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In–situ Synthesis and characterization of composite of polyaniline with cobaltmonoethanolamine complex

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ABSTRACT

The present paper involves the synthesis of polyaniline (PANI) composite with cobaltmonoethanolamine $[Co(mea)_2(H_2O)_2Cl_2]$ complex via in situ oxidative polymerization by ammonium persulphate. The complex has been synthesized by refluxing method. The composite has been subjected to elemental analysis, FTIR, and SEM characterization techniques. FTIR absorption peaks confirm the insertion of complex in the backbone of PANI. SEM of the composite also supports its successful synthesis.

Introduction

Polymers are generally used in a wide range of applications often for their low cost, light weight and mechanical properties, or for the three characteristics combined. One of the main characteristics required for electrical and/or optical activities to occur in a polymer is a conjugated backbone which can be subject to oxidation or reduction by electron acceptors or donors. Among the conducting polymers, Polyaniline [PANI] and its derivatives have attracted much interest because of their higher environmental, thermal and chemical stability along with high conductivity [1]. Conducting polymers and its composites have found application as transducers of biosensor [2], electrodes of rechargeable batteries [3], artificial nerves and muscles [4], gas sensors [5], solid electrolytic capacitor, diodes, transistors [6], anti-static electromagnetic shielding [7], and biomedical applications [8]. The composites of PANI with various metal-oxides, inorganic, organic, nanoparticles have been synthesized and properties of PANI have improved significantly. Various composites of PANI with various fillers, binders and dopants have been synthesized, characterized and explored for many applications. For example, composites of PANI with dopants like MoO_3, Zro_2, TiO_2, WO_3, Mn_3O_4, MnO_2 have been synthesized, characterized, and have shown significant applications [9]. The composites of PANI with other oxides, inorganic and organic substances like iron oxides, MoS_2, MnO_2, graphite, and platinum have also been reported [10]. Therefore, literature shows that the chemical modification of PANI with suitable chemical species, induces varied dimensions in the composite material and desired characteristics can therefore be achieved by suitable chemical synthesis and modifications. Ethanolamines commonly known as aminoalcohols include mono-, di- and triethanolamines. Because of their basic nitrogen atom and the hydroxyl group, the chemical properties resemble those of both amines and alcohols. We here report the synthesis and characterization of PANI and its composite with cobaltmonoethanolamine complex.

Experimental

Aniline was obtained by Loba Chemicals and was used after distillation. HCl, ammonium peroxidisulphate, Cobalt Chloride, Monoethanolamine were also provided by Loba Chemicals. All other reagents used were of Analytical grade. UV–visible spectra were taken on Shimadzu UV-190 double-beam spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on Perkin Elmer RX-1 FTIR spectrophotometer. The spectra were taken in KBr disks. Surface morphology of the samples was studied on a Hitachi SEM Model S-3600N.

Synthesis of PANI

PANI was prepared by known methods of oxidation with ammonium persulphate $(NH_4)_2S_2O8$. To precooled solution of 10 ml distilled aniline dissolved in 150 ml of distilled water with 10 ml concentrated HCl, 4.5 g of $(NH_4)_2S_2O_8$ dissolved in 30 ml of water was added drop wise to the solution with constant stirring. The solutions were kept stirring for about 2 h and were left for more than 1 h. The precipitate resulting from this solution was filtered and washed repeatedly in Buckner funnel under vacuum with distilled water. The precipitate was collected and dried in an oven at about 40 ^{0}C.

Synthesis of $[Co(mea)(H_2O)_2Cl_2]$ complex

The cobalt monoethanolamine $[Co(mea)_2(H_2O)_2Cl_2]$ complex was prepared by mixing 50 ml of 1M solution of monoethanolamine to 50 ml of 1M cobalt chloride solution. A pale violet precipitate resulting from this reaction upon refluxing is filtered and repeatedly washed with distilled water.

Synthesis of PANI/$[Co(mea)(H_2O)_2Cl_2]$ composite

The polyaniline composite was synthesized by in situ polymerization procedure. A typical preparation process for the PANI composite is as follows:

10 ml distilled aniline and 10 ml HCl were added to 100 ml distilled water and the mixture was allowed to pre cool. A calculated amount of $[Co(mea)(H_2O)_2Cl_2]$ complex and ammonium persulphate was slowly added to the pre cooled mixture upon constant stirring for about 3 hours. The mixture was allowed to react for 24 hours. A dark green precipitate

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obtained from the above reaction was washed repeatedly in the filtering funnel with distilled water. The precipitate was then dried in an oven at 40 ^{0}C for 24 hours.

Results and Discussion

Elemental Analysis

The complex formed was analyzed for C, H and N and the empirical formula for the complex was found to be $[Co(mea)(H_2O)_2Cl_2]$. The observed percentages of C, H, and N are 10.67%, 4.90%, and 6.20%, respectively, against the calculated percentages C= 10.57%, H= 4.85%, and N= 6.16%.

FTIR characterization

The FT-IR spectra of (a) PANI, (b) $[Co(mea)(H_2O)_2Cl_2]$ complex and (c) PANI/$[Co(mea)(H_2O)_2Cl_2]$ composite are shown in Fig. 1. PANI shows a hump at 3305 cm^{-1} because of N–H stretching. The strong peak at 2922 cm^{-1} because of C–H stretching is observed. This absorption is also as a result of overtones or combination of some modes of benzene and quinoid units in PANI. A weak peak at 2852 cm^{-1} is observed because of C–H stretching. The absorption peaks observed in the region of 1600–1450 cm^{-1} are because of aromatic ring breathing, N–H deformation and C-N stretching. The peak at 1590 cm^{-1} is because of stretching of N=Q=N in PANI. A weak peak at 1377 cm^{-1} is also present in PANI. The peak at 1164 cm^{-1} in case of PANI can be because of a mode of N=Q=N. The peak at 830 cm^{-1} in PANI is because of C–H out of plane bending.

The complex formed is assigned molecular formula $[Co(mea)(H_2O)_2Cl_2]$ on the basis of elemental analysis. Further FTIR shows the presence of different moieties as well. In case of this complex, we expect the vibrational frequencies due to ethanolamine, alcohol, and amine group. Alcohol group involves O-H stretch which appears at 3349 cm^{-1} in alcohols. Moreover, we observe C-C-O symmetric stretch at about 817 cm^{-1} and O-H in plane and out of plane bending vibrations at 1309 cm^{-1} and 655 cm^{-1} respectively since there is water present as a ligand in the complex which is clearly supported by FTIR. Though the appearance of O-H stretch due to H_2O at about 3446 cm^{-1} is similar in alcohols but the presence of water is very clear from absorption peak at 1627 cm^{-1} due to scissoring of two O-H bonds. This vibration is unique to water only, therefore, the presence of this band along with the O-H stretch vibration at 3446 cm^{-1} is a very strong evidence of presence of water molecule as a ligand in the complex also. The peaks at 1502 cm^{-1}, 1116 cm^{-1}, 1064 cm^{-1}, 731 cm^{-1}, and 438 cm^{-1} are also observed in the complex which can be because of δ-CH_2, ρ-CH_2, ν-(C-N), ν-C-O, τ-CH_2, ν-(C-C) and ν-(M-N) respectively.

For successful synthesis of PANI composite with synthesized complex, we compare the FTIR of PANI (Fig.1a), $[Co(mea)(H_2O)_2Cl_2]$ complex (Fig.1b) and PANI composite (Fig.1c) PANI having a hump at 3305 cm^{-1} because of N–H stretching shows a significant shift of 149 cm^{-1} and appears at 3447 cm^{-1} in case of composite. The strong peak at 2922 cm^{-1} because of C–H stretching remains unchanged. The presence of complex as the dopant in the composite is evident from the observation that in case of complex we observe the absorption peak due to ν-(O-H) of alcoholic group. This ν-(O-H) is also because of presence of coordinated water, which is further confirmed by appearance of a peak at 1627cm^{-1}. This peak is also present in case of composite with a less intensity and slight shifting at 1697 cm^{-1}, therefore proves the presence of complex as a dopant in PANI composite. The presence of dopant in the composite is also evident from the appearance of finger print region absorption peaks like 721 cm^{-1}.

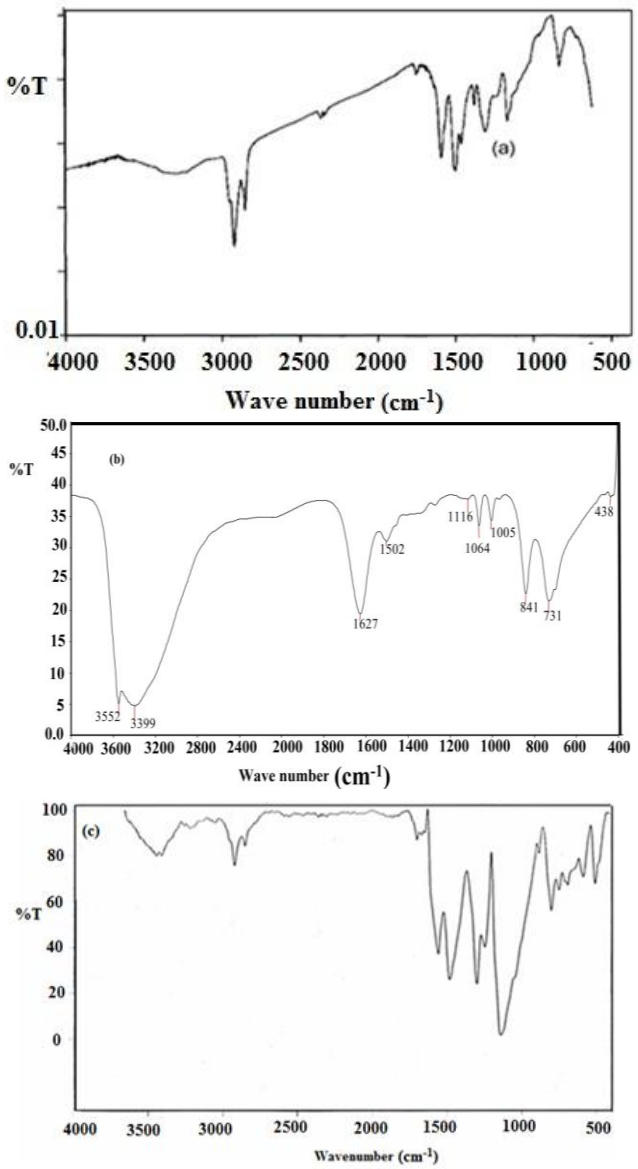
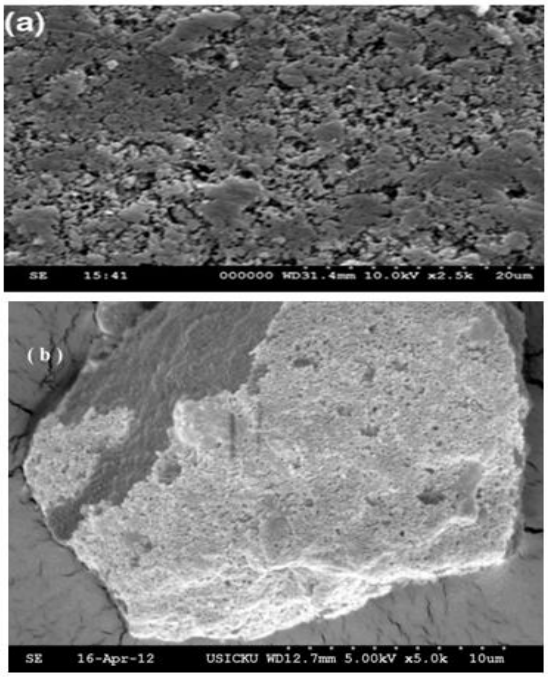


Fig.1. FTIR of (a) PANI, (b) $[Co(mea)(H_2O)_2Cl_2]$ complex, and (c) composite of $[Co(mea)(H_2O)_2Cl_2]$ complex with PANI



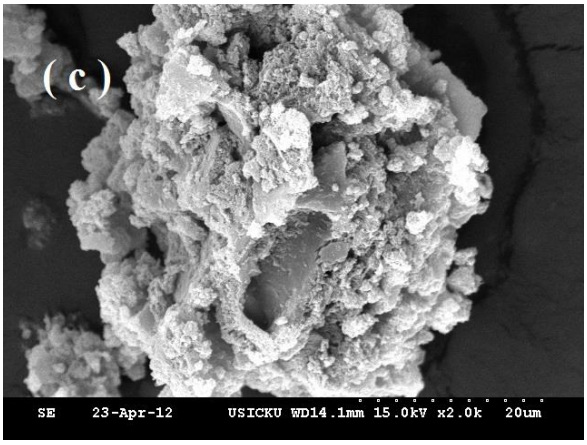


Fig.2. SEM micrographs of (a) pure PANI, (b) $[Co(mea)(H_2O)_2Cl_2]$ complex, and (c) composite of $[Co(mea)(H_2O)_2Cl_2]$ complex with PANI

Therefore, from the discussion of FTIR of pure PANI, $[Co(mea)(H_2O)_2Cl_2]$ complex, and the composite of PANI with synthesized complex, the successful synthesis of composite of PANI with this complex is proved.

SEM

Fig. 2 shows the SEM images of PANI (Fig. 2a), $[Co(mea)(H_2O)_2Cl_2]$ complex (Fig. 2b) and PANI/$[Co(mea)(H_2O)_2Cl_2]$ complex composite (Fig. 2c) respectively. Surface morphology of PANI sample shows amorphous structure. The SEM of $[Co(mea)(H_2O)_2Cl_2]$ complex is showing a very compact morphology, which has dominated the surface morphology of PANI/$[Co(mea)(H_2O)_2Cl_2]$ complex composite, clearly showing that the composite has been synthesized successfully. Further, SEM image of composite is showing improvement in compactness.

Conclusion

The preparation of PANI/$[Co(mea)_2(H_2O)_2Cl_2]$ composite was successfully performed by in situ polymerization method and incorporation of $[Co(mea)_2(H_2O)_2Cl_2]$ complex in the polyaniline matrix was confirmed by FTIR and SEM.

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