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Influence of Reaction Conditions on Synthesis of PAni/MnO_2 Composites

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An investigation of the parameters as aniline:MnO_2 and temperature on synthesis of polyaniline/MnO_2 composites was performed. The composites were chemically prepared in H_2SO_4 media using different aniline: MnO_2 ratios at 0°C. After the ratio optimization, the syntheses were performed at 20°C. The polyaniline/MnO_2 composites were characterized by scanning electron microscopy (SEM), ultraviolet-visible, near infrared and infrared spectroscopic techniques. Composites obtained with a uniform, homogeneous and thicker coating of polyaniline films under oxide was considered as the best condition for synthesis.

Keywords Composite; manganese oxide; polyaniline; synthesis

Introduction

Composites of conducting polymers and inorganic particles have received much attention in several applications, as protective coating against corrosion [1], catalyst [2] and sensors [3,4]. Polyaniline (PAni)/WO_3 and PAni/CeO_2 composites have been studied as humidity sensors [3] meanwhile PAni/TiO_2 can be applied as protective coating for steel [1] and trimethylamine [4] sensor. PAni/MnO_2 composites have been used as catalysts for the removal of textile dyes from aqueous solutions [2], catalysis [5], lithium battery electrodes [6] and supercapacitors [7].

Polyaniline/MnO_2 composites combine the advantages of MnO_2, as low cost and environmental friendship, with the PAni characteristics as high electrical conductivity, processability, low cost and easy polymerization. PAni/MnO_2 composites can be prepared by either chemical [8,9] or electrochemical [9] methods. By the electrochemical method the reactions, electropolymerization of aniline and MnO_2 electrodeposition, from solutions containing aniline H_2SO_4 and $MnSO_4$, occur simultaneously [9]. In the chemical syntheses, PAni/MnO_2 composites can be obtained by direct oxidation of aniline by MnO_2 or by using ammonium persulphate as oxidant agent in the presence of MnO_2 suspended in the reaction medium.

In the literature it is possible to find some works describing the preparation and properties of PAni/MnO_2 composites. However, no systematic study describing the

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optimization of the reactional conditions, such as temperature and monomer: oxidizing agent ratio was found. Thus, the aim of this work was to study the effect of temperature and the best monomer:oxidizing agent ratio for the synthesis of PAni/MnO_2 composites. The PAni/MnO_2 composites were characterized by scanning electron microscopy (SEM) and ultraviolet-visible, near infrared and infrared spectroscopic techniques.

Experimental

The chemical synthesis of PAni was performed by dissolving aniline (0.1 mol L^{-1}) in 0.5 mol L^{-1} H_2SO_4 at 0°C under stirring. To this solution, 0.1 mol L^{-1} ammonium persulphate ($(NH_4)_2S_2O_8$) was added. After 90 minutes of reaction, the polymerized material was filtered, washed with water and dried at 50°C under dynamic vacuum for 48 hours. A weight fraction of the polymer was conditioned in 0.1 mol L^{-1} NH_4OH solution for 24 hours under stirring to be undoped. The undoped polymer was filtered, washed with water and dried in an oven at 50°C under dynamic vacuum for 48 hours.

The PAni/MnO_2 composites were synthesized using 0.5 mol L^{-1} H_2SO_4 solutions containing 0.1 mol L^{-1} aniline and MnO_2 particles with the following aniline:MnO_2 ratios: 1:4, 1:6, 1:8, and 1:10, at 0°C under stirring for 180 minutes. The PAni/MnO_2 composites were filtered, washed with water and dried under dynamic vacuum at 50°C for 48 hours. After optimization of the aniline:MnO_2 ratio, the synthesis was performed at 20°C.

The PAni/MnO_2 composites were previously prepared in our laboratory in different acidic media at 0°C and they showed morphology dependent on the nature of acid used, as well as, no arrangement of crystalline oxide. In the present work one the focus was to prepared a material using a process that can be applied in the industry. So, the option was to prepare the composites at 20°C in order to minimize the scale up problems and to guarantee the material processability.

Infrared spectra of KBr pellets containing the samples (MnO_2, PAni/MnO_2 or PAni) were obtained in a Bomem MB-102 – FTIR spectrometer in the range of 400–4000 cm^{-1}. The electronic structures of PAni and PAni/MnO_2 composites were determined by analysis of the UV-Vis-NIR spectra using a VARIAN Cary-spectrometer model 2315. The undoped PAni was dissolved in NMP (N-methyl-2-pyrrolidone) and doped by addition of 0.5 mL of HCl 5 mol L^{-1} and the spectra of both states of PAni were recorded. When PAni/MnO_2 composites are dispersed in NMP (N-methyl-2-pyrrolidone), the PAni is solubilized and the oxide is precipitated. The supernatant containing the dissolved PAni was separated from the oxide and the UV-Vis-NIR spectrum was recorded. With the addition of HCl 5 mol L^{-1}, the polymer was doped and then, another spectrum was recorded. Scanning electron microscopy (SEM) using a LEICA microscope ZEISS model DSM 960, operated with an electron beam of 15–20 kV was used to study the morphology of MnO_2, PAni and PAni/MnO_2 composites.

Results and Discussion

FT-IR Analysis. The spectrum of commercial MnO_2 is shown in Figure 1. One can observed the main characteristic bands of the oxide: (i) a strong band at 620 cm^{-1} due to distortion of MnO_6 octahedral, (ii) a band at 1630 cm^{-1} attributed to O–H

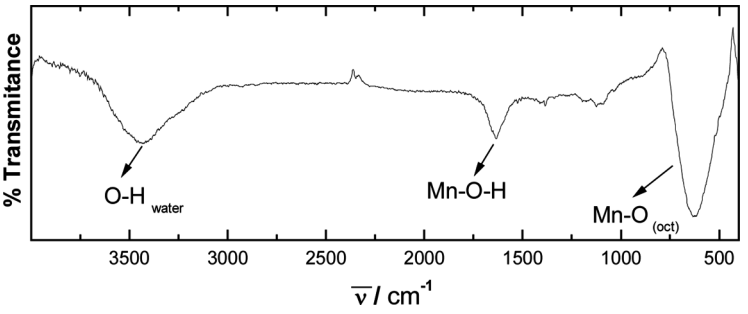


Figure 1. Infrared spectrum for commercial MnO_2.

bending vibrations combined with Mn and (iii) a large band at 3415 cm^{-1} attributed to O–H stretching vibration of constitutional water.

The spectra of undoped and doped PAni synthesized using the ammonium persulphate are concordance with several authors [10–12]. In the spectra in Figure 2 it is possible to identify the characteristic bands of PAni and the respective values are presented in Table 1. So, it is possible to identify bands at around 1245 and 1302 cm^{-1} corresponding to N–H bending and the symmetric component of the C–N connections (or C–C) stretching modes, bands at 1583 and 1494 cm^{-1} corresponding to quinoid and benzenoid rings, respectively. In the spectrum of doped PAni (Fig. 2b) showed a strong band at 1103 cm^{-1}, attributed to C–H out-of-plane bending mode and can be associated at conductivity of polymer.

Figure 3 illustrates the infrared spectra of PAni/MnO_2 synthesized using different aniline:MnO_2 ratio. By these infrared spectra it can be observed a strong band at around 620 cm^{-1}, attributed to distortion of MnO_6 octahedral. With the increase of aniline:MnO_2 ratio, the characteristic bands of PAni become less evident. This result can indicate that amount of PAni is higher in composites obtained using 1:4 (aniline:MnO_2) (Fig. 3a). When PAni/MnO_2 composites are conditioned in

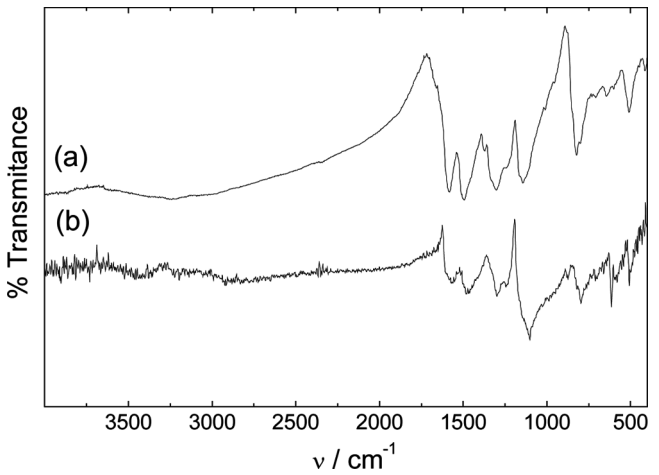
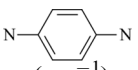
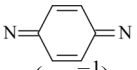


Figure 2. Infrared spectra of PAni obtained using $(NH_4)_2S_2O_8$ as oxidizing agent in (a) undoped and (b) doped state.

Table 1. Main characteristic bands the in infrared spectrum of PAni

	C–H out-of-plane (cm^{-1})	C–H in-plane (cm^{-1})	 (cm^{-1})	 (cm^{-1})	C–N (cm^{-1})	N–H (cm^{-1})
Undoped	823	1143	1494	1583	1302	1245
Doped	796	1103	1475	1566	1298	1244

$0.1\,mol\,L^{-1}$ NH_4OH solution, the detachment of polymer (consequently the undoping process of polymer) and oxide sedimentation occur. The supernatant containing the undoped PAni was separated from the oxide. The materials separated were washed with purified water (Milli-Q-Millipore), dried and characterized by FT-IR.

The spectra of PAni/MnO_2 using aniline:MnO_2 ratio of 1:4, MnO_2 and PAni obtained after undoping process are showed in Figure 4. By this figure is clearly observed that bands characteristic of MnO_2 and PAni are merged. A strong and large band at around $1100\,cm^{-1}$ indicates the doped state of PAni. After the undoped process, in the spectrum of MnO_2 is observed the main characteristic band of oxide (Fig. 4b) and in the spectrum of PAni removed from oxide's surface, a similar spectra of PAni corresponding to the undoped state.

SEM Analysis

The Figure 5a shows the SEM image of commercial MnO_2 used in this work. The morphology of MnO_2 is granular and shows cubic and hexagonal shapes. The

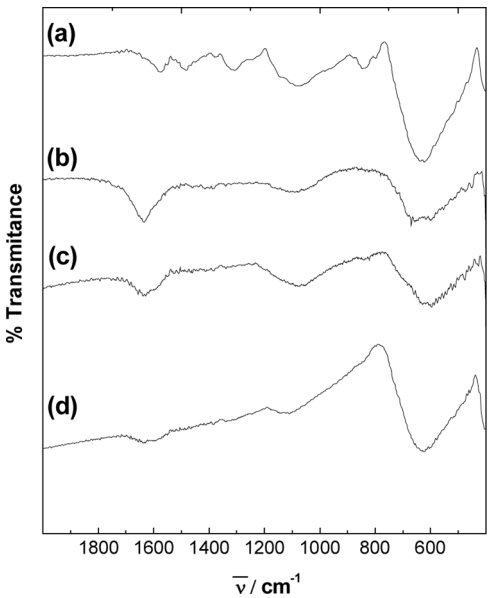


Figure 3. Infrared spectra of PAni/MnO_2 composites synthesized using the aniline:MnO_2 ratios: (a) 1:4, (b) 1:6, (c) 1:8, and (d) 1:10.

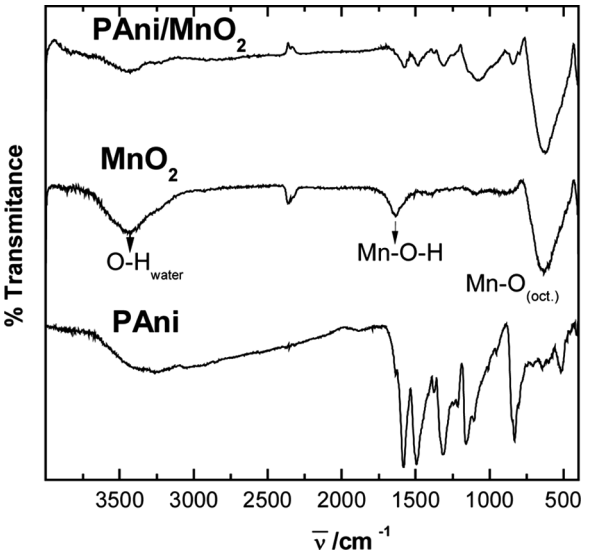
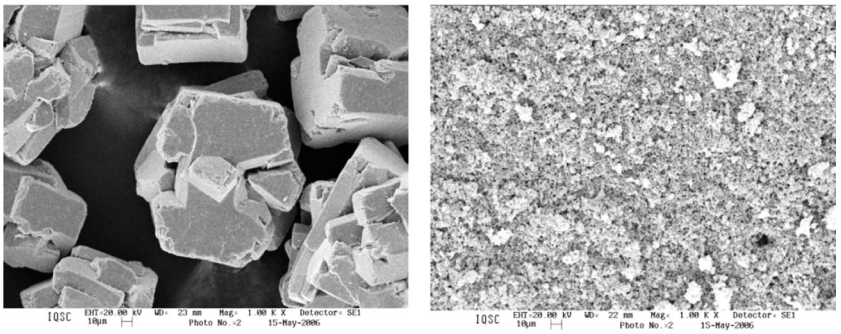


Figure 4. Infrared spectra of PAni/MnO_2 obtained by synthesis using 1:4 (aniline:MnO_2), MnO_2 and undoped PAni.

micrographs of PAni synthesized chemically using ammonium persuphate as oxidizing agent is shown in Figure 5b. PAni presents a globular structure and compact.

In the Figure 6 the SEM images of PAni/MnO_2 composites obtained using different aniline:MnO_2 ratio (1:4, 1:6, 1:8, and 1:10) are presented. The oxide is covered by PAni layers, with a structure layer by layer. With the increase of the aniline:MnO_2 ratio, the oxide particles begins to be covered by a thin layer of PAni. Moreover, the MnO_2 particles are not completed covered and it is possible to observe failures in PAni film, which is hard to distinguish between parts of the particle surface are not covered or the presence of a thin PAni layer. Better coatings were obtained by syntheses using 1:4 and 1:6 ratio (aniline:MnO_2). So, by the visual analysis of the micrographs of covered particles 1:4 ratio was selected by the criteria of thickness and recovering capability of the PAni film.



(a) (b)

Figure 5. SEM images of (a) commercial MnO_2 and (b) PAni obtained with $(NH_4)_2S_2O_8$.

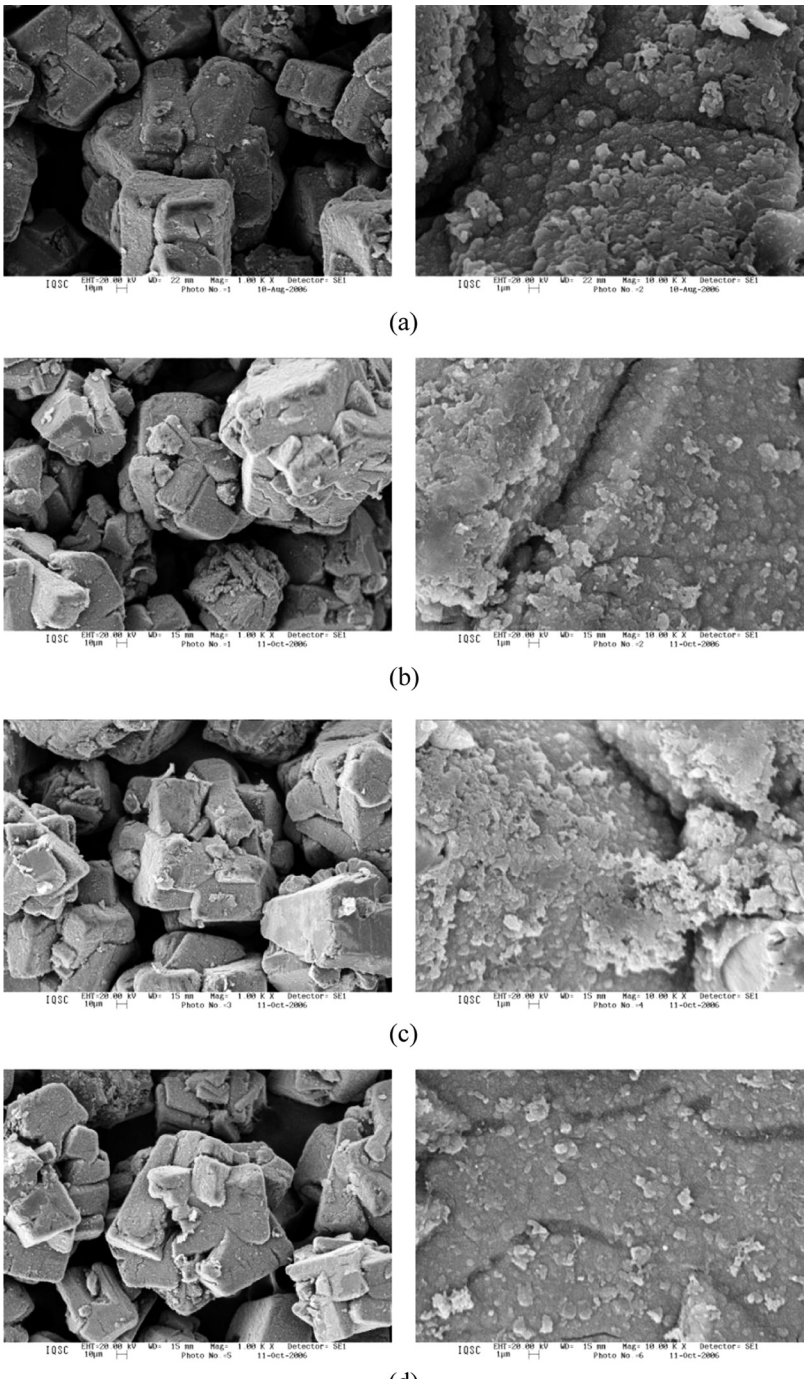
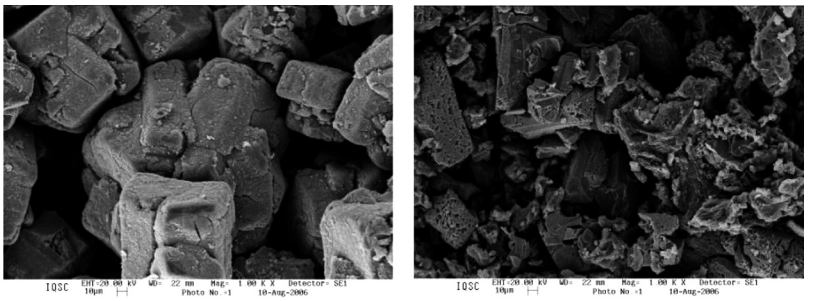


Figure 6. SEM images of PAni/MnO_2 composites obtained using different aniline:MnO_2 ratio in: (a) 1:4, (b) 1:6, (c) 1:8, and (d) 1:10. Magnification: 1000 × (right) e 10.000 × (left).



(a) (b)

Figure 7. SEM images of PAni/MnO_2 (1:4) obtained at 0 (a) and 20°C (b).

For comparative morphology analysis of the composites obtained at different temperatures (0 and 20°C), the micrographs used are shown in Figure 7. When PAni/MnO_2 composites were prepared using the ratio of 1:4, at 20°C, the film of PAni formed on the oxide particles is extremely porous. At low temperatures, the polymerization rate is slower, favoring an uniform and homogeneous coating by layers of PAni on the surface of the MnO_2 particles.

The composites synthesized at 20°C can be used for lithium battery electrodes with higher insertion of lithium ions due to the film porosity. On the other hand, the composites prepared at 0°C, with the MnO_2 removal, present a core shell structure with PAni film more homogenous.

UV-vis-nir Analysis

The Uv-vis-nir analysis of PAni/MnO_2 composites dissolved in NMP (N-methyl-2-pyrrolidone) presents the characteristic bands of PAni in the emeraldine base oxidation state, in accordance with the literature [10,11]: band at 330 nm, attributed $\pi-\pi^*$ transitions of the aromatic rings, and other at 630 nm corresponding to charge transfer between quinoid and bezenoid rings. After the doping with 0.5 mL of HCl 5 mol L^{-1}, a band at around 440 nm, assigned to radical cations and a broad band around 830 nm, associated with the charge carried in the polymer chain are revealed.

Conclusions

PAni/MnO_2 composites were chemically prepared by using different aniline:MnO_2 ratio, therefore, the best aniline:MnO_2 ratio was determined as 1:4 based on the greater oxide coating of the particles by PAni. The possibility of removing the PAni film from the surface of the oxide particles becomes the MnO_2 a promising recyclable oxidizing agent, producing PAni with interesting properties as PAni nanostructure and "core shell" structures. The syntheses at 20°C produce porous PAni, which increases the efficiency of this material for application in lithium battery electrodes. On the other hand, when the syntheses are performed at 0°C, a highly homogenous film is obtained, which after the oxide removal can produce "core shell" like structures.

Acknowledgments

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