

ABSORBANCE OF NICKEL NANOPARTICLES / POLYANILINE COMPOSITE FILMS PREPARED BY RADIATION TECHNIQUE

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ABSTRACT

Composites of conducting polymer – metal nanoparticles are of great interest in modern physical and chemical researchers due to their unique physical and chemical properties, which are distinct from those of the bulk metal and molecules. Conducting polymer – metal nanoparticles can be used in diverse fields such as electronics, electrocatalytics and optoelectronics. Conducting polyaniline and nickel nanoparticles blended in polyvinyl Alcohol (PVA) was synthesized by irradiating films containing aniline and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ salt at different concentrations with gamma radiation technique. In the same time the polyaniline and nickel nanoparticles were formed due to oxidation of aniline and reduction of nickel ion respectively by radiation. The structure analysis of polyaniline – nickel nanoparticles films were studied by X-Ray diffraction system which appears different diffraction peak angles at ($2\theta = 31.7, 45.5, 56.6$) respectively. The optical properties were investigated using UV –Vis spectrophotometer that show optical absorbance peak at $\lambda = (725, 395)$ nm of polyaniline and nickel nanoparticles respectively. From the UV-spectrum the band gap energy (E_g) was deduced and found to be decreases from (1.54, 2.88) eV at 10 kGy to (1.35, 2.62) eV at 50 kGy for polyaniline and nickel nanoparticles respectively.

INTRODUCTION

In the 1960s, conducting polymers and conjugated polymers were synthesized and characterized. Natta et al. reported the preparation of a dark powder of polyacetylene that was insoluble in organic solvents. After that the discovery of the metallic conductivity and superconductivity of poly(sulfurnitride) was an important step in developing the research on these materials. Conducting polymers are commonly known as a (synthetic metals) because they possess the electric, electronic, magnetic and optical properties of a metal or a semiconductor, while retaining the processing advantages and mechanical properties of conventional polymers. Since the discovery of electrically conducting polymer by MacDiarmid, Heeger and Shirakawa in 1976, intensive investigations have been carried out on the new generation of “synthetic metals” due to their unique combination of electronic and optical properties and processing advantages [1,3]. They have relatively high conductivity, light in weight, flexible, air-stable, and can be used as a support for metal-polymer transitions.

In the another hand Faraday carried out groundbreaking work wherein it was

established that the intense red color of stained glass indeed derives from small particles of gold in 1857. He described a relatively simple way to make colloidal gold nanoparticles suspended in water that are quite stable over time. Faraday realized that these colloids are stabilized by the adsorption of ions onto the nanoparticle surfaces during growth and noted that they must be stabilized against aggregation. In the early 20th century, the optical properties of nanoparticles were addressed by both Mie and Maxwell-Garnett theories for the first time and the field remained relatively quiet for some time due to lack of instrumentation with sufficient resolution to observe and study nanoparticles [4]. In 1953, Turkevich and co-workers synthesized gold nanoparticles in a similar manner to Faraday and observed them with electron microscopy, which proved the existence of nanoparticles gold. Through the late 1970's until the early 1990's, work proceeded involving the synthesis of nanoparticles contained within micelles or surfactants which were studied utilizing Mie theory, and significant agreement between experiment and theory was observed and the size and shape control with reverse micelle water content allowed for further investigation into size-dependent optical properties[3,5,8].

Both of conducting polymers and metal nanoparticles are considered relatively new materials and at present are extensively investigated. Recently, nanostructuring of conducting polymers and metal nanoparticles and their composites emerge as new fields of research and development in nanotechnology.

Several methods have been developed to prepare the electroactive polymer – metal composite nanospheres. These include the use of templates for arranging the metal nanoparticles and electroactive polymers into well defined structure, spontaneous reduction of metal salt by the electroactive polymers, or incorporation of the metal clusters during electrosynthesis of the polymer [4,8,9]. In this work, we want to report the structure and optical properties of polyaniline-nickel nanoparticles as thin films synthesized using gamma rays.

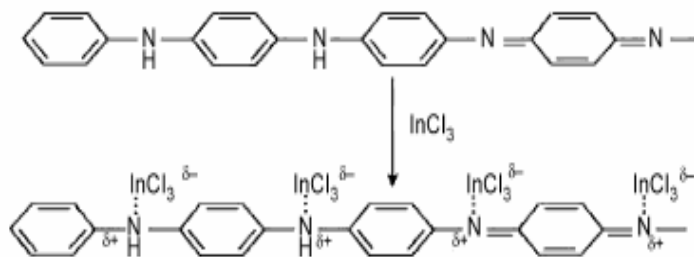


Figure 1: Doping of polyaniline with metal as InCl_3 [6].

EXPERIMENTAL

Preparation of the polyaniline - metal nanoparticles in PVA matrix.

Polyvinyl alcohol (PVA) 99 – 100 % hydrolyzed supplied by Sigma Aldrich Mw = 85000 g/mol, Aniline monomer supplied by Fulka (Mw = 93.13 g/mol) and Nickel chloride – 6 – hydrate pure supplied by Hamburg Chemical GmbH ($\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, Mw = 237.7 g / mol) were used. The PVA bulk solution was first prepared by dissolving PVA powder in distilled water under controlled temperature of 90 °C and continuous stirring for 2 h then left to cool at room temperature. Nickel chloride solution was prepared by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solid in distilled water. Nickel chloride and aniline formed 0.4M in solution form was added into the PVA solution at room temperature and stirred continuously 3 h using a magnetic stirrer. The blend solution was allowed to dry from casting glass and under ambient temperature and free standing casting film formed after several days and the blend film was peeled off and cut into several pieces. The average thickness of the blend film was (1.95 ± 0.4) mm.

Irradiation for polyaniline-nickel nanoparticles

Thin films of aniline – $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ / PVA composite were irradiated with gamma rays from ^{60}Co radiation facility (Excel 220 model) of dose rate 4.11kGy/h. The irradiation was performed at room temperature and the doses were delivered up to 50 kGy in a step of 10 kGy.

Characterization

The structure analysis of polyaniline – nickel nanoparticles films were studied by X-Ray diffraction system model 7602EA Philips. The optical characteristics of the composite were studied by a UV-VIS spectrophotometer (SHIMADZU 1650 PC) for the absorption spectra measured in the wavelength range from 200 to 1000 nm. The optical properties of polyaniline-nickel nanoparticles/PVA composites are strongly dependent on the amount of conducting polyaniline formed in the films and all measurements were performed at room temperature.

RESULTS AND DISCUSSION

X-Ray diffraction characteristics

X-Ray diffraction (XRD) can be used to determine the degree of crystallinity of compound as well as the unit cell shape and lattice parameters and possibly Debye-Scherrer's equation can be used to estimate particle size depending on the full width at half maximum of diffraction peaks [7] as the particle size increases, the broadening increases.

Polyaniline – nickel nanoparticles films figure 2 has different diffraction peak angles at ($2\theta = 31.7, 45.5, 56.6$) respectively corresponding to polyaniline – nickel nanoparticles crystallinity, this peaks being influenced by the radiation in a sequence reduction of the crystalline counts from amorphous phase at dose 0 kGy.

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where k is a constant (often taken as 1), λ represents the X-ray wavelength, β and θ are the full width at half maximum (in radians) and the Bragg angle, respectively.

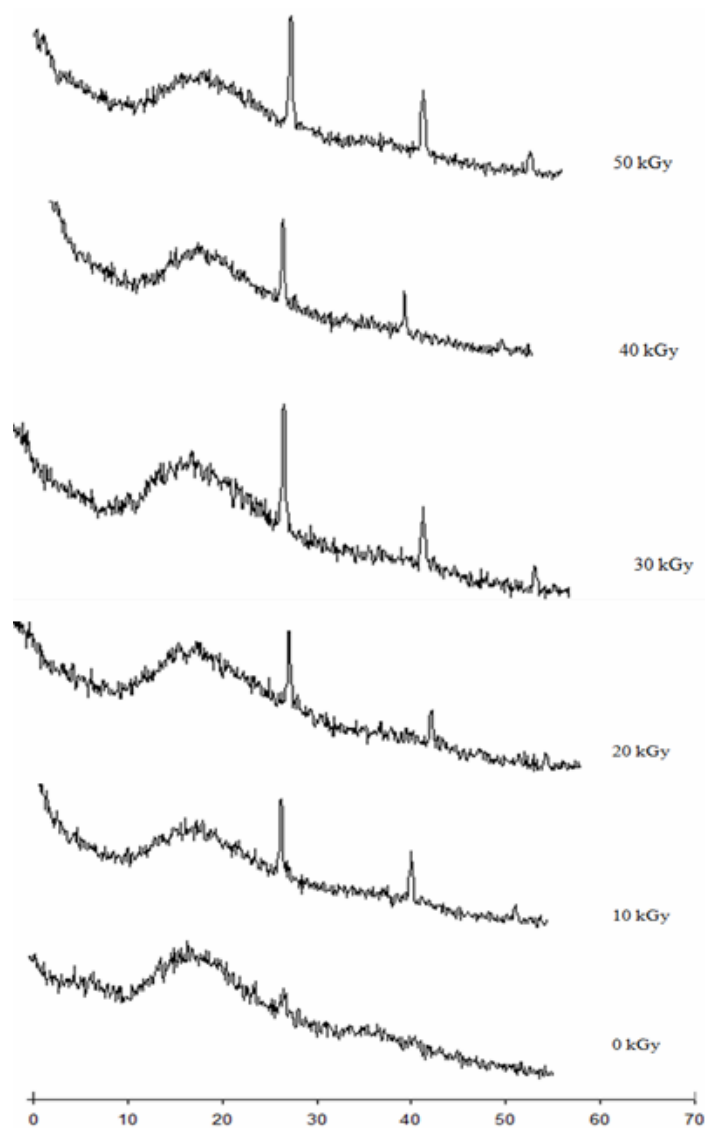


Figure 2: The variation XRD at different dose for metal nanoparticles.

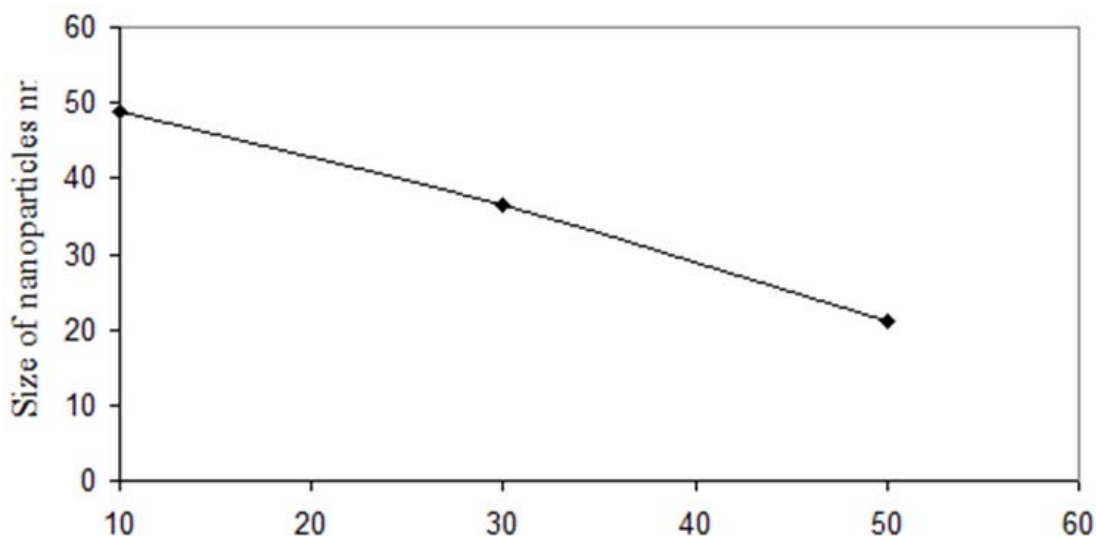
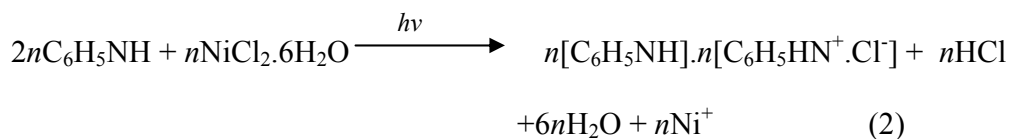


Figure 3: The variation of size of particles (nm) at different for nickel nanoparticles by use Debye-Scherrer's equation.

Optical characteristics

It is very interesting to understand the mechanism of radiation doping in the formation of polyaniline from irradiated aniline with metal chloride. Gamma rays imparted energy in the medium mainly through various processes such as ionization and excitation of atoms. In our case after irradiation, aniline C_6H_5N with nickel chloride hydrate $NiCl_2 \cdot 6H_2O$ as thin films by oxidizing agent to polymerize aniline molecules for the formation conducting polymer of polyaniline and by reduction agents for the formation nanoparticles for nickel. The possible reaction for the formation of polyaniline from aniline and nickel chloride hydrate by radiation doping may be written as follow [9]:



The UV-Vis absorption spectra in Figure 4 show two absorption bands peaking at 395 nm and 725 nm for nickel and polyaniline respectively. The absorbance of both bands increased with increasing the dose. The optical absorption at 725 nm is associated with the electronic transitions from highly occupied molecular orbital (HOMO) π -band to lowly unoccupied molecular orbital (LUMO) π^* -band of electronic states and the absorbance at 395 nm band is due to the electronic transitions from highly occupied

electron orbital which called the valance band (VB) to unoccupied electron orbital which named the conduction band (CB).

The formation nickel nanoparticles by radiation reduction process shows the absorbance increases with the increase of dose, suggesting more nanoparticles formed at higher doses as shown by the increase of plasmon resonance. The chlorine ions removed from nickel salt act as oxidant and in turn polymerized aniline monomer into conducting polymer polyaniline due to formation of polarons represented by C=N molecules. The absorption band at 725 nm is due to absorbance of polyaniline which increases with the increase of dose.

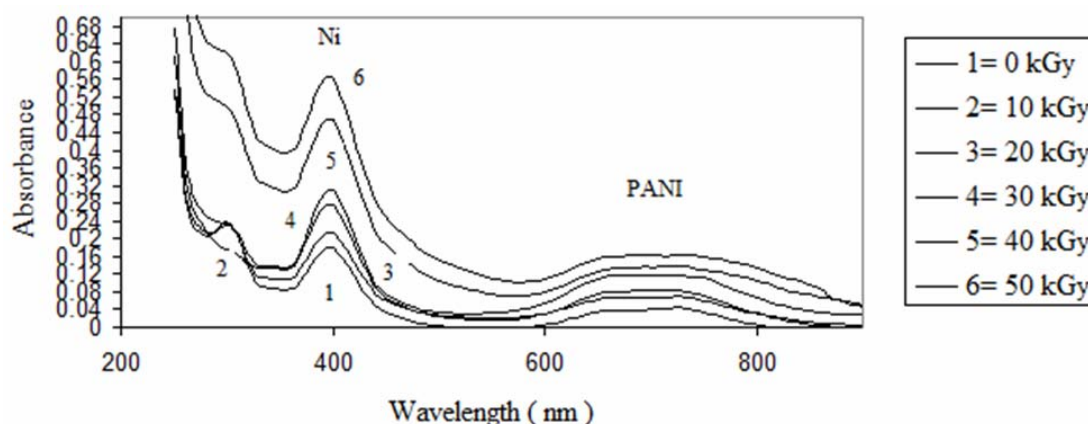


Figure 4: UV-visible absorption spectra of polyaniline - nickel nanoparticles of films irradiated at different doses up to 50 kGy.

The absorption coefficient $\alpha(\nu)$ of the optical absorption near the band edge shows an exponential dependence on photon energy $h\nu$ given by the formula :

$$\alpha(\nu) = \alpha_0 \exp \frac{h\nu}{\Delta E} \quad (4)$$

Where α_0 is a constant, ΔE is an energy that represents the width of the tail of localized states in the normally forbidden band gap associated with the amorphous nature of the materials, and ν is the angular frequency of the absorbed UV radiation equation 4 has been modified to a more general form by Davis and Mott [10,11]:

$$\alpha(\nu)h\nu = \beta(h\nu - E_g)^n \quad (5)$$

where β is a constant, E_g is the optical energy gap and n is an index determined by the nature of the electronic transitions during the absorption process, which is equal to 2 for many amorphous materials. The variation of $(\alpha h\nu)^{1/2}$ with $h\nu$, the values of E_g are

obtained according to equation 5 extrapolating the linear portions of the curves to $(\alpha hv)^{1/2} = 0$ to gives the ΔE_g values . We found the band gap energy was decreased from 1.54 to 1.35 eV and 2.88 to 2.62 eV for polyaniline and nickel nanoparticles respectively when the dose was increased from 10 to 50 kGy.

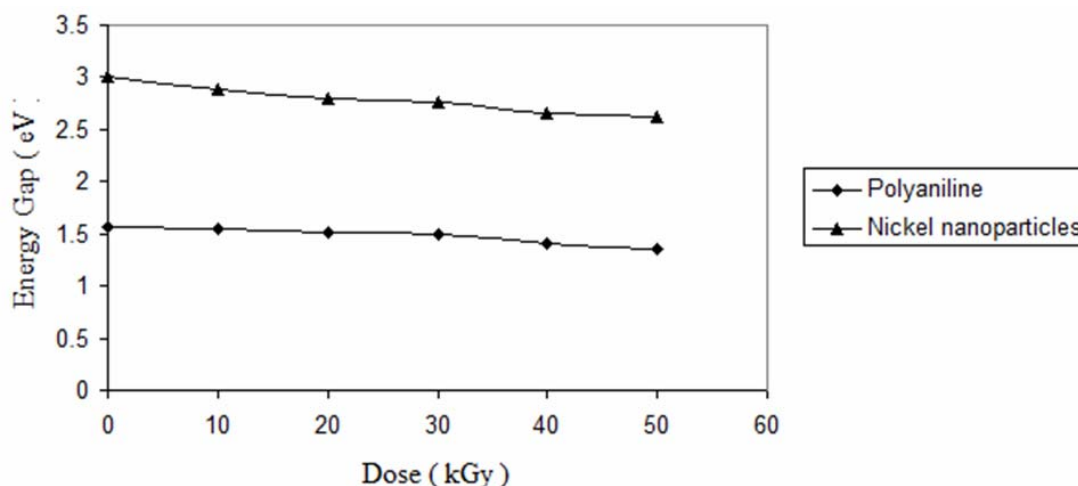


Figure 5: The variation of band gap energy vs. radiation dose for polyaniline and nickel nanoparticles.

CONCLUSION

Polyaniline - nickel nanoparticles / PVA has been synthesized directly from aniline – nickel chloride / PVA blend as thin films by radiation doping at different dose under ambient conditions. The polyaniline and nickel nanoparticles were formed due to oxidation of aniline and reduction of nickel ions respectively by radiation. The structure of polyaniline – nickel nanoparticles films was crystalline where x-ray diffraction appears different peaks angles. The formation of polyaniline and nickel nanoparticles has been detected at the absorption band of 725 nm, 395 nm respectively. We found the band gap energy of polyaniline and nickel nanoparticles was decreased when the dose was increased.

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