ISSN : 2393-8188 (print)
2393-8196 (online)
www.milliyasrcollege.org.journal.php

100 MEV O^{7+} SHI IRRADIATION INDUCED MODIFICATION IN NICKEL OXIDE/POLYANILINE NANOCOMPOSITES: A SPECTROSCOPIC STUDY

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ABSTRACT:

A metal oxide based polymer composite materials consisting of nickel oxide nanoparticles dispersed in a polyaniline (PANI) were synthesised by an in-situ polymerization method using potassium peroxysulfate $K_2S_2O_8$ as an oxidant in acidic medium at room temperature. The composites in the form of thin film over a glass slide were prepared by drop casting method. Nickel oxide/Polyaniline (NiO/PANI NCs thin films) have been then irradiated with 100 MeV O^{7+} ions at different fluences (1x 10^{10}- 1x10^{12} ions/cm^2) using 15 UD pelletron under ultra high vacuum. The prestine and irradiated samples were investigated by FTIR in order to study the modifications in structural properties. IR spectroscopy indicates that transmittance intensity decreases in the range 1200- 4000 cm^{-1} with increasing fluence which reveals a benzenoid to quinoid transition in PANI chain upon SHI irradiation. Creation of some new absorption peaks in the range 600-1200 cm^{-1} suggests formation of new functional groups due to irradition in the polymer composites.

KEYWORDS: Metal oxide polymer nanocomposites; SHI irradiation; FTIR.

1. INTRODUCTION

Metal oxide polymer nanocomposites have attracted increasing interest owing to their unique properties and numerous potential applications in optoelectronics, gas sensors etc. Polymer nanocomposites based on conducting polymer and metallic/metal oxide or semiconducting nanomaterial have become one of the most active research areas in materials science due to their improved magnetic, optical, electrochemical and catalytic properties [1,2] Amongst conducting polymers, polyaniline (PANI) is considered the most technologically important material for its ease of preparation, environmental stability and special doping mechanism. Composites of PANI and inorganic nanoparticles were prepared to obtain special combining properties which could be difficult to attain separately with the individual components [3,4].

Bulk NiO has a cubic (NaCl-type) structure with a lattice parameter of 0.4177 nm and is classified as a Mott–Hubbard insulator with very low conductivity of the order of 10 $^{-11}$ Ω^{-1} m $^{-1}$ at room temperature [5] However, the conductivity of NiO is drastically increased when prepared in the form of thin films or consolidated nanoparticles (2.5–17 nm) due to the holes generated by Ni vacancies in the lattice [6]. The electrical conduction is primarily ascribed to the hopping of holes associated with the Ni^{2+} vacancies. NiO nanoparticles are p-type semiconducting with band gap 3.51 eV. It is considered as promising electrode material for electrochemical capacitor [7,8] and gas sensor for NO_2, NH_3, and H_2 [9].

Swift heavy ion (SHI) irradiation has already been used as an efficient tool for enhancing the physico-chemical properties of conducting polymers and their composites such as conductivity, electrochemical stability, sensing properties etc.

[10,11]. The primary phenomena associated with the interaction of ion beam and polymers are cross-linking, chain scission and emission of atoms, molecules and molecular fragments [12].

In the past decade, there have been continuous attempts to combine conducting polymers with metal oxides to form hybrid nanostructured materials. A wide variety of synthesis methods for nanocomposites of PANI with NiO have been reported in the literature. NiO/PANI NC's were synthesised by EG (Ethylene Glycol) route. The incorporation of NiO into PANI has shown synergistic properties such as enhancement in thermal stability, electrical conductivity, electrochemical cyclability and magnetic properties [13]. Song *et al.* successfully synthesized NiO/PANI nanobelts and NiO/PANI rectangular tube powders via chemical polymerization [14]. Han *et al.* have reported the synthesis of PANI/NiO rectangular tubes through a self-assembly process in the presence of sodium dodecyl benzene sulfonate [15]. The crystalline PANI/NiO rectangular tubes showed good thermal stability and satisfactory conductivity. Xia *et al.* prepared highly porous NiO/PANI composite films on Indium-tin-oxide (ITO) glass by combining the chemical bath deposition and electro-polymerization methods successively [16]. The NiO/PANI thin film exhibited a noticeable electrochromism with reversible color changes from transparent yellow to purple. The porous NiO/PANI composite film also showed good reaction kinetics with fast switching speed, and the response time for oxidation and reduction was 90 and 110 ms, respectively. However, in most cases the preparation of polymer composites is done by the *in situ* polymerization technique. NiO/PANI nanocomposites were developed via liquid/liquid interfacial polymerization [17].

In the present investigation, we have prepared PANI/NiO nanocomposites by an in-situ polymerization followed by drop casting method. Addintionally, we irradiated these composites with 100 MeV oxygen ions with different fluences in order to study modification in their structural properties.

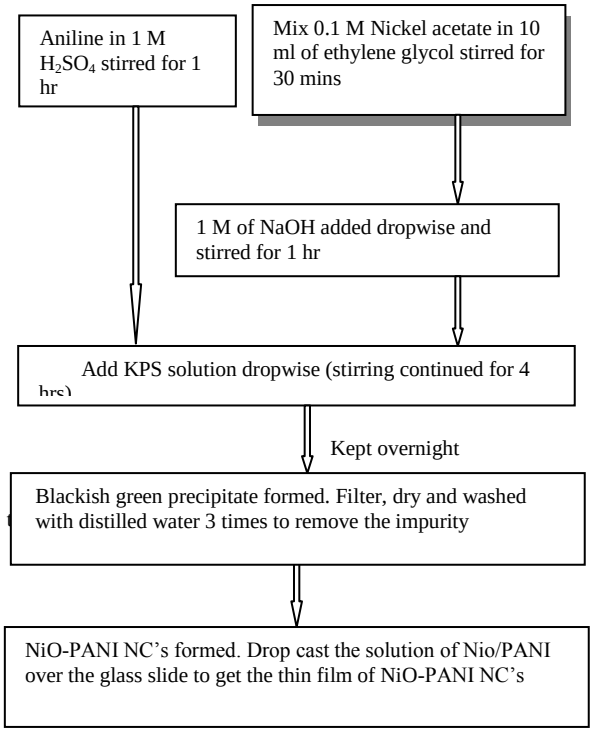
2. EXPERIMENTAL

Chemicals

Aniline (SpectroChem. Ltd., 99.5%) was vacuum distilled prior to use. All other chemicals like nickel acetate and ethylene glycol (Rankem), Hydrochloric acid, potassiun peroxydisulfate (KPS), sulphuric acid, N, N-dimethyl sulfoxide (DMSO) were bought from S. D. Fine-Chem. Ltd. and used as received without further purification. All chemicals were of analytical grade. Solutions were prepared in deionized water.

Synthesis of NiO/PANI Nanocomposites

Nanocomposite material of NiO/PANI have been synthesized by in situ chemical oxidative polymerisation. In 250 ml of conical flask, 0.1M of nickel acetate and ethylene glycol was stirred for half an hour. To this viscous solution, 1M of NaOH added drop wise. The broad ppt. of $Ni(OH)_2$ forms in the solution. The solution was stirred for 1 hour and then in another flask 10 ml of aniline was uniformly stirred with 1M H_2SO_4 and the synthesized $Ni(OH)_2$ was then poured to the aniline solution. Polymerization was carried out in ice-cold condition in presence of potassium peroxydisulfate and solution was kept overnight. The blackish green colour ppt. formed on addition of oxidizing agent. The solution was stirred 4 hours and then washed with distilled water 3 times to remove impurity and then the ppt. was filtered and dried. NiO-PANI NC's were formed. Thin films ($1x1cm^2$) of these composites were prepared by drop casting the solution of NiO/PANI over the glass slide. A schematic presentation of PANI/NiO nanocomposite preparation in the form of flow chart is described in **Scheme 1**



Scheme 1. Schematic presentation of PANI/NiO nanocomposite thin film

SHI Irradiation and Characterisation

Thin films of the metal oxide polymer were irradiated with 100 MeV O^{7+} ions with 0.5 pnA Current. The irradiation fluence was varied from $1x\ 10^{10}$- $1x10^{12}$ ions/cm^2 using the 15UD Pelletron accelerator at the Inter University Accelerator Centre (IUAC), New Delhi. Vacuum inside the

irradiation chamber was maintained with the help of a rotary and turbomolecular pump at ~10^{-6} torr during irradiation. The sample was irradiated at normal beam incidence.

Fourier Transform Infra Red (FTIR) spectra were recorded on Alpha T Bruker Spectrophotometer in the wavelength range of 600–4500cm^{-1}.

3. RESULTS AND DISCUSSION

FTIR spectra of NiO/PANI (a) prestine, and irradiated with fluences (b) 1x 10^{10} (c) 1x10^{11} and (d) 1x10^{12} ions/cm^2 composite are shown in Fig. 1.

In figure 1(a), The characteristic peaks of NiO/PANi nanocomposite occur at 3696, 3598, 2335, 1648, 1356 and 624 cm^{-1}. The strong transmittance peaks at 3696 and 2335 cm^{-1} are assigned to the N-H stretching vibration of amino group of Polyaniline. The peaks at 1648 cm^{-1} are attributed to the characteristic C=C stretching of the Quinoid rings of polyaniline; the peaks at 1474, 1356 cm^{-1} correspond to asymmetric C–N stretching modes of the benzenoid ring. However, the characteristic peaks of NiO can be observed at higher wavenumbers 624 cm^{-1} indicating that there is an interaction between NiO nanoparticles and PANi chain.

In fig.1 (b) i.e. at fluence 1x10^{10} ions/cm^2, transmittance intensity decreases slightly without changing their peak positions. In fig (c) transmittance intensity decreases significantly in the range 600-1400 cm^{-1} and some new peaks (1207, 1060, 964, 927, 785 and 705 cm^{-1}) arise in this region which may be due to the crosslinking among polymeric chain inside the nanocomposites. New functional groups are creating due to irradiation at the fluence 1x 10^{11} ions/cm^2. In fig.1 (d) it was observed that transmittance intensity increases in the range 600- 1200 cm-1 while decreases slightly in the range 1200-4000 cm^{-1} with increasing fluence (1x10^{12} ions/cm^2) which suggests that benzenoid to quinoid transition in PANI chain upon SHI irradiation.

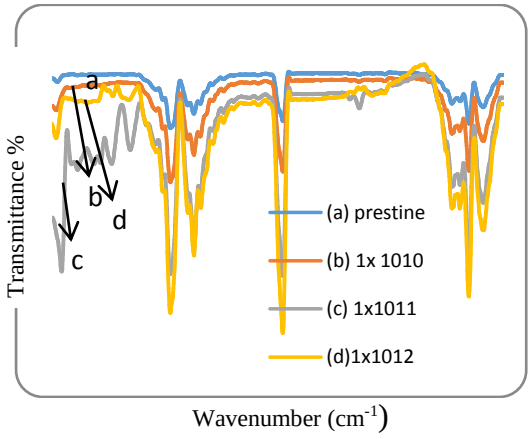


Figure 1. *FTIR spectra of NiO/PANI (a) prestine, and irradiated with fluences (b) 1x 10^{10} (c) 1x10^{11} and (d) 1x10^{12} ions/cm^2*

4. CONCLUSIONS

NiO/PANI nanocomposites have been successfully prepared by in situ polymerization and thin films were obtained by drop casting method. NiO/PANI NCs thin films have been irradiated with 100 MeV O^{7+} ions at different fluences (1x 10^{10}- 1x10^{12} ions/cm^2). FTIR results show the presence of NiO and PANI in the composite material and their interactions exist between PANI and NiO nanoparticles. IR spectra indicates that transmittance intensity decreases in the range 1200-4000 cm^{-1} with increasing fluence which reveals a benzenoid to quinoid transition in PANI chain upon SHI irradiation. At higher fluences, creation of some new absorption peaks in the range 600-1200 cm^{-1} suggests formation of new functional groups due to the crsslinking among polymeric chain in the nano composites.

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