

# APPLICATIONS OF NANOSTRUCTURED MATERIALS AND BIOMOLECULES FOR ELECTROCATALYSIS AND BIOSENSORS

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## ABSTRACT

Electronically conducting polymers are important materials, and composites of these materials with metal nanoparticles have also been drawn significant research attention in recent years. We prepared a highly stable Ag<sub>nano</sub>-Poly (3, 4-ethylenedioxythiophene) (PEDOT) nanocomposite by one-pot synthesis method. Here, 3, 4-ethylenedioxythiophene (EDOT) is used as the reductant and polystyrene sulfonate (PSS<sup>-</sup>) as a dopant for PEDOT as well as particle stabilizer for silver nanoparticles (AgNPs). Ag<sub>nano</sub>-PEDOT/PSS<sup>-</sup> nanocomposite was characterized by infrared (IR) spectroscopy, transmission electron microscopy (TEM). AgNPs are distributed uniformly around PEDOT polymer with an average particle size diameter of 10–15 nm and the nanocomposite film showed catalytic activity towards 4-nitro phenol. Some types of including Ag bimetallic nanoparticles and nanostructured materials could be directly applied for the electroanalysis and biosensing applications.

**Key words:** Nanoparticles, nanocomposite, PSS, PEDOT, catalytic activity, electroanalysis.

## INTRODUCTION

Silver colloidal particles play important roles as substrates in the studies of surface-enhanced Raman scattering [1] and catalysis [2]. A number of reports are available in the literature to synthesize AgNPs by reducing silver salts as precursors. Reduction routes involved in these studies fall into three broadly defined categories. The first one involves the use of relatively strong reducing agents, such as sodium borohydride [3] and hydrazine [4], while the second one is irradiation of the solution containing silver ions [5,6], and the third route involves heating the solution of silver salt under prolonged reflux of silver solution in the presence of weak reducing agents, such as glucose [7].

Recently, AgNPs have been prepared using polymer, like poly (vinyl alcohol) (PVA) [8], and conducting polymer [9] as the reductant to reduce silver salts and obtained AgNPs- polymer nanocomposite.

Among conducting polymer monomers, thiophenes including, terthio-

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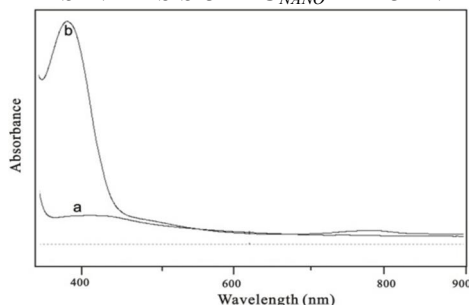
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phene and (3, 4-ethylenedioxythiophene) (EDOT) [10] are examples of such reductants. In the course of our investigations, we have found that EDOT reduces  $\text{AgNO}_3$  into AgNPs in acidic condition. Since the silver metal ions have suitable oxidation potentials to polymerize the monomer unit, EDOT, consequently it may be getting reduced into AgNPs. In the present work  $\text{PSS}^-$  used as stabilizer. Since,  $\text{PSS}^-$  is negatively charged and plays dual role. Such as, first, it stabilizes AgNPs and secondly, it is a good dopant for PEDOT and helps to enhance solubility of EDOT as well as PEDOT polymer. Since, PEDOT in its oxidized state is not soluble in aqueous medium.

Herein, we report a one-pot synthesis of  $\text{Ag}_{\text{nano}}$ -PEDOT/ $\text{PSS}^-$  nanocomposite in aqueous solution using EDOT as a reductant and  $\text{PSS}^-$  as a dopant for PEDOT as well as a particle stabilizer for AgNPs. Further, stability of  $\text{Ag}_{\text{nano}}$ -PEDOT/ $\text{PSS}^-$  nanocomposite compared with  $\text{Ag}_{\text{nano}}$ -PEDOT nanocomposite and it was found that  $\text{Ag}_{\text{nano}}$ -PEDOT nanocomposite is not stable. In addition,  $\text{Ag}_{\text{nano}}$ -PEDOT/ $\text{PSS}^-$  nanocomposite was found to effectively catalyze activation of the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of excess  $\text{NaBH}_4$ .

## EXPERIMENTAL

### SYNTHESIS OF $\text{Ag}_{\text{NANO}}$ -PEDOT NANOCOMPOSITE



**Fig. 1** – UV-vis spectra of (a)  $\text{Ag}_{\text{nano}}$ -PEDOT nanocomposite and (b)  $\text{Ag}_{\text{nano}}$ -PEDOT/ $\text{PSS}^-$  nanocomposite

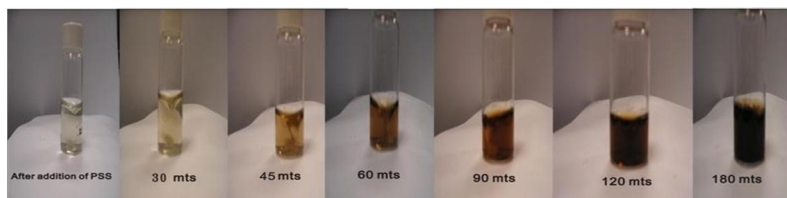
nanance (SPR) band at 400 nm [11], as shown in *Fig. 1a*.

### SYNTHESIS OF $\text{Ag}_{\text{NANO}}$ -PEDOT/ $\text{PSS}^-$ NANOCOMPOSITE

0.05M  $\text{AgNO}_3$  was added into 10 ml of 1M  $\text{HNO}_3$  solution containing 0.01 M EDOT, and 0.1%  $\text{PSS}^-$ . After  $\text{AgNO}_3$  addition, the solution turns slightly yellow. The yellow color resulted from the plasma absorption of silver nanoparticles (AgNPs). After extending time of stirring, the solution color changes initially from yellow to brownish yellow followed slightly brownish and finally dark brown solution was obtained, as shown in *Fig.2*.

## RESULTS AND DISCUSSION

0.05M  $\text{AgNO}_3$  was added into 10 ml of 1M  $\text{HNO}_3$  solution containing 0.01M EDOT. The mixture was stirred at room temperature and after 15min white color solution was changed into slight yellow and finally, changed into blackish brown after stirring long time. The appearance of slight yellow color solution indicates formation of AgNPs, which exhibits surface Plasmon resonance



**Fig. 2** – Different color solution of Agnano-PEDOT/PSS- nanocomposite.

The color change indicates complete formation of AgNPs and the corresponding surface plasmon resonance (SPR) band observed at 375 nm [12] as shown in *Fig. 1b*. With extension of reaction time the color of Ag<sub>nano</sub>-PEDOT/PSS<sup>-</sup> nanocomposite changed from slight yellow to bright yellow to deep yellow to yellowish brown and finally brown as shown in *Fig. 2*. This is attributed to the increase of the silver loading and complete reduction of Ag<sup>+</sup> to Ag<sup>0</sup> state.

In addition to color change, particles size have calculated from the full widths at half maximum of absorbance of Ag<sub>nano</sub>-PEDOT/PSS<sup>-</sup> nanocomposite and Ag<sub>nano</sub>-PEDOT nanocomposite are 20 and 90 nm, respectively. Moreover, SPR bands of AgNPs in Ag<sub>nano</sub>-PEDOT/PSS<sup>-</sup> nanocomposite are symmetrical and sharp, which indicates formation well dispersed smaller size nanoparticles. On the other hand, Ag<sub>nano</sub>-PEDOT nanocomposite peak shifts to longer wavelength, which might be due to agglomeration and increasing size of AgNPs.

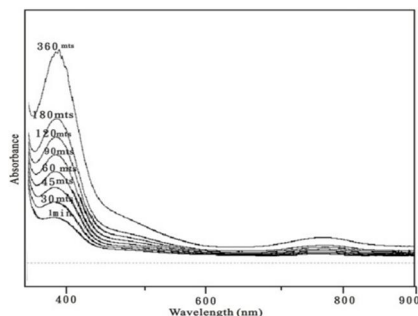
Moreover, the relatively larger absorbance of Ag<sub>nano</sub>-PEDOT/PSS<sup>-</sup> nanocomposite (*Fig. 1b*) in comparison with Ag<sub>nano</sub>-PEDOT nanocomposite (*Fig. 1a*) probably is due to substantial reduction of AgNPs took place when PEDOT doped with negatively charged PSS. The synthetic approach followed in the present work incorporates all the features typical of one-pot synthesis, such as aqueous solubility of PEDOT/PSS<sup>-</sup> and in-situ encapsulation of AgNPs into PEDOT/PSS<sup>-</sup>. The improved solubility of EDOT is due to the formation of a pseudo-complex similar to the ones reported by Sakmeche et al. [13]. PSS<sup>-</sup> is well known stabilizer for metal nanoparticles and reaction of EDOT with AgNO<sub>3</sub> in its presence leads to formation of a yellow dispersion, as shown in *Fig. 2*. This indicates that EDOT is oxidized by Ag<sup>+</sup>. The strong absorbance at 375 and above 700 nm corresponds to SPR of AgNPs and oxidized PEDOT, respectively. It is consistent with the fact that effective stabilization of radical cations by PSS<sup>-</sup> during oxidative polymerization of PEDOT leads to the formation of PEDOT in its highly oxidized form. The above discussion accounts for the formation of PEDOT and also relatively larger absorbance of Ag<sub>nano</sub>-PEDOT/PSS<sup>-</sup> nanocomposite in comparison to Ag<sub>nano</sub>-PEDOT nanocomposite.

**FORMATION AND STABILITY OF AGNPS IN AG<sub>NANO</sub>-PEDOT/PSS<sup>-</sup> NANOCOMPOSITE**

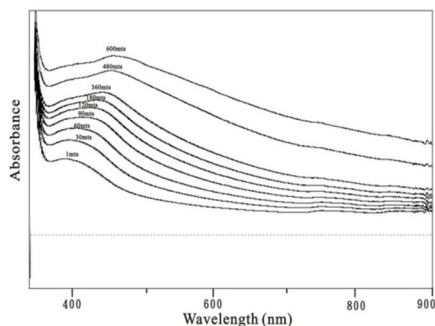
The formation of  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite was followed by UV-vis spectroscopy at various time intervals as shown in *Fig. 3*. After the addition of  $\text{AgNO}_3$  into  $\text{HNO}_3$  solution containing EDOT and  $\text{PSS}^-$ , absorption peaks at 375 nm and above 700 nm developed and increased gradually with time as shown in *Fig.3*. This indicates the formation of AgNPs with concomitant EDOT oxidation as shown by the broad absorption above 700 nm that is attributable to polaronic and bipolaronic states of oxidized (doped) PEDOT [14].

We have examined the stability of  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite and  $\text{Ag}_{\text{nano}}\text{-PEDOT}$  nanocomposite and their respective UV-vis spectrums are shown in *Fig.3* and *Fig.4*, respectively. In the UV-vis spectrum of  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite, with extending time the absorbance of AgNPs increased regularly and neither shift in wavelength towards neither longer nor shorter this indicates that particles are highly stable. In contrast,  $\text{Ag}_{\text{nano}}\text{-PEDOT}$  nanocomposite, the absorption intensity of AgNPs decreased and shift in wavelength towards longer with extending reaction time. This is an indication that AgNPs are not stable as shown in *Fig.4*.

The formation of stable  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite can be reasoned as follows. PEDOT/ $\text{PSS}^-$  as a stabilizer, the interaction of  $\text{AgNO}_3$  with the reductant EDOT is through oxidative coupling of EDOT by the action of  $\text{AgNO}_3$ , being a strong oxidant, can completely oxidize both the EDOT monomer and its polymer, PEDOT. FT-IR spectrum of  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite confirmed that the  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite is a combination of PEDOT with  $\text{PSS}^-$ . TEM investigation revealed that silver nanoparticles are dispersed around polymer without any agglomeration with an average diameter of 10-15 nm.



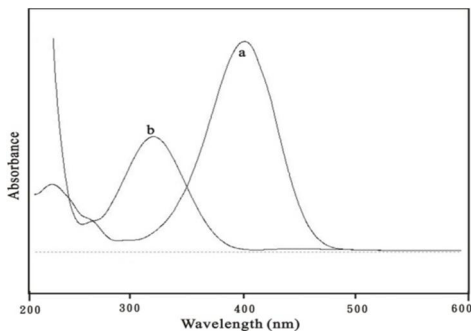
**Fig. 3** – UV-vis spectra of  $\text{Ag}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite at different time intervals



**Fig. 4** – UV-vis spectra of  $\text{Ag}_{\text{nano}}\text{-PEDOT}$  nanocomposite at different time intervals

*CATALYTIC REDUCTION OF NITROPHENOL USING  $\text{Ag}_{\text{NANO}}\text{-PEDOT/PSS}^-$  NANOCOMPOSITE*

We have studied the catalytic reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP) by  $\text{NaBH}_4$  in the presence of the  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite composite. The reactions have been monitored spectrophotometrically, as shown in Fig. 5.



**Fig. 5** – UV-vis spectra of the reduction of 4-nitrophenol by  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite

Also, important to mention here is the use of excess  $\text{NaBH}_4$  so that the kinetics of the reaction could be followed as a function of concentrations of AgNPs. An aqueous solution of 4NP shows a distinct spectral profile with absorption maximum at 317 nm, which shifts to 400 nm in the presence of  $\text{NaBH}_4$  due to the formation of the 4-nitrophenolate ion. The anionic species remain stable for weeks in the absence of any

other reagent. Interestingly, addition of very small aliquots (2  $\mu\text{L}$ ) of  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite to the previous solution was found to cause fading and finally discoloration of the yellow green color of 4-nitrophenolate in aqueous solution. This is unambiguously proved by the disappearance of the absorption peak at 400 nm after the addition of  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite, with a concurrent appearance of new absorbance peak at 315 nm, corresponding to the formation of 4-aminophenol [15]. From the control experiment, we observed that PEDOT-PSS dispersion alone cannot reduce 4-nitrophenol. Hence, it can be concluded that reduction is catalyzed only due to AgNPs in  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite.

### CONCLUSION

We reported one-pot synthesis of stable  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite using EDOT as reductant for  $\text{AgNO}_3$  and PSS<sup>-</sup> was a particle stabilizer for AgNPs as well as dopant for PEDOT. The prepared composite was characterized by UV-vis spectrum, XRD, IR and TEM. TEM studies revealed that the in-situ occurrence of monomer polymerization and metallic ion reduction should be more beneficial to the formation of well dispersed and narrow size-distributed nanoparticles. It also reveals that AgNPs distributed uniformly around polymer with an average particle diameter of 10-15 nm. The  $\text{Ag}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite was tested for catalytic activity towards reduction of 4-nitrophenol in presence of excess of  $\text{NaBH}_4$ .

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