Potential -dependent band gap of Polypyrrole composite

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Introduction

Studies on electrical and optical properties of conducting polymers have attracted much attention in the view of their application in electronic and optical devise, in the last few years. During oxidation of polymer, some polaron and bipolaron states are formed which associated to the intermediary energy levels within the electronic band gap region. These new electronic levels decrease the energy required for the electronic transition between the valance band (VB) and conduction band (CB), leading to a red shift in the UV–vis spectrum [1]. Researchers used the optical absorption and particularly the absorption edge study to investigate the band structure and energy gap of crystalline and non-crystalline materials [2]. Since the potential plays an important role in electrochemical polymerization technique, we studied the effect of applied potential on the electrical and optical properties of polymers. In this research polypyrrole-chitosan (PPy-CHI) thin films were electrodeposited on the ITO glass at different potential at room temperature.

Materials and methods

All composite polymers were potentiostatically prepared in solution containing Pyrrole (provided by Acros and pre-distilled), *p*- toluene sulfonate as dopant (Fluka), and chitosan (88% degree of deacetylation) in acetic acid at room temperature in one minute. Electrochemical deposition of PPy–CHI was performed using a potentiostat (Model: PS 605, USA).

I-V characteristic technique was used to measure the conductivity of the PPy-CHI thin films. Current-voltage source (Keithley, model 236) was used to provide the necessary voltage and measuring the resulting currents. A Perkin-Elmer UV/Vis Lambda 20 spectrophotometer was used to obtain the optical absorption data. The optical band gap (E_g) in an amorphous semiconductor for a direct transition, is determined by Tauc equation.

$$[\alpha h\nu]^2 = K(h\nu - E_g)$$

Where α represents absorption coefficient, K is constant and *h*ν is energy of photon [1].

Results and Discussion

The band gaps of the films were determined by extrapolation of the plot of $(Ah\nu)^2$ vs $h\nu$ and the results are shown in Figure 1. Extrapolation of the line to the base line, where the value of $(Ah\nu)^2$ is zero, produced a band gap value of 2.05 eV for PPy film which was in good agreement with the results obtained by Santos *et al*. [3].

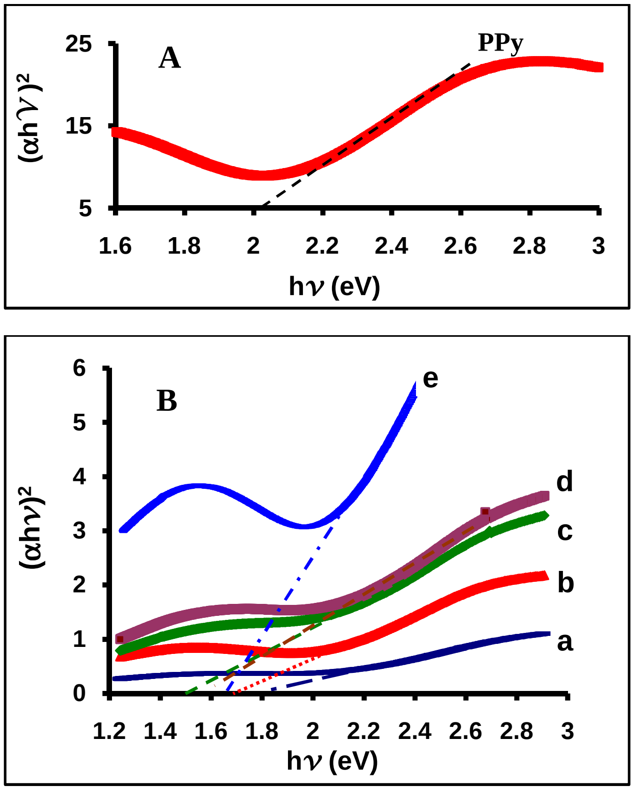

Figure 1. Determination of the band gap from the plot of $(\alpha h\upsilon)^2$ vs hυ for (A) PPy and (B) PPy-CHI composite films prepared at (a) 0.8V (b) 1V (c) 1.2V (d) 1.4V (e) 1.6V (vs SCE).

Electrical conductivity of the PPy-CHI thin films prepared in 1min was measured by I-V characteristic technique and the results are shown in Table 1.

Overoxidation of the polymer composite occurred at potential higher than 1.2 volt which led to less conductivity and rougher surface of polymer product. A decrease in conductivity at high anodic potential can be caused by the reaction of nucleophiles, like H_2O and/or OH^- with the polymer backbone (OH^- is the product of reduction of H_2O at the surface of auxiliary electrode). This reaction stabilizes charge carriers (polarons or bipolarons), interrupts the conjugated structure and lowers the conductivity of the polymer [4].

Table 1. Optical band gap (E_g) and conductivity of PPy-CHI composite films prepared at various applied voltages

Applied voltage (volt vs SEC)	Thickness (nm)	Conductivity (Scm^{-1}) $\times10^{-7}$	E_g (eV)
0.8	123	8.22	1.82
1.0	142	11.59	1.72
1.2	159	15.33	1.53
1.4	167	11.92	1.63
1.6	193	12.90	1.72

Conclusion

Overoxidation of the polymer composite occurred at potential higher than 1.2 volt which led to less conductivity and rougher surface of polymer product. The optical band gaps (E_g) of composite thin films were found between 1.53–1.82 eV as estimated from optical absorption data.

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