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Characterization and electrochemical properties of conducting nanocomposites synthesized from p-anisidine and aniline with titanium carbide by chemical oxidative method

I. Radja a, H. Djelad a,b, E. Morallon b, A. Benyoucef a,*

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Graphical abstract
Characterization and electrochemical properties of conducting nanocomposites synthesized from p-anisidine and aniline with titanium carbide by chemical oxidative method

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- A simple and facile method was used to synthesize prepared a nanocomposite.
- Intercalation of monomers on TiC was followed by oxidative polymerization.
- Characterizations confirm the presence of polymers on TiC.
- The PPA/TiC are more thermally stable than those of PANI/TiC.
- Good electrochemical response has been observed for polymers grown on TiC.
Characterization and electrochemical properties of conducting nanocomposites synthesized from \( p \)-anisidine and aniline with titanium carbide by chemical oxidative method

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Abstract

A novel polymer/TiC nanocomposites “PPA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC” was successfully synthesized by chemical oxidation polymerization at room temperature using \( p \)-anisidine and/or aniline monomers and titanium carbide (TiC) in the presence of hydrochloric acid as a dopant with ammonium persulfate as oxidant. These nanocomposites obtained were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and thermogravimetric analysis (TGA). XRD indicated the presence of interactions between polymers and TiC nanoparticle and the TGA revealed that the TiC nanoparticles improve the thermal stability of the polymers. The electrical conductivity of nanocomposites is in the range of 0.079–0.91 S cm\(^{-1}\). The electrochemical behavior of the polymers extracted from the nanocomposites has been analyzed by cyclic voltammetry. Good electrochemical response has been observed for polymer films; the observed redox processes indicate that the polymerisation on TiC nanoparticles produces electroactive polymers. These nanocomposite microspheres can potentially used in commercial applications as fillers for antistatic and anticorrosion coatings.

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1. Introduction

Intrinsically conducting polymer thin films have been used in various kinds of electronic devices. Conducting polymers are combined with metal oxides because of their enhanced physical and electronic properties and find useful applications in different devices, such as sensors, electrodes, batteries, and photovoltaics [1,2]. Conducting-polymer-based solar cells have gained much importance in the last decade because of their low cost, easy processability, low toxicity, and high environmental stability [3,4]. Among conducting polymers, polyaniline (PANI) is unique because it can be easily doped with various acids and it also exhibits good thermal and environmental stability [5,6]. Metal oxides can also replace fullerenes (electron-acceptor materials) in bulk hetero-junction solar cells because of their high electron mobilities [1,2].

Organic–inorganic hybrid materials, which combine excellent performances of the two materials, are extremely innovative, and such materials promise new applications in many fields, such as electronics, optics, electrochemistry, supercapacitor, mechanics and biology [7–10]. Any organic–inorganic hybrid materials can be obtained by intercalative reactions of layered solids based on self-assembly approaches [11–14].

Recently, on the basis of conducting polymers and inorganic nanoparticles, the nanocomposites have attracted attention as it seems to be the potential route to improve the performance of materials in devices. Several reports on the synthesis of the nanocomposites of polyaniline with Fe\(_3\)O\(_4\) [15], ZnO [16], ZrO\(_2\) [17], TiO\(_2\) [18] and montmorillonite [19] nanoparticles have already been published.

Titanium carbide (TiC) is one of the most important metal carbides with excellent properties, such as high melting temperature, hardness, strength, wear, corrosion resistance, electrical conductivity, and thermal conductivity [20,21]. TiC is an important material from technological applications because of its high melting point, hardness, elastic modulus, electrical conductivity and low coefficient of thermal expansion. Composite systems consisting of a polymer matrix and conductive particles of titanium carbide have been considered as a novel class of smart materials, because of their ability to switch from negative to positive temperature coefficient of conductivity [22–25]. Negative temperature coefficient of conductivity (NTCC) is useful in applications such as self controlled heaters, current limiters,
sensors, thermostors and over current protectors, while it is considered as detrimental in cable engineering [26].

Moreover, the synthesis of poly(p-anisidine)/TiC (PPA/TiC), poly (p-anisidine-co-aniline)/TiC (poly[PA-co-ANI]/TiC) and PANI/TiC nanocomposites has not been reported before. Herein, we look forward to synthesis nanocomposites by using an in-situ chemical polymerization route and used it as new material and characterized by UV–vis, FT-IR, XRD, thermogravimetric analysis (TGA) and further study for electrochemical properties. The p-anisidine is a substituted derivative of PANI with methoxy (–OCH3) group substituted at para positions. The PPA was chosen as an organic counterpart for this study to explore the possibility of utilizing it as an alternative to PANI for technologies application. The purpose of this paper is to give a preliminary account of our research on the use of polymer/TiC nanocomposites as suitable anodic materials for hydromet larly.

2. Experimental

2.1. Materials

The monomers aniline (ANI) (from Aldrich) was distilled under vacuum prior to use and p-anisidine (PA) (from Aldrich) was used as received. Perchloric acid and hydrochloric acid (from Merck) was Suprapur quality and all the solutions were freshly prepared with distilled-deionised water was obtained from an Elga Labwater Purelab Ultra system. A titanium carbide (TiC) (99%) is purchased from the Sigma–Aldrich Company. Ammonium persulfate (NH4)2S2O8 (APS) and ammonium solution (NH4OH) were all of analytical purity and used without further purification.

2.2. Chemical synthesis of nanocomposites

In the preparation of PPA/TiC nanocomposite process, firstly, TiC nanoparticles (1.0 g) were dispersed in 1 M HCl aqueous solution with ultrasonic vibration for 1 h to obtain a uniform suspension. A 1.35 g quantity of PA monomer was added to this mixture dropwise under strong stirring in an ice-water bath and stirred for 1 h. Then 2.51 g of APS in 20 mL of 1 M HCl solution was slowly added dropwise to the suspension mixture (using 1:1 monomer/oxydant mole ratio), and the solution was stirred at room temperature for 24 h. A solid product was obtained after filtration and washed with 1 M HCl and deionized water to remove residual aniline and ammonium sulfate. The final products were bathed using 50 mL of 1 M NH4OH at room temperature while magnetically stirring for 2 h. The product was collected by filtering and washing the precipitate with deionized water, and dried under vacuum at 60 °C for 24 h [27,28].

For the synthesis of the PANI/TiC and poly(PA-co-ANI)/TiC nanocomposites and also the polymer PPA (without TiC), the same procedure was repeated.

2.3. Nanocomposite characterization

The X-ray diffraction of the powder nanocomposites were taken using a Bruker CCD-Apex equipment with a X-ray generator (Cu Ka and Ni filter) operated at 40 kV and 40 mA. For recording the UV–vis absorption spectra, a Hitachi U-3000 spectrophotometer was used. The solution of the homo- and co-polymer in N-methyl-2-pyrrolidone (NMP) was used for recording the spectrum. Fourier transform infrared (FT-IR) spectroscopy was recorded using a Bruker Alpha in transmission mode after dissolving the sample in KBr.

Transmission electron microscopy (TEM) was performed to determine the morphology of the samples using JEOL microscope, JEM-2010 model. This TEM microscope is equipped with an X-ray detector Bruker XFlash 3001 for microanalysis energy dispersive spectroscopy (EDS) for the elucidation of chemical composition of the samples. A simultaneous TG-DTA (METTLER TOLEDO model TGA/SDTA851e/SE/1100) thermogravimetric analyzer was employed to perform the thermal analysis under a 100 mL/min nitrogen flow at 10 °C/min until 900 °C.

2.4. Electrochemical studies

The electrochemical behaviour of the polymers was studied by cyclic voltammetry after their extraction from the polymer by dissolving in the N-methyl-2-pyrrolidone (NMP). It is known that this kind of conducting polymers is soluble in NMP [14,29], while the TiC remains in solid state. Thus, both components can be separated by filtration. The electrochemical measurements were carried out using a conventional cell of three electrodes. The counter and reference electrodes were a platinum foil and a hydrogen reversible electrode (RHE), respectively. For all the electrochemical and spectroelectrochemical experiments the polymers were separated from the catalyst by dissolving the mixture in NMP. Then polymer films were obtained by casting a drop of these solutions over the working graphite carbon electrode and heating with an infrared lamp to remove the solvent. The electrolyte used was 1 M HClO4 and all experiments were carried out at 50 mV/s.

2.5. Electrical conductivity measurements

Electrical conductivity measurements were carried out using a Lucas Lab resistivity equipment with four probes in-line. The samples were dried in vacuum during 24 h and pellets of 0.013 m diameter were prepared using a FTIR mold by applying a pressure of 7,4, 10⁸ Pa.

3. Results and discussion

3.1. XRD characterization

Fig. 1 shows the X-ray diffractograms for all the three nanocomposites and TiC pure. The XRD pattern of the TiC particles presents the hexagonal structure with no extra reflections, and perfectly indexed to (001), (100), (101), (110), (002), (111), (200), (102) and (201) crystal plane of hexagonal TiC (JCPDS Card No. 200097). In XRD of nanocomposites, all the peaks of TiC are observed. The XRD pattern for the polymer/TiC shows new low diffraction peaks at 2θ = 22.81 ° (Fig. 1, inset.). In addition, the intensities of this broad diffraction peak corresponding to polymer “PA, poly([PA-co-ANI]) and PANI” in the nanocomposite become weakened with introducing TiC nanoparticles, which indicates that TiC nanoparticles have an effect on the crystallinity of polymer [30]. This indicates that the crystal structure of TiC is not modified due to the presence of polymer. This result also shows the interaction between the TiC nanoparticles and polymer molecular chains due to the adsorption of polymer molecular chains on the surface of the TiC nanoparticles.

The average crystallite sizes of TiC nanoparticles, and the three samples of nanocomposites were estimated from the X-ray diffraction patterns using Scherrer formula [31]:

\[ d = \frac{k \times \lambda}{\beta \times \cos\theta} \]  

(1)

where \( d \) is the average crystallite size, \( \lambda \) is the X-ray wavelength, \( \beta \) is the full-width at half-maximum and \( \theta \) is the diffraction angle. The value of \( k \) depends on several factors, including the Miller index of reflection plane and the shape of the crystal. If shape is
unknown, $k$ is often assigned a value of 0.9. So the crystallite size of TiC nanoparticle, and the nanocomposites was computed from XRD patterns see Table 1.

### 3.2. FT-IR spectroscopy

The typical FT-IR spectra for TiC, pure PPA, pure PANI and PPA/TiC, poly(PA-co-ANI)/TiC, PANI/TiC nanocomposites containing 5 wt% TiC nanoparticles are shown in Fig. 2.

The characteristic bands for pure PPA are observed in the spectrum at 3425, 2935, 1207, 1169 and 800 cm$^{-1}$, in agreement with the reported literature [32]. The bands at approximately 1498 and 1591 cm$^{-1}$ are due to the benzenoid and quinoid ring units, respectively. It was found that the PPA film formed by galvanostatic conditions contained both benzenoid and quinoid moieties. There are other characteristic bands at 1275 and 1114 cm$^{-1}$, due to 1,2,4-trisubstituted benzene rings. The characteristic bands of pure PANI were assigned as follows: at 3450 cm$^{-1}$ it was associated to N–H stretching mode, C=N and C=C stretching modes for the quinoid and benzenoid rings are observed at 1573 cm$^{-1}$ and 1480 cm$^{-1}$ respectively, the bands at about 1309 cm$^{-1}$ and 1243 cm$^{-1}$ can be associated to C–N stretching mode for the benzenoid ring, while the band at 1126 cm$^{-1}$ was assigned to a in plane bending vibration of C–H (mode of N=Q=N, Q=N–H–B and B–N–H–B), which was formed during protonation [33].

It was evident that the FTIR spectra of the nanocomposites (PPA/TiC, poly(PA-co-ANI)/TiC, PANI/TiC) contained contributions from both TiC and polymers. However, some bands of doped polymer had shifted due to interactions with TiC nanoparticles. For example, in PPA/TiC nanocomposite, the bands at 1275 cm$^{-1}$, 1215 cm$^{-1}$ and 1169 cm$^{-1}$ corresponding to the stretching mode of C–C, C=N and C–H, all shifted to higher wavenumbers, and C–N stretching band at 1591 cm$^{-1}$ shifted to lower wavenumber. Similarly, the band at 3425 cm$^{-1}$ also shifted to 3220 cm$^{-1}$ this band was attributable to N–H stretching mode. These changes suggest that C–C, C=N and C–H bands became stronger in PPA/TiC nanocomposite, but the N–H band became weaker. This was probably because of the action of hydrogen bonding between the surfaces of TiC nanoparticles and the N–H groups in PPA polymer. And the presence of TiC nanoparticles had effect on the doping of PPA.

The spectra of poly(PA-co-ANI)/TiC and PANI/TiC nanocomposites, display bands between 1565–1596 cm$^{-1}$ and 1497 cm$^{-1}$ ($\nu(C=N)$ and $\nu(C=C)$), indicating that the PA-co-ANI and ANI

![Fig. 1. XRD diffraction patterns of PPA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC nanocomposites and TiC nanoparticles.](image)

![Fig. 2. FT-IR spectra of nanocomposites (PPA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC), pure polymers (PPA and PANI) and TiC nanoparticles.](image)

Table 1

<table>
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<tr>
<th>Samples</th>
<th>TiC</th>
<th>PPA/TiC</th>
<th>poly(PA-co-ANI)/TiC</th>
<th>PANI/TiC</th>
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<td><strong>d (nm)</strong></td>
<td>30.80</td>
<td>46.64</td>
<td>31.73</td>
<td>42.45</td>
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polymers are present in the matrix. The spectra also display a broad band between 3251 cm⁻¹

The increases in the intensity of the band between 1014 cm⁻¹ and 1021 cm⁻¹ corresponding to the stretching mode of C–O–C may be attributed to the signal from the methoxy group in the anisidine [34].

Despite the slight shifts of these bands compared with the matrix, we can suppose that the overall framework is preserved after the reaction, in agreement with the X-ray powder diffraction data (Fig. 1).

3.3. Electrical conductivity characterization

Table 2 shows the electrical conductivities of nanocomposites that are in the range of 0.12–1.45 S cm⁻¹. An increase in the content of aniline in the polymerization produces the increase in conductivity. In the case of nanocomposites a reduction in the electrical conductivity is observed as compared to the pure polymers. This fact can be explained by the interactions between the polymers and TiC nanoparticles which probably led to the reduction in conjugation length of polymers [35–37]. Moreover, the presence of TiC nanoparticles hindered the transport of carriers between different molecular chains of polymer [37,38]. The presence of TiC particles may also have hindered the transfer of carriers between molecular chains of polymers.

3.4. UV-vis spectroscopy

Fig. 3 shows the UV–vis absorption spectra of PPA/TiC, poly[PA-co-ANI]/TiC and PANI/TiC nanocomposites, these samples dissolved in NMP solution for separate the polymer from TiC. Although the three samples show two characteristic absorption bands, the three spectra look somewhat different. The absorption bands at ~317–329 nm can be ascribed to π–π* transition of the benzenoid rings, whereas the bands at ~443–545 nm can be attributed to polaron–π* transition [39]. Therefore, it can be concluded from the UV–vis absorption spectrum of PPA/TiC that the doped state can be enhanced with the incorporation of PA units in the polymer chain, which may resulted with a strong electronic effect that can stabilize the doping state of polymer. Based on the previous research, the doping level can roughly be estimated from the absorption spectra of PPA/TiC at 450 nm (π–π* transition). The poly[PA-co-ANI]/TiC exhibits this band at higher wavelength which implies that the doping level of copolymer nanocomposite is lower than that of homopolymer nanocomposites.

This is in consistent with the results of FTIR spectra. When comparing the absorption spectra, a notable red shift of the bands are observed for copolymer poly[PA-co-ANI]/TiC nanocomposite as compared to homopolymers nanocomposites. This indicates a higher conjugation length appearing in copolymer nanocomposite. The effective conjugation length favors planar chain structures and steric factors that prevent to give twisted chains. Evidently, the steric hindrance connected with –OCH₃ substituent results in twisting, thus lowering the conjugation length in PPA [40]. These results suggest that the proportion of PA perhaps plays a significant role toward the determination of the chain length and other properties of these conducting copolymers.

3.5. Thermogravimetric analysis (TGA)

The thermal stability of a conducting polymer is very important for its potential application. Thermogravimetry (TGA) is a significant and useful dynamic way to detect the degradation behavior in which the weight loss of a polymer sample is measured continuously while the temperature is changed at a constant rate. In order to investigate the thermal stability of the PPA/TiC, poly[PA-co-ANI]/TiC, PANI/TiC nanocomposites and the pure PANI, pure PPA and TiC, the thermal analyses of samples were tested, the results are shown in Fig. 4. In the first stage, the weight loss starting practically from room temperature to 110 °C is due to the loss of water molecules and moisture present in the samples. Note that the degradation of nanocomposites is slower than that of pure polymers with the temperature increase, and the thermal stability of PPA/TiC is higher than that of poly[PA-co-ANI]/TiC and that PANI/TiC respectively; these results also demonstrates that the

<table>
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<th>Samples</th>
<th>PPA/TiC</th>
<th>Poly[PA-co-ANI]/TiC</th>
<th>PANI/TiC</th>
<th>PPA</th>
<th>poly[PA-co-ANI]</th>
<th>PANI</th>
</tr>
</thead>
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<tr>
<td>Conductivity (S cm⁻¹)</td>
<td>0.08</td>
<td>0.09</td>
<td>0.91</td>
<td>0.22</td>
<td>0.82</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Fig. 3. UV–vis spectra of PPA/TiC, poly[PA-co-ANI]/TiC and PANI/TiC nanocomposites.

Fig. 4. Thermogravimetric analysis (TGA) of nanocomposites (PPA/TiC, poly[PA-co-ANI]/TiC and PANI/TiC), pure polymers (PPA and PANI) and TiC nanoparticles obtained in nitrogen atmosphere at heating rate of 10 °C/min.
The thermo stability of nanocomposites depends on the polymer type used (structure of the polymers and the interaction between two components) [41].

The thermal behaviour of PPA pure is similar to that of PANI pure and exhibits a four-stage decomposition pattern. In the first stage, is due to the loss of water molecules and moisture present in the polymer. The second- and third-stage losses that occur from 110 °C to 350 °C are attributed to the loss of the dopant from the polymer chains. While the fourth stage loss from 350 °C to 600 °C is the result of the complete degradation and decomposition of the polymer backbone [42].

The results implied that the incorporation of nanoparticles TiC into polymer resulted in the improvement of the thermal stability of nanocomposites.

One of the common uses of TGA analysis in the technology is to determine the polymer amount of a nanocomposite. The definition of each sample is based on its relative volatility. The success of the method depends on each component having a different thermal stability range in an inert atmosphere. The amount of polymer was calculated by difference between the initial amount to 20 °C and after a temperature 700 °C (the degradation behavior), according to the following equation:

\[
\Delta w = \frac{w_i - w_f}{w_i} \times 100
\]

where \(w_i\) and \(w_f\) are the amounts of polymer at 20 °C and at 700 °C (g), respectively. \(\Delta w\) is the percentage of the amount of polymer formed on TiC (see data in Table 3).

### Table 3
The amount of nanocomposites at 20 °C, 700 °C and the percentage of the amount formed on TiC nanoparticle.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(w_i) (g) at 20 °C</th>
<th>(w_f) (g) at 700 °C</th>
<th>(\Delta w) %</th>
</tr>
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<tbody>
<tr>
<td>PPA/TiC</td>
<td>7.06</td>
<td>6.71</td>
<td>5.0</td>
</tr>
<tr>
<td>Poly(PA-co-ANI)/TiC</td>
<td>6.92</td>
<td>6.06</td>
<td>12.4</td>
</tr>
<tr>
<td>PANI/TiC</td>
<td>4.16</td>
<td>2.29</td>
<td>44.9</td>
</tr>
</tbody>
</table>

Fig. 5. Cyclic voltammograms recorded for a graphite carbon electrode covered by PPA/TiC, Poly(PA-co-ANI)/TiC and PANI/TiC nanocomposites in 1 M HClO₄ solution. Scan rate 50 mVs⁻¹.

Fig. 6. TEM images of: (a) TiC nanoparticle, (b) PPA/TiC, (c) Poly(PA-co-ANI)/TiC and (d) PANI/TiC nanocomposites.
3.6. Electrochemical properties

Cyclic voltammetry experiments were performed to test the electroactivity of the polymers. Fig. 5 shows the steady voltammograms for polymers from PPA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC samples, obtained in 1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. In the case of PANI/TiC nanocomposite, two overlapped redox processes are observed. The first one appears at 0.45/0.27 V, which results in a potential peak separation (ΔEₚ) close to 180 mV, the second process is observed at 0.77/0.59 V and gives an ΔEₚ value of 180 mV. The first redox process is due to the oxidation of the leucoemeraldineto emeraldine form and the second one to the oxidation of the emeraldine to pernigraniline of polyaniline [43,44]. The voltammetric profile of copolymer poly(PA-co-ANI)/
TiC also show two redox process, however in this case the two processes are more overlapped.

The voltammetric profile for PPA/TiC nanocomposite shows three redox process, the first centered at 0.22/0.36 V gives a ΔEₚ value of 140 mV; the second processes at 0.41/0.50 V (ΔEₚ = 90 mV) and finally, the third process centered at 0.66/0.70 V with a ΔEₚ value of 40 mV.

3.7. Transmission electron microscopy (TEM)

Fig. 6 shows the TEM images of the nanocomposites (PPA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC) and nanoparticle (pure TiC), and after evaporation of the solvent. In Fig. 6(b-d), one can observe the formation of a homogeneous film of polymer particles, whereas in Fig. 6(a), we present a TEM image of pure TiC nanoparticles. However, as it can be seen in Fig. 6(d), a more fibrous structure seems to be associated to the PANI/TiC nanocomposite [45].

Energy dispersive spectroscopy (EDS) analysis of nanocomposites and nanoparticle revealed the presence of Ti and C elements peaks which confirmed the existence of TiC nanoparticles (Fig. 7). In this paper, the spectra of PPA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC nanocomposites indicates that the intensity of Ti decreased; on the contrary, the intensity of C increased, which demonstrates that the TiC nanoparticles are successfully coated by the polymers [46]. However, the elements weight contains signals of Ti, C, Cl and O together with those of the nanocomposites (Tables in Fig. 7).

3.8. Mechanism of formation of polymer/TiC nanocomposites

Scheme 1 shows the proposed reaction scheme for the deposition of polymer on the surface of TiC nanoparticles and the chemical oxidative polymerisation of monomers (PA and/or ANI) with APS to form partially encapsulated nanocomposite particles (PA/TiC, poly(PA-co-ANI)/TiC and PANI/TiC).

There are a bond interaction at the interface between TiC nanoparticles and polymer. Hydrogen bonds can be formed via the amido –NH₂ group in the monomers (PA and/or ANI) and the large amount of hydroxides produced on the surface of TiC nanoparticles when they come into contact with water.

Simultaneously, the N atom in the –NH₂ group has a lone pair of electrons and can be coordinated with the Ti atom. Thus there may be hydrogen bonding and coordinate bonding between TiC and polymer.

When the TiC nanoparticles are introduced into the reaction mixture, the surfaces of individual nanoparticles act as template...
4. Conclusions

Polymer/TIC nanocomposites were prepared from in situ intercalative oxidative polymerization of p-anisidine and/or aniline with TIC nanoparticles. The synthesized nanocomposites were characterized by X-ray diffraction pattern (XRD), fourier transform infrared (FTIR), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA) and electrical conductivity techniques. The electrochemical behavior of polymer/TiC shows that these nanocomposites exhibit a redox processes indicate that the polymerization on TIC nanoparticles produces electroactive polymers.

Acknowledgements

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