designated as the split peak of C-H plane bending vibration, indicating the strong interaction between the layer of PANI and SVO.$^{[92]}$

![Fig.22 FTIR spectra of PANI-SVO nanocomposites](image)

**Fig.22 FTIR spectra of PANI-SVO nanocomposites**

### 3.3.7 Thermogravimetric analysis of PANI NFs and PANI-SVO nanocomposite

Thermogravimetric analysis (TGA) of PANI and layer of PANI on SVO NCs were recorded at 50-600°C and is presented in Fig. 23. On comparison, it is observed that, in pure polyaniline there are three stage decomposition pattern is obtained. The first step weight loss (50-120°C) is due to the loss of adsorbed water molecules present in the polymer matrix.
The second step weight i.e. 120-250°C is due to the loss of dopant ion (thermal dedoping). The third step weight loss i.e. 250 °C onward is found to be very steep and major weight loss is observed in this step over a small temperature range. The complete degradation and decomposition of the polymer backbone was taken place at the temperature range i.e.250-650 °C. However, in SVO-PANI nanocomposite, there is very small weight loss is observed in the first and second step of decomposition as compared to pristine polyaniline. Also, the third step weight loss is initiated at 400°C and the percentage of weight loss observed is also very less upto 450°C. Above 450°C, no weight loss is observed, which clearly demonstrates the enhanced thermal stability of SVO-PANI nanocomposite due to the growth of SVO nanospheres in polymer matrix. It is noteworthy that, SVO nanospheres increases stability of the nanocomposite and hence will be useful for electronic devices as well as advanced study in physical properties of materials where thermal stability is important.

3.3.8 Growth of ultrathin layer of polyaniline on SVO nanospheres

In-situ polymerization of aniline in presence of ammonium metavanadate, silver nitrate along with APS in acidic condition successfully yields SVO dispersed in layer of PANI NCs. The formation of PANI layer on SVO nanospheres during in-situ
polymerization is difficult at lower temperature, because the formation of SVO is always favorable at very high temperature. However, we have demonstrated at considerably low temperatures (60 & 80°C). From experimental data, it is believed that ratio of Ag:V (1:1) is favorable for the formation of SVO and supposed to have better electrochemical performance.

During polymerization, net formation of silver vanadium oxide is given in reaction (1).

\[
2\text{NH}_4\text{VO}_3 + 2\text{AgNO}_3 \xrightarrow{\text{HNO}_3} 2\text{AgVO}_3 + 2\text{NO}_3^- + 4\text{H}_2\text{O}
\]

The free energy of reaction (1) could be - 23.44 kJ mole\(^{-1}\) \([19]\) implying tendency of reaction to progress toward the right-hand side.

Ammonium metavanadate in water gives vanadium pentaoxide shown in reaction (2)

\[
2\text{NH}_4\text{VO}_3 \xrightarrow{\text{H}_2\text{O}} \text{V}_2\text{O}_5 + 2\text{NH}_3 + \text{H}_2\text{O}
\]

Vanadium pentaoxide (V\(_2\)O\(_5\)) is an amphoteric oxide. Thus, it reacts with strong non-reducing acids (HNO\(_3\)) to form pale yellow solution according to reaction (3)

\[
\text{V}_2\text{O}_5 + 2\text{HNO}_3 \rightarrow 2\text{VO}_2(\text{NO}_3^-) + \text{H}_2\text{O}
\]

\[
2\text{VO}_2(\text{NO}_3^-) + 2\text{AgNO}_3 \xrightarrow{2\text{H}_2\text{O}} 2\text{AgVO}_3 + 4\text{HNO}_3
\]

However, according to Porn et al. \([93]\) the polymerization of aniline is not dependent on reduction potential of any oxidizing agent, but it is believed that the growth of SVO in ultrathin layer of PANI is not assisted by acid. The reduction potential of Ag is E\(^0\) +0.79 V, which is lower than 1.02 V of aniline. Thus, it is hard for AgNO\(_3\) to act as an oxidant in the early stages of aniline polymerization. Hence, the oxidation of aniline by AgNO\(_3\) may require more than 96 hrs. V\(_2\)O\(_5\) is an oxidizing agent which forms at early stages of reaction and later converted into VO\(_2\)(NO\(_3\)) which doesn’t act as an oxidant. During experimentation, we have observed instantly the green color by the addition of aniline which is prima facie indication of the formation of PANI. Aniline is oxidized by APS (2.001V) but not by vanadate because reduction potential (1.00 V) is slightly lower than 1.02 V of aniline. It may act as an oxidizing agent for prolonged reactions but in our case the reaction was carried out within short period of time (6 hrs).
During polymerization, the silver nitrate reacts with VO$_2$ (NO$_3$) solution as per reaction (3) and forms stable nuclei of β-AgVO$_3$ nanospheres in ultrathin layer of PANI by forming NFs (Fig. 11(a, b) and Fig.13). The nucleation is further engendering into control crystal growth over a period of complete polymerization. The reactions (2) and (3) are the key steps because in reaction (3) there is formation of β-AgVO$_3$, which is simultaneously anchored /dispersed by/in PANI as per reaction (4).

The reaction mechanism is simplified by scheme 1
From the above results, it is understood that the core of the nanospheres is $\beta$-AgVO$_3$ and the outermost layer is PANI. When the liquid aniline monomers were added in the mixture of SVO, some of them first adsorbed on the surface of solid SVO nanospheres uniformly. At the solid-liquid interface a small amount of Ag$^+$ dissolved from the SVO nanospheres with aniline monomers which lead to the formation of middle part of SVO. As a result, some of the aniline monomers transformed to liquid oligomers and small amounts of metallic silver particles. After addition of APS the polymerization was further carried out completely and NCs of layer of PANI - SVO was obtained on hydrothermal treatment.\cite{94}

3.4 Synthesis and characterization silver vanadium sulfide (SVS) – polyaniline nanocomposite

In the present investigation, PANI anchored silver vanadium sulfide (SVS) nanocomposite (NC) was synthesized by \textit{in situ} polymerization of aniline. For the preparation of NC, aniline, silver nitrate, ammonium metavanadate and thiourea (TU) were used as the precursors. TU was used as a metal ion complex forming agent as well as a source of sulfur. Fourier transform infrared (FTIR) and energy
dispersive X-ray (EDS) spectroscopic investigations indicate the PANI is as at outermost and SVS at the middle layer. Field Emission Scanning Electron Microscopy (FESEM), High resolution transmission electron microscope (HRTEM) and Atomic Force Microscopy (AFM) study shows PANI anchored spherical particle of SVS.

Polyaniline (PANI) is one of the most attractive conducting polymer due to high conductivity, better stability and ease of synthesis.\textsuperscript{[95]} It has been extensively studied and synthesized for electronic applications.\textsuperscript{[96]} Nanoparticles (NPs) of transition metal sulfides have been anchored into the PANI layer, because of different valence states, which are more useful in various applications, like electric vehicles and high power tools.\textsuperscript{[95,96]}Layered transition-metal dichalcogenides such as MoS\textsubscript{2}, WS\textsubscript{2}, Ag\textsubscript{2}S, and VS\textsubscript{2} etc. have been successfully established a new paradigm in the chemistry of nanomaterials. The nanomaterials viz nanotube, fullerene-like nanostructure and the graphene analogues shown huge potentials during the past decades.\textsuperscript{[97-100]} There is a growing interest in development of binary metal sulfide conducting polymer NCs by the scientific community. It is difficult to prepare binary / ternary metal sulfide alone in an H\textsubscript{2}S atmosphere because it requires high temperature and hence the bulk metal sulfide is obtained instead of nanomaterial.\textsuperscript{[97]} These sulfides are non-oxidizing and hence they are not suitable for polymerization. However, other synthetic methods for introducing non-oxidizing sulfides into polymers can be used. There is a considerable amount of interest in layered NCs, assembled from the two-dimensional inorganic hosts and organic guests or vice-versa. Such materials are prepared by mixing of components at the molecular level and design the new materials with novel properties. Most of binary metal sulfides generally show the cubane like crystal structures.\textsuperscript{[101-103]} However, a very limited study was reported on the conducting polymer binary or ternary metal sulfides NCs.\textsuperscript{[104]} To the best of our knowledge, this is the first report where ternary metal chalcogenides are anchored by PANI which are obtained from the metal oxide. The anchoring of metal sulfide is more predominant in PANI than oxide.

In view of this, we have attempted the synthesis of SVS–PANI NCs by \textit{in situ} polymerization without destructing the host material property.\textsuperscript{[105-106]} However, there are certain reports on successful synthesis of metal sulfide conducting polymer NCs by \textit{in situ and ex-situ} polymerization of aniline. Vadivel \textit{et al}\textsuperscript{[98]} reported the VS\textsubscript{2}–
poly (3, 4 ethylene dioxythiophene, PEDOT) NCs with improved conductivity at room temperature. Very recently, polyvinyl alcohol- MoS$_2$ was also reported with enhanced properties.\cite{107} Thin films of Ag$_2$S- polyvinyl pyrrolidone (PVP) NCs was reported by Qian et al.\cite{108}. Hence, the various metal and metal sulfide– conducting polymer NCs synthesized by in situ polymerization is observed to be a very effective universal approach.\cite{109} In view of this, we have explored this approach.

In this study, we have successfully synthesized hexagonal binary metal chalcogenides (Ag$_2$V$_2$S$_4$) at low temperature and anchored by PANI matrix which shows good electrochemical performance. Synthesis of PANI, PANI anchored SVS nanospheres is discussed in section 2.1.7 and 2.3.5 in chapter 2.

### 3.4.1 Characterization of PANI, PANI anchored SVS nanospheres NCs

XRD patterns of PANI anchored SVS nanospheres NCs, PANI were recorded at room temperature in the 2 theta range 10–70$^\circ$ using a Cu Ka (k = 1.5418 Å) radiation source. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech ESCA 3000 instrument. The morphology was examined by FESEM (Hitachi S-4800) and the elemental composition was examined by EDAX. HRTEM analysis was performed on a JEOL, JEM 2100 instrument. AFM images were recorded with a NTEGRA aura model (NT MDT) SPM instrument in semi contact mode using an NSG 01 silicon nitride probe. For the detection of functional groups, Fourier Transform Infrared (FTIR) (SHIMADZU 8300) spectroscopy was used.

#### 3.4.1.1 X-ray diffraction analysis

Fig. 24 presents the XRD patterns of PANI (Fig.24a) and PANI anchored SVS nanospheres NCs. The XRD pattern of PANI anchored SVS nanospheres NCs shows the probable formation of Ag$_2$V$_2$S$_4$anchored by PANI matrix (Fig.24b). There is no report of a probable structure (by XRD) of SVS, however few researchers presented it on the basis of theoretical study.\cite{109-110} We have determined the lattice parameters by using a standard software package “POWD” \cite{111-113} The XRD peaks of SVS are well indexed and given in the Table 1. On the basis of the best agreement between the observed and calculated d-spacing ($\sum \Delta d = d (\text{obs}) - d (\text{Cal}) = \text{minimum}$), the unit cell lattice parameters are calculated to be $a=b=7.8551$ (5), $c=18.6801$ (5). The most probable crystal system is observed to be hexagonal.
### Table 1. Indexing of SVS

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<tr>
<td>61.84</td>
<td>2 2 8</td>
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</table>

The nature of diffraction peaks of PANI anchored SVS nanosphere NCs
indicate the good crystallinity\cite{114, 115}. The peaks of SVS anchored PANI, shows that there is no change in the structure of SVS. There is no change in peak position of NCs as compare to SVS, attributed to SVS nanospheres anchored on surface of PANI. \cite{116} The XRD peaks of PANI clearly shows slightly amorphous nature while the peaks of PANI anchored SVS NCs are sharp with high intensity indicates high loading of crystalline SVS.\cite{94}

![XRD patterns of (a) PANI (b) PANI anchored SVS NCs](image)

**Fig. 24** XRD patterns of (a) PANI (b) PANI anchored SVS NCs

### 3.4.1.2 UV-Vis.spectroscopy

The UV-Visible absorption spectra of PANI anchored SVS nanospheres NCs is shown in Fig.25. Fig.25a indicate the UV.Vis. spectra of PANI anchored SVS NCs. PANI shows a peak at 330 nm (Magnified spectra is shown in Fig. 25b) and a small hump at ~ 800 nm which may be due to $\pi-\pi^*$ transition of the benzenoid rings and the conducting emeraldine salt phase of the PANI respectively.\cite{117, 118} The shift of SVS peak was masked by the sharp peak of PANI $\pi-\pi^*$ transition at 330 nm. The SVS anchored PANI NCs shows the broad absorption band in the range of 350-600 nm.
which is due to the cluster of SVS NPs (10-40nm) anchored PANI matrix. (Magnified spectra is shown in Fig. 25c)[119-122]

![Graph](image1.png)

**Fig.25** The UV-Visible absorption spectra of PANI anchored SVS nanospheres NCs

**3.4.1.3 Morphological study: FESEM**

Fig. 26 shows the FESEM image of the PANI anchored SVS nanosphere NCs at different magnification. The clusters of SVS were anchored over the very thin layer (black color) of PANI as observed in the FESEM images. The particle size of SVS is observed to be in the range of 10-40 nm. The careful observations indicate the spherical morphology of SVS anchored PANI (Fig. 26a, b). To ascertain the complete conversion of AgVO$_3$ to Ag$_2$V$_2$S$_4$, we performed additional energy dispersive X-ray (EDS) analysis of the product (Fig. 26c). The spectra show signals arising from Ag, V and S atoms. [123-125] The composition is nearly matching with the theoretical one. The exact composition is difficult to obtain in polymer NCs because EDS can give only surface analysis which will not give a clear idea of embedded particles.
Fig. 26 (a-b) FESEM images of PANI anchored SVS nanospheres NCs with (c) corresponding EDS

<table>
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</tr>
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</tr>
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</tr>
</tbody>
</table>
3.4.1.3 High Resolution Transmission Electron Microscopy (HRTEM)

Fig. 27 (a-c) HRTEM images of PANI anchored SVS nanospheres NCs at different magnification and (d) its SAED pattern.

Fig. 27 shows the HRTEM images of PANI anchored SVS nanospheres NCs at different magnification with corresponding selected area electron diffraction (SAED). The images (Fig. 27 a-c) clearly show SVS NPs of size 10-20 nm is anchored in PANI matrix. The particle morphology obtained is spherical in nature. Very tiny SVS nanoparticles anchored by PANI were obtained because of in-situ polymerization. The SAED pattern shows single crystalline nature of SVS anchored by PANI (Fig. 27).

3.4.7 Atomic Force Microscopy (AFM) study

Fig. 28 reveals the AFM images of PANI anchored SVS nanospheres NCs (a) 2D and (b) 3D.
The surface morphology of the 2D image clearly shows SVS nanospheres (white colour spots in images) of size 10-20 nm and they are anchored by PANI matrix (brown color). The SVS NPs those are comparatively higher in size are partially anchored by PANI (white in colour). The 3D image also shows small white colour spot surface roughness and height of the SVS NPs which is in the range of 10-20 nm. The surface morphology obtained using AFM is in good agreement with FESEM and HR-TEM.\cite{125-127}

### 3.4.8 X-ray photoelectron spectroscopy (XPS)

The XPS spectrum of the PANI anchored SVS nanospheres NCs synthesized at 60 °C is depicted in Fig. 29. In Fig. 29b, peak at 286.9 eV suggests the presence of the C 1s and N 1s at 401.0 eV (Fig. 29d) indicates the existence of PANI matrix. Significantly, the peak at around 397.4 eV (Fig.29 d) is attributed to the amine nitrogen of the polymer while the other two peaks at 399.5 and 400.5 eV correspond to positively charged nitrogen. The two different environments at ~ 400 eV can be interpreted as to undoped quinonoid imine (-N)) and benzenoid amine (-NH-), states of nitrogen. The presence of two nitrogen indicates that PANI is still in the conducting state. The doublet peaks of vanadium with binding energy 517.8 and 531.4 eV can be attributed to the V$^{5+}$ (Fig. 29e).
Fig. 29 (a-f) XPS spectra of PANI anchored SVS nanospheres NCs

The 3d_{3/2} electrons located at 368.8 eV and 3d_{5/2} electrons at 376 eV, indicating the presence of different valencies of silver (Fig. 29c) i.e. Ag^+ and Ag^0 and there are the spectra of both silver and vanadium indicating the formation of SVS obtained from silver vanadium oxide (SVO). These two spectrums (Fig. 29c & e) suggest that during
the electrochemical reactions, there may be the immense probability of reductions of $\text{Ag}^{+}$ to $\text{Ag}^{0}$ and $\text{V}^{5+}$ to $\text{V}^{4+}$.

Fig. 29f represents the XPS of sulfur (2P$_{3/2}$) present in the SVS. The peak at 168 eV is absent indicates the absence of oxygen. This is the particular peak of sulfonate group. There are certain undefined peaks are also present indicate that the sulfur is present in different environment particularly of low-valence-state. These low-valence sulfur ions are more reactive. The 2p$_{3/2}$ electrons located at 162.1 eV of sulfur shown by (#) predominantly indicated the lower loading and S 2s at 165.9 eV is an indication of the higher loading (**) . Sulfur can not be detected clearly because of low sensitive instrument. It is important that these both peaks are originating from the PANI anchored SVS nanospheres NCs. The asymmetric tail on the high binding-energy side of this component is due to the positive charge stored along the anchored PANI layer and partially localized on the sulfur atoms. The doping charges lead to an intermediate electronic structure of the PANI chains between quinoid and benzoid structures.\cite{128,129} The survey of XPS spectrum of PANI anchored SVS nanospheres NCs is shown in the Fig. 29a. All data are carbon corrected.

3.4.9 Fourier Transforms Infrared Spectroscopy (FTIR) study

The FTIR spectra for PANI anchored SVS nanospheres NCs is depicted in Fig. 30. The presence of sharp peaks near 1423.51 and 1591.02 cm$^{-1}$ are attributed to stretching of the benzenoid and quinoid rings of PANI respectively. The appearance of the characteristic absorption band at around 1165.04 cm$^{-1}$ was due to the C–N stretching in bipolaron structure in PANI. These results indicate that PANI in the form of thin layer highly anchored to surface of SVS and existing in the conducting emeraldine salt form. The peak at 1290.42cm$^{-1}$ corresponds to C–N stretching of secondary amine of PANI. The existence of absorption band at 1124.54cm$^{-1}$ may be originating from plane bending vibration of C–H, which is formed in the PANI.\cite{128,129} The 599.98 and 538.16 cm$^{-1}$ band absorptions are assigned to the antisymmetric stretching mode of Ag–S and V–S of SVS anchored by PANI matrix. The 538.16 cm$^{-1}$ band is weak compared to the 599.98 cm$^{-1}$ also partially coincident with the V–S and Ag–S absorption.\cite{79,130-133}
Band at 1020 cm\(^{-1}\) can be designated as the split of C-H plane bending vibration, indicating the strong interaction between the PANI shell and SVS core. The relative intensity of the band at 553 cm\(^{-1}\) strongly decreased due to introduction of Ag(I) into vanadium sulfide (inset of Fig. 30).

The thermal behavior of PANI anchored SVS nanospheres NCs was investigated by TGA and depicted in Fig. 31.
TGA shows the weight loss in three steps. The first step weight loss at 30 to 120 °C is due to the elimination of water and unreacted monomers. The additional weight loss between 150 and 200 °C for the PANI-SVS nanosphere NCs is probably attributed to the removal of the dopant molecules and some oligomers. The third step major weight loss observed at around 450 °C was attributed to the degradation of polymer main chain. The structural decomposition of the PANI occurred fairly at high temperature (450 °C) which suggest the good thermal stability of the polymer NCs. The weak peak at temperature 750 °C is because of the instrumental error (Fig.31).

Fig. 31 TGA of PANI anchored SVS nanospheres NCs.

Fig.32 Structure of PANI [139]
An enormous amount of work has been reported on microstructure/morphology of PANI. The molecular structure of the PANI (Fig. 32) is also known. Overall chain conformation and packing, degree of cross-linking etc., remain dubious. How these factors affect collective properties of PANI is still unknown. However, the formation of PANI matrix is quite well known that has been discussed in the experimental section 1. We strongly believe that there is formation of PANI anchored SVS which is supported by XRD, FESEM and HR TEM.

Net formation of silver vanadium oxide (SVO, i.e.\(\text{AgVO}_3\)) is given in reaction (1) \([127]\)

\[
2\text{NH}_4\text{VO}_3 + 2\text{AgNO}_3 \xrightarrow{\text{HNO}_3} 2\text{AgVO}_3 + 2\text{NO}_3^- + 4\text{H}_2\text{O}
\]

The free energy of reaction (1) could be - 23.44 KJ mole\(^{-1}\)\([128]\) implies the tendency of reaction to progress toward the right-hand side at temperature 60\(^\circ\)C.

The formation of \(\text{Ag}_2\text{V}_2\text{S}_4\) from \(\text{AgVO}_3\) is explained with following allied reactions. Ammonium metavanadate in water gives vanadium pentaoxide shown in reaction (2). \([140;141]\)

\[
2\text{NH}_4\text{VO}_3 \xrightarrow{\triangle \text{H}_2\text{O}} \text{V}_2\text{O}_5 + 2\text{NH}_3 + \text{H}_2\text{O}
\]

Vanadium pentaoxide (V2O5) is an amphoteric oxide. Thus, it reacts with strong non-reducing acids (HNO3) to form a pale yellow solution according to the reaction (3).\([142]\)

\[
\text{V}_2\text{O}_5 + 2\text{HNO}_3 \xrightarrow{} 2\text{VO}_2(\text{NO}_3^-) + \text{H}_2\text{O}
\]

\[
2\text{VO}_2(\text{NO}_3^-) + \text{AgNO}_3 \xrightarrow{2\text{H}_2\text{O}} 2\text{AgVO}_3 + 4\text{HNO}_3
\]

The conversion of SVO into \(\text{Ag}_2\text{V}_2\text{S}_4\) is important. Here, it is important that, the repulsive force increases more rapidly for the sulfides because the more diffuse ‘S’ valence electron density shields the ‘S’ nucleus weakly. In effect, this makes the ‘S’ atom larger than the ‘O’ atom, contributing to its larger empirically defined radius. The attractive force, approximated as valence electron molecular orbital delocalization energy is greater for the sulfides by which equilibrium will attain. The long bond distances for the oxides increases the repulsive energy. At equilibrium, the attractive and repulsive energy components are similar for the sulfides and oxides. The
differences in bond strengths are due to the metal to chalcogenides charge-transfer energy.\textsuperscript{[143]} In the presence of a high percentage of sulfur source by which effect of oxygen became negligible and surrounding become favorable for formation of SVS. The detailed mechanism of formation of cluster of Ag$_2$V$_2$S$_4$ is described elsewhere in detail which is given in reaction (4).\textsuperscript{[127,128]}

![Reaction Diagram]

The SVS formed in reaction is anchored by PANI during polymerization as shown in reaction (5)\textsuperscript{[106,144]} During the reaction, precursors like silver nitrate, ammonium metavanadate are themselves acts as oxidizing agent but the reaction time will affect the formation because of redox capacity. The addition of (NH$_4$)$_2$S$_2$O$_8$ as an oxidizing agent improved the conductivity of the NCss. The NCs subject to post-oxidative treatment show enhanced electrochemical performances and conductivity.

The reaction of the resulting phase of SVS with water can form SVS dispersions with a partial negative charge. In the presence of positively charged guest species (PANI), the SVS host layers re-stack and result in the formation of novel materials.\textsuperscript{[107,145]}
3.5 Synthesis and characterization of reduced graphene oxide – polyaniline nanocomposite

The nanoroseflowers, nanosheets, nanorods and nanoferns of reduced graphene oxide were demonstrated by using oxalic acid as a reducing agent. The various morphologies of reduced graphene oxide have been obtained on time dependent reduction of graphene oxide. The composites of reduced graphene oxide based polyaniline nanofibers, nanobooky of flowers (bouquet) and honeycombs were grown at a low temperature (60°C) by \textit{in situ} polymerization of aniline. The electrochemical study of reduced graphene oxide and its composites with polyaniline nanostructures was performed. The composite of honeycomb reduced graphene oxide – polyaniline nanofibers showed enhancement in the electrochemical performance. Such type of composites is the best contender for supercapacitor.

Reduced graphene oxide (RGO) has been synthesized using a simple chemical method which has potential applications in various nanoelectronic devices. Many methods have been reported for the preparation of RGO, such as lithography, sonochemical, chemical vapor deposition (CVD) etc.\textsuperscript{[146]} Controlled morphology of RGO has not yet been well studied due to different process parameters and steps involved in the synthesis. The CVD is one of the most popular, powerful and well controlled method to synthesize desired morphology and structures of RGO\textsuperscript{[146-154]}. But, the problem remains with CVD method, it yields poor quality of RGO and also shows low electrochemical performances,\textsuperscript{[148,150,155]}. Chemical methods were found to be economical and effective for producing RGO in large scale. Therefore, chemical methods are more suitable for synthesizing high-performance RGO and RGO based composites\textsuperscript{[156]}. The challenge of preparation of highly crystalline, most excellent quality with a large area single sheet of RGO has not yet been resolved.\textsuperscript{[157]} However, the reduction of graphene oxide (GO) to RGO is not possible completely by using hydrazine hydrate as a reducing agent. It is also well known that, the hydrazine
hydrate is toxic, carcinogenic and unstable. Hence, it is necessary to investigate highly efficient, low toxic and eco-friendly reducing agent for the synthesis of RGO.

The conducting polymer like polyaniline, will overcome all these issues even though there is a weak attraction between RGO and polyaniline. In view of this, we synthesized highly populated nanorose flower, nanorods, nanofern and nanosheets of RGO in various and interesting morphologies from GO. Such unique morphologies of RGO from GO have been demonstrated for the first time by simple chemical treatment. The chemical treatment is more efficient for the production of RGO which was further used for the synthesis of RGO based polyaniline composites. The composites of RGO-polyaniline in different morphologies are synthesized by in situ polymerization in the presence of mild oxalic acid (O. A.). The RGO and RGO-polyaniline composites have been characterized and electrochemical performance was demonstrated.

3.5.2. Experimental section:

3.5.2.1 Materials

Graphite powder was obtained from Carbon Everflow Ltd. Concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) (98%), potassium permagnate (KMnO\textsubscript{4}), sodium nitrate (NaNO\textsubscript{3}), O.A, ammonium persulfate (A.P.S.), Aniline, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), hydrochloric acid (HCl) were purchased from S D Fine Chem. company and used as received.

3.5.2.2 Synthesis of polyaniline nanofibers

In 100 ml distilled water (DI), A.P.S. (22.81 gm, 1 mol/l) was dissolved. 1 mol/l of aniline (9.1 ml) was added in above A.P.S. Solution (1:1 mol ratio) and stirred for 15 minutes. On constant stirring, 3 mol/l (48.9 gm) of O.A. was added slowly in small fractions in above mixture. The green color suspension obtained and stirred for 36 hours at room temperature. The final product was filtered, washed and dried.

3.5.2.3 Synthesis of GO

GO was synthesized from graphite powder by a modified Hummers method. In a typical synthesis, 1 gm of graphite and 0.5 gm of NaNO\textsubscript{3} were mixed
in 25 ml concentrated H₂SO₄ (98%) in a 100 ml flask. The mixture was stirred for 30 min in ice bath. While maintaining vigorous stirring, 3gm of KMnO₄ was added to the above mixture. The reaction temperature was maintained ~ 20°C and reaction was carried out overnight. As the reaction progressed, the mixture gradually became pasty, and the color turned into light brownish. At the end, 30 ml of water was slowly added to the paste with vigorous agitation. The reaction temperature was rapidly increased more than 90°C along with effervescence, and the color changed to yellow. The diluted suspension was stirred at 90°C for 24 hrs. Then, 10 ml of 30% H₂O₂ was added to the mixture. For purification, the mixture was washed by rinsing and centrifugation with 5% HCl and then DI for several times. After filtration and dry under vacuum, the GO was obtained as a gray powder.

3.5.2.4 Synthesis of nanoroseflowers, nanorods, and nanosheets of RGO

The 7 gm of O.A. dissolved in 90 ml DI. and to this 10 ml GO suspension (4.1 mg ml⁻¹) was added. The solution was stirred vigorously for 2h at 60°C. The same procedure was used for 4 and 6h. The products were washed with distilled water several times. The various morphologies of RGO were obtained.

3.5.2.5 Synthesis of nanofibers Hierarchical composites

RGO nanosheets (2 mg) were dispersed in 100 ml DI containing 3 gm (3%) of O.A. Liquid aniline with 100% weight percentage of RGO nanosheets were slowly added into above solution. After 2 h, A.P.S. with 1:1 mole ratio of monomer was added. The mixture was allowed to react for another 4, 8 and 12h.

3.5.2.6 Characterizations

The crystallographic structures of the RGO – polyaniline nanofibers hierarchical composites and RGO were determined by X-ray diffraction (XRD, Brucker D8-diffractionometer) equipped with a Cu Ka radiation (λ= 1.544Å). While the initial changes in the surface chemical bonding as well as the coating behavior of the hybrids were recorded by Fourier transformed infrared spectrophotometer (FT-IR, SHIMADZU 8300) in the range of 2000-800 cm⁻¹. Ultraviolet –visible spectroscopy (Perkin Elmer, Lambda 950) measurements of dispersed of honeycomb RGO-polyaniline nanofibers composite and RGO in DI were recorded for transition
detection in the range of 300-900nm. Raman spectra for the honeycomb RGO-polyaniline nanofibers composite and RGO were obtained with a micro-Raman system. Microstructure and structural morphologies of the hybrids were investigated by a field emission scanning electron microscopy (FE-SEM) performed on a Hitachi S-4800 and by High Resolution Transmission Electron Microscope (HRTEM) on a JEOL-2010. BET method is used for surface area analysis of honeycomb RGO-polyaniline nanofibers composites and hierarchical RGO-polyaniline nanofibers composites and RGO pressed into tablets under a hydraulic press to mirror finishing were subjected to the standard four point probe method for conductivity measurements. The polyaniline nanofibers were also characterized by XRD.

3.5.2 Chemistry of reduced graphene oxide and reduced graphene oxide – polyaniline nanocomposite/composites

It has been well studied that the O.A. acts as a reducing agent for GO \cite{157,158} and also act as a dopant for aniline polymerization, which further improves the solubility of polyaniline composites. Further, it reduces the impurities and most importantly it helps to coating of polyaniline on RGO. \cite{158-161}

*Fig.33: Photographs of suspension of (a) GO (b) RGO (c) Honeycomb RGO-polyaniline nanofibers composites*
The synthesis scheme of nanorose flowers, nanofern, nanosheets, nanorods of RGO and composites of nanobooky of flower, nanosheets, honeycombs of RGO-polyaniline nanofibers are shown in Fig. 34 and the corresponding FESEM images shown in Fig. 36

Mostly, any reduction of GO is to produce RGO from direct mechanical exfoliation. Recent few reports describe the reduction of GO by O.A, ascorbic acid and silver at high temperature. [157,162,164] The reaction for reduction of GO of carboxylic acids is given below. [164-172]

\[
\text{GO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{RGO} + \text{H}_2\text{O} \quad \text{(1)}
\]

The RGO based polyaniline composites have been reported to the supercomputer application and hence have been synthesized by *in situ* polymerization using RGO and aniline [157, 159,160]

The reactions involved in the synthesis of RGO and RGO-polyaniline nanofibers are given below.

\[
\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^- \quad \text{(2)}
\]

\[
\text{GO} + 2\text{e}^- \rightarrow \text{RGO} + \text{e}^- \quad \text{(3)}
\]

\[
\text{RGO} + \text{e}^- + \text{Ph} - \text{NH}_2 \rightarrow -[\text{Ph} - \text{NH}_3^+]n - \text{RGO} \quad \text{(4)}
\]
COOH

H₂O

O

C

C

O

O

\[ \text{Reduction} \quad \text{GO} + xH^+ + ye^- \rightarrow \text{RGO} + 2H_2O \]

Fig. 34 (a) Preparation of GO (b) RGO in the morphologies of (i) Nanorose flower (4h), (ii) Nanosheets (2h), (iii) Nanorods (6h), (iv) Nanoferns (12h) (c) Composites of (i) Nanobooky of flower RGO-polyaniline nanofibers (8h), (ii) Nanosheets RGO-polyaniline nanofibers (4h), (iii) Honeycomb RGO- polyaniline nanofibers (12h).
Fig.35: Schematic of functionalized RGO \cite{174}. Resulting in different morphology (Phenyl functionalized GO (Ph- GO) and GO can be thermally reduced. 4-iodophenyl functionalized GO (I-Ph-GO) can be thermochemically reduced at 60 °C)

3.5.3 Field Emission Scanning Electron Microscopy (FESEM)

Fig. 36 reveals the FESEM images of RGO (a, b) nanorose flowers, (c, d) nanofern, (e, f) nanosheets, (g, h) nanorods and composites of (i to l) RGO-polyaniline nanofibers in the form of flower of nanobooky (bouquet) (i, j), honeycombs RGO-polyaniline (k, l). These morphologies are quite interesting with size in the range of 0.5-10 μm. Such morphologies were obtained due to the mismatch of strain with GO and RGO during treatment.
Fig. 36: FESEM images of nanorose flower RGO (a-b), nanofern RGO (c-d), nanosheets RGO (e-f), nanorods RGO (g-h), flower of nanobooky (bouquet) (RGO-polyaniline nanofibers composites (i-j), and honeycombs of RGO-polyaniline nanofibers composites (k-l).

The effect of mismatch strain is considered, which predicts a strain induced instability under a compressive strain of GO and RGO under a tensile strain. Most interesting morphology formed were composites of honeycomb RGO with polyaniline nanofibers as shown in FESEM images Fig. 36 (k, l) having larger sheet size.\textsuperscript{[153, 173]} In this nanocomposite, the polyaniline nanofibers are embedded in the hexagonal and pentagonal space of RGO honeycomb. These types of morphology were obtained in 12 h chemical treatment at low temperature (60$^\circ$C). For the formation of different types of morphology of RGO and RGO-polyaniline based composites, the concentration of defects/edges were responsible and caused by the effect of temperature and reaction time.\textsuperscript{[175-178]} In the present work it is observed that, the RGO nanosheets shows the less edges / defects due to the less chemical reaction time i.e.
2h. As reaction time increases, the edges / defects along with population increases as depicted in FESEM image Fig. 36. On treatment of GO with O. A., The GO can be activated due to the rapid loss of oxygen and can be modulated for desired morphology. \cite{157} However, plausible mechanism of formation of various kinds of RGO and RGO based composites in the presence of O.A. as shown in above reactions (1-4) and Fig.34. The reaction of formation of magnate ester is the rate determining reaction which further formed alcohol after reduction.\cite{178-179} As the process continues, due to strains there is a chance to react the carbonyl group. Further, as the bond angle strain increases, the edges or defects in RGO nanosheets increases by which finally the honeycomb morphology was obtained.

### 3.5.4 High Resolution Transmission Electron Microscopy (HRTEM)

Fig.37 shows the TEM images of (a, b) RGO nanosheets, (c, d) composites honeycombs RGO-polyaniline nanofibers (e, f) composites of nanobooky of flower, (g, h) composites of RGO nanosheets- polyaniline nanofibers. Fig.37 (a, b) shows the TEM images of RGO layers which is one of the most common morphology. \cite{172} We have recorded selected area electron diffraction (SAED) pattern of composites of RGO-polyaniline nanofibers (inset of Fig.37 (h)), composites of nanobooky of flower (inset of Fig.37 (f)), honeycombs (inset of Fig.37 (d)), in order to show the good crystallinity of the composites with periods of \textit{in situ} polymerization in the present work.
Fig. 37: TEM images of (a-b) Nanosheets of RGO, (c,d) Honeycombs of RGO-polyaniline (Pani) composites, (e-f) Nanobooky of flower –polyaniline nanofibers composite and (g,h) nano sheet RGO-polyaniline nanofibers composite.
The well-defined diffraction spots in the corresponding SAED pattern indicated the multilayer structure of the as-prepared honeycomb RGO–polyaniline nanofibers composite. A comparison study discloses that, the composites show an increasing of crystalline behavior with in situ polymerization period. The crystallinity of honeycomb was observed to be (inset of Fig. 37 (d)) >flower of nanobooky (inset of Fig. 37(f)) >composites of RGO nanosheets -polyaniline nanofibers (inset of Fig.37 (h)). This also indicates the electrochemical performances and conductivity of RGO based composites depend with period of chemical treatment and the amount of polyaniline nanofibers coated on RGO shown later in this thesis. The more amount of polyaniline nanofibers is coated on RGO nanosheets as shown in Fig.38. Its conductivity and capacitance is less as compared to other two RGO based composites.

![Image](image.png)

**Fig. 38** it is shown that the Polyaniline nanofibers are coated on the surface of RGO nanosheets

### 3.5.5 X-ray diffraction (XRD) study

Fig. 39 reveals the XRD patterns (JCPDS 065-6212) of (c) RGO nanosheets, composites of (b) RGO-polyaniline nanofibers in the form of nanobooky of flower (a) honeycombs and (d) nanosheets. The XRD of RGO shows fairly intense peaks at $2\theta = 26.23$ and $43.3^\circ$. However, all composites show broad peaks at $2\theta = 20.0$ and $25.1^\circ$ ascribed to polyaniline nanofibers. The broadness of peak indicates the amorphous nature of all composites (in respect of crystallinity to each other). However, broadness is not same in the all peaks. The absence of RGO peak at $2\theta = 20^\circ$. 

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=43.3° clearly shows homogeneous formation RGO-polyaniline nanofibers composites.

Fig. 39: XRD patterns of (a) Honeycomb RGO-polyaniline nanofibers composites (b) flower of nanobooky (c) RGO nanosheets (d) RGO nanosheets- polyaniline nanofibers composites

It is noteworthy that the presence of weak peak at 2θ = 6.34° indicates composites of polyaniline nanofibers. Fig. 40 reveals the FTIR study of RGO nanosheets and the hierarchical composites of RGO-polyaniline nanofibers. The featureless FT-IR spectrum of RGO indicates that the chemical reduction of GO is relatively complete (Fig. 40d). In case of all hierarchical RGO- polyaniline nanofibers composites FTIR spectrum is shown in Fig. 40 (Fig. 40 a- c) the characteristic bands at 1503 cm⁻¹ ascribed to C=C stretching vibration in rings, whereas the bands at 1296, 1242 and 1040 cm⁻¹ were related to the C–N and C=N stretching modes and C-H plane bending vibration respectively.[157,159,182-187]
The presence of these bands suggests the successful coating of polyaniline nanofibers on RGO nanosheets and all above characteristic peaks strongly indicate the successful polymerization of polyaniline nanofibers in and on RGO. The increase in the intensity of the band at 1140 cm\(^{-1}\) was attributed to charge delocalization indicating that the interactions existed between RGO and polyaniline nanofibers.

Fig. 40: FTIR study of (a) Honeycomb RGO-polyaniline nanofibers composites (b) composites of flower of nanobooky (c) RGO nanosheets- polyaniline nanofibers composites (d) RGO nanosheets
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The peaks observed at 1595 and 1699 cm\(^{-1}\) in doped polyaniline nanofibers are due to the carboxyl group may be originating from oxalic acid.\(^{[158,187]}\)

### 3.6. Synthesis and characterization of metal/ metal oxide nanocomposite

Uniformly embedded silver (Ag) nanoparticles in orthorhombic nanotubes (NTs) of lithium vanadium oxide (LVO) synthesized via a facile template-free hydrothermal treatment at low temperature exhibited an excellent morphology with good crystallinity and may act as an exceptional contender for electronic applications. Controlled low-temperature hydrothermal method has been developed for the synthesis of LVO/silver (Ag) 1D nanostructure by using LiNO\(_3\), AgNO\(_3\) and NH\(_4\)VO\(_3\) at lower temperature.

Polymorphic forms of lithium vanadium oxide (LVO) NTs,\(^{[188-191]}\) and they have distinctive properties and are now widely used in electronic applications.\(^{[192]}\) The operating properties and applications of electronic devices depend not only on the oxidation state of vanadium, but also on its structure. So far, great efforts have been made in the field of synthesis of bulky or Nanocrystalline LVO with different structural properties. However, due to the low conductivity, the efforts have not been highly successful. However, to the best of our knowledge, the synthesis of one dimensional (1D) nanostructures of silver–lithium vanadium oxide (LVO/Ag) nano composites of different morphologies with the same crystallographic structures has not yet been reported for electronic applications. Moreover, 1D nanostructure is excellent for the efficient transport of electrons.\(^{[193]}\) Recently, the 1D silver–vanadium oxide (SVO) nanowires showed excellent applications in electrochromic devices (ECDs) synthesized at higher temperatures with high conductivity.\(^{[194]}\) 1D nanostructure appears to be an exciting field of research and could show case great potential in addressing the problem...
of the space-confined transport phenomenon. The key to preparing 1D nanostructure lies in the way in which atoms or other building blocks are rationally assembled into a structure with nano meter sizes but are much larger in length under properly controlled conditions. This means that the formation of 1D nanostructures is thermo-dynamically preferable for many substances under certain conditions. Since, LVO is well known for its electronic applications. We have attempted the facile synthesis of the 1D nanostructured LVO/Ag nanocomposite.

Fig. 41 elucidates the intercalation of silver in the layers of LVO

Synthesis of LVO/Ag nanotubes are explained in section 2.3.6

3.6.1 Characterizations

3.6.1.1 X-ray diffraction (XRD) study

The phase purity of the product was examined by X-ray diffraction (XRD) (Fig.42). The peak at $2\theta = 19.0^\circ$ existence of $\varepsilon$-LiV$_2$O$_5$ and is in good agreement with JCPDS data (Card No. 01-0089-8320, ICSD-88643) with the lattice constants $a = 11.3552$, $b = 4.6548$, $c = 3.5732$ nm of space group Pmn. The corresponding strong (010) plane indicates the existence of orthorhombic structure of the LVO. Two weak peaks at $2\theta = 38.1^\circ$ (111) and $44.3^\circ$ (200) shown by (*) are the characteristics of silver. It is concluded that due to the layered structure of LVO, silver is intercalated and forms nanocomposites in the form of NT’s under the present
synthetic conditions at particular composition. The domain structure influences the intensities and line widths of all reflections. At given temperature, the conductivity of LVO/Ag having (010) plane is more than 1 order of magnitude.\textsuperscript{[195]} This indicates electron conduction preferentially depends on concentration of lithium.\textsuperscript{[191]} Hence, we choose 1D NT’s of LVO/Ag for further study which has lower concentration of lithium.

![XRD pattern of LVO/Ag nanocomposite NT’s.](image)

**Fig. 42** XRD pattern of LVO/Ag nanocomposite NT’s.

### 3.6.1.2 Morphological study (FESEM and HRTEM)

Fig. 43 shows LVO/Ag NT’s of LVO with silver. HRTEM images reveals, silver nanoparticles of size 2-10 nm were embedded in LVO NT’s having diameter 40-50 nm and length 5-10 µm. The single tube has been indexed, and shows existence of LVO NT’s and silver with (010), (200) plane respectively (Fig. 43). The top - view of images in Fig. 43 (e, f) is the indication of formation of NT’s.

The chemical reaction can be formulated as \textsuperscript{[142]}

\[
\text{AgNO}_3 + 2\text{NH}_4\text{VO}_3 + \text{LiNO}_3 \rightarrow \text{LiV}_2\text{O}_5/\text{Ag} + 2\text{NH}_3 + \text{H}_2\text{O} + 2\text{NO}_3^- \quad (1)
\]

The entropy change may be considered as a cumulative effect of structural, electric and order-disorder processes. Assuming that these effects are additive, it may be possible to make a quantitative estimate of the individual contributions so as to
determine the predominant factor in driving the reaction. Entropy of the reaction (1) is \( \sim 32.42 \text{ J mol}^{-1} \text{K}^{-1} \) implying tendency of reaction to progress toward the right-hand side. Basically the silver was to be mobile in LVO at appropriate concentration of lithium reported by West et al. \cite{195}

![Fig. 43](image_url)

Fig. 43 (a) FESEM image of LVO/Ag NT’s (b) Silver nanoparticles are coated on LVO NT’s (c) Silver nanoparticles are intercalated in LVO NT’s with their corresponding TEM images.

![Fig. 44](image_url)

Fig. 44 (a) SAED pattern (b) HRTEM (c) clear fringes of silver- LVO NT’s

It is apparent that Ag\(^+\) and V\(_2\)O\(_5\) coexisting with the corresponding ions of Li\(^+\) in all typical reactions reported herewith. Li\(^+\) ions concentration plays an important role in synthesis for the desired crystal structure and morphology of the product. According to Dznies \cite{53} the only nanofibers/ NT’s does not show the results as expected rather than nanocomposite. A certain amount of V\(_2\)O\(_5\) is required as stabilizing ions for the development of LVO from which it can be seen that the Li\(^+\) concentration will result in a decrease in the formation rate and growth of SVO.
From our XRD, FESEM and TEM observations, it appears that the mechanism of Ag$^+$ with LVO entails for thermodynamically feasible and thereby expected.[195]

Li et al.[196] demonstrated decoration of silver on NT’s of vanadium oxide, however, we presented the silver not only decorated but also intercalated in LVO NT’s. During the synthesis process, the products may be influenced by two factors: (a) the dispersion effect of Ag in LVO layer and (b) concentration of lithium nitrate, which is directly controlling the morphology.

The specific surface area of the vanadium oxides is 11.26 m²/g[197] whereas Ag-LVO is 8.2771 m²/g, indicate the growth of LVO-Ag NT’s. In the IR spectrum (Fig 45), the relative intensity of the band at 542 cm⁻¹ is strongly decreased due to introduction of Ag$^+$ into the LVO NT’s framework, which interrupts the linkages of Li-O-V and produces more edge-sharing V-O bonds and terminal V=O bonds. The introduction of silver in LVO framework enlarged the interlayer spacing as well as coordinated water. These contributed to a Li ion diffusion coefficient for LVO NTs.

![FTIR study of LVO/Ag nanocomposites nanotubes](image)

**Fig.45 FTIR study of LVO/Ag nanocomposites nanotubes**

### 3.7 Characterization of metal oxides synthesized by CVD method
The synthesis of various metal oxides by CVD method is described in section 2.2.3 to 2.2.8

3.7.1 Characterization

3.7.2 TGA of ammonium metavanadate

![Graph showing TGA pattern of ammonium metavanadate](image)
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Fig. 47 represents the TGA pattern of pure ammonium metavanadate (NH$_4$VO$_3$). The TGA pattern indicates the three weight loss steps between 200-380°C. The first two steps presented the decomposition of ammonium metavanadate. The constant weight loss at 380°C indicates the formation of vanadium oxide as a final product. [142,199-205]

3.7.3 SEM study of MoO$_3$

![Image of MoO$_3$ microstructure sheet]

Fig. 48 SEM image of MoO$_3$ microstructure sheet

The synthesis of MoO$_3$ is carried out by the procedure given in section 2.2.8. The formation of MoO$_3$ microstructure sheets are in layered forms.

3.7.4 XRD study of V$_2$O$_5$

![Image of XRD pattern of V$_2$O$_5$]

Fig 49: XRD pattern of V$_2$O$_5$
Fig. 49 shows the XRD pattern of V$_2$O$_5$ as synthesized by the procedure given in section 2.2.5 [206]

3.7.5 SEM image of V$_2$O$_5$

Fig. 50 shows nanowires of V$_2$O$_5$ synthesized by the procedure given in section 2.2.5 (CVD method). The SEM study clearly shows that, the formation of nanowires. The growth of V$_2$O$_5$ nanowires are in vertical and in well defined direction (1 dimensional).

![SEM image of V$_2$O$_5$ nanowires](image_url)

Fig.50 SEM image of V$_2$O$_5$ nanowires
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