Synthesis and Characterization of Poly O-Anisidine Nanoparticles and their Nanocomposite

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Abstract

In this work, Poly o-anisidine nanoparticles were prepared by using cationic surfactant. Poly o-anisidine nanoparticles/ nanocomposites filled with constant content 1.0 wt% of Ag2O, ZnO, CuO and TiO2 powder have been prepared. The sample microstructure was established by FTIR spectroscopy and transmission electron microscopy. The thermal properties, sulfate reducing bacteria and electrical conductivity were investigated. The influence of the inorganic nanoparticles on the thermo stability of poly o-anisidine nanoparticles is very complicated. It was found that POA/Ag2O nanocomposite microspheres have good effects to sulfate reducing bacteria than POA nanoparticle. The value of the electrical conductivity, $\sigma$, of the nanocomposites was investigated. It was found that the poly o-anisidine nanoparticles was improved by adding metal oxides which converted the polymer nanoparticles from insulator behaviour $10^{-16}$ (S/cm) to semiconductor behaviour $10^{-11}$ (S/cm) in case of POA/Ag2O and $10^{-12}$ (S/cm) in case of POA/ZnO. The conductivity increased by increasing the temperature.

Keywords: o-Anisidine; Cationic surfactant; Metal oxide nanoparticles; Sulfur reducing bacteria; Thermal and electrical properties

Introduction

Among conducting polymers, polyaniline and its derivatives have attracted much attention due to its ease of synthesis; by chemical or electrochemical polymerization; ammonium persulfate is generally used as the oxidizing agent for the preparation. Although the chemical method offers mass production at a reasonable cost; the electrochemical method involves the direct formation of conducting polymer thin films with better control of thickness and morphology; which are suitable for application in electronic devices [1-6]. A novel poly (o-anisidine) (POA)/CoFe2O4 nanocomposite was synthesized by a facile in situ polymerization of o-anisidine in the presence of CoFe2O4 nanoparticles which were obtained by a simple refluxing process in ethylene glycol [7]. However their properties depend on the synthesis conditions such as type of supporting electrolyte; reagent concentration; applied potential; type of solvent and pH of polymerization bath [8-9]. Polyaniline and its derivatives are mainly used as coating to improve the corrosion resistance of oxidizable metals. These coatings have also been considered for several applications such as the electronic industry; biosensor applications [10-16]. Polyaniline has shown variety of applications such as in rechargeable batteries; electro catalysis; electrochromic displays; gas separation; and biosensors. However; the role of structural and mechanical behaviour of polyaniline and its derivatives for their applications to biosensor has not yet been explored [17].

Scheme of homo polymerization of poly (o-anisidine)

The incorporation of metal in the form of nanoparticles in the polymer matrix forms composite materials; which have proved to exhibit improved performances over those of the polymer alone [18,19]. Most of the effective corrosion-resistant paint formulations that are popular in industries are based on chromic compounds; which need to be replaced with alternative materials such as polyaniline (PANI) and poly-o-anisidine (POA) [20-23].

Recently; the antibacterial performance of PANI against Escherichia coli and Gram-positive staphylococcus aurous were reported by different research groups [24,25]. Sulphate Reducing Bacteria (SRB) implicated in the deterioration of metals in the oilfield; water recirculation system and marine environments. Mollica and Trevis report that the presence of SRB bio film (sessile) SRB on the metal surface resulted in a higher corrosion rate as compared to the corrosion rate due to plank tonic bacteria alone [26]. In order to control bio corrosion; preventing materials from bio films is a very important method. Currently; the environmental friendly antifouling coating attracts more interest. The present paper described optimized conditions for a successful formation of PNMA microspheres by a simple chemical polymerization method using monomer; acid; and oxidant without any templates. And the resulting PNMA microsphere had good effect to control Sulphate Reducing Bacteria (SRB) and SRB bio films accumulation and then reduced the corrosion rate [27]. In the present work; we report the fabrication of POA nanostructure using cationic surfactant. This study was also focused on the preparation of nanocomposites using different metals oxide nanoparticles. Sulphate Reducing Bacteria (SRB); thermal and electrical properties of the nanostructured POA/metal oxide nanocomposites were investigated.

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Experimental Procedure

Materials

Monomer; O-anisidine; Redox initiator; ammonium persulfate (APS) and -dodecyloxy carbonylmethyl-N-triethanol ammonium chloride as cationic surfactant were purchased from Aldrich (Milwaukee; WI; USA); (TiO2) nanopowder; average particle size: 25-70 nm; Cat # 634662; CuO nano powder; average particle size: 50 nm; Cat # 544868; AgO powder; Cat # 221163; ZnO nano powder; average particle size: 100 nm; Cat # 544906; product from Aldrich.);

Synthesis of poly-o-anisidine nanoparticle

A variable amount of cationic surfactant N-dodecyloxycarbonylmethyl-N-triethanol ammonium chloride [28] was prepared according to Gad et al. [29] was magnetically stirred in 40 ml of distilled water at 3°C. In a typical fabrication of POA nanoparticles; 1.305 g (10.7 m mol) of O-anisidine monomers were added dropwise to the surfactant solution and 1.23 g (5.3 m mol) of APS and 22 g (33 m mol) of 1.5 M HCl were added to the mixed solution. The chemical oxidation polymerization proceeded with magnetically stirring for 3 hr. After polymerization; the reaction product was placed in a separating funnel. An excess ethanol and distilled water were poured into the funnel alternately to remove the surfactants and to precipitate POA nanoparticles. The POA nanoparticles were retrieved and dried in a vacuum oven at room temperature.

Synthesis of poly-o-anisidine metal nano-oxides

1.0 wt% of polymer nanoparticles prepared from different metal oxide nanopowder was added to 0.2 gm. of poly-o-anisidine nanoparticles and stirring until the mixture became homogeneity and the metal oxide nanopowder distributed in the polymer nanoparticles. The polymer-nanocomposites were pressed into pellets 1cm diameter and 1mm thickness.

Characterization

Molecular weight

Molecular weight determination was done by gel permeation chromatography (GPC); The weight average molecular weight was determined by using CRYETTEA instrument- Automatic cryoscope. The method is based on Avogadro-Gerhardt law. The weight average molecular weight; M_w was found to be 75457 for poly-o-anisidine nanoparticles.

FTIR spectroscopy

FT-IR characterizations were performed using a Perkin-Elmer 1650 FTIR spectrophotometer using the KBr technique.

Transmission electron microscopy (TEM)

JEOL JEM-1230; 1000 Kv Electron Microscope measured TEM Micrograph of the prepared poly-o-anisidine and for poly-o-anisidine nanoparticles.

Thermogravimetric analysis (TGA)

The thermal stability of the prepared poly-o-anisidine and for poly-o-anisidine compounds were studied using a thermo gravimetric analyzer. All TGA spectra were recorded under a nitrogen atmosphere up to 600°C using a programmed rate of 10°C/min.

Antibacterial effect (SRB)

The antimicrobial activities of the synthesized compounds were evaluated at the Micro Analytical Center (Cairo University) using the modified Kirby-Bauer disc diffusion method [30] against sulfur reducing bacteria (Desulmonomas Pigra); then the activities of the most efficient compounds against SRB strain were further investigated.

Electrical conductivity

The samples prepared were pressed into pellets of 1.33 cm diameter and 1 mm thickness in a hydraulic press (Kimaya Engineers; India; Model WT-324) at five metric ton pressure. The conductivity measurements were carried out by a four-probe technique recorded by a Keithly electrometer type 614. The pellet used in this measurement is placed between two copper electrodes; which were connected to the two terminal of the Keithley electrometer.

Results and discussion

FTIR spectroscopy

The spectrum of POA nanoparticles samples table (1) shows that; disappearance of the band 3411 cm\(^{-1}\); new bands at 3646 and 3394 cm\(^{-1}\) appear due to single bridge compounds polymeric association [31]. There is also a band at 3174 cm\(^{-1}\) showing the presence of chelate compounds. The C-H stretching vibration is represented by the band 2920 cm\(^{-1}\). The band at 1481 cm\(^{-1}\) may be due to CH\(_2\) group or to aromaticity. Additional bands at 1283; 1199; 1050 and 1004 cm\(^{-1}\) could be assigned to vibrations of the C–O–C bonds of the ether group [32] and aromatic C–O; [33] respectively. Small bands at 608 and 444 cm\(^{-1}\) are due to the presence of CuO nanopowder; the band at 441 cm\(^{-1}\) is due to Ag2O; the band at 44 cm\(^{-1}\) showing the presence of ZnO and the bands at 533 and 438 cm\(^{-1}\) are due to TiO2.

TEM analysis

Figure 1 represents TEM image of the POA nanoparticles. Due to preparation of the polymer nanoparticle in the presence of cationic surfactant (N-dodecyloxycarbonylmethyl-N-triethanol ammonium chloride); POA nanoparticles are shown in the range of nanoscale. Figures 1(a) and (b) of POA nanoparticle pure and POA /TiO\(_2\) nanocomposite; the particle size ranged between 5-7 nm and 35-36 nm in diameter and had spherical shape. But in presence of POA / AgO nanopocomposite; their sizes varied from 28 to 32 nm in diameter and appeared as rod shape

(1c).

Table 1: IR absorptions POA nanoparticles/nanocomposites.

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>POA</th>
<th>POA +CuO</th>
<th>POA+AgO</th>
<th>POA +ZnO</th>
<th>POA+TiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single bridge compounds</td>
<td>3646</td>
<td>3646</td>
<td>3646</td>
<td>3646</td>
<td>3646</td>
</tr>
<tr>
<td>C-H stretching vibrations</td>
<td>3394</td>
<td>3394</td>
<td>3394</td>
<td>3394</td>
<td>3394</td>
</tr>
<tr>
<td>Alkane monosubstituted group</td>
<td>2853</td>
<td>2853</td>
<td>2853</td>
<td>2853</td>
<td>2853</td>
</tr>
<tr>
<td>C-O aromatic</td>
<td>1114</td>
<td>1114</td>
<td>1114</td>
<td>1114</td>
<td>1114</td>
</tr>
<tr>
<td>CH(_2) group</td>
<td>1481</td>
<td>1481</td>
<td>1481</td>
<td>1481</td>
<td>1481</td>
</tr>
<tr>
<td>C-O-C ether</td>
<td>1283</td>
<td>1283</td>
<td>1283</td>
<td>1283</td>
<td>1283</td>
</tr>
<tr>
<td>CuO</td>
<td>-</td>
<td>608</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AgO</td>
<td>-</td>
<td>-</td>
<td>444</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>444</td>
<td>-</td>
</tr>
<tr>
<td>TiO2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>533-438</td>
</tr>
</tbody>
</table>
POA/CuO nanocomposite; and POA/ZnO nanocomposite; it seems as cubed shape with 9 to 12 nm in diameter. It was found that; with different nano metal oxides different shapes and sizes were appeared [34].

**Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA) is one of the thermal analysis techniques used to quantify weight change and thermal decomposition of the sample. The TGA curves of pure TiO$_2$ nanoparticles only show a small weight loss; occurring below 400°C and can be ascribed to the elimination of water; ethanol and partial dehydroxylation of the TiO$_2$ nanoparticles. The 17.8% weight loss observed until 347°C in the TGA curve of the pure ZnO nanoparticles is attributed to the elimination of the adsorbed water and to the dehydroxylation process (Figure 2).

In fact; the influence of the inorganic nanoparticles on the thermal stability of POA nanocomposites is very complex; which is related to many factors; such as the synthetic method; type of inorganic nanoparticles; structure of composites; the interaction between two components; and so on [35]. TGA curves of the pure POA nanoparticle and its composites with different metal oxide nanopowder at the same concentration are shown in figure 2.

The TGA curve of the POA/nano-ZnO composites also show weight losses between 22.16°C and 93.77°C attributed to the loss of water from both ZnO and polymer surfaces; besides a differentiated behaviour marked by a strong weight loss in the 94.69–443.45°C range. Comparing POA/nano-composites with POA pure; it can be seen that the incorporation of ZnO; Ag; CuO and TiO$_2$ nanoparticles was lower than that of pure POA. This is the same results of Kumar et al. [36]; who found the decomposition temperature of the PANI nanocomposites with Cu$_2$O nanoparticles was lower than that of pure PANI. But different in the result of Yongjun He [37] who found that ZnO nanoparticles improves the thermal stability of PANI to a certain extent. However; Kim et al. [38] observed that the thermal stability of PANI was relatively enhanced by forming the nanocomposites with montmorillonite. It seems that the influence of the inorganic nanoparticles on the thermal stability of PANI nanocomposites is very complicated; its mechanism remaining to be addressed.

By comparing the different metal oxides nanopowder; it was found that the weight loss of POA/CuO nanocomposite; is -1.625mg (-63.177%) between 39.38°C to 600.06°C which is more stable than POA/Ag$_2$O nanoparticle whose weight loss is -1.410mg (-64.453%) from 38.48°C to 600.04°C which is more stable than POA/ZnO nanocomposite whose weight loss is -2.090 mg (-72.096%) between 22.16°C to 600°C which is more stable than POA/TiO$_2$ nanocomposite whose weight loss is -2.365mg (-74.279%) from 24.06°C to 600.01°C.

**Antibacterial effect (SRB)**

It is clear from the data that; the antibacterial activities of the POA/Ag$_2$O nanocomposite microspheres have good effects to sulfate reducing bacteria than POA nanoparticles. It can be used in antibacterial coating in water environment against biocorrosion. As it is shown in table [3a].

**Conductivity measurements**

From studying TGA and SRB of poly o-anisidine nanoparticles which prepared by using cationic surfactant N-dodecylxoycarbonylmethyl-N-triethanol ammonium chloride; we chosen Ag$_2$O and ZnO as nanopowder to studying the effect of these metal oxides on the electrical conductivity of poly o-anisidine nanoparticles. We can observe that the electrical conductivity of POA nanoparticles pure is in the range of insulator $10^{-16}$ as shown in figure (3); but when added different metal oxides nanopowder; it was found that the electrical conductivity of poly anisidine nanoparticles was improved.

While $\ln R = 2.303 \log R$ then $\log R = 1/2.303 \ln R$
Figure 3: Electrical conductivity of (a) POA nanoparticle pure (b) POA nanoparticles+ AgO (c) POA nanoparticles+ ZnO

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Temperature (°C)</th>
<th>Weight Loss % at 1000/T (K^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POA</td>
<td>440</td>
<td>59.543%</td>
</tr>
<tr>
<td>POA/ZnO</td>
<td>500</td>
<td>72.096%</td>
</tr>
<tr>
<td>POA/AgO</td>
<td>405</td>
<td>64.453%</td>
</tr>
<tr>
<td>POA/CuO</td>
<td>515</td>
<td>63.177%</td>
</tr>
<tr>
<td>POA/TiO₂</td>
<td>470</td>
<td>74.279%</td>
</tr>
</tbody>
</table>

Table 2: TGA data of POA/metal oxides powder nanocomposites.

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Conductivity σ (S/cm)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(o-anisidine)</td>
<td>6.25 x 10^-14</td>
<td>40°C</td>
</tr>
<tr>
<td>(o-anisidine/AgO)</td>
<td>2.0 x 10^-11</td>
<td>40°C</td>
</tr>
<tr>
<td>(o-anisidine/ZnO)</td>
<td>8.1 x 10^-13</td>
<td>40°C</td>
</tr>
</tbody>
</table>

The electrical conductivity σ = 1/R Ω⁻¹; so

\[ \ln R = 2.303 \log R \]
\[ \log R = 10^{10}/2.303 \ \Omega^{-1} \text{ near 40°C; and} \]
\[ \ln R = 2.303 \log R \]
\[ \log R = 10^{10}/2.303 \ \Omega^{-1} \text{ at 120°C}. \]

When the polymer was mixed with AgO figure (4-d):

\[ \ln R = 2.303 \log R \]
\[ \log R = 10^{10}/2.303 \ \Omega^{-1} \text{ near 40°C and} \]
\[ \ln R = 2.303 \log R \]
\[ \log R = 10^{10}/2.303 \ \Omega^{-1} \text{ at 120°C}. \]

In the case, when the polymer impregnated with ZnO; figure (4-c):

\[ \ln R = 2.303 \log R \]
\[ \log R = 10^{10} / 2.303 \ \Omega^{-1} \text{ at 40°C; and} \]
\[ \ln R = 2.303 \log R \]
\[ \log R = 10^{10} / 2.303 \ \Omega^{-1} \text{ at 120°C}. \]

It was found that the resistance of the polymer nanoparticles decreases with increase of temperature. Also the electrical conductivity of the polymer nanoparticle increases when the polymer was impregnated with metal oxide nanopowder. The increase in electrical conductivity differs with the metal oxide used. Accordingly, it’s shown that poly (o-anisidine/AgO) the highest electrical conductivity than poly (o-anisidine/ZnO). Table 3b show the effect of temperature on the electrical conductivity. This means that by adding metal oxides poly o-anisidine nanoparticles converted from insulator behaviour to semiconductor behaviour which can uses in electronic industry.

**Conclusion**

The following conclusions have been drawn from the present study. A poly-o-anisidine nanoparticles was prepared in presence of cationic surfactant N-dodecylxycarbonylmethyl-N-triethanol ammonium chloride. FTIR spectra of pure POA nanoparticles and POA nanoparticles in presence of CuO; ZnO; TiO₂ and AgO were determined. The transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA) were studied. From TGA; it was found that the influence of the inorganic nanoparticles on the thermal stability of poly-o-anisidine nanoparticles is very complicated. The antimicrobial activities of the synthesized compounds were evaluated; it was found that the POA/AgO nanocomposite microspheres have good effects on the sulfate reducing bacteria than POA nanoparticles. The electrical measurements declare that the poly o-anisidine nanoparticles was improved by adding metal oxides which converted the polymer nanoparticles from insulator behaviour 10^-10(S/cm) to semiconductor behaviour 10^-10(S/cm) in case of POA/AgO and 10^-14(S/cm) in case of POA/ZnO. Also the conductivity was increased by increasing the temperature.

**References**