

Electrochemical and *in situ* spectroelectrochemical studies of gold nanoparticles immobilized Nafion matrix modified electrode

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Abstract. Electrochemical and *in situ* spectroelectrochemical behaviours of phenosafranine (PS⁺) were studied at the gold nanoparticles (Au_{Nps}) immobilized Nafion (Nf) film coated glassy carbon (GC) and indium tin oxide (ITO) electrodes. Cyclic voltammetric studies showed that the PS⁺ molecules strongly interact with the Au_{Nps} immobilized in the Nf matrix through the electrostatic interaction. The presence of Au_{Nps} in the Nf film improved the electrochemical characteristics of the incorporated dye molecules. The emission spectra of Nf–Au_{Nps}–PS⁺ films showed that the incorporated PS⁺ was quenched by Au_{Nps} and it could be explained based on the electronic interaction between the Au_{Nps} and PS⁺ molecules. The *in situ* spectroelectrochemical study showed an improved electrochemical characteristic of the incorporated PS⁺ molecules at the ITO/Nf–Au_{Nps} electrode when compared to the ITO/Nf electrode.

Keywords. Gold nanoparticles; Nafion; modified electrode; phenosafranine; *in situ* spectroelectrochemistry.

1. Introduction

In recent years, interest in electrocatalysis and sensors has soared because of the technological advances that have been made, especially in materials science and device miniaturization (Eggs 2002). The preparation of thin films with high density of metal nanoparticles is often desired for catalysis and electronics (Niemeyer 2001). The integration of metal nanoparticles in thin films is particularly important for various applications, for example, in biological sensing and in the preparation of optoelectronic, advanced photonic and nanodevices (Rodriguez *et al* 2002; Xiao *et al* 2003; Haruta 2004; Xu *et al* 2004). Although gold is a poor catalyst in bulk form, nanometer-sized gold particles can exhibit excellent catalytic activity due to their relative high surface area-to-volume ratio, arrangement of atom, electronic structure and their interface dominated properties, which significantly differ from their bulk counterparts (Henglein 1989; Kreibitz and Vollmer 1995; Shipway *et al* 2000; Hu *et al* 2001; Ipe *et al* 2002; Sudeep *et al* 2002; Thomas and Kamat 2003; Campbell 2004; Daniel and Astruc 2004; Clapp *et al* 2005). The modification of electrode surface with nanosized noble metals can enhance the sensing activities of the electrode by mediating the electron transfer properties (Linsebigler and Lu 1995; Selvaraju and Ramaraj 2005). However, only a few studies have reported the effect of metal nanoparticles modification on the electrode surface and its applications (Yao *et al* 1998; George *et al* 2000; Wildgoose *et al* 2006).

We are interested in developing the gold nanoparticles immobilized Nafion film coated electrode for the study of electrochromic properties of molecules and to develop electrochemical sensors. The *in situ* spectral measurements of molecules under potential scanning have rarely been carried out especially in metal nanoparticles incorporated systems. It is, therefore, important to investigate the redox behaviour of molecules, especially electroactive and photoactive molecules at metal nanoparticles modified electrodes (Radovic 1999; Gonzalez-Garcia *et al* 2002; Aray *et al* 2003; Eckenrode *et al* 2005). Phenazine dye, such as phenosafranine, has been used in the studies of photoelectrochemical cells (Newmann-Spallart and Kalyana Sundaram 1982; Ramaraj and Natarajan 1989), photosensitization of large band-gap semiconductor such as TiO₂ (Gopidas and Kamat 1989, 1990; Easwaramoorthy and Natarajan 2005), electrocatalysis of NADH (Tanaka *et al* 1993) and electrochromism when loaded in Nafion membrane (Abraham John and Ramaraj 1997; Ganesan *et al* 2001). In this paper, a novel approach of dispersing the Au_{Nps} in a Nf matrix is reported. Thus it brings together the advantageous properties of microheterogeneous structure with permselective and preconcentration properties of Nf matrix (Olah *et al* 1986; Abraham John and Ramaraj 1996; Mauritz and Moore 2004) and catalytically active Au_{Nps} with high surface area-to-volume (Shenhar and Rotello 2003; Subramanian *et al* 2004; Barazzouk *et al* 2005). While the solid Au_{Nps} were embedded in the hydrophobic and interfacial regions, the cationic molecules were ion-exchanged into the Nf matrix. This type of approach will find applications in electrocatalysis, sensors, photoelectrochemical cells and electrochromic systems. In view of these considerations, we have chosen a cationic pheno-

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safranin dye and gold nanoparticles to prepare the modified electrode and to investigate the influence of Au_{Nps} on the immobilized dye molecules in the Nf film.

2. Experimental

2.1 Chemicals

Chloroauric acid (HAuCl₄) and sodium citrate of analar grade were used as received. Phenosafranin (Aldrich) was used after purification (Gopidas and Kamat 1990). A 5% Nafion (Nf) solution (Aldrich, EW 1100, dissolved in a mixture of lower aliphatic alcohol and water) was diluted to 1% with ethanol. Double distilled water was used throughout the experiments. Nitrogen gas was used for deaerating the solution. One side deposited indium tin oxide plates (CG-411N-1507, Delta Technologies Ltd., USA) with a surface resistance of 4–8 Ωsq⁻¹ was used to fabricate transparent electrodes. The ~0.7 mm thickness strips (1.5 × 1 cm) were incised and cleaned in acetone, ethanol and in double distilled water.

2.2 Preparation of spherical colloidal Au nanoparticles by sodium citrate reduction method

Spherical colloidal Au nanoparticles were prepared by citrate reduction of HAuCl₄ in aqueous solution using reported procedure (Daweipan 2004). 1.8 ml of 1% sodium citrate solution was added to 50 ml of 0.01% HAuCl₄ boiling solution. The solution was refluxed for 15 min until a wine red colour was observed. The surface plasmon band observed at 519 nm confirmed that the colloidal Au nanoparticles have been successfully synthesized by sodium citrate reduction method. The citrate ions act as capping agent and prevent colloidal Au nanoparticles from further agglomeration. The literature reports show the size of Au nanoparticles to be in the range of 15–20 nm (Daniel and Astruc 2004; Daweipan 2004).

2.3 Immobilization of colloidal Au nanoparticles in Nafion matrix

The glass vials were washed and dried in the oven. The required volume (v/v) of 0.5 ml of 1% Nafion[®] solution was taken in the sample tube and a known amount of (0.25 ml/0.5 ml) colloidal Au nanoparticles was added slowly to the Nafion[®] solution and the mixture was stirred for 10 min using magnetic stirrer. The volume ratio with respect to Nafion and colloidal Au nanoparticles were 1 : 1 and 2 : 1 (v/v). The immobilized colloidal Au nanoparticles in Nafion matrix containing viols were corked tightly and stored in refrigerator. By cast coating method, the Au_{Nps} dispersed Nafion was coated on the GC and ITO electrodes (GC/Nf–Au_{Nps} and ITO/Nf–Au_{Nps}) and from the amount of Nf taken the film thickness was calculated as 1.6 μm.

2.4 Equipment and measurements

All the electrochemical and *in situ* spectroelectrochemical experiments were performed in an EG&G PAR model 283 potentiostat/galvanostat with Echem software and HP diode array spectrophotometer (Agilent technologies-8453) with HPchem software loaded computers. The electrochemical and *in situ* spectroelectrochemical experiments were carried out with a single compartment three-electrode system, which has platinum wire as the counter electrode, saturated calomel electrode (SCE) or Ag wire as the reference electrode and GC (0.07 cm²) (CH Instruments) or ITO (1 cm²) coated glass electrode as the working electrode. Prior to every experiment, the GC electrodes were polished with an aqueous suspension of 1 μm alumina on a soft surface, rinsed copiously with doubly distilled water and sonicated in a water bath for 3 min. The electrode was then rinsed with distilled water and ethanol. The cleaned electrode was transferred to the electrochemical cell and pretreated by cycling the potential between –0.2 and 1.2 V at a scan rate of 20 mVs⁻¹ in 0.1 M phosphate buffer (pH 7.2) until a stable cyclic voltammogram was obtained. For the activation of electrode surface, the potential was stepped to 1.2 V for 2 min. The activated electrode was immediately used for electrochemical experiments.

3. Results and discussion

3.1 Spectral characterization of Au_{Nps} in Nafion film

The absorption spectra of the colloidal Au_{Nps} and Au_{Nps} dispersed in 0.5% Nafion solution (Nf–Au_{Nps}) are shown in figure 1. The surface plasmon absorption bands for the Au_{Nps} and Nf–Au_{Nps} were observed at 519 and 521 nm, respectively with an average diameter of Au_{Nps} in the range

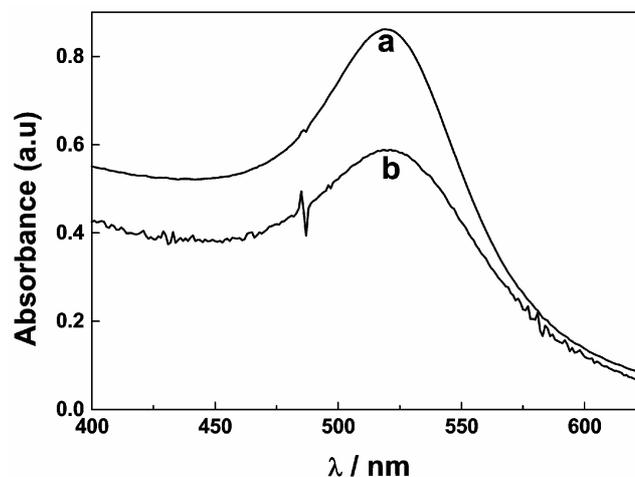


Figure 1. Absorption spectra of Au_{Nps} (a) and Nf–Au_{Nps} (b) in aqueous and 0.5% Nafion solution.

15–20 nm (Daniel and Astruc 2004; Daweipan 2004). The surface plasmon band of the Nf–Au_{Nps} exhibits a small red shift of 2 nm with bandwidth broadening. The change in the steady-state spectrum of the Nf–Au_{Nps} was due to the difference in the dielectric constant of the surrounding medium and embedding material (Su *et al* 2003; Yan *et al* 2003). When known amount of Nf–Au_{Nps} was coated on a glass plate (the amount used to prepare modified electrodes), the Nf–Au_{Nps} film did not show observable absorption band due to very small amount of Au_{Nps} dispersed in the Nf film.

3.2 Characterization of Au_{Nps} immobilized Nafion film coated GC electrode

The voltammetric procedure was used to study the ‘fingerprint’ characteristics of gold nanoparticles. The voltammetric responses were recorded for plain GC and Nf–Au_{Nps} modified GC electrodes in 0.1 M H₂SO₄. In the absence of Nf–Au_{Nps} on the GC electrode, no electrochemical peak was observed either in the anodic or cathodic scan. However, the Nf–Au_{Nps} modified GC electrode exhibited a sharp reduction peak at 0.8 V due to the reduction of surface oxides of gold nanoparticles (figure 2) (Trasatti and Petrii 1991; Dai *et al* 2006). This observation shows that the Au_{Nps} in Nf film are indeed formed from the dispersed gold nanoparticles and that they are in good electrical contact with the macroelectrode surface (Trasatti and Petrii 1991; Hoogvliet *et al* 2000; Dai *et al* 2006). One of the well established advantages of using the metal nanoparticles (e.g. metal nanoparticles modified electrode) is the significantly large electroactive surface area when compared to the bulk metal electrode.

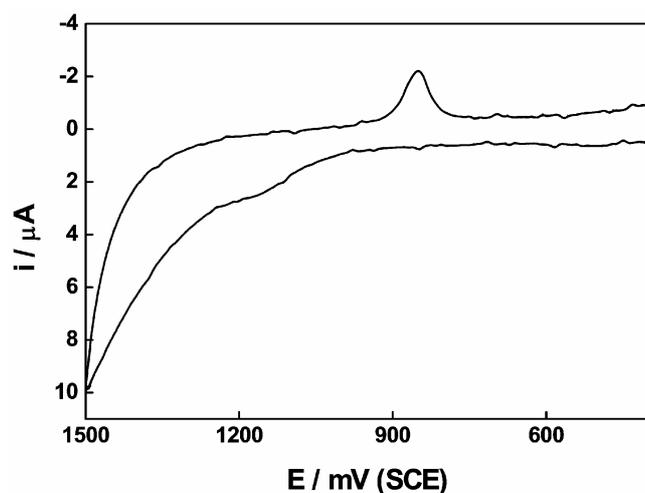


Figure 2. Cyclic voltammogram of Au_{Nps} immobilized Nf film modified GC electrode (GC/Nf/Au_{Nps}) in 0.1 M H₂SO₄. (Scan rate = 50 mV s⁻¹. [Au] = 2.57 × 10⁻¹³ mol).

3.3 Electrochemical behaviour of PS⁺ dye in GC/Nf and GC/Nf–Au_{Nps} electrodes

The electrochemical properties of PS⁺ were studied by recording the cyclic voltammograms for GC/Nf/PS⁺ and GC/Nf–Au_{Nps}/PS⁺ electrodes in 0.1 M H₂SO₄ at different scan rates as shown in figures 3 and 4, respectively. The PS⁺ dye undergoes two-electron and two-proton reduction (1) (Tanaka *et al* 1993). The PS⁺ dye showed an $E_{1/2}$ value of -0.07 V and -0.06 V (SCE) at the GC/Nf/PS⁺ and GC/Nf–Au_{Nps}/PS⁺ electrodes, respectively. This observa-

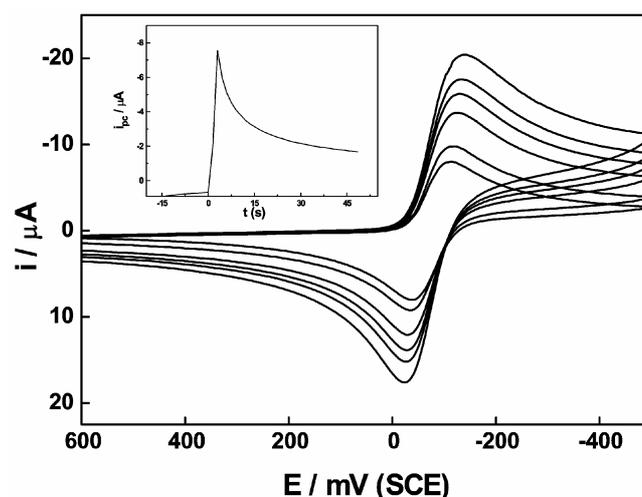


Figure 3. Cyclic voltammograms observed for GC/Nf/PS⁺ electrode in 0.1 M H₂SO₄. Scan rate = 10, 20, 50, 75, 100 and 150 mV/s. Inset: Chronoamperometry response observed for the same electrode in 0.1 M H₂SO₄. (Electroactive PS⁺ (Γ) = 0.88 × 10⁻⁸ mol/cm²).

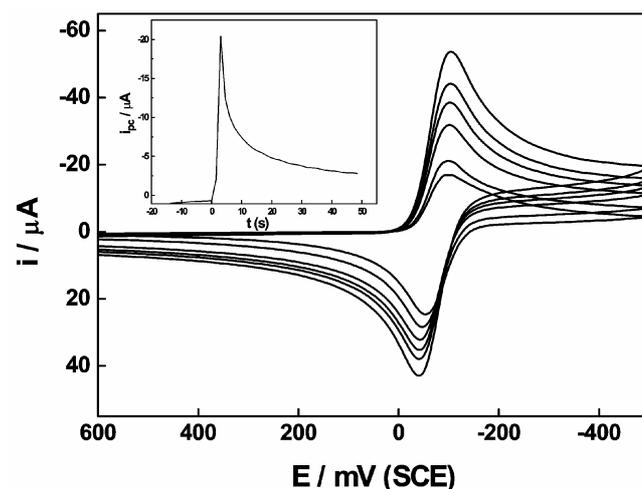
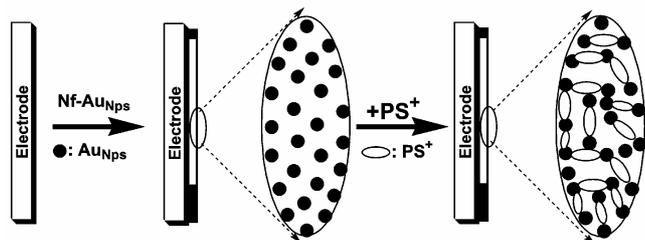


Figure 4. Cyclic voltammograms observed for GC/Nf–Au_{Nps}/PS⁺ electrode in 0.1 M H₂SO₄. Scan rate = 10, 20, 50, 75, 100 and 150 mV/s. Inset: Chronoamperometry response observed for the same electrode in 0.1 M H₂SO₄. (Electroactive PS⁺ (Γ) = 1.53 × 10⁻⁸ mol/cm². [Au] = 2.57 × 10⁻¹³ mol).

tion shows that the redox potential of PS^+ is not changed significantly at the GC/Nf- Au_{Nps} electrode.



The reversibility was improved and enhanced peak currents were observed at the GC/Nf- Au_{Nps} / PS^+ electrode for PS^+ molecule (figure 4) when compared to GC/Nf/ PS^+ electrode without Au_{Nps} (figure 3). The increase in the peak currents due to PS^+ redox process observed at the GC/Nf- Au_{Nps} / PS^+ electrode (figure 4) when compared to the GC/Nf/ PS^+ electrode (figure 3) clearly shows that the redox reaction of PS^+ at Au nanoparticles is significantly improved with fast electron transfer kinetics. The nitrogen atoms of the $-\text{NH}_2$ moieties of the cationic PS^+ bind strongly to Au_{Nps} (Ding et al 2006) immobilized in Nf matrix and hence the electrostatic interaction plays an important role in increasing the reversibility and peak currents. Scheme 1 depicts the schematic representation of the interaction of dispersed Au_{Nps} and their interaction with the incorporated PS^+ dye at the Nf- Au_{Nps} modified electrodes. The linear plot observed for the cathodic (i_{pc})



Scheme 1. Schematic representation of interaction of PS^+ molecules with dispersed Au_{Nps} in Nf film.

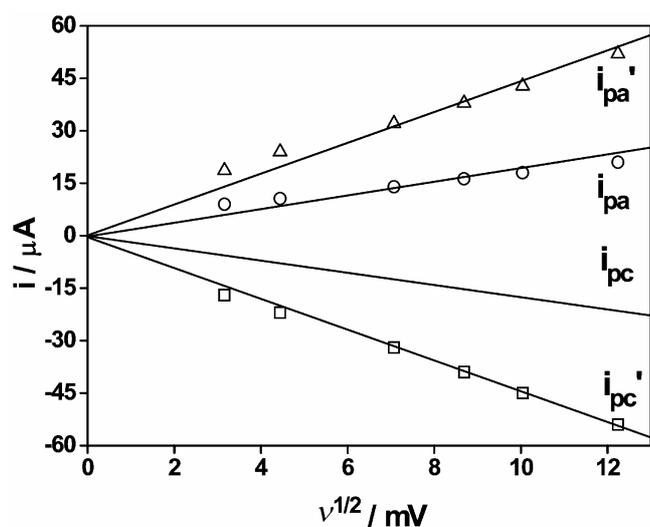


Figure 5. Plots of cathodic (i_{pc} and $i_{\text{pc}'}$) and anodic (i_{pa} and $i_{\text{pa}'}$) peak currents against square root of scan rate ($v^{1/2}$) at the GC/Nf/ PS^+ and GC/Nf- Au_{Nps} / PS^+ electrodes, respectively.

and anodic (i_{pa}) peak currents against square root of scan rate ($v^{1/2}$) for GC/Nf/ PS^+ and GC/Nf- Au_{Nps} / PS^+ electrodes confirm the diffusion-controlled processes at both the electrodes (figure 5). The rate of charge or mass transport associated with redox reaction at the modified electrode is commonly studied by determining the apparent diffusion coefficient (D_{app}) (Martin et al 1984). The chronoamperometry method (Martin and Dollard 1983) was used to estimate the value of D_{app} . The typical reductive single step chronoamperometry responses recorded for GC/Nf/ PS^+ and GC/Nf- Au_{Nps} / PS^+ electrodes are shown in figures 3 (inset) and 4(inset). From the chronoamperometry plots, the molar concentration of electroactive PS^+ dye (C_p) (Chiba et al 1987) and the apparent diffusion coefficient (D_{app}) were calculated as $5.51 \times 10^{-5} \text{ mol/cm}^3$ and $0.94 \times 10^{-9} \text{ cm}^2/\text{s}$ at GC/Nf/ PS^+ electrode and $8.34 \times 10^{-5} \text{ mol/cm}^3$ and $1.34 \times 10^{-9} \text{ cm}^2/\text{s}$ at GC/Nf- Au_{Nps} electrode. The molar concentration of electroactive PS^+ dye (C_p) was increased at the GC/Nf- Au_{Nps} electrode when compared to the GC/Nf electrode at the same amount of Nf in the film. The PS^+ dye incorporated into the hydrophobic region of the Nf film are electroinactive (Guadalupe et al 1991). When Au_{Nps} were embedded into the Nf film, in addition to the hydrophobic and interfacial regions, more amount of PS^+ dye would occupy the expanded $-\text{SO}_3^-$ ionic cluster region of the Nf film. The molecules occupying the ionic cluster and interfacial regions of the Nf- Au_{Nps} film are electroactive. This means that more amount of PS^+ molecules incorporated into the Nf- Au_{Nps} film occupy the $-\text{SO}_3^-$ ionic cluster and interfacial regions and are electroactive.

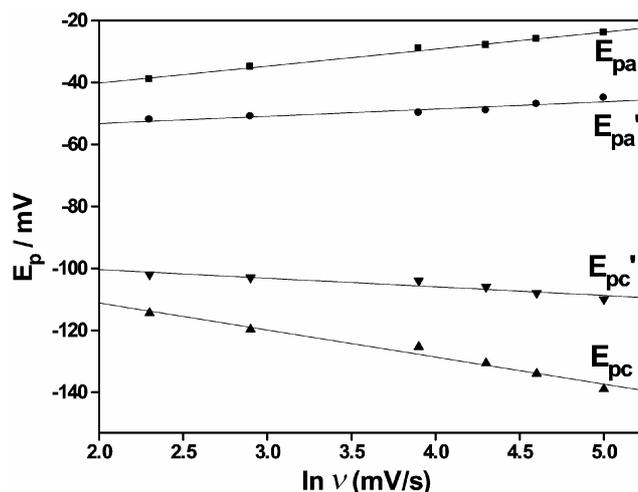


Figure 6. Plot of $\ln v$ against E_p for both anodic (E_{pa}) and cathodic (E_{pc}) peak potentials obtained from the cyclic voltammograms shown in figures 3 and 4. The value of α was estimated to be 0.38 and 0.46, respectively from the slope of the plots obtained for GC/Nf/ PS^+ (E_{pa} and E_{pc}) and GC/Nf- Au_{Nps} / PS^+ ($E_{\text{pa}'}$ and $E_{\text{pc}'}$) electrodes.

3.4 Measurement of electron-transfer rates at modified electrodes

Cyclic voltammetry is a classical technique used for the determination of electron-transfer rate based on the separation of peak potentials (ΔE_{peak}) (Nicholson 1965; Moses and Murray 1976; Laviron 1979; Bard and Faulkner 2000). The electrochemical behaviour of redox molecules at modified electrode deviates from Nernstian behaviour at higher scan rates i.e. becomes quasi-reversible, and the ΔE_{peak} increases. The voltammograms shown in figure 3 for GC/Nf/PS⁺ electrode show that the peak potential separation (ΔE_{peak}) values increased up to 45 mV when the scan rate increased from 10 to 150 mV/s. However, at the GC/Nf-Au_{Nps}/PS⁺ electrode (figure 4), relatively a small increase of 18 mV was observed for the same scan rate change. In an attempt to determine the electron transfer coefficient ' α ' and the rate constant ' k ', Laviron's approach was used, which is valid for an electroactive species immobilized on the electrode surface (Laviron 1979). The peak potential (E_p) values observed for PS⁺/PSH₂⁺ and PSH₂⁺/PS⁺ couples at 10, 20, 50, 75, 100 and 150 mV/s scan rates in the cyclic voltammograms are shown against $\ln \nu$ (figure 6) to understand the electron transfer process at the GC/Nf/PS⁺ and GC/Nf-Au_{Nps}/PS⁺ electrodes.

The ' α ' and ' k ' values can be determined from the following relationships

$$\alpha = s_a / (s_a - s_c), \quad (2)$$

$$k = \alpha n F \nu_c / RT \quad \text{or} \quad (1 - \alpha) n F \nu_a / RT, \quad (3)$$

where ν_c and ν_a are the cathodic and anodic scan rates, respectively and s_a and s_c are the slopes of the anodic and

cathodic peak currents. Figure 6 shows linear variation of $\ln \nu$ against E_p for both the anodic and cathodic peak currents. The estimated values of α are 0.38 and 0.46, which shows that the energy barrier for double layer charging is not symmetric, and the average rate constant, k values are calculated as 1.99 and 2.82 s⁻¹ for GC/Nf/PS⁺ and GC/Nf-Au_{Nps}/PS⁺ electrodes, respectively. A higher rate constant value was observed for GC/Nf-Au_{Nps}/PS⁺ electrode when compared to the GC/Nf/PS⁺ electrode. The ' k ' values are comparable to the reported values at other modified electrodes (Zhao *et al* 2005). The presence of immobilized Au_{Nps} at the GC/Nf electrode not only improved the reversibility of voltammograms but also improved the rate of reaction.

3.5 Emission spectra of PS⁺ incorporated into Nf-Au_{Nps} matrix

The PS⁺ is an emissive dye and we used emission spectroscopy to probe the interaction between dye and Au_{Nps} in the Nf matrix. The emission spectra of PS⁺ incorporated into Nf and Nf-Au_{Nps} films are shown in figure 7. PS⁺ in Nf film exhibits an intense emission band at 598 nm when excited at 520 nm (figure 7a). The incorporated PS⁺ molecules into the Au_{Nps} dispersed Nf films show the emission band at 598 nm with lower emission intensity (figure 7(b-c)) when compared to plain Nf film (figure 7a). The amount of Au_{Nps} dispersed in 1.6 μm thick Nf films are calculated as 1.28 $\times 10^{-13}$ mol (figure 7b) and 2.57 $\times 10^{-13}$ mol (figure 7c). The dye incorporation was carried out in the Nf and Nf-Au_{Nps} film coated glass plates under similar experimental conditions. Using chronocoulometry experiments the amounts of PS⁺ dye in the Nf-Au_{Nps}

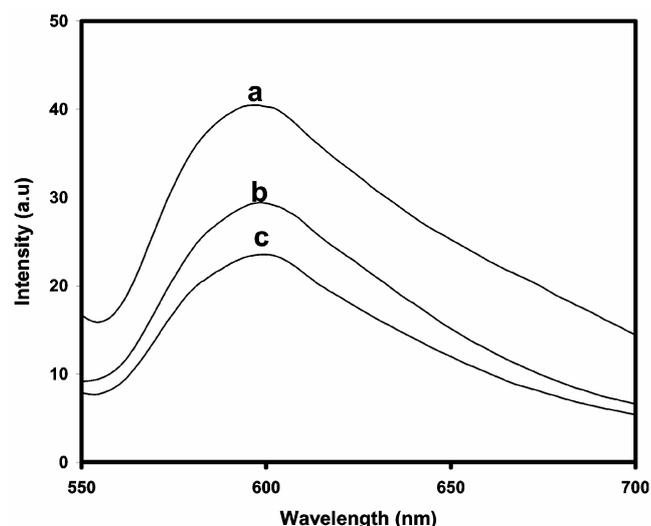


Figure 7. Emission spectra of PS⁺ in Nf (a) and Nf-Au_{Nps} (b-c) films coated glass plates. The amount of Au_{Nps} in the Nf films are 1.28 $\times 10^{-13}$ mol (b) and 2.57 $\times 10^{-13}$ mol (c). λ_{ex} = 520 nm.

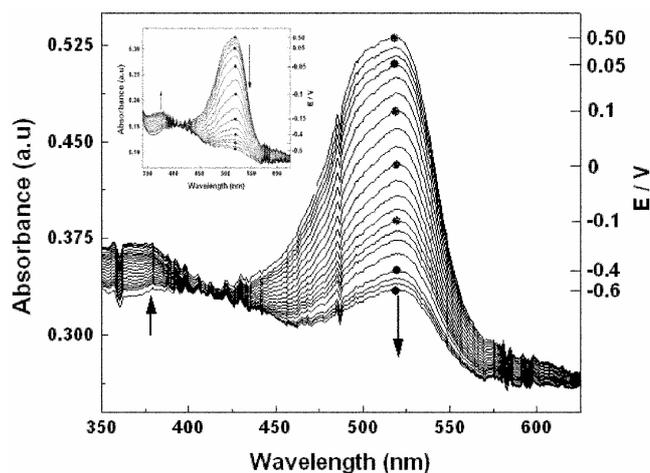


Figure 8. *In situ* absorption spectral changes observed for ITO/Nf-Au_{Nps}/PS⁺ in 0.1 M H₂SO₄ during the reductive scan from 0.5 to -0.6 V. Scan rate = 5 mV/s. Absorption spectra were recorded at an interval of 2 s. Other conditions are as in figure 4. Inset: *In situ* absorption spectral changes observed at ITO/Nf/PS⁺ electrode in 0.1 M H₂SO₄.

modified electrodes with same film thickness were calculated as 1.34×10^{-8} mol/cm² and 1.53×10^{-8} mol/cm², respectively. From the emission spectra, a decrease in the emission intensity was observed for PS⁺ in the Nf–Au_{Nps} films. The decrease in the emission intensities indicates that a fraction of excited state PS⁺ molecules were deactivated by the Au_{Nps}. The immobilization of both Au_{Nps} and PS⁺ in the Nf film would enhance the interaction between the PS⁺ dye and Au_{Nps} (Ipe et al 2002; Ding et al 2006). The interaction between the cationic dye (PS⁺) and the electron rich Au_{Nps} is further enhanced by the micro-heterogeneous environment provided by the Nf film. The improved electrochemical characteristics and the excited state quenching of PS⁺ in the presence of Au_{Nps} at the Nf film clearly indicate that this system will find applications in photo-based nanodevices and sensor devices.

3.6 *In situ* spectroelectrochemical properties of PS⁺ dye incorporated into Nf and Nf–Au_{Nps} film modified electrodes

The *in situ* absorption spectral changes of PS⁺ at the ITO/Nf–Au_{Nps}/PS⁺ electrodes were recorded during potential scan. The *in situ* spectroelectrochemical study provides a tool to understand the redox reaction at the Nf–Au_{Nps} modified electrode and the electrochromic behaviour of the incorporated molecules in the presence of Au_{Nps}. The *in situ* spectral changes observed at the ITO/Nf–Au_{Nps}/PS⁺ and ITO/Nf/PS⁺ electrodes in the reductive scan from 0.5 to –0.6 V at a scan rate of 5 mV/s are shown in figure 8 and figure 8 (inset), respectively. Similarly, *in situ* spectral changes observed in the oxidative scan from –0.6 to

0.5 V at a scan rate of 5 mV/s are shown in figure 9 and figure 9 (inset), respectively. The *in situ* absorption spectra recorded for PS⁺ incorporated into Nf–Au_{Nps} and Nf films during the reductive scan from 0.5 to –0.6 V at a scan rate of 5 mV/s showed a decrease in the absorbance at 520 nm due to the reduction of PS⁺ molecules with a simultaneous appearance of a new absorption band at 370 nm (figure 8) with an isobestic point at 410 nm. At –0.6 V, most of the PS⁺ molecules underwent reduction and the appearance of a new absorption band was clear at 370 nm. The absorption band at 370 nm was identified as the two-electron reduced leuco PSH₂⁺ (Martin and Dollard 1983; Abraham John and Ramaraj 1997). The formation of leuco PSH₂⁺ by photochemical reduction of PS⁺ dye was reported by Gopidas and Kamat (1989, 1990) using laser flash photolysis technique. During the oxidative scan from –0.6 to 0.5 V, an increase in absorbance was noticed at 520 nm with a simultaneous decrease in absorbance at 370 nm. At the end of the oxidative scan from –0.6 to 0.5 V, the original absorption spectrum was recovered (figure 9).

The absorption spectra of PS⁺ in water and Nf film exhibited the characteristic absorption band due to monomer PS⁺ at 520 nm. When Au nanoparticle (2.57×10^{-13} mol) was dispersed in 0.5% Nf solution and coated on the electrode surface an increase in the absorbance due to PS⁺ in the Nf–Au_{Nps} film was observed when compared to the ITO/Nf/PS⁺ electrode. The absorption band due to PS⁺ was not shifted at the ITO/Nf–Au_{Nps} electrode. The Au_{Nps}-dye (Au–PS⁺) assemblies combine to form larger clusters within the film because of surface charge neutralization (Awan and Shah 1997) and modulate the arrangement of PS⁺ molecules in the Nf film.

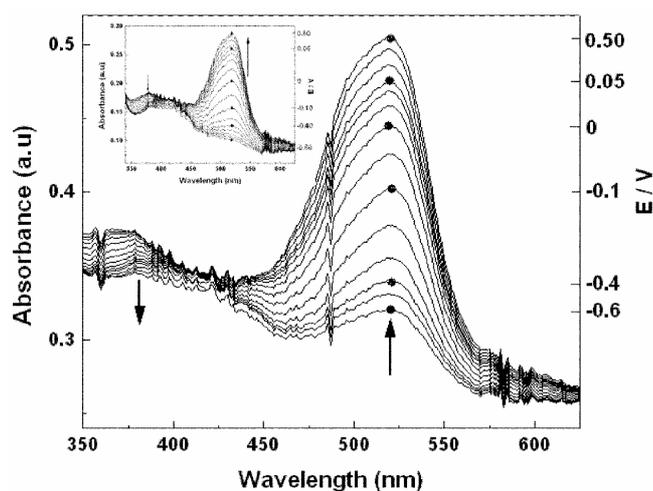


Figure 9. *In situ* absorption spectral changes observed for ITO/Nf–Au_{Nps}/PS⁺ in 0.1 M H₂SO₄ during the oxidative scan from –0.6 to 0.5 V. Scan rate = 5 mV/s. Absorption spectra were recorded at an interval of 2 s. Other conditions are as in figure 4. Inset: *In situ* absorption spectral changes observed at ITO/Nf/PS⁺ electrode in 0.1 M H₂SO₄.

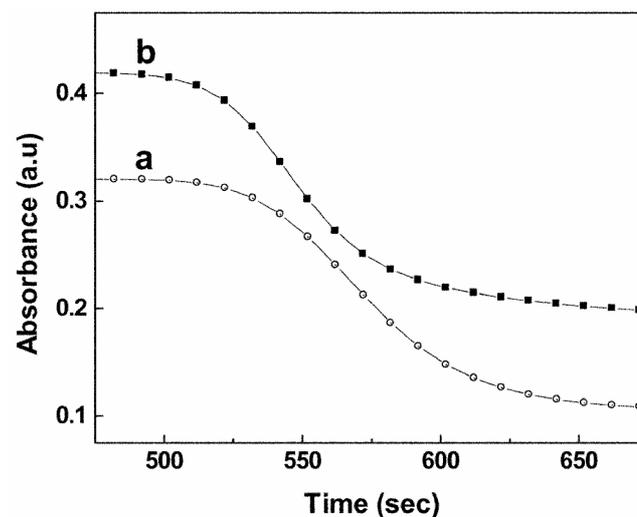


Figure 10. Absorbance changes observed at 520 nm due to PS⁺ reduction with time during the reductive scan from 0.5 to –0.6 V. Spectral changes recorded for ITO/Nf/PS⁺ (a) and ITO/Nf–Au_{Nps}/PS⁺ (b) electrodes in 0.1 M H₂SO₄. Absorption spectral changes were recorded at 2 s interval.

Figure 10 shows the plot of change in absorbance of PS^+ at 520 nm with respect to time during the reductive scan at ITO/Nf/Au_{Nps} (figure 10a) and ITO/Nf (figure 10b) electrodes. During the reductive scan between 0.5 and -0.6 V, the absorbance due to PS^+ decreased rapidly at the ITO/Nf-Au_{Nps} electrode in about 80 s whereas at the ITO/Nf electrode the absorbance due to PS^+ decreased slowly in about 150 s. The redox process of PS^+ dye with the formation of short lived leuco PSH_2^+ dye is clearly shown in the *in situ* spectral changes. The *in situ* spectral study clearly shows that the dispersion of Au_{Nps} in the Nf film mediates the electron transfer of PS^+ molecule and improves the redox switching process. The rapid spectral change during the redox process observed at the Nf-Au_{Nps}/ PS^+ film shows that the Nf-Au_{Nps} modified electrode could be used for electrochromic display devices, electrocatalysis and sensor applications. The advantageous properties of this modified electrode are the permselective and microheterogeneous nature of Nf film, the large surface area and the fast electron mediation effect of Au_{Nps}.

4. Conclusions

The electrochemical and *in situ* spectral characteristics of PS^+ dye incorporated into the Nf-Au_{Nps} film modified electrode were studied by means of electrochemical and *in situ* spectroelectrochemical techniques. The PS^+ molecules interact strongly with Au_{Nps} as confirmed by cyclic voltammetric and spectroelectrochemical studies. The incorporation of PS^+ dye into Au_{Nps} immobilized Nf modified electrode enhances the absorption sensitivity of PS^+ and modulates the molecular arrangement of PS^+ molecules. The Au_{Nps} immobilized in Nf matrix improved the reversibility of PS^+ molecules and the rate of the reaction. The incorporated PS^+ into the Nf-Au_{Nps} film is fluorescent, and this property suggests possible applications in fabricating biomolecular labels and design of novel photo-based nanodevices for sensing and switching. The rapid *in situ* spectral changes of the PS^+ redox process shows that the Au_{Nps} immobilized Nf matrix could be useful in electrocatalytic and electrochromic applications.

Acknowledgements

The financial support from the Department of Science and Technology (DST) is gratefully acknowledged. One of the authors (TS) is recipient of a CSIR-SRF fellowship.

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