In-Situ Preparation of Conducting Polymers/Copper (II)-Maghnite Clay Nanocomposites

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Abstract
In this work we report a simple way for the conducting polymer nanocomposites synthesis using on algerian hydrophilic natural Montmorillonite (MMT) nanoclay named Maghnite (Mag) as dopant. The electrochemical properties study of the following conducting polymers: poly(4-aminobenzylamine) (P4ABA) and polyaniline (PANI) nanocomposites with copper maghnite (Mag-Cu) were successfully prepared by In-Situ polymerization, in presence of inorganic nanolayers of clay, and oxidizing agent ammonium persulfate. The synthesis of copolymers was developed at different feed mole fractions of monomer. The products were characterized by the Fourier transform Infrared (FT-IR), the ultraviolet-visible (UV–vis) spectroscopies and X-ray diffraction (XRD). The results showed that the in-situ polymerization produced real nanocomposites containing aniline and 4-aminobenzylamine units.

Introduction
Recently, clay/polymer nanocomposites have aroused high interest, both in industry and in academia1,2 especially polymer-layered silicate nanocomposites. These nanocomposites are currently prepared by various methods: in-situ polymerization, intercalation from a polymer solution, and direct intercalation by molten polymer (melt compounding)3. The growing interest in polymer nanocomposites initiates from the improvement

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of enhanced mechanical, flame retardant, gas barrier and polymer recycling properties and also, the development of new materials to find potential applications.

At present, Montmorillonite is a hydrophilic clay mineral of the smectites group with a 2:1 aluminosilicate layered structure and it can be used in the preparation of polymer nanocomposites (PNCs). The use of MMT in PNCs due to their unique characteristic of intercalation and exfoliation in the polymeric matrices. MMT can be used in the polymer/Clay nanocomposites preparation, only with MMT-Surface modification to make her compatible with hydrophobic polymers. It was generally needed ion exchange reaction between cationic surfactants. However, the MMT-modification allows enlarging the clay interlayer distance. Due to this interlayer space enlargement, polymer chains can enter in the MMT-Clay gallery and can enhanced properties including improved physical and chemical environment for the polymer.

Maghnite(Mag) is Algerian Montmorillonite(MMT) sheet silicate clay with very high cation exchange property. She is a natural and non-toxic montmorillonite with a lamellar structure, which was developed at the Polymer Chemistry Laboratory of the University of Oran1 Ahmed Ben Bella, Algeria. Montmorillonites are phyllosilicates minerals comprising a crystal structure of TOT layer (Figure 01), they are specific clays showing both Bronsted and Lewis acid sites, and they own net negative charge can be neutralized by cations such as Na⁺, K⁺, Ca²⁺, etc., which occupy the interlamellar space, which can be intercalated or exfoliated, then, industrial applications are all quite dependent on the dispersion of MMT in polymer matrix.

Experimental Materials
4-Amino benzylamine (4ABA) and Aniline were purchased from Aldrich Co. Ammonium persulfate (Merck). A natural montmorillonite clay (named Maghnite) used was supplied by a local company (ENOF Maghnalia-ALGERIA).

Modification of Maghnite (Mag-Cu)
The raw-maghnite (Mag-Na) 10 g was crushed for 30 min then dried for 24 h and stored for later use. Mag-Cu was prepared by Cu²⁺-exchanged reaction. Ten grams of the Mag treated were dispersed in 1M CuSO₄ solution, the mixture was stirred for 24h, this product was then filtered and given several washings with distilled water, to eliminate SO₄⁻. The product was exsiccated at 110 °C, overnight and its composition was determined by X-ray fluorescence (Table1).

Polymer/Mag-Cu Nanocomposites Synthesis
Polymer/Mag-Cu Clay nanocomposites were synthesized by firstly the intercalation of Copper-
Maghnite (0.25 g), then utilizing 4-amino benzyl amine and/or aniline monomers.

The monomers were appended by different mole fractions. In all preparations, the mole ratio of oxidant to the total monomer was 0.5. For instance, the method for poly(aniline-co-4-amine benzylamine)/Mag-Cu nanocomposites mole fraction for f1=0.50 were as fellow; aniline (0.39g, 4.2mmol), 4-amino benzyl amine (0.25g, 4.3mmol) were added to Mag-Cu, and the mixture was kept under stirring and heated at 60°C. A solution of ammonium persulfate (0.49g, 4.1mmol) dissolved in 100ml distilled water, was then added to the reaction mixture. It was stirred for 24h.

**Measurements**

The XRD patterns of the obtaining nanocomposites were carried out at room temperature on a Bruker AXS D8 Advance diffractometer equipped with LynxEye linear detector, with a X-ray generator Cu Kα1 (λ = 1.54056 Å) and operated at (40kV, 40mA). In the range of 2θ = 0° – 70° and scanning speed of 0.02°/s.

Voltammetric measurements are carried out using an electrochemical cell made up of three electrodes immersed in a solution containing the analyte and an excess of a non-reactive electrolyte called the supporting electrolyte. One of the three electrodes is the working electrode, which is in this work made of glassy carbon. The redox process occurs at this electrode. The second electrode is the reference electrode, which provides calibration for the applied potential. Example of this work the reference used was the reversible hydrogen electrode (RHE). The third electrode is the counter electrode, which is often a platinum wire that simply serves to conduct electricity from the signal source through the solution to the other electrodes.

The cell electrolyte was 1M HClO₄, and all measurements were carried out at 0.50 V/s, after extraction the polymers using NMP (N-Methyl-2-pyrrolidone).

**Results and Discussion**

**Maghnite Structure Composition**

Table 1 shows the chemical compositions of the Maghnites determined by X-ray fluorescence spectrometry (XRF). It is necessary to note that Maghnite-Na shows the increase of the content of Na₂O, and cation exchange of copper in the Mag-Cu is detected by the appearance of the content of CuO.

<table>
<thead>
<tr>
<th>Chemical Compositions wt.%</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CuO</th>
<th>Na₂O</th>
<th>MgO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mag-Na</td>
<td>72.77</td>
<td>24.15</td>
<td>1.95</td>
<td>-</td>
<td>2.66</td>
<td>3.37</td>
<td>0.17</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Mag-Cu</td>
<td>67.66</td>
<td>17.17</td>
<td>1.78</td>
<td>2.15</td>
<td>0.01</td>
<td>2.56</td>
<td>0.11</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Nanocomposites Characterization**

**FT-IR Spectroscopy**

The representative FTIR spectra of the maghnite before and after ion exchange and attachment of polymers chains in the nanocomposites were given in Fig.1 and Table 2. The peaks between 3500 and 3100 cm⁻¹ (3351 and 3219 cm⁻¹ for the P4ABA/Mag-Cu, 3337 cm⁻¹ for the PANI/Mag-Cu, and 3340 cm⁻¹ for the P(4aba-co-ani)/Mag-Cu (50/50) nanocomposites associated to N-H bending. Broad absorption peaks between 1580 and 1400 cm⁻¹ from the spectrum of P(4aba-co-ani)/Mag-Cu and
P4ABA/Mag-Cu nanocomposites are typical for secondary amines. Absorption above 1600 cm\(^{-1}\) from the spectrum of P4ABA/Mag-Cu nanocomposites correspond the presence of C=N.\(^{14}\)

The Peaks between 1040 and 450 cm\(^{-1}\) indicate the Mag clay inside nanocomposites, while the peaks at 1487 cm\(^{-1}\), 1448 cm\(^{-1}\) and 1310 cm\(^{-1}\) for PANI/Mag-Cu and P(4aba-co-ani)/Mag-Cu (50/50) nanocomposites correspond to quinone- and benzene-ring stretching deformations, respectively.\(^{15}\)

**Ultraviolet-Visible Absorption Measurements**

Fig. 2 Show typical Ultraviolet-Visible spectra of homo- and co-polymer nanocomposites doped with Mag-Cu. However, the absorption depends on the polymerization conditions and the medium in which the film is examined. For the homopolymers nanocomposites (spectra (a) and (d) for P4ABA/Mag-Cu and PANI/Mag-Cu, respectively) two characteristic peaks, can be observed at about 234/325 nm and 277/480 nm, corresponds to

![IR-FT spectra of the Mag-Na, Mag-Cu and the nanocomposites (P4ABA/Mag-Cu, PANI/Mag-Cu and P(4aba-co-ani)/Mag-Cu).](image1)

**Table 2: Important IR bands of Montmorillonites (Mag-Na, Mag-Cu) and Nanocomposites:**

(a) PANI/Mag-Cu; (b) P(4aba-co-ani)/Mag-Cu (50/50); (c) P4ABA/Mag-Cu

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wave number range (cm(^{-1}))</th>
<th>Assignments</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mag-Na, Mag-Cu</td>
<td>3620</td>
<td>O-H str. (hydroxyl group)</td>
<td>[16-20,22]</td>
</tr>
<tr>
<td></td>
<td>3385, 3418</td>
<td>H-OH hydrogen bonded water</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>1630</td>
<td>O-H deformation of entrapped water</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>996, 1000</td>
<td>Si-O in-plane str.</td>
<td>[22, 24]</td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>(Si-O-Al) deformation</td>
<td>[22, 24]</td>
</tr>
<tr>
<td>Nanocomposites</td>
<td>3337-3351 (a, b, c)</td>
<td>N-H str.</td>
<td>[22-25]</td>
</tr>
<tr>
<td></td>
<td>1580-1400 (b, c)</td>
<td>Vibration of secondary amine</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>1600 (c)</td>
<td>C=N vibration</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>1043 (c)</td>
<td>1,2,3-trisubstitution of 4-aminobenzylamine</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>1573, 1586 (a, b)</td>
<td>C=C str. vibrations of quinoid ring</td>
<td>[15,26]</td>
</tr>
<tr>
<td></td>
<td>1487, 1498 (a, b)</td>
<td>C=C str. vibrations of benzoid ring</td>
<td>[15, 26]</td>
</tr>
<tr>
<td></td>
<td>1266 (a, b)</td>
<td>C-N str. of secondary aromatic amine</td>
<td>[15,25-26]</td>
</tr>
<tr>
<td></td>
<td>1011-1040 (a, b, c)</td>
<td>Si-O in-plane str.</td>
<td>[15,21]</td>
</tr>
<tr>
<td></td>
<td>515 (a, b, c)</td>
<td>(Si-O-Al) deformation</td>
<td>[22, 24]</td>
</tr>
</tbody>
</table>
the n→π* transition and to the π→π* transition, respectively, these transition-related absorbance peaks clearly revealed the transition of the benzenoid rings and quinine-imine groups.

For the copolymers/Mag-Cu nanocomposites two major absorption peaks, can be seen in the spectra (b) and (c) at about 269/376 nm and 327/464 nm. These peaks are due to the presence of the –CH2-NH2 groups in the copolymer chain. The absorption results obtained from electrochemical polymerization of the mixture of Aniline and 4-Aminobenzylamine clearly show the incorporation of monomers into the polymer during polymerization.

**XRD Spectroscopy**

The X-ray diffraction of Mag-Na, Mag-Cu and nanocomposites (PANI/Mag-Cu, P(4aba-co-ani)/Mag-Cu, P4ABA/Mag-Cu) are shown in Fig.3 and quantitative data are given in Table 3. The change in the interlayer spacing of maghnite after ion exchanging Na+ with Cu2+ was found to increase from 12.79Å in the Mag-Na to 14.60Å in the Mag-Cu. In the case of nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing, in comparison with the spacing of the modified Clay used. The interlayer spacing was estimated according to Bragg’s diffraction formula: \( \lambda = 2d \sin \theta \), where \( \lambda \) is the X-ray wavelength and \( 2\theta \) is the scattering angle. X-ray diffraction (XRD) patterns were obtained with a Japanese Rigaku D/max X-ray diffractometer equipped with graphite monochromatized Cu K radiation (\( \lambda = 1.54 \) Å).

**Table 3: Basal spacing \([d_{(001)}]\) of Maghnite-Na, Maghnite-Cu and Nanocomposites**

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ max (deg)</th>
<th>( d_{(001)} ) (Å)</th>
<th>( \Delta d ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mag-Na</td>
<td>6.95</td>
<td>12.79</td>
<td>-</td>
</tr>
<tr>
<td>Mag-Cu</td>
<td>6.09</td>
<td>14.6</td>
<td>1.81</td>
</tr>
<tr>
<td>P(4aba_co-ani)/Mag-Cu</td>
<td>5.84</td>
<td>15.32</td>
<td>2.53</td>
</tr>
<tr>
<td>/Mag-Cu (50/50 P4ABA/Mag-Cu)</td>
<td>5.72</td>
<td>15.63</td>
<td>2.84</td>
</tr>
<tr>
<td>PANI/Mag-Cu</td>
<td>5.98</td>
<td>14.88</td>
<td>2.09</td>
</tr>
</tbody>
</table>

**Fig. 3: X-ray diffraction patterns of two montmorillonite (Mag-Na and Mag-Cu), and the nanocomposites (PANI/Mag-Cu, P(4aba-co-ani)/Mag-Cu, P4ABA/Mag-Cu).**

**Fig. 4: Cyclic voltammograms recorded of polymer and copolymer films formed in 1.0 M HClO4 on graphite carbon electrode**
Electrochemical Response

Comparative cyclic voltammetric (CV) of polymer and copolymer films obtained from P(4aba-co-ani)/Mag-Cu (20/80) at a graphite carbon electrode in 1 M HClO₄ solution at a scan rate of 50 mV s⁻¹, is shown in Figures 5A and 5B. The significance of this study was to explore the best electron transport properties of obtaining nanocomposites. In the case of PANI/MMT-Cu, two overlapped redox processes are observed. The first one appears at 0.32/0.26 V, which results in a potential peak separation (ΔEp) close to 60 mV; the second process is observed at 0.63/0.48 V and gives an ΔEp value of 150 mV. This redox process corresponding to leucoemeraldine/emeraldine and emeraldine/pernigraniline transitions, respectively. On the contrary, the P4ABA/MMT-Cu shows the electrochemical response that is only one redox peak at 0.32/0.49 V. This can be due to the differences in the structures of the polymer.

On the other hand, the nanocomposite P(4aba-co-ani)/Mag-Cu (20/80) displayed different redox properties that hinged on the other samples synthesized. Which present two good and higher redox processes at 0.34/0.47 V and 0.79/0.84 V. This redox process leads to the dependence on the amounts PANI of nanocomposite.

Therefore, the comparative cyclic voltammetry studies reveal that the best electron transport properties is the nanocomposite P(4aba-co-ani)/Mag-Cu (20/80) due to the presence of polar functional groups that may promote covalent cross-link chains in copolymers.

Conclusion

In this study, a poly(4-aminobenzyl amine) (P4ABA), polyaniline (PANI), and copolymer(4aba-co-ani) doped with copper-maghnite clay nanocomposites was successfully synthesized by In-Situ polymerization in the presence of ammonium persulfate a oxidant. The X-ray diffraction, FT-IR spectra and UV-Vis spectroscopy shows some peaks shifts, which indicate the formation of some new bonds and support the intercalation of polymer chains into the interlayer spacing of maghnite (Mag-Cu). Good electrochemical response has been observed for copolymers grown into Mag-Cu in which the cyclic voltammogram shows a broad anodic peak that consists on the overlapping of one redox processes; this indicates that the copolymerisation into Mag-Cu is electroactive.

References


