Sulfonated Polyaniline–20% MgO Nanocomposites: Possible Biomedical Material

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Abstract: In situ chemical oxidation route has been adopted to prepare the nanofiber-nanosheet (NF-NS) network of sulfonated polyaniline emeraldine salt (PANI-ES) using APS as oxidant and H2SO₄ as dopant. Composite of PANI with 20% magnesia mineral (MgO) nanoparticles has synthesized by placing magnesia mineral powder gradually in the polymerization solution of aniline by keeping monomer to dopant ratio 0.4:1. All the samples are characterized by SEM and UV-vis spectroscopy. NF-NS morphology of PANI, nanoparticles of MgO and linked nanosheet–nanorod (NS-NR) agglomerated by MgO nanoparticles (NP) morphology of PANI/20%MgO composite have been examined by SEM micrographs. Optical band gaps of PANI-ES and PANI/20%MgO have been calculated by UV-vis spectrographs. Electrical conductivity (dc) of the prepared samples was calculated by four probe method.

Keywords: Polyaniline, Emeraldine Salt, Sulphate Anions, Sulphuric Acid, Chemical Oxidation Route.

1. Introduction

During the past two decades, both fundamental and applied research in conducting polymers (CPs) like polyaniline (PANI), polycrylonitrile, polythiophene and polypyrrole has grown enormously. PANI is one of the most studied CPs of the past 50 years. The most common chemical synthesis of PANI is by oxidative polymerization with ammonium per sulfitre as an oxidant. PANI owing to its ease of synthesis, remarkable environmental stability and high conductivity in the doped form has remained thoroughly studied due to their varied applications in fields like biological activity, drug release systems, rechargeable batteries and sensors [1]. PANI (leucoemeraldine base form), which becomes truly conjugated only after protonic acid doping [2]. Doping the polymers creates new states (donor or acceptor states), which exist within the band gap and are energetically accessible to the pi electrons, resulting in significant increase in conductivity [3]. In fact, the conductivity of doped polymers may be up to ten orders of magnitude greater than that of the neutral (undoped) polymers [4]. Emeraldine base form of PANI, upon doping with acid, the resulting emeraldine salt form of PANI is electrically conducting [5]. Conductivity of H2SO4 doped PANI has been reported up to ~10⁸ S/cm [1]. The antimicrobial properties of conductive functionalized PANIs have been investigated by exploring their interaction with bacterial cells. Lower concentrations of PANI strongly inhibited the growth of many bacteria as well as several antibiotic resistant clinical pathogens. Functionalized PANIs (PANI NFs) tested for its antifungal properties [6]. PANI-Zr (IV) sulphosalicylate has also been tested against the various bacterial and fungal strains and relatively higher activities have been observed than the known antibiotics [7]. PANI Grafted Chitosan (Chit-g-PANI) has been tested for its antimicrobial activity. PANI and Chit-g-PANI also shows a potent antifungal activity compared to antimicrobial activity [8]. There are numerous potential applications using CPs as actuators, artificial muscles, and transducers [9].

CPs has immense applications in the fields of drug delivery, neuroprosthetic devices, cardiovascular applications, bioactuators, biosensors and the food industry. Functionalization of CPs with different biomolecules/dopants has allowed biomedical engineers to modify CPs with biological sensing elements [10]. A conducting polymer, PANI, was prepared in globular and nanotubular morphologies. The protonated forms were converted to the corresponding bases and both types of samples were tested for cytotoxicity [11]. Excellent biocompatibility properties in terms of dermal irritation and sensitization are reported in case of both PANI hydrochloride and PANI base. The main challenge for using PANI and its derivatives for biological applications arises from its poor cell compatibility, poor processibility, lack of flexibility, and non-biodegradability. However, PANI has been investigated for use in biomedical applications such as biosensors, neural probes, controlled drug delivery, and tissue engineering applications with promising outcomes [12, 13].

Application of metal oxide (MO) MgO nanomaterials in the fields such as high dense ceramics, additives in
bactericide, refractory, and superconductor products has been reported. MgO nanoparticles (NPs) may find applications in high-densed ceramics. They can be used as additives in bactericide, refractory and superconductor products. [14]. MgO NPs are a promising antibacterial agent due to their high resistance to harsh processing conditions. The antibacterial activity of MgO NPs is size and concentration dependent. In the future, more research should be focused on the preparation of MgO NPs with low cost and studies of the antibacterial mechanism of MgO NPs. Also, more studies should be carried out on the activity of MgO NPs towards other micro-organism species [15]. The MgO is eco-friendly; non toxic, thermally stable flame retardant and suppressing fumes under fire conditions [16]. Preparation of MgO NPs by sonication method to understand their antibacterial property is reported. PANI/MgO nanocomposites (NCs) synthesized by low temperature solution combustion and chemical oxidative polymerization method is reported so far [17].

All above literature survey has inspires the author to synthesize and study the PANI/MgO NCs by wet chemical (chemical oxidation) sol-gel process. The data yet has not been reported so far on the composite of H2SO4 doped (sulfate doped) PANI with MgO.

2. Experimental

The chemical oxidation route has been used to synthesize the PANI and its composites with MgO. Pallets of seven tons. The four probe set up model DFP-RM (SES Roorkee) was used to measure surface electrical conductivity of samples. The MgO, PANI and PANI/ MgO in their powder form were characterized by UV-VIS spectroscopy and SEM techniques at Sophisticated Test & Instrumentation Centre (STIC) Cochin University of Science and Technology. The optical absorption (UV-VIS spectroscopy) by samples in the ultraviolet, visible and near infrared regions is measured by instrument Varian, Cary 5000 in the spectral range 175 – 3300 nm with wavelength accuracy: ±0.1nm (UV-Vis), ±0.4nm (NIR). Scanning Electron Microscopy (SEM) is a method for high resolution surface imaging. The morphology of samples has been studied by the instrument JEOL Model JSM - 6390LV with resolution 3 nm (Acc V 30 KV, WD 8 mm, SEI), 8 nm (Acc V 3.0 KV, WD 6 mm, SEI) and 15 nm (Acc V 1.0 KV, WD 6 mm, SEI) in the magnification range 5 X to 300,000 X (Both in High and Low Vacuum Modes) using probe Current 1 μA to 1mA.

2.1 Materials

Aniline monomer, magnesium oxide (MgO), ammonium persulfate (APS), acetone, methanol and sulphuric acid all of GR grade, are purchased from a Merck (India) company, and they were used as received without further purification process. Double distilled water was used throughout this work.

2.2 Synthesis of Polyaniline NFs-NSs

The chemical polymerization of aniline was carried out in the presence of aqueous sulphuric acid solution. Appropriate amount of aniline (0.4 M) and (1M) H2SO4 acid were added into 100 ml deionized water into the polymerization beaker. APS (0.4 M) was dissolved in sulphuric acid (1M) in 100 ml deionized water in beaker. Both solutions were stirred at 2°C for one hour. Then the second solution was added slowly to the aniline solution by drop wise fashion for 20 minutes. The color of the polymerization mixture has changed initially to light blue and then finally into dark green. The dark green colour of precipitate ensures the formation of electrically conductive sulfonated PANI (SO3-) emeraldine salt. The final solution was kept at constant stirring for 7 hrs. Then the solution was allowed to settle overnight. At the end of polymerization reactions, the final product was filtered, washed with distilled water and methanol, until the filtrate become colorless and dried at 60°C in the oven, for 12 hours. The synthesized sulphonated polyaniline salt was finally crushed, and the product is obtained in the form of fine dark-green powder [18, 19, 20].

2.3 Synthesis of Polyaniline / MgO NCs

The polymerization of the monomer (aniline) was initiated by the drop-wise addition of the oxidizing agent (ammonium per sulphate APS) in an acidified solution prepared, using doubly distilled water under constant stirring at 0 to -2°C. During this stirring for one-hour, MgO nanoparticles in different proportion with aniline was added to synthesize the composites. The monomer to oxidizing agent ratio and monomer to dopant ratio was kept at 1:1 and 0.4:1 respectively. After complete addition of the oxidizing agent the reaction mixture was kept under constant stirring for seven hours. The resulting dark green precipitated was kept overnight and then filter. The precipitated polymer was filtered and washed with distilled water and methanol until the filtrate become colorless. Finally, the polymer composite was dried in an oven at 60°C for 12 hours [21,22, 23].
3. Results and Discussion

3.1 dc Conductivity

The Arrhenius equation \( \sigma_{dc} = \sigma_0 \exp \frac{E_a}{k_B T} \) is used to calculate the surface conductivities (\( \sigma_{dc} \)) of sulfonated PANI and PANI/20%MgO. The \( \sigma_{dc} \) of samples at respective temperatures are given in Table 1, and their dc conductivity graphs against temperature are given by Fig. 1. The dc conductivity of both, PANI and composite increases with rise in temperature (semiconductor nature) from 193 K to 368 K. The electrical conductivity of polyaniline is expected to be high, since the polymerization reactions were carried out in highly acidic conditions at low temperature 0°C to -2°C. The calculated room temp conductivity of pure PANI is 0.178 S/cm at 293 K, which increases with temperature up to 0.267 S/cm at 368 K, shows the semiconductor behavior as reported by authors in their previous work [21], and that have been found for PANI/20%MgO are 0.065 S/cm at 298K and 0.119 S/cm at 368 K. The dc conductivity of PANI is well agreed with reported data [17, 24, 25].

The plot of dc conductivity conducting PANI and its composite with temperature is shows the exponential increase in \( \sigma_{dc} \) with temperature, thereby indicating the behavior of disordered semiconductor. The analysis of temperature dependent conductivity data suggests that the charge transport mechanism in PANI as well as its composite can be explained by the variable range hopping (VRH) model [26]. The linear portion of particular slope on temperature dependent dc conductivity graphs of PANI and its composites follow the Arrhenius behavior and equations. For the Arrhenius model, the conductivity is given by: \( \sigma_{dc} = \sigma_0 \exp \frac{E_a}{k_B T} \); \( E_a \) is the activation energy. Charge transport behaves by tunneling between conductive grains/clusters. Increment in conductivity with rise in temperature, which is the characteristic of thermal activated behavior, indicated that the tunneling is the most prominent transport mechanism [27].

On the graphs of log \( \sigma \) verses \( 1/T \) of the composite, depression of slopes at high temperature range indicates the low values of activation energy with rise in temperature and thus reveals good agreement with the Sheng’s model of CELT of carriers [28], or it may be due to moisture content which has get loss at high temperature. Conductivity of doped PANI increases in large order because dopant acting as an electron acceptor creates positive charges on polymer chain, and as a result the polaron state arises. Thus, it may consider that the polarons acts as charge carriers hopping from state to state in the sample. The increase in conductivity is attributed to the increase of efficiency of charge transfer between the polymer chains and the dopant (and/or additive ions) with increase in the temperature [29]. It is also possible that the thermal curing affects the chain alignment of the polymer, which leads to the increase of conjugation length and hence conductivity. There may be molecular rearrangement on heating, which made the molecular confirmation favorable for electron delocalization [30]. Calculated dc conductivities of all samples are agreed with the reported conductivities [24, 25, 17, 31, 32, 33, 34].

Table 1: dc conductivity of PANI and PANI/20%MgO

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \sigma_{dc} ) S cm(^{-1} ) at 298K</th>
<th>( \sigma_{dc} ) S cm(^{-1} ) at 368K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>0.178</td>
<td>0.267</td>
<td>24, 25</td>
</tr>
<tr>
<td>PANI/20%MgO</td>
<td>0.065</td>
<td>0.119</td>
<td>17</td>
</tr>
<tr>
<td>MgO</td>
<td>insulator</td>
<td>high temp. Insulator</td>
<td>31, 32</td>
</tr>
</tbody>
</table>

3.2 Characterization

UV-vis Spectroscopy

Fig. 2 (a, b and c) shows UV-Visible spectra of PANI, MgO and PANI/MgO composite, and their respective energy gap is given in Table 2. Each of their spectra except MgO reveals the presence of two absorption bands, one in the UV region which assigned to \( \pi-\pi^* \) transitions about intra chain charge transfer and another in visible region ensures the \( n-\pi^* \) transition about inter chain charge transfer excitation from benzoid to quinoid moieties. In case of PANI, three characteristics bands appear at 330 nm, 609 nm
and 649 nm which are attributed to $\pi-\pi^*$ intrachain, exciton and polaron transition respectively. For pure PANI salt (converted in to base in DMF), two absorption peaks in DMF at 330 nm and 609 nm assigning the $\pi - \pi^*$ transition band (transition in the benzenoid rings) and $n-\pi^*$ exciton band (exciton transition from HOMO of benzenoid to LUMO of quinoid ring, or exciton absorption in quinoid rings). The excitation (n-$\pi$*) leads to formation of molecular exciton, i.e., positive charge on the benzenoid units and negative charge centred on quinoid unit. This interchain charge transfer may lead to the formation of positive and negative polarons. All the absorption peaks of PANI are well agreed with reported peaks [34, 35, 36, 37].

Reported data reveals the synthesized PANI is with hydrogen sulfate $\text{HSO}_4^-$ or sulfate $\text{SO}_4^{2-}$ group. It has been reported that $\text{H}_2\text{SO}_4$ may interact with PANI by donating either hydrogen sulfate $\text{HSO}_4^-$ or sulfate $\text{SO}_4^{2-}$ anions as dopant anions. In the emeraldine salt (ES), the $\text{HSO}_4^-$ species are ionically bonded with the $\cdot\text{NH}$ groups presented in the polymer chain. Actually, these kinds of bonds are very weak and can be removed very easy by changing the system’s pH [38, 39].

![Figure 2: UV-vis spectrographs of a) sulfonated PANI, b) MgO and c) PANI/20% MgO](image)

**Table 2: Absorption peaks and band gaps from UV-vis Spectrographs**

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV nm</th>
<th>Band gap eV</th>
<th>Vis nm</th>
<th>Band gap eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>330</td>
<td>3.756</td>
<td>609</td>
<td>2.038</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>649</td>
<td>1.912</td>
</tr>
<tr>
<td>MgO</td>
<td>289</td>
<td>4.294</td>
<td>628</td>
<td>1.976</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>663</td>
<td>1.872</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>689</td>
<td>1.801</td>
</tr>
<tr>
<td>PANI/20%MgO</td>
<td>326</td>
<td>3.807</td>
<td>654</td>
<td>1.897</td>
</tr>
</tbody>
</table>

Much less absorbance 0.1336 at 289 nm reveal the presence of nanoparticles (NPs) in the used MgO powder [37, 40]. The absorbance peak at 326 nm and 654 nm in case of PANI/20% MgO ensures the both intrachain transition band and interchain excitation band respectively as that of PANI. The spectra of composite show the blue shift of band in UV region and red shift of band in visible region compare with spectra of PANI.

**Scanning Electron Microscopy (SEM)**

*Morphology of PANI, MgO and PANI/Metal Oxide Nanocomposites*
**Fig. 3** shows, SEM micrographs of PANI (a), MgO (b) and PANI/20% MgO (c). **Table 3** highlighted the effect of percent weight of metal oxide while the polymerization of aniline on morphology of resultant composites. The addition of MgO not only affects the size but also the surface morphological features of PANI nanosheets (NSs) & nanofibers (NFs). All these SEM analysis was previously reported by author [22].

It is clear that the use of $\text{H}_2\text{SO}_4$ as dopant produced NS-NF network/cluster of PANI structure with the NFs having diameters 94.28 nm to 80.00 nm (Fig.1a). The nanosheets with thickness ranging 30 – 80 nm are abundant on PANI SEM. A.Y. Obaid et al (2014) [41] and Hyung-Kee Seo et al (2013) [42] has been reported the formation of NSs of PANI by protonic acid (H$_2$SO$_4$, HCl) doping. NSs and NFs network in the SEM of sulphuric acid doped PANI salt has been reported in the present work as reported by author in his previous work [22].

The SEM picture of MgO reveals the presence of MgO NPs (<100nm). The reports by S. Devi Meenakshi et al (2012) [14] and Chandrappa K.G. et al (2015) [37] supported the NP nature MgO powder used in present work. Significant changes in morphology are seen in the PANI/MO composite prepared using $\text{H}_2\text{SO}_4$ as dopant. SEM of PANI/20% MgO NC (Fig.1c) shows the presence of network includes the NSs of reduced thickness and nanorods (NRs) of 113 nm to 63 nm in widths with agglomeration of adsorbed particles below 100 nm size. With incorporation of MgO NPs in the SO$_4^{2-}$ doped PANI, the size of NSs gets reduced. NFs converted in to NRs remarkably (encircled on the figure 3 c) and NPs of MgO get agglomerated with NSs of PANI. This change in morphology of PANI salt by the incorporation of MOs is well agreed with as results reported by Ngo Trinh Tung et al (2011) [43].

**Table 3: SEM analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>NSs</td>
<td>NS thickness &lt; 100 nm</td>
</tr>
<tr>
<td></td>
<td>NFs</td>
<td>NFs - 94.28 nm to 80.00 nm</td>
</tr>
<tr>
<td>MgO</td>
<td>NPs</td>
<td>NPs &lt; 100nm</td>
</tr>
<tr>
<td>PANI/20% MgO</td>
<td>NSs</td>
<td>Reduced</td>
</tr>
<tr>
<td></td>
<td>NRs</td>
<td>NR - 113 nm to 63.00 nm</td>
</tr>
<tr>
<td></td>
<td>NPs</td>
<td>NPs &lt; 100 nm</td>
</tr>
</tbody>
</table>

**Conclusions**

The sulfonated (SO$_4^{2-}$ doped) PANI ES and PANI/20% MgO have been prepared by wet chemical method through the chemical oxidation route using APS oxidant and $\text{H}_2\text{SO}_4$ dopant. Dark green coloured powdered samples ensure the formation of conducting form of PANI and it’s composite with MgO. All the peaks on UV-vis spectra reveals the formation of PANI and the shifts on UV-vis spectra with addition of MgO in PANI matrix shows the formation of PANI/20% MgO composite. The peak in UV region supported the presence of NPs in the used MgO powder. All the literature taken as references agreed with formation semiconducting PANI ES and PANI/20% MgO composite. SEM analysis shows the NSs-NFs network in the PANI samples. Also the SEM study of PANI/MO shows that with the addition of MgO in PANI matrix the NFs of PANI becomes NRs in some extent, the size of PANI NSs reduces and the size of agglomerated MgO NPs on PANI
nanostructure is also reduces. The adopted chemical oxidation route is the good method for the preparation of nanostructured PANI and PANI/MO composite. All this study makes the author’s attention to find the antibacterial and bacteria repellant nature of the PANI/20% MgO.

5. Acknowledgement

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6. References
