A Green Facile in Situ Synthesis and Characterization of Cerium Doped Polyaniline (PANI-Ce) Nanocomposite

Z. Khanam\textsuperscript{a}, F. Adam\textsuperscript{b}

\textsuperscript{a}Faculty of Agro Based Industry, Universiti Malaysia Kelantan, Campus Jeli, Kelantan, 17600, Malaysia
\textsuperscript{b}School of Chemical Sciences, Universiti Sains Malaysia, 11800, Penang, Malaysia

Email: zakiakhanam09@gmail.com

Abstract

PANI is an unique conjugated polymer because of its controllable doping and dedoping properties. The rare earth metal doped PANI composites in nanorange reported to have several potential applications in magnetic devices and catalyses. In the present study cerium doped PANI composite (PANI-Ce) was prepared by green in situ synthesis with water as solvent and mild oxidizing agent, H\textsubscript{2}O\textsubscript{2}. Spectroscopic studies (FT-IR and UV-Vis) revealed successful polymerization of PANI-Ce. EDX analysis further supported the presence of Ce in polymer matrix with 5.81 weight percentage. TEM results exhibited that the composite, PANI-Ce exist in nanorange with particle size 3-7 nm. Based on previous finding further study is warranted as nanostructured cerium doped polyaniline hold promise for heterogenous catalysis, sensors and magnetic materials.

Keywords: Polyaniline; cerium; green synthesis; characterization

1. INTRODUCTION

Polyaniline (PANI) was discovered in early 1980s, since then it has been most investigated conducting polymers due to its environmental stability and interesting redox properties (Arora et al., 2015a; Arora et al., 2015; Palaniappan & John, 2008). PANI is also considered unique among conjugated polymers because of its controllable doping and dedoping process and reversible acid-base chemistry (Khanam et al., 2014). These outstanding features of PANI made this material attractive for light weight battery electrodes, electromagnetic shielding devices, photovoltaic devices, solar cells, antistatic materials, anticorrosion coatings, chemical and biological sensors, infrared polarizers, and light emitting diodes (Drury et al., 2007; Lei et al., 2007). The electrical conductivity of the polyaniline can be varied over the full range from insulator to metal by doping. Depending upon the doping and oxidation states of polymer, six different forms of PANI can exist. Among these forms only emeraldine salt form is electrically conducting which can be formed from acid doping of semiconducting emeraldine base or prepared by chemical oxidation of aniline in the presence of acid (Zhang, 2007).

The incorporation of metal and metal oxide particles in conducting polymers has attracted considerable attention in the last two decades because of the ability of the polymer to alter its properties on doping. Polyaniline-metal composite is particularly useful as they combine the electrical properties of metal and the mechanical and processing properties of polymer (Neelgund et al., 2008). Various PANI-metal showed enhanced electrocatalytic activity and increased gas sensing properties. Various techniques can be employed to incorporate metallic nanoparticles into polymer matrixes like electropolymerisation, electrochemical deposition and spontaneous reduction of metal salts with the polymer (Sofiane et al., 2006). There have been many reports of chemical methods by which unique morphology of PANI composite can be obtained. These methods include use of template
or surfactant, electro-spinning, interfacial polymerization, seeding and oligomer assisted polymerization (Khanam et al., 2014).

Metal doped PANI in nanorange have attracted broad attention due to their special physical and chemical properties (Bandgar et al., 2012). Nanostructured PANI-metal composite has vital influence on its enhanced performance. It has shown good electrical conductivity compared to those of powder or thin film forms of the same polymer (Khanam et al., 2014). Interest in conducting polymer nanoparticles derives mainly from their potential utility in catalysis, molecular electronics, and energy conversion devices and as a potential media for controlled drug release (Dutta et al., 2010). The PANI composites in nanorange have many potential applications in nanodivices [29]. In sensor application they showed greater sensitivity and faster time response relative to its conventional bulk counterpart due to higher effective surface area and shorter penetration depth for target molecules [30]. In recent years polyaniline-metal composites gained widespread application as an efficient heterogenous catalysts for various organic transformations (Kantam et al., 2007). Recently Mallik et al. prepared paramagnetic polyaniline nanospheres doped with cerium ions via interfacial polymerization method (Mallick et al., 2010). Based on these findings, the present work reported a green facile in situ synthesis of cerium doped polyaniline (PANI-Ce) nanocomposite by simple chemical oxidation method using mild oxidizing agent, H2O2 and water as solvent.

2. MATERIALS AND METHOD

2.1. Materials

The double distilled aniline monomers (R & M chemicals) were used to prepare polyaniline composite in the presence H2O2 as oxidizing agent (30%, QREC). The source of cerium was obtained from cerous (III) nitrate hexahydrate (R&M chemicals) for the preparation of PANI-Ce complex. Other reagents required for synthesis and characterization were 1-methyl-2-pyrrolidinone (NMP, Sigma Aldrich) and acetone (QREC). All chemicals were of AR grade and were used as received.

2.2. Synthesis of PANI-Ces

To a magnetically stirred solution of aniline (5 g), 10% by weight cerous (III) nitrate hexahydrate dissolved in 100 ml water was added. The reaction mixture was stirred for 30 minutes. Then 25 ml of H2O2 (30%) was added dropwise in 15 minutes. The reaction was allowed to proceed for further 2 hours while stirring. The precipitate formed was filtered by suction pump and washed with copious amount of water followed by acetone.

3. Results and Discussion

3.1. FT-IR spectroscopy

The FT-IR spectrum (Figure 1) shows characteristic peaks at 1584 and 1495 cm⁻¹ attributed to benzenoid and quinoid ring indicating the formation of polyaniline. The bands at 752 and 695 cm⁻¹ corresponded to deformation vibration modes of the aromatic rings. The C-H out of plane bending of 1,4 disubstituted aromatic ring appear at 827 cm⁻¹ (Yang & Chen, 2006). The broad peaks at 1306 and 1117 cm⁻¹ due to C-N stretching and bending vibrations while a broad peak at 1215 cm⁻¹ ascribed to C=N stretching vibration, respectively. The broadening of these peaks suggests incorporation of metal at N site of polyaniline. The peak at 496 cm⁻¹ can be related to metal-nitrogen bond.

3.2. UV-Vis spectroscopy

The UV-vis spectrum (Figure 2) of cerium doped polyaniline shows absorption band at 275 nm attributed π- π* transitions of benzenoid rings in polymer chain. The band at 424 nm corresponds to polaron/bipolaron transition. While broad band at 549 nm was due to benzenoid to quinoid excitonic transition (Mallick et al., 2010; Izumi et al., 2006).
3.3. **EDX analyses**

The mass and atomic percentages of all the elements in PANI-Ce are tabulated in Table 1. The predominant elements found in composite are carbon, oxygen, cerium and nitrogen. The percentage of cerium in composite was 5.81% by weight, suggesting incorporation of cerium in polyaniline matrix.
Table 1: Elemental percentage of PANI-Ce by EDX analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>66.26</td>
<td>74.24</td>
</tr>
<tr>
<td>N</td>
<td>14.18</td>
<td>13.63</td>
</tr>
<tr>
<td>O</td>
<td>13.75</td>
<td>11.57</td>
</tr>
<tr>
<td>Ce</td>
<td>5.81</td>
<td>0.56</td>
</tr>
</tbody>
</table>

3.4. TEM analyses

TEM images of the PANI-Ce represented in Figure 3 at 60 K magnification. The micrographs particularly revealed agglomeration of particles. It also showed formation of granular, short range porous structure of the composite. These granular nanoparticles of PANI-Ce composite approximately ranges from 3-7 nm in diameter (Khanam et al., 2014).

![Figure 3](image_url)

Figure 3: TEM image of PANI-Ce at 60 k magnification

4. Conclusions

In summary, the above results demonstrated a simple green route towards in situ synthesis of cerium doped polyaniline as it utilizes water as solvent and mild oxidizing agent H2O2. FT-IR and UV-Vis spectroscopy revealed successful polymerization of PANI-Ce. EDX analysis further supported the presence of metal in polymer matrix. TEM results showed that the composite exist in nanorange (3-7 nm). Nanostructured metal doped polyaniline previously showed various applications, so this material may also hold promise for exploration of applications such as heterogeneous catalysis, sensors and magnetic materials.

REFERENCES


