

Enhancement of Optical Absorption by Incorporation of Plasmonic Nanoparticles in PANI Films

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Abstract Recently 1D nanostructured polyaniline (PANI) are the focus of intense research owing to their high mobility, good environmental and chemical stability. PANI has various applications in the areas like solar cell, sensor, electrocatalysis, supercapacitor, electrochemical capacitor, rechargeable batteries, electrochromic displays and anticorrosion coating. Metal nanoparticles (NPs) incorporated in solid materials have received enormous interest in recent years because of the possibility of tuning the optical, electrical and electrocatalytic properties. To increase the efficiency of organic-inorganic solar cell, plasmonics phenomenon can be used to trap the light inside the absorber material to increase the absorbance. Here we have studied the light trapping using gold nanoparticles embedded in the emeraldine salt form of PANI. Highly conducting PANI thin films with fibrous morphology have been successfully synthesized by electropolymerization. Gold nanoparticles of size ~ 10 -20 nm were used to form the PANI-Au nanocomposites by a simple chemical route. The dose of Au nanoparticles was increased systematically and studied the optical, structural, morphological and electrical properties. XRD pattern confirms the amorphous nature of PANI. The peaks corresponds to emeraldine salt form, π - π^* interband transition (317 nm), polaron band transition (371-427 nm) and bipolaron band transition (750 nm) were observed in the UV-Vis absorption spectra for pristine PANI thin films. The PANI has found to be changed from the emeraldine salt to emeraldine base in the presence of Au NP's. The peaks observed in photoluminescence spectra at 395 nm and 610 nm corresponds to π^* - π interband transition and excitonic transition, respectively were found to be increased due to presence of Au nanoparticles. FESEM images reveal the growth of long fibers of diameters ~ 100 nm decorated with gold nanoparticles having size 20-30 nm. This nanocomposite layer can be directly used as absorber layer in hybrid solar cells to form graded band-gap structure.

Keywords Polyaniline, Electrodeposition, PANI-Au nanocomposite, Absorption spectra and Plasmonic

1. Introduction

Conducting polymers are a special class of organic polymers having good conductivity due to presence of alternate single-double bond conjugation. Among them, Polyaniline (PANI) demonstrates outstanding properties due to its unique electrical, electrochemical properties, high mobility, good environmental and chemical stability [1]. PANI has variety of applications [2]. PANI is well known for its ease of synthesis and can be synthesized by either chemical oxidation or electrochemical polymerization [3, 4]. Electrochemical polymerization is preferable than chemical oxidation since a good quality polymer film is formed using electropolymerization.

PANI can be found in one of the three oxidation states: fully reduced state Leucoemeraldine, half oxidized state Emeraldine and fully oxidized state Pernigraniline. The most common green protonated emeraldine salt (ES) has highest

conductivity among all forms of PANI. These emeraldine salt can be converted into non-conducting blue emeraldine base (EB) when treated with base. The EB form of PANI can be again protonated (doped) to form emeraldine salt (ES) by an acid and EB form can be dedoped back by base. The doping process causes a conductivity variation from $\sim 10^{-10}$ to $10 \Omega^{-1}\text{cm}^{-1}$ [5].

ES form of PANI shows absorption in region of 300 nm to 400 nm and in near IR region. To increase the absorption of in visible region, Au were incorporated in PANI since gold shows strong surface plasmon resonance in visible region. Incorporation of metal nanoparticles into PANI has been proposed as a way of increasing its electrochemical and electrocatalytic activities. PANI-Au nanocomposites are considered to be particularly unique materials because Au NPs have attractive electrical and optical properties. In organic/hybrid solar cell these NPs can be used to increase the efficiency of solar cell by trapping more light inside the absorber layer.

Here, PANI thin films were prepared by using electropolymerization. The doses of Au NPs were varied systematically in PANI films and characterized with a range of characterization techniques to study various properties.

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Published online at <http://journal.sapub.org/nn>

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2. Experimental Section

Analytical reagent grade aniline ($C_6H_5NH_2$) and perchloric acid ($HClO_4$) was used for the electropolymerization of PANI. Chloroauric acid ($HAuCl_4$), sodium borohydride ($Na_2B_4O_7$) and hexadecyl-trimethyl-ammonium bromide (CTAB) were used for the synthesis of gold nanoparticles. The synthesis procedure for PANI thin films [6] and Au NPs [4] are reported elsewhere.

The pristine PANI thin films were functionalized with different doses of Au NPs. The green color of PANI films were then changed to blue color, indicating the formation of EB form of PANI. These samples were dried under argon flow and used for further characterization.

Electropolymerization of PANI was carried out by potentiostat/galvanostat AUTOLAB, $\mu 3AUT$ 70762. X-ray diffraction (XRD) measurements were performed using a Bruker D8 advance diffractometer. Optical absorption measurements were carried by JASCO UV-vis spectrophotometer. Photoluminescence spectra's (PL) were recorded using JASCO-photometer. The surface morphology was studied by using HITACHI, S 4800 field emission scanning electron microscope (FESEM). Raman spectra's were obtained with Invia Renishaw Raman Microscope coupled with Philips CCD camera with 785 nm excitation laser.

3. Results and Discussion

3.1. Electropolymerization of PANI

PANI films were electropolymerized using cyclic voltammetry technique. Figure 1 (a) shows X-ray diffraction pattern of PANI thin film. Intense bands observed at $2\theta \sim 15.40^\circ$, 24.20° and $\sim 25.00^\circ$ confirm the synthesis of emeraldine salt of PANI [7]. Presence of prominent peaks suggests the formation of highly crystalline PANI thin films.

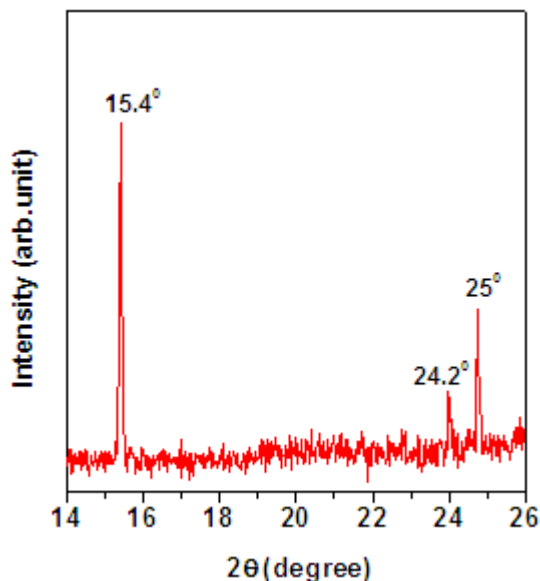


Figure 1a. XRD pattern for PANI thin film

Raman spectra of PANI recorded using 785 nm excitation are shown in figure 1 (b). The bands appeared in the wavenumber range of $1100-1700\text{ cm}^{-1}$ corresponds to the stretching modes of different bonds. The band from $1000-400\text{ cm}^{-1}$ gives information about deformation vibrations of the benzene rings. The band at 874 cm^{-1} , 812 cm^{-1} and 424 cm^{-1} are in plane and out of plane vibrations of ring of protonated emeraldine form of PANI [8].

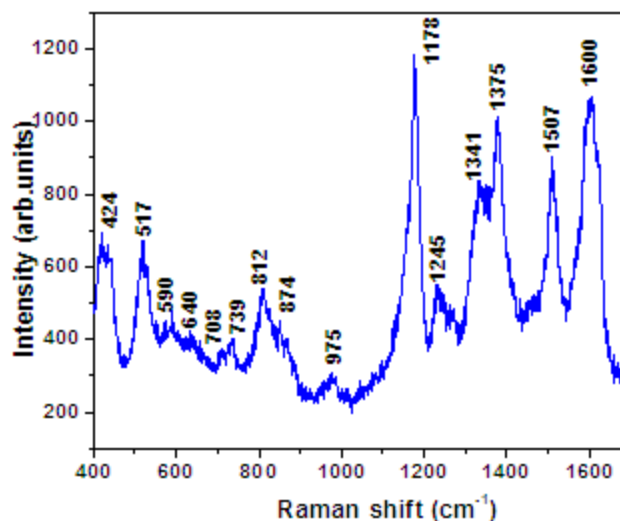


Figure 1b. Raman spectra for PANI thin film

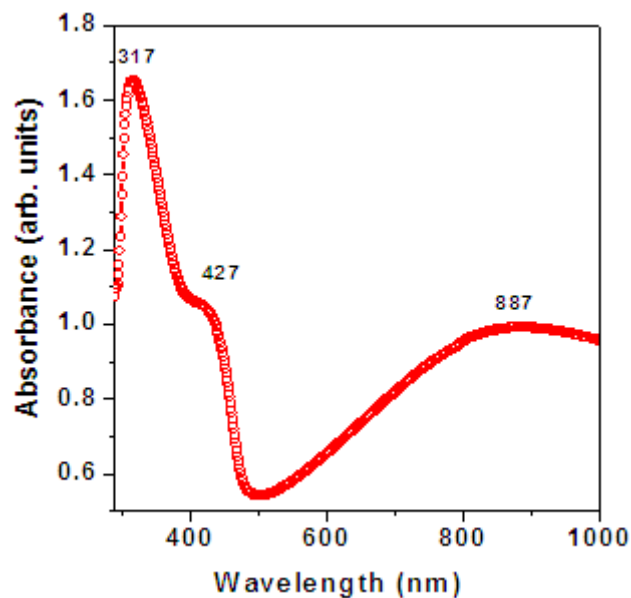


Figure 2a. Optical absorption spectra for PANI thin film

Optical absorption spectra of PANI films obtained during the electropolymerization is as shown in figure 2 (a). Three strong absorption peaks attributed at 317 nm, 427 nm and 887 nm are corresponds to the $\pi-\pi^*$ electronic transition, polaron and bipolaron band transition of PANI, respectively. Presence of these three peaks confirm the formation of PANI in emeraldine salt form [9].

Figure 2 (b) depicts the photoluminescence spectra for PANI thin film. Peaks at 397 nm, 463 nm and 722 nm are

originated due to π^* - π transition of the benzoid units, de-excitation from polaron band and bipolaron de-excitation, respectively.

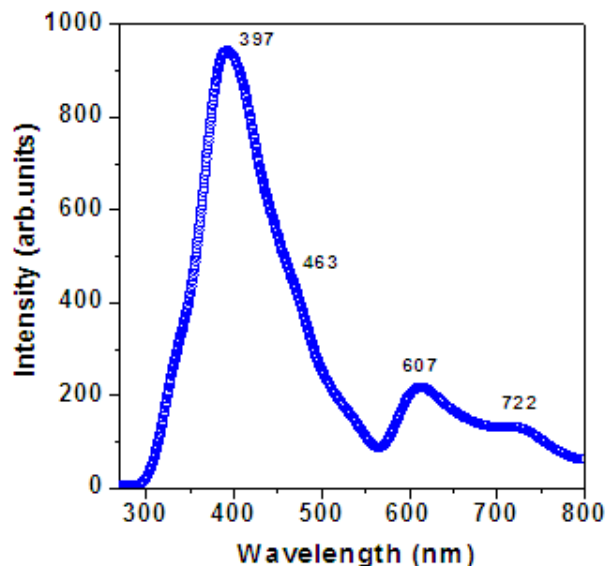


Figure 2b. Photoluminescence spectra for PANI thin film

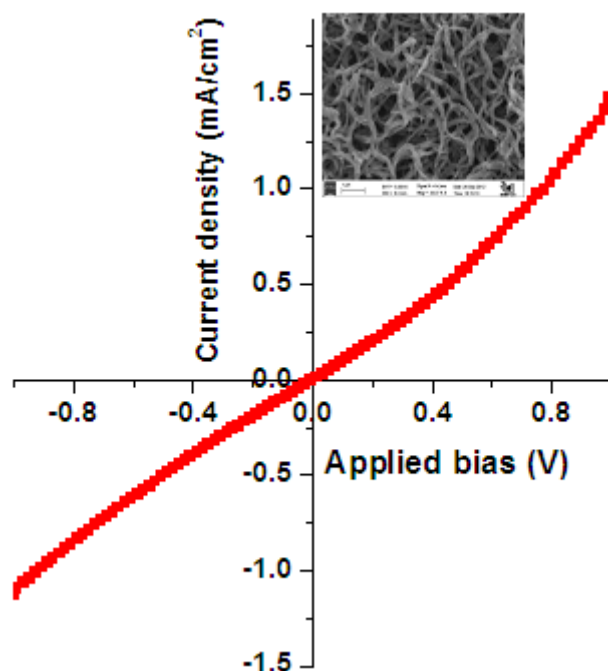


Figure 3. J-V curve for PANI thin films. Inset shows SEM micrograph of PANI thin film

Current density- Voltage (J-V) curve for electrodeposited PANI film is depicted in figure 3, which shows ohmic behavior. Value of electrical conductivity was calculated for PANI film is $1.89 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$. Inset shows the SEM micrograph of electropolymerized PANI film. Uniform, compact and fibrous morphology of PANI with fiber having length of few micron and diameter ~ 50 nm are observed.

3.2. Growth of Au NPs

Au NPs were synthesized using a simple colloidal route.

These nanoparticles were dispersed in aqueous solution and used for further characterization.

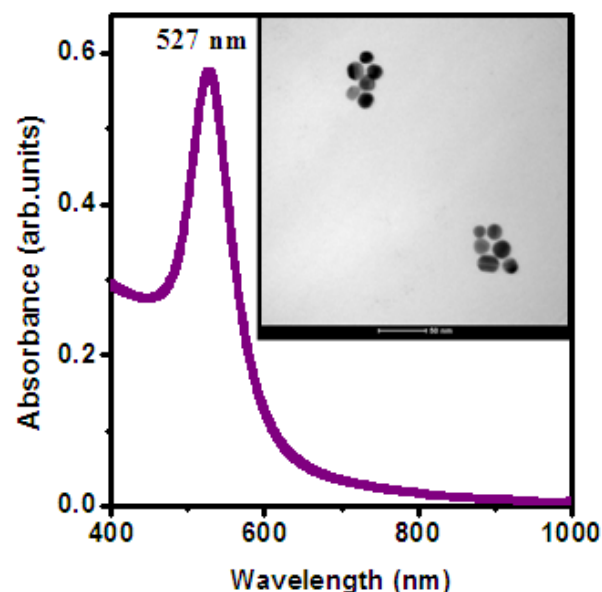


Figure 4. Optical absorption spectra for Au nanoparticles (Inset shows corresponding TEM image)

Optical absorption spectrum for Au NPs prepared with CTAB is shown in figure 4. Absorption spectra attributed sharp SPR peak at 527 nm indicates the narrow size distribution, which is further confirmed by TEM. Inset shows the TEM image of Au NPs. The size of Au NPs observed from TEM was $\sim 10-20$ nm.

3.3. PANI-Au Nanocomposite

Pristine PANI films were embedded by Au NPs with different dose. These samples were characterized by different technique to study their various properties.

Figure 5 (a) shows the optical absorption spectra of as-prepared PANI and PANI-Au thin films with different doses of Au NPs. Three peaks observed in pristine PANI films at 317 nm, 427 nm and 887 nm are associated to the formation of emeraldine salt form of PANI. A clear enhancement in the absorption of PANI in visible area is observed upon increasing the dose of Au NPs in PANI films. Conversion of PANI from emeraldine salt to emeraldine base takes place as the dose of Au NPs implemented onto PANI films. The peak attributed around 600 nm in the nanocomposites sample dipped in Au solution for 30 mins is due to the excitonic transition.

Photoluminescence spectra recorded for as-prepared PANI and PANI-Au nanocomposite thin film are shown in figure 5 (b). The wavelength of excitation was 270 nm. Presence of three emission peaks appeared at 397 nm, 457 nm and 620 nm are assigned to emeraldine salt form of PANI. The same features were observed in PANI-Au nanocomposite thin films for different Au doses. As the Au doses in PANI films increases enhancement the in the emission intensity is observed. The presence of distinct peaks in the UV-visible region in photoluminescence spectra

indicates the possibility of the existence of multiple electronic states participating in the photo-excitation process [10].

Figure 6 shows the FESEM images for PANI-Au nanocomposite thin film. Presence of around 10-20 nm gold NPs along with PANI fibers were clearly seen in FESEM image.

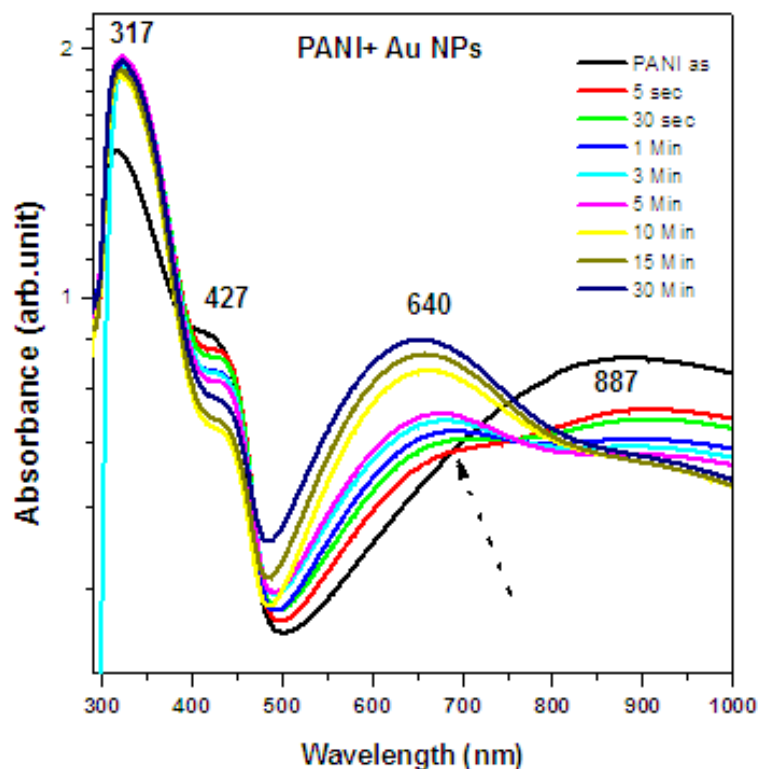


Figure 5a. Optical absorption spectra of as-prepared PANI and PANI-Au nanocomposites with different doses of Au NPs

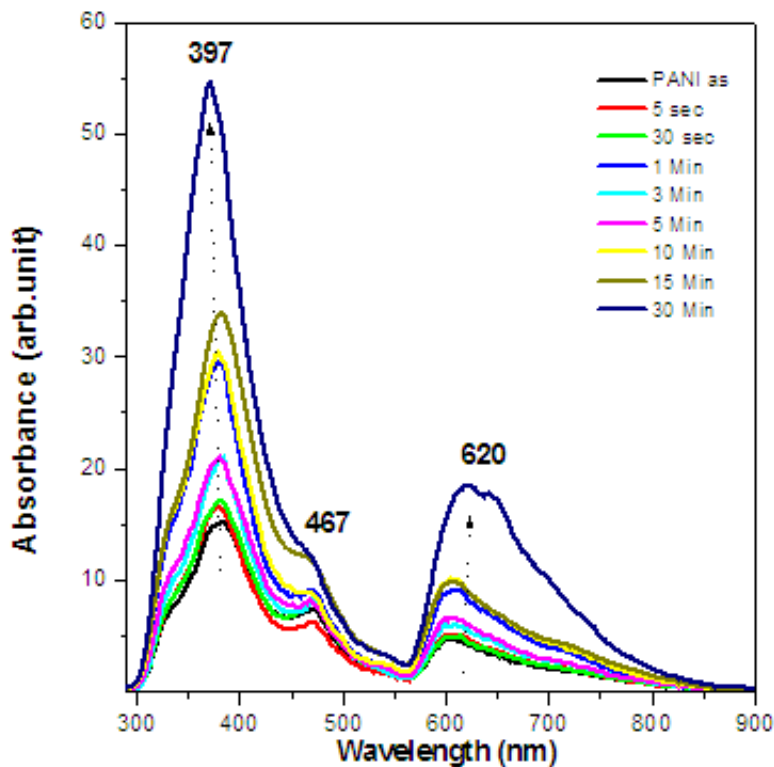


Figure 5b. Photoluminescence spectra of as-prepared PANI and PANI-Au thin films with different doses of Au NPs

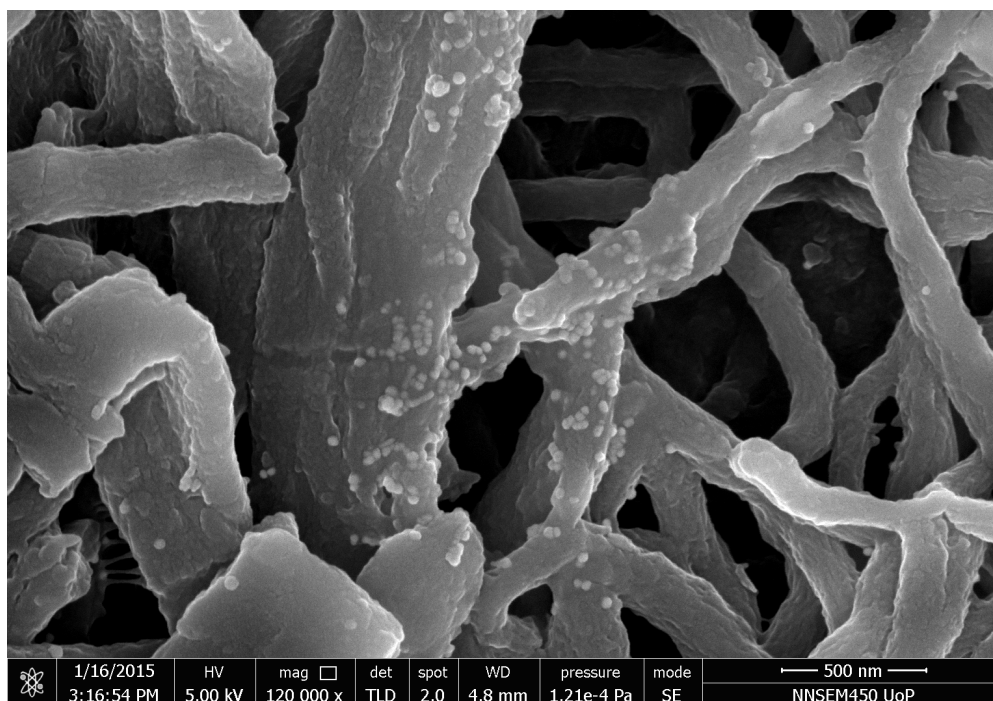


Figure 6. FESEM image for PANI-Au nanocomposite (Au dose for 3 mins)

4. Conclusions

Polyaniline with fibrous morphology were successfully electropolymerized using perchloric acid. The effect of different Au doses on PANI films was studied. Optical absorption spectra showed absorption peak for π - π^* , polaron and bipolaron transition for pristine PANI films, while the excitonic transition related peak was observed with Au NPs. The emeraldine form of PANI has been changed to emeraldine base form after the incorporation of Au NPs in PANI. Photoluminescence study shows the formation of PANI in emeraldine salt form, with increase in Au doses the emission intensity was found to be increased. FESEM micrographs shows presence of around 10-20 nm gold NPs along side with PANI fibers. The prepared PANI-Au nanocomposite layer with increase in absorption in visible region can be directly used as absorber layer in hybrid/organic solar cells.

ACKNOWLEDGEMENTS

The authors are thankful for the financial support received from Defence Research and Development Organisation, New Delhi, India under the major research project, ERIP/ER/10003866/M/01/1388.

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