

Microstructure and optical properties of ultra thin film of gold nanocomposite polyaniline

P J Saikia^a, P C Sarmah^{b*} & A Rahman^c

^aDepartment of Electronics, J B College, Jorhat 785 001, India

^bElectronics Division, CSIR-North-East Institute of Science & Technology, Jorhat 785 006, India

^cDepartment of Physics, Gauhati University, Guwahati 781 014, India

Received 25 September 2013; revised 11 December 2015; accepted 21 January 2016

Conductive polymer, polyaniline and its nanocomposite have attracted much attention due to their potential applications. The incorporation of gold nanoparticles to ultra thin polyaniline film has been done and its effects on structural and optical properties have been discussed. The SEM and TEM spectra for polyaniline and gold nanocomposite polyaniline clearly show different states of surface morphology of two samples. FTIR and TEM spectra display the presence of gold nanoparticles in the nanocomposite polyaniline sample. The increase of conductivity and change of band gap in gold nanocomposite film have been observed. The band gap calculated for polyaniline and gold nanocomposite polyaniline films are 2.90 eV and 2.73 eV, respectively. Intense photoluminescence effect is observed in gold nanocomposite samples.

Keywords: Polyaniline, Gold nanocomposite, Band gap, Microstructure, Photoluminescence

1 Introduction

Conductive polymers, like polyaniline, polypyrrol, polythiophene, etc. are important candidates in modern electronic technology as they have several potential applications, such as optical, microelectronics, sensors, solar cells, etc.¹⁻⁵. Considerable research interests have been grown over the last few years on nanocomposite of these polymers materials. Inorganic materials and their oxides have been used to such polymers in forming inorganic polymer matrix. These are used in various devices for optical, gas sensing, solar photovoltaic, etc.⁶⁻⁸ Among these conductive polymers, polyaniline (PANI) is one of the important material and has been used in various forms. Due to its different important properties, like easy processing, cheap, antistatic, flexibilities, etc. these materials have been gaining popularity among the researchers⁹. The incorporation of metallic or semiconducting nanoparticles in polyaniline is of interest because of the strong electronic interaction between the nanoparticles and the polymer materials. This product not only changes the physical properties but also enhances electrical conductivity¹⁰. More recently, structural, electrical, optical properties of nano structural polyaniline and nanocomposite polyaniline have been under intense investigation. A

good number of literatures indicate the use of these materials in various device fabrications, like microelectronics, photonics, sensor applications, etc. This material is also studied for various optical applications both in linear and non linear regimes¹¹. In this paper, various properties of ultra thin gold nanocomposite films are presented and compared to the base material, polyaniline ultrathin film. In this process, surface morphology and optical properties of these materials are investigated.

2 Experimental Methods

2.1 Preparation of sample

The preparation of polyaniline and gold nanocomposite polyaniline ultra thin film were performed by electrochemical method using Autolab Potentiostat/Galvonostat (EcoChemie, Netherlands, Model 101N) with NOVA software in which working electrode was replaced with PANI/ITO and AuNPs/PANI/ITO. Platinum wire and Ag/AgCl (3 M KCl) were used as counter and reference electrodes, respectively. Prior to the electro-polymerization, the ITO glass plate (0.80 cm²) was thoroughly cleaned with methanol and then rinsed with de-ionized water. Polymerization was achieved in a potentiodynamic mode in 0.2 M aniline per 1 M HCl solution following methodology of Radhapyari *et al.*¹² The nanocomposites of AuNPs-PANI were prepared

*Corresponding authors (E-mail: pratap_sarmah@yahoo.com)

by electrochemical deposition of a mixture of HCl (1.0 M), aniline (0.2 M) and 500 μL AuNPs (2 mgmL^{-1} of KAuCl_4) and thoroughly sonicated for 15 min; introduced in a three-electrode electrochemical cell of Autolab Potentiostat/Galvonostat (EcoChemie, Netherlands, Model 101N). The cell consists of Ag/AgCl (3M KCl) as reference, Pt wire as counter electrode and ITO glass plate (0.80 cm^2) as working electrode. The electro-polymerization was demonstrated at a scan rate of 20 mVs^{-1} for seven (7) cycles in the potential range of -2.0 - 1.1 V. The AuNPs/PANI/ITO electrode is washed with de-ionized water to clean off the untreated AuNPs-PANI. Two set of films were prepared in the range of 110 - 130 nm thickness.

2.2 Studies on various parameters

The surface morphology of the samples was carried out by SEM (JEOL Asia PTE Ltd.) and TEM (JEM-2100) analysis. FTIR studies were conducted by FTIR spectrometer (Perkin Elmer System 2000). UV-Vis spectra were recorded by UV-Vis spectrometer (model Shimadzu UV-Vis Spectrometer) within the range of 330-2500 nm. Photoluminescence study was performed by a spectrofluorophotometer (Perkin Elmer, Singapore) in the wavelength range of 340-550 nm.

3 Results and Discussion

3.1 Structural morphology

Figures 1(a) and 1(b) represent the SEM spectra of the samples for the polyaniline and gold nanocomposite polyaniline, respectively. The polyaniline and its gold nanocomposite morphology of the films have been displayed by the observed SEM spectra. It has been seen that the gold nanoparticles are uniformly distributed in the gold polyaniline matrix. The particles are of almost spherical in nature and average size is about 7 nm and dispersed within the range of 2-20 nm.

TEM spectra of the polyaniline and gold nanocomposite polyaniline are shown in Figs 2(a) and 2(b), respectively. The TEM images of the samples and corresponding particle size histograms have been shown in Fig. 3. The average size distribution of the gold nanoparticles was found to be 5-7 nm. The micrographs of the sample indicate the spherical morphology of the particles and almost evenly dispersed in the media.

Figures 4(a) and 4(b) show FTIR spectra of polyaniline and gold nanocomposite polyaniline film, respectively. FTIR analysis of the finger print region

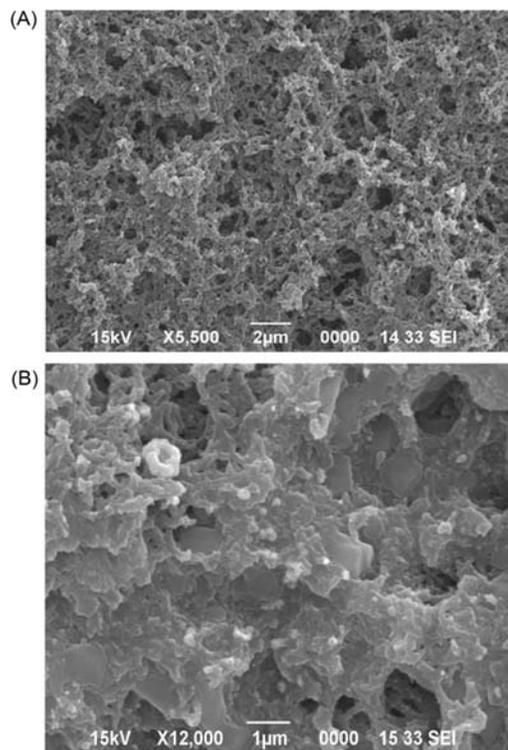


Fig. 1(a) – SEM spectra of polyaniline sample and (b) SEM spectra of gold nanocomposite polyaniline sample

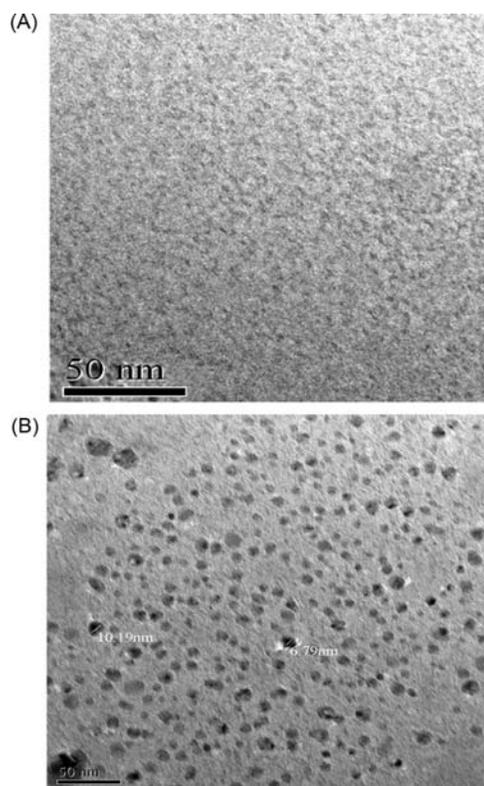


Fig. 2(a) – TEM image of polyaniline and (b) TEM image of gold nanocomposite polyaniline

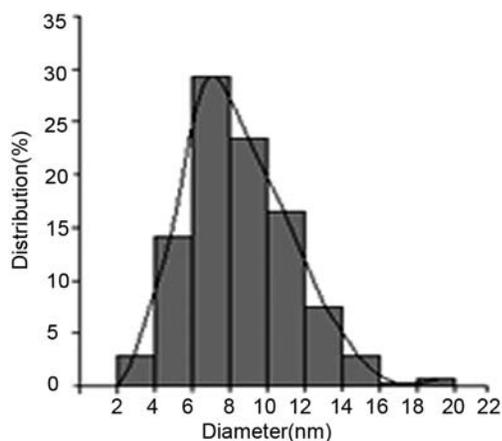


Fig. 3 – Particle size distribution for polyaniline in TEM image of gold polyaniline matrix

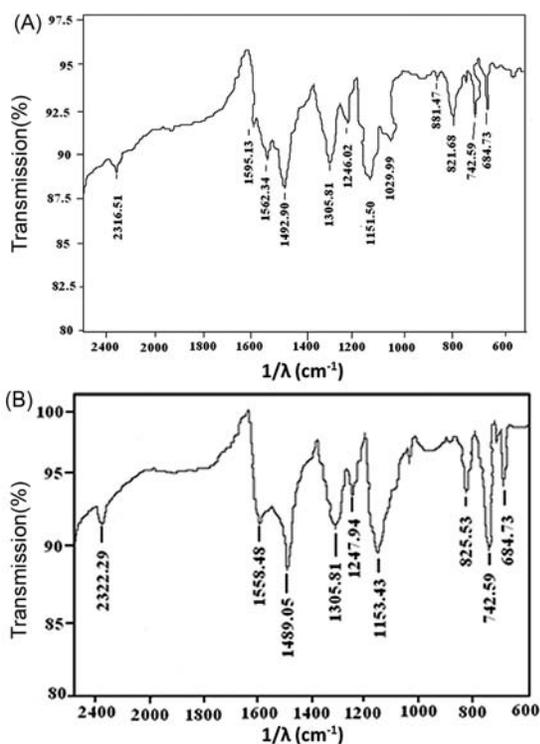


Fig. 4(a) – FTIR spectra of polyaniline sample and (b) FTIR spectra of gold nanocomposite polyaniline sample

between 600 and 2000 cm^{-1} is particularly useful for examining the resonance mode of the benzenoid and quinoid unit. From these spectra, it has been observed that all peaks corresponding to polyaniline are present in gold nanoparticle samples. However, there has been shifting of peaks in sample for gold nanocomposite polyaniline. It has been seen from the two figures that the shifting of about 5 cm^{-1} of peak has taken place in Fig. 4(b), which is due to the effect of incorporation of gold nanoparticles to polyaniline material. The peaks at about 1153 and 1305 cm^{-1} may be combination modes of benzenoid and quinoid unit and C-N stretching, respectively¹³. The shifting of peak may be attributed to the interaction of gold particles with amine and imine nitrogen site of benzenoid and quinonoid moieties¹⁴. Similar observations have been reported by earlier researcher in gold nanocomposite materials¹⁵.

The conductivity of gold nanocomposite films as measured by four probe method (not shown in figure) is found to be slightly higher than that of pure polyaniline film. The increase of conductivity of nanocomposite polyaniline (Table 1) may be attributed to charge transfer from polyaniline to gold nanoparticle through tunneling process¹⁶. This has been supported by the slight decrease of band gap as observed in optical study.

3.2 Optical properties

Figure 5 shows the UV-Vis spectra of the films for polyaniline and gold nanocomposite polyaniline. Two main peaks observed for these samples are at 587 nm (2.1 eV) and 295 nm (4.1 eV), respectively. The absorption peaks at 2.1 and 4.1 eV may be attributed to the transition from lower polaron to the upper polaron and to the conduction band, respectively¹⁷. The slight shifting of the peak observed in gold polyaniline matrix by an amount of 5 nm is due to the combine effect of bonding of polyaniline and gold nanoparticles. Thus, shifting of peaks towards the longer wave length may be due to the strong

Table 1 – Various parameters of polyaniline and gold nanocomposite polyaniline thin film sample

Sample	Thickness (nm)	UV-Vis absorption peak (nm)	Conductivity (S cm^{-1})	Band gap (eV)	Photoluminescence peak (nm)	Structure
Polyaniline	120	587, 295	$\sim (10^{-9}-10^{-10})$	2.90	380	Amorphous (for thin film); Polycrystalline (for thick film)
Gold nanocomposite polyaniline	120	592, 296	$\sim (10^{-8}-10^{-9})$	2.73	367	Polycrystalline

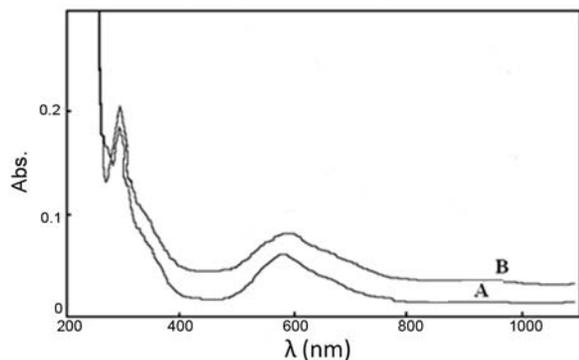


Fig. 5 – UV-Vis spectra of two types of samples (a) polyaniline and (b) gold nanocomposite polyaniline

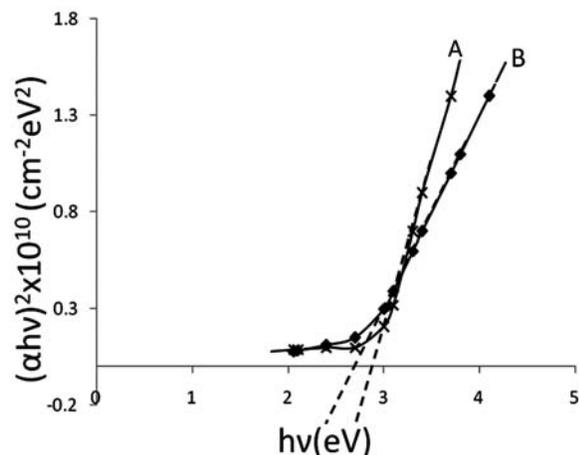


Fig. 6 – Plot of $h\nu$ versus $(ah\nu)^2$ for two types of samples (a) polyaniline and (b) gold nanocomposite polyaniline

interaction of polymer with gold particles and could be attributed to spill out of s-electrons or due to increase of effective mass of conduction electrons as was observed by earlier researchers in Ag nanoparticles¹⁸. The band gaps of the films were calculated by plotting $(ah\nu)^2$ versus $h\nu$ using the relation $\alpha = (h\nu - E_g)^n / h\nu$, where, n , is 2 for indirect band gap and $1/2$ for direct band gap.

The band gaps evaluated from the plot are 2.90 eV and 2.73 eV for polyaniline and gold nanocomposite polyaniline matrix, respectively as shown in Fig. 6. The slight decrease of band gap may be either reduction of disordered state or increase in density of defect states in polycrystalline polyaniline sample¹⁸. The various sample parameters for both types of films have been shown in Table 1

Photoluminescence of these samples were recorded to study the effect of illumination with an excitonic wavelength of 295 nm. Figure 7 shows the photoluminescence spectra for both types of samples.

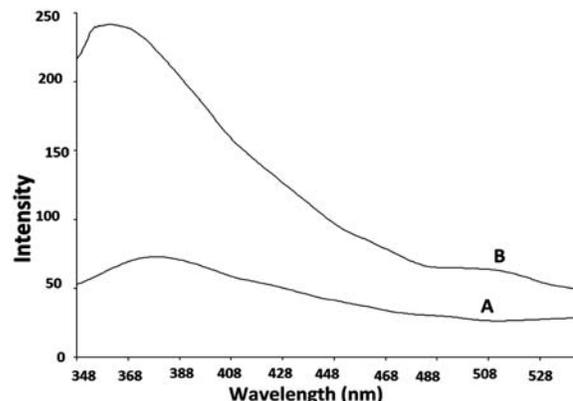


Fig. 7 – Photoluminescence spectra for two types of samples (a) polyaniline and (b) gold nanocomposite polyaniline

Both the spectra indicate a small peak around 380 nm. However, with increase of intensity and slight shifting of peak has been observed for nanocomposite polyaniline. The slight shifting of peak may be attributed to the presence of aggregation of gold nanoparticles in polymer chain, which might change band gap²⁰ as has been discussed in band gap measurement.

4 Conclusions

Ultrathin polyaniline and gold nanocomposite polyaniline samples were studied to evaluate various parameters required for device fabrication. It has been observed that the incorporation of gold nanoparticles greatly affect the physical and optical parameters of the samples. A considerable increase of conductivity and decrease of band gap have been observed due to incorporation of gold particles to polyaniline films. The gold nanocomposite film indicates higher photoluminescence effect than that of polyaniline film. These factors are essential for device fabrication of these materials in microelectronics and gas sensing applications⁸.

Acknowledgement

The authors wish to thank the Director, CSIR-NEIST, for providing necessary facilities to carry out this work.

References

- 1 Yakovlev Y O & Zolin V F, *Synth Met*, 91 (1997) 205.
- 2 Malachowski M J & Zmija J, *Opto-electro Rev*, 18 (2) (2010) 121.
- 3 Yu G, *Synth Mat*, 80 (1996) 143.
- 4 Bredas J L, Beljonne D, Cornil J & Santos D A D, *Int J Polym Mater*, 44 (1999) 341.
- 5 He H, Zhu J, Tao N J, Nagahara L A, Amlani I & Tsui R, *J Am Chem Soc*, 123 31 (2001) 7730.

- 6 Huang K, Yuanjian Z, Dongxue Han, Yanfei S, Zhijuan W, Junhua Y, Qixian Z & Li N, *Nanotechnology*, 17 (1) (2006) 283.
- 7 Beecroft L L & C K Ober, *Chem Mater*, 9 (6) (1997) 1302.
- 8 Saikia P J, Sarmah P C & Rahman A, *European Physical Journal, Appl Phys*, 60 (2012) 10202.
- 9 Dias H V Rasika, Rajapakse R M Gamini, Krishantha D M Milan, Fianchini Mauro, Wang Xiaoyu & Elsenbaumer Ronald L, *J Mater Chem*, 17 (2007) 1762.
- 10 Sarmah T K, Chowdhury D, Paul A & Chattopadhyay A, *Chem Commun*, (2002) 1048.
- 11 Anand P B, Hasna K, Anilkumar K M & Jayalakshmi S, *Polym Int*, 61 (2012) 1733.
- 12 Radhapyari K, Kotoky P & Khan R, *Mater Sci Eng C*, 33 (2013) 583.
- 13 Saikia P J, Sarmah P C & Rahman A, *Polym Sci Ser A*, 55 (2013) 48.
- 14 Sridevi V, Malathi S & Devi C S, *Chem Sci*, 26 (2011) 1.
- 15 Afzal A B, Akhtar M J, Nadeem M & Hassan M M, *J Phys Chem C*, 113 (2009) 17560.
- 16 Tseng R J, Baker C O, Shedd B, Huang J, Kaner R B, Ouyang J & Yang Y, *Appl Phys Lett*, 90 (2007) 053101.
- 17 Saikia P J & Sarmah P C, *Mater Sci Appl*, 2 (2011) 1022.
- 18 Choudhury A, *Sensor Actuat B-Chem*, 138 (2009) 318.
- 19 Safenaz M, Sheikhha M & Al-Ghannam, *Adv Mater Phys Chem*, 2 (2012) 75.
- 20 Ameen S, Ali V, Zulfiquar M, Haq M M & Hussain M, *J Appl Poly Sci*, 112 (2009) 2315.