

# Stabilized Gold Nanoparticles by Reduction Using 3,4-Ethylenedioxythiophene-polystyrenesulfonate in Aqueous Solutions: Nanocomposite Formation, Stability, and Application in Catalysis

Shanmugam Senthil Kumar, Chinnaiyah Siva Kumar, Jayaraman Mathiyarasu, and Kanala Lakshminarasimha Phani\*

*Electrodics and Electrocatalysis Division, Central Electrochemical Research Institute, Karaikudi 630 006, India*

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Herein, we report a one-pot synthesis of highly stable Au nanoparticles (AuNPs) using 3,4-ethylenedioxythiophene (EDOT) as a reductant and polystyrene sulfonate (PSS<sup>-</sup>) as a dopant for PEDOT and particle stabilizer. The synthesis demonstrated in this work entails the reduction of HAuCl<sub>4</sub> using EDOT in the presence of PSS<sup>-</sup>. The formation of AuNPs with concomitant EDOT oxidation is followed by UV-vis spectroscopy at various time intervals. Absorption at 525 nm is due to the surface plasmon band of AuNPs (violet), and broad absorption above 700 nm is due to oxidized PEDOT that was further characterized to be in its highly oxidized (doped) state, using FT-Raman spectroscopy. Transmission electron microscopy shows a polydisperse nature of the particles, and the selected area electron diffraction pattern reveals the polycrystalline nature of AuNPs. With stabilizers such as sodium dodecylsulfate (SDS) (green) and polyvinylpyrrolidone (PVP) (blue), the absorbance around 525 nm was found to be negligibly small, while PSS<sup>-</sup> showed high absorbance at 525 nm (violet) and above 700 nm (oxidized PEDOT). PSS<sup>-</sup> also allows complete oxidation of EDOT and serves as an effective dopant for PEDOT. While AuNPs covered by PEDOT alone cannot be dispersed in aqueous solutions, PSS<sup>-</sup> renders Au-PEDOT water soluble. The hydrodynamic diameter of the nanocomposite estimated from the dynamic light scattering (DLS) measurements increases in the order Na-PSS < SDS < PVP. Interestingly, the color of the Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> aqueous dispersion changed reversibly between violet and blue and vice versa on addition of NaOH and HCl, respectively. This reversible color change appears to be a combination effect of acid/base on the properties of PEDOT, in turn changing the environment around the embedded AuNPs. The nanoparticle dispersion also exhibited very high stability in presence of 3.0 M NaCl. Remarkably, the nanocomposite Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> was found to function as an effective catalyst to activate the reduction of 4-nitrophenol to 4-aminophenol in the presence of excess NaBH<sub>4</sub>, and the calculated apparent rate constant value of  $4.39 \times 10^{-2} \text{ s}^{-1}$  is found to be higher than those obtained using other nanocomposites with SDS and PVP and comparable to the values reported in the case of other encapsulants.

## Introduction

The synthesis and use of Au nanoparticles constitute a major research area that attracts both academic and industrial interest.<sup>1</sup> Many applications require these particles to be water dispersible and to remain suspended in water with no loss of physical or chemical properties over extended periods of time.<sup>2–3</sup> Moreover, the usefulness of these particles in biological applications, however, will require much more than mere water solubility. The stability of these nanoparticles in high ionic strength environments becomes very important. Nevertheless, water based synthesis of nanoparticles is beset with problems as a result of ionic interactions, which are typically overcome by using low reactant concentrations<sup>4</sup> (about  $5 \times 10^{-4} \text{ M}$ ) or because the synthesis is carried out in the presence of stabilizers that are subsequently difficult to remove.<sup>5</sup> In contrast, particles synthesized in organic solvents can be made at relatively high concentrations<sup>6</sup>

(up to 1 M reactant) with a predefined size and shape<sup>7,8</sup> and with improved monodispersity as compared to those prepared in aqueous solutions. Such particles are, however, water immiscible, which limits their range of application. Hence, phase transfer to aqueous solutions was used. Several routes for chemical reduction of hydrogen tetrachloroaurate (III) for preparing gold colloids have been evolved in the past few decades. The classic citrate reduction method has been extensively used for the generation of aqueous solutions of gold colloids with very narrow size distribution. Biphasic syntheses were performed to produce organic soluble gold colloids (<5 nm). Recently, Au nanoparticles with a high colloidal uniformity were prepared in aqueous solution and organic systems by reducing gold salts with *o*-anisidine.<sup>9</sup> In addition, a variety of Au nanoparticles was synthesized using ascorbic acid, oxalic acid, or hydrazine as the reducing agents, and it was found that the reactivity and concentration of the reducing agents have a significant effect on the size and dispersity of the metal nanoparticles.<sup>1</sup> Many molecules such as pyrrole,<sup>10</sup> aniline,<sup>11</sup> thiophene, or substituted molecules<sup>12,13</sup> can be oxidized

\* Corresponding author. Tel.: +914565227555. Fax: +914565227779. E-mail: kanalaphani@gmail.com.

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and polymerized to conducting polymers when they are used as reductants to prepare gold nanoparticles. Several chemical approaches have been developed to prepare nanocomposites of metallic NPs and conducting polymers. Generally, these follow one of two routes: (a) where the monomer or polymer acts as a reductant for the metal, yielding the nanocomposite in powder or thin film forms or (b) preparation of the NPs followed by either chemical polymerization around the particles or dispersion of the NPs in a polymer matrix.

Among the thiophene class of compounds, terthiophene and 3,4-ethylenedioxythiophene (EDOT) are examples of such reductants. Recently, terthiophene coated magnetic nanoparticles were produced and self-assembled into uniform spherical aggregates through  $\pi$ - $\pi$  interactions.<sup>14,15</sup> A water soluble terthiophene derivative was used as a reductant for the reduction of HAuCl<sub>4</sub> to prepare Au NPs, wherein terthiophene was oxidatively coupled into sexithiophene in the reaction.<sup>12</sup> The synthesis of regioregular poly(3-hexylthiophene) stabilized gold nanoparticles was accomplished using a room temperature, two-phase, one-pot reaction involving the reduction of tetrachloroauric acid by sodium borohydride in the presence of regioregular poly(3-hexylthiophene)s.<sup>16</sup> In the course of our investigations, we found that EDOT reduces HAuCl<sub>4</sub> to gold nanoparticles while also undergoing oxidation to form an insoluble mass in aqueous medium. The oxidation potential of EDOT is close to that of terthiophene, which makes it possible for it to be used as a reducing agent in the preparation of Au nanoparticles.<sup>14</sup> In the meantime, Li et al. have reported studies on the self-assembly of gold nanoparticles prepared using EDOT as a reductant in tetrahydrofuran solutions with alkylamines as stabilizers.<sup>14,17</sup> They concluded that by using XPS (a) there was a formation of Au nanoparticles, (2) the -C-O-C- unit in EDOT was intact without ring opening during oxidation, and (3) as-formed PEDOT was coated on the surface of AuNPs, as also supported by the red-shift of the surface plasmon absorption. Although EDOT was capable of reducing gold salt, the resultant nanocomposite could not be dispersed in solvents for further use in any applications. Hence, they resorted to refluxing a gold salt solution with EDOT and long-chain alkylamine stabilizers at 120 °C for several hours in an organic solvent like tetrahydrofuran. This procedure led to the formation of a self-assembled structure as a consequence of ordered aggregation.<sup>14</sup> The formed PEDOT, being insoluble in water, forced AuNPs to aggregate and sediment. In spite of the fact that these self-assembled structures can be deposited as thin films on solid substrates, achieving aqueous dispersions of Au<sub>nano</sub>-PEDOT is not possible since the stability is offered by alkylamines only in an organic solvent. However, there is a caveat here: PEDOT in its oxidized state is not soluble in aqueous medium. To be able to achieve an aqueous dispersion, (a) PEDOT polymer solubility in aqueous medium needs to be promoted and (b) the positive charge on the oxidized PEDOT should effectively be compensated by a water soluble macromolecular negatively charged species. We work with a premise that the surfactants/polymeric stabilizers like cetyltrimethylammonium bromide, sodium dodecylsulfate, polyvinylpyrrolidone, and sodium polystyrenesulfonate can serve these purposes. Among these, polystyrenesulfonate is known to act as (a) a solubility enhancer for EDOT, (b) a dispersion stabilizer and solubilizing agent for the PEDOT polymer and AuNPs, and (c)

an effective dopant<sup>18</sup> for the formed PEDOT, to be able to bring about aqueous compatibility of the AuNPs and stability against a high ionic strength environment. It is well-known that among various dopants known in the conducting polymer literature, poly(styrenesulfonate) increases the solubility of both EDOT and PEDOT, rendering it processible in water.<sup>19</sup> Although Mayer and Mark<sup>20</sup> prepared AuNPs in the presence of protective polymers including PSS<sup>-</sup>, their results showed that PSS<sup>-</sup> is not as effective as other polymers having a hydrophobic backbone in stabilizing smaller AuNPs. In recent years, PEDOT has become commercially important as a dispersion in aqueous poly(styrenesulfonic acid) for industrial applications because of its remarkable stability and possibility of synthesizing both chemically and electrochemically.<sup>21</sup>

Herein, we report a one-pot synthesis of highly stable AuNPs in aqueous solutions using EDOT as a reductant and PSS<sup>-</sup> as a dopant for PEDOT and as a particle stabilizer. In this work, the swelling and expandability of a PEDOT/PSS composite<sup>18</sup> are taken advantage of to allow enhanced direct contact with the aqueous solutions. It is found that the reducing ability of EDOT plays a major role during the formation of AuNPs. In this work, we employ the pH of the synthesis medium as a parameter to control the reducing ability of EDOT and follow AuNP formation spectrophotometrically. Studies also include aspects relating to stability in environments of high ionic strength and acid/base. The first results of the dependence of the reducing ability of EDOT on the type of the stabilizer and pH of the medium are also discussed briefly. Remarkably, the AuNPs thus prepared (protected by a sheath of PEDOT/PSS<sup>-</sup>) were found to effectively catalyze activation of the reduction of 4-nitrophenol to 4-aminophenol in the presence of excess NaBH<sub>4</sub> with an apparent rate constant that is significantly higher than those reported using other systems.<sup>22-24</sup> Earlier, metal nanoparticles stabilized by dendrimers,<sup>22</sup> thermosensitive polymer gels,<sup>23</sup> and  $\beta$ -D-glucose<sup>24</sup> have been reported to be catalytically active toward the reduction of nitrophenol. The work presented here is the first report of a PEDOT based Au nanocomposite aqueous dispersion acting as a catalyst.

## Experimental Procedures

**Materials and Methods.** 3,4-Ethylenedioxythiophene (EDOT) (Aldrich), HAuCl<sub>4</sub>·3H<sub>2</sub>O (Aldrich), sodium 4-polystyrenesulfonate (Aldrich), cetyltrimethylammonium bromide (Ranbaxy), sodium dodecylsulfate (Ranbaxy), polyvinylpyrrolidone (Sisco), hydrochloric acid (Ranbaxy), sodium hydroxide (Ranbaxy), sodium chloride (Ranbaxy), potassium chloride (Ranbaxy), sodium nitrate (Ranbaxy), 4-nitrophenol (Ranbaxy), and sodium borohydride (Merck) all of analytical grade were used as received. Aqueous solutions were prepared using Milli-Q water of 18 M $\Omega$ .

The UV-vis absorption spectra of the colloidal dispersions were collected on a Cary 500 scan UV-vis-NIR spectrophotometer with incident light normal to the 1 cm path length quartz cuvette. Spectra were collected between the wavelengths of 200 to 1100 nm. XRD pattern of the Au-PEDOT (precipitate) was recorded in a PANalytical diffractometer system Model PW3040/60 X'pert PRO operating

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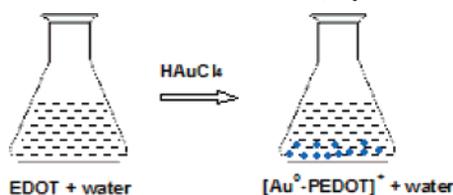
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## Scheme 1. Formation of Au-PEDOT (Sky Blue Precipitate)



with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) generated at 40 kV and 20 mA. Scans were done at  $3^\circ \text{min}^{-1}$  for  $2\theta$  values between 20 and  $90^\circ$ .

TEM examination of the samples was carried out with a Philips CM200 microscope working at 200 kV. A single drop of the aqueous solution of the Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> dispersion was placed onto a copper grid coated with a carbon film (400-mesh). The grid was left to dry in air for several hours at room temperature. The selected area electron diffraction (SAED) was taken at an accelerating voltage of 200 kV. For infrared and Raman spectroscopic measurements, a Thermo-Electron Corp. FT-Raman module (InGaAs detector and Nd:YVO<sub>4</sub> laser operating at 1064 nm) coupled with a Nexus 670 model FT-IR spectrometer (DTGS detector) was used.

The hydrodynamic diameter of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> was determined by the dynamic light scattering method at 25 °C with a light scattering photometer (Brookhaven Instruments (BI-200SM) with a He/Ne gas laser). A measurement time of a minimum of 5 min was allowed for setting and stabilizing of the sample before the first data points were obtained. All solutions were filtered using appropriate filters before the light scattering measurements (0.1 and 0.45  $\mu\text{m}$  MillexVV).

The catalytic reduction reaction was carried out in a standard quartz cell with a 1 cm path length and about 3 mL volume. The procedure entailed mixing excess NaBH<sub>4</sub> (15 mM) with a 4-NP (0.1 mM) solution in water in the quartz cell. Mixing leads to a color change from light yellow to green–yellow. The absorption spectra were recorded immediately after the addition of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> (10  $\mu\text{L}$  of 0.5  $\mu\text{g}$  of Au in aqueous dispersion) with a time interval of 50 s in a scanning range of 200–600 nm at 25 °C.

## Results and Discussion

We begin with a description of the synthesis of Au-PEDOT with and without stabilizers. The characterization of these new dispersions was performed with UV–vis spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared/Raman spectroscopy, and the results of studies on stability and catalytic activity are discussed in the following sections.

**Au-PEDOT System.** A slow addition of an aliquot of 250  $\mu\text{L}$  of HAuCl<sub>4</sub> ( $2.5 \times 10^{-4}$  M) to a solution containing EDOT ( $1 \times 10^{-2}$  M) yields initially a deep sky blue precipitate (Scheme 1). As its oxidation potential is sufficient to reduce Au<sup>3+</sup> to Au<sup>0</sup>, EDOT reduces HAuCl<sub>4</sub> to Au<sup>0</sup> and in turn undergoes oxidative polymerization to PEDOT, poly(3,4-ethylenedioxythiophene). The precipitate is a composite of Au<sup>0</sup> particles in the PEDOT matrix. Precipitation occurs as PEDOT is insoluble in aqueous media and the formed Au<sup>0</sup> particles are surrounded by water insoluble PEDOT, in consonance with the observation of Li et al.<sup>14</sup> of polymer capped AuNPs. The precipitate was washed several times with Milli-Q water and acetone and dried under vacuum. The dry sample of the composite was characterized by powder X-ray diffraction analysis to confirm the formation of a crystalline phase. The XRD pattern of the Au-PEDOT (precipitate) clearly shows the diffraction peaks at  $38.43$ ,  $44.60$ ,  $64.91$ ,  $77.73$ , and  $81.91^\circ$  corresponding to the (111), (200), (220), (311), and (222) lattice planes (Figure 1). These features corroborate the *fcc* structure of Au in Au-PEDOT formed in the previous synthesis. No peaks corresponding to PEDOT were observed.

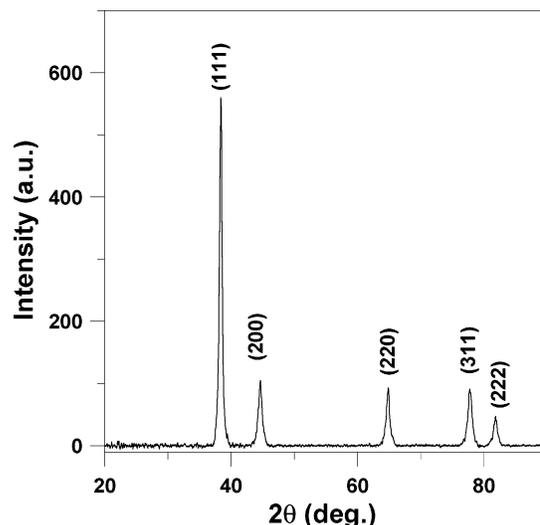


Figure 1. X-ray diffraction pattern of Au-PEDOT sky blue solid.

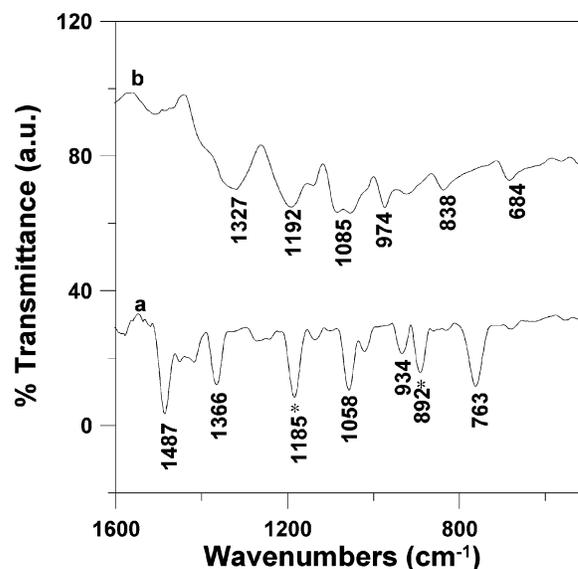


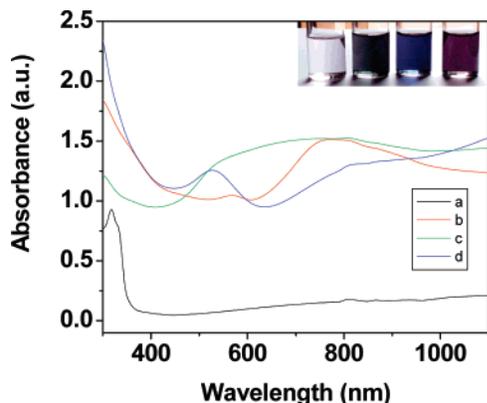
Figure 2. FT-IR spectra of (a) pure EDOT monomer and (b) Au-PEDOT sky blue solid.

The FT-IR spectrum of pure EDOT (Figure 2a) shows bands at 1185 and  $895 \text{ cm}^{-1}$  attributed to the =C–H in-plane and out-of-plane deformation vibrations, respectively. These two bands are found to be absent for the sky blue precipitate that is formed upon the oxidation of EDOT by the action of Au<sup>3+</sup> (Figure 2b). This clearly indicates the formation of PEDOT in oxidized form by  $\alpha$ – $\alpha'$  coupling.<sup>25</sup> The other band at  $1327 \text{ cm}^{-1}$ , due to C–C and C=C stretching of quinoidal structure, originates from the thiophene ring. Further, the vibration bands at 974, 835, and  $684 \text{ cm}^{-1}$  are due to a –C–S bond in the thiophene ring, whereas vibrational bands at 1192 and  $1085 \text{ cm}^{-1}$  are assigned to stretching in the –C–O–C– bond.<sup>26</sup>

**Synthesis of Au<sub>nano</sub>-PEDOT in the Presence of Various Stabilizers.** To obtain stable aqueous dispersions of Au<sub>nano</sub>-PEDOT, its synthesis in the presence of various stabilizers was attempted. It is well-known that AuNPs can be stabilized using a variety of polymeric and monomeric surfactants, charged and uncharged.<sup>1</sup> The dispersions prepared using these stabilizers exhibited different colors as displayed in Figure 3 (inset). Among

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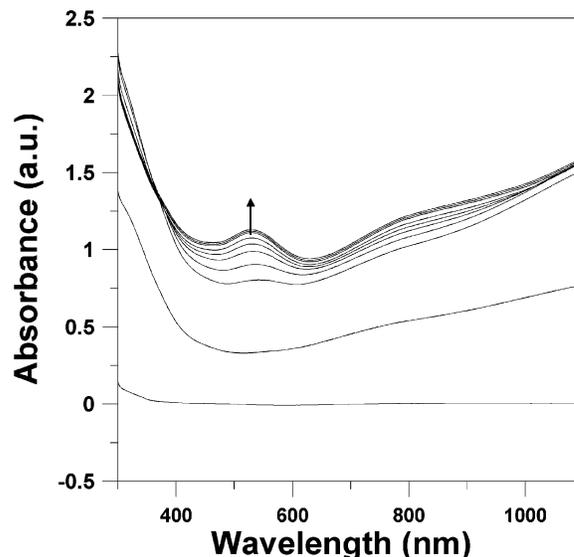
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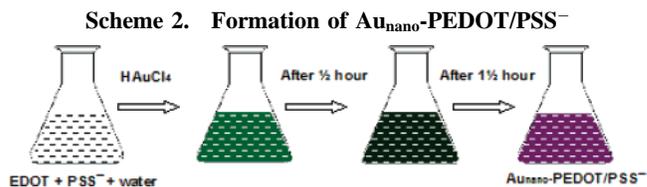
**Figure 3.** UV-vis spectra of AuNP dispersions synthesized using various stabilizers: (a) CTAB (black line), (b) SDS (red line), (c) PVP (green line), and (d) Na-PSS (blue line). (The photograph in the inset shows different colors of the corresponding dispersions).

the monomeric surfactant-type (cationic) stabilizers employed, cetyltrimethylammonium bromide (CTAB) at concentrations above its critical micelle concentration (cmc) was found to inhibit oxidation of EDOT by  $\text{Au}^{3+}$ , thereby preventing AuNP formation. With the other stabilizers, viz. sodium dodecylsulfate (anionic) and polyvinylpyrrolidone, the absorbance peak at 525 nm was negligibly small, although the solutions turned green and blue, respectively. Dodecylsulphate ( $\text{DS}^-$ ), being anionic, has been reported to form a pseudo-complex with EDOT.<sup>25</sup> It is also known to increase EDOT solubility in water from 11 to 73 mM, shift its electro-oxidation to lower anodic potentials, and stabilize the cation radicals formed upon the oxidation of EDOT.<sup>22</sup> The interaction of  $\text{AuCl}_4^-$  with several monomers has been examined previously by a number of groups,<sup>9,10,11,14</sup> and in some cases, the polymer was produced separately and then reacted with  $\text{AuCl}_4^-$ .<sup>16</sup> 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 AuNPs into PEDOT/PSS<sup>-</sup>. EDOT is partially soluble in water at room temperature (14 mM) but dissolves well in solutions containing surfactants like SDS (ca. 73 mM), molecular encapsulants like cyclodextrin<sup>27</sup> (26 mM), and polyelectrolytes like polystyrene-sulfonate (PSS<sup>-</sup>) (90 mM).<sup>28</sup> The improved solubility of EDOT is due to the formation of a pseudo-complex similar to the ones reported by Sakmeche et al.<sup>25</sup> Polyvinylpyrrolidone (PVP) is a well-known stabilizer for AuNPs, and reaction of EDOT with  $\text{AuCl}_4^-$  in its presence leads to the formation of a blue dispersion. This indicates that EDOT is oxidized by  $\text{Au}^{3+}$ . However, due to broad absorption of the resultant oxidized PEDOT, the plasmon band of AuNPs is masked in the UV-vis absorption spectrum (Figure 3). Such observations have been reported, for example, in the case of polyaniline-Au nanocomposites,<sup>11</sup> whereas PSS<sup>-</sup> showed strong absorbance at 525 nm (violet) and above 700 nm, corresponding to the plasmon resonance of AuNPs 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 synthesis of  $\text{Au}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> aqueous dispersion in this work entails the reduction of  $\text{HAuCl}_4$  using EDOT in the presence of PSS<sup>-</sup>. Briefly, EDOT ( $1 \times 10^{-2}$  M) was dissolved in 25 mL of water along with 1% Na-PSS (w/v) under continuous stirring. Complete dissolution of Na-PSS and the presence of



**Figure 4.** UV-vis spectra obtained during the formation of AuNPs at different time intervals after the addition of  $\text{HAuCl}_4$  to the solution containing EDOT and Na-PSS. (Spectra were collected every 15 min until no change in absorbance at 525 and 700 nm was observed).



EDOT ensures formation of a pseudo-complex analogous to that reported in the case of EDOT- $\text{DS}^-$ <sup>25</sup> and ter- and semi-thiophene-PSS.<sup>12</sup> Then, an aliquot of 250  $\mu\text{L}$  of  $\text{HAuCl}_4$  ( $2.5 \times 10^{-4}$  M) was added slowly to the previous solution. Immediately, the initially colorless solution changed to bright green, and as the reaction was allowed to proceed for over 30 min, it turned dark brown and gradually to violet, indicating complete reduction of  $\text{Au}^{3+}$  to the  $\text{Au}^0$  state (the pH of the EDOT-PSS<sup>-</sup> solution was measured to be 6.0 and 3.0 after the addition of  $\text{HAuCl}_4$ ) (Scheme 2).

The formation of AuNPs was followed by UV-vis spectroscopy at various time intervals (Figure 4). Absorption at 525 nm was due to the plasmon resonance of AuNPs (violet) in the size range of  $>3$  nm,<sup>29,30</sup> and broad absorption above 700 nm was due to the oxidized PEDOT. After the addition of  $\text{HAuCl}_4$ , absorption peaks at 525 nm and above 700 nm developed and increased gradually with time. This indicated the formation of AuNPs with concomitant EDOT oxidation occurring simultaneously as shown by the broad absorption above 700 nm that is attributable to polaronic and bipolaronic states of oxidized (doped) PEDOT.<sup>31</sup> Further, to analyze the doped state of PEDOT in the  $\text{Au}_{\text{nano}}$ -PEDOT/PSS<sup>-</sup> nanocomposite, FT-Raman spectroscopy was employed (Figure 5), as it has proven to be useful for studying the doping processes in the conjugated polymers.<sup>25,32,33</sup> The most intense band at  $1416\text{ cm}^{-1}$  was assigned to the symmetric stretching mode of  $-\text{C}=\text{C}-$  bond, whereas the less intense one at  $1531\text{ cm}^{-1}$  is characteristic of a

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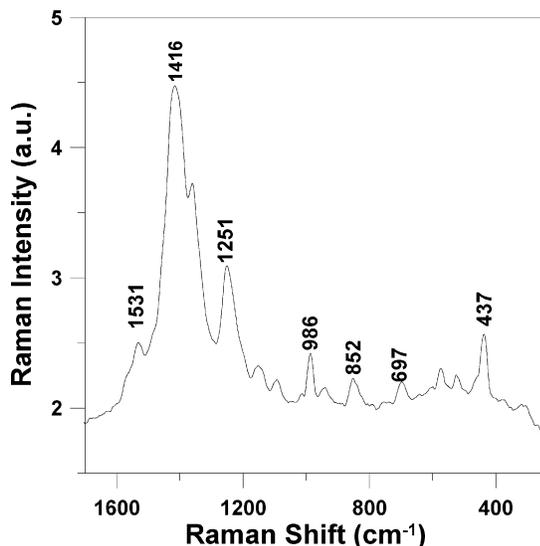


Figure 5. FT-Raman spectrum of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$ .

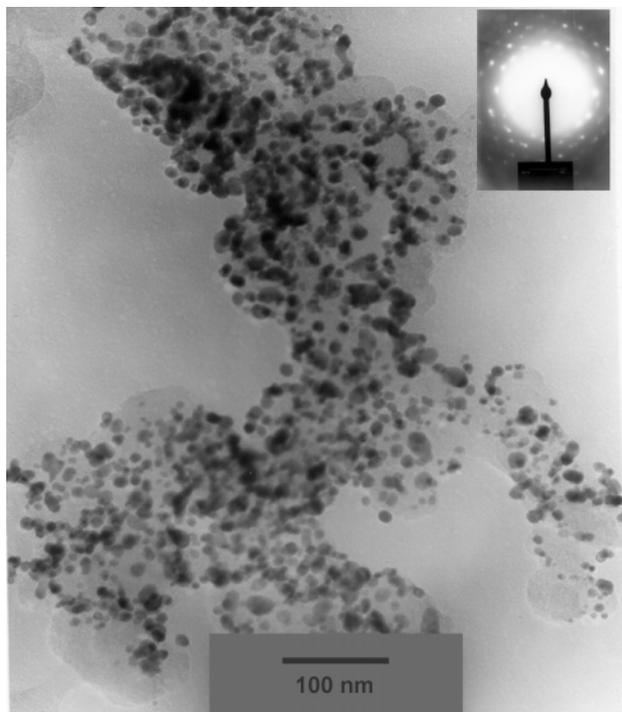


Figure 6. Transmission electron microscopy and selected area diffraction pattern (inset) of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  composite.

$\text{—C=C—}$  asymmetric stretching vibration, in accordance with the results reported in refs 30 and 33. Other weaker bands at 1251, 986, and  $697\text{ cm}^{-1}$  are attributed to the  $\text{—C—C—}$  inner ring bond,  $\text{—C—C—}$  asymmetric bond, and  $\text{—C—S—C—}$  bond, respectively. All these spectral data clearly show that PEDOT in the  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite is in a highly doped state.<sup>32</sup>

The morphology and size distribution of AuNPs were determined by transmission electron microscopy by placing a drop of the aqueous solution of the  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  dispersion onto a copper grid coated with a carbon film. A typical TEM image of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  presented in Figure 6a shows the polydisperse nature of the particles and the presence of a number of aggregates. Since the present work is concerned with metal particle–polymer nanocomposite dispersion, a more appropriate technique like dynamic light scattering (DLS)<sup>22</sup> was employed here. While the TEM measurements are sensitive only

to the electron-dense metal particle, the DLS measurements are sensitive to the size of the whole nanocomposite. The hydrodynamic diameter of the nanocomposite particle should then include the dimensions of the PEDOT/PSS<sup>-</sup> protecting layer, and DLS should reveal the structure of the nanocomposite. Values of an average hydrodynamic diameter of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$ ,  $\text{Au}_{\text{nano}}\text{-PEDOT/DS}^-$ , and  $\text{Au}_{\text{nano}}\text{-PEDOT/PVP}$  were measured to be  $26.3 \pm 1.5$ ,  $45.3 \pm 3.6$ , and  $220.0 \pm 0.5$  nm, respectively.

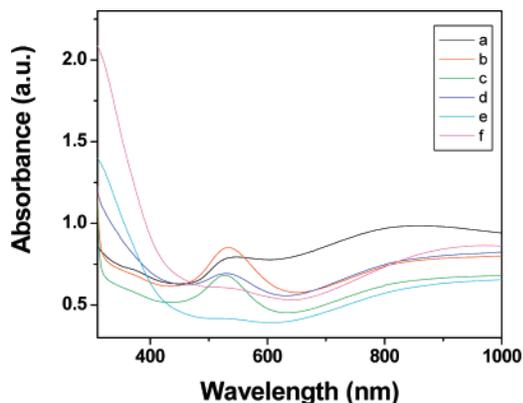
To clarify the crystal structure of  $\text{Au}_{\text{nano}}$  in the nanocomposite, selected area electron diffraction (SAED) measurements were carried out (inset in Figure 6). The spherical spot-like electron diffraction pattern of  $\text{Au}_{\text{nano}}$  shows the polycrystalline nature of the Au nanoparticles in the composite.

A discussion of the mechanism of formation and stabilization is in order now. It is reasonable to think that PSS<sup>-</sup> alone could act as the protecting agent if  $\text{Au}^{3+}$  is reduced by a reducing agent like  $\text{NaBH}_4$ . However, the dispersions thus prepared were not stable as shown by gradual destabilization that is in agreement with the observations of Mayer and Mark.<sup>20</sup> They found that the negatively charged poly(sulfonates) like PSS<sup>-</sup> are less suitable stabilizers for gold colloids in comparison with the poly(styrenesulphonic acids). They reasoned that the interaction of the negatively charged poly(sulfonates) with the gold surface necessary for stabilization might be less favored, whereas in the case of PEDOT/PSS<sup>-</sup> as a stabilizer, the interaction of  $\text{AuCl}_4^-$  with the reductant EDOT is through oxidative coupling of EDOT by the action of  $\text{HAuCl}_4$ .  $\text{HAuCl}_4$ , being a strong oxidant, can completely oxidize both the EDOT monomer and its polymer, PEDOT. In the PEDOT/PSS<sup>-</sup> used in the present work, the polymeric counteranion, poly(styrenesulfonate) (PSS<sup>-</sup>), is in excess with respect to the positively charged PEDOT chain. The molar ratio of the monomer units of EDOT/PSS<sup>-</sup> is reported to be about 0.8:1.<sup>34</sup> The colloidal particles of PEDOT/PSS<sup>-</sup> are negatively charged, which stabilizes them in aqueous media and are in a highly swollen state.<sup>18</sup> This presumably leads to the formation of a non-stoichiometric soluble polyelectrolyte complex around the gold nanoparticle.

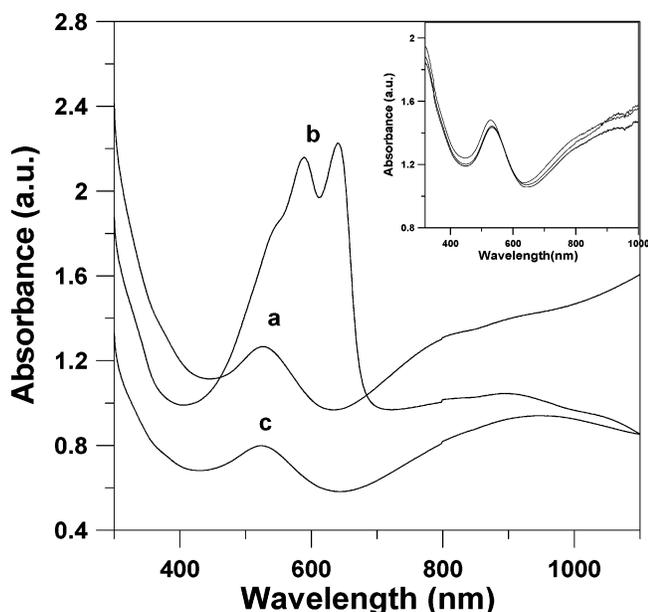
**Role of Solution pH in the Synthesis of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  Nanocomposites.** As seen from the previous discussion, EDOT oxidation and the reduction of  $\text{Au}^{3+}$  to  $\text{Au}^0$  are interdependent. As there are no reactive protons involved in its oxidation, EDOT chemistry/electrochemistry is apparently not pH dependent. However, in as yet unpublished work, we observed that EDOT oxidation depends on the added electrolyte and/or solution pH. At pH values  $>6$ , the oxidation of EDOT becomes difficult as observed through linear sweep voltammetric studies carried out from  $-0.3$  to  $1.0$  V (saturated calomel electrode, SCE). The oxidation peak potential was found to shift to more anodic values with increasing pH, indicating that the oxidation process is slowed down.

Figure 7 presents the absorption spectra obtained at different pH values ranging from 2 to 8. As can be seen from the spectra, the plasmon resonance peak of AuNPs is noticeable only for reduction in a pH range of 3–5. As the pH increases beyond 5, the intensity gradually decreases to finally disappear totally at pH 8. These results can be rationalized using the behavior of EDOT oxidation. In aqueous solutions, thiophene oxidation takes place at high oxidation potentials, and the nucleophilic attack by the solution  $\text{OH}^-$  ions and water consumes the radical cations produced in the thiophene oxidation process, thus inhibiting the growth of the PEDOT polymer. Even whatever little PEDOT may have formed can undergo transformation to the reduced form. The cation radicals are compensated by the electrons

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**Figure 7.** UV-vis spectra of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  dispersion at different pH values ranging from 2 to 8. (a) 2 (black line), (b) 3 (red line), (c) 4 (green line), (d) 5 (blue line), (e) 6 (teal line), and (f) 8 (magenta line).



**Figure 8.** UV-vis spectra of (a)  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  dispersion, (b) after addition of 1 M NaOH to  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  dispersion, and (c) after addition of 1 M HCl to conditions in panel b. The inset shows the effect of concentration of NaCl up to 3M.

produced by the base.<sup>35</sup> Hence, pH conditions above 5 are not favorable for the oxidation of EDOT, and the latter cannot act as a reductant toward  $\text{Au}^{3+}$ . Thus, it is reasonable to select an optimum pH range of 3–5 for the synthesis of aqueous  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$ .

**Stability and Catalytic Activity of AuNPs in  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  Composite. (a) Effect of Externally Added Electrolytes.** The studies on the stability aspects of the AuNPs in the  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  composite involved comparison of the effect of addition of HCl and NaOH to the nanocomposite dispersion. It is intriguing that the color of the  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  aqueous dispersion changed reversibly between violet and blue and vice versa on the addition of NaOH and HCl, respectively. The pH of the corresponding solutions with a violet and blue color was measured to be 3.0 and 12.0. The absorption behavior of the nanocomposite under the previous two conditions is depicted in Figure 8. The absorption at 525 nm is found to be unaffected by the addition of HCl, whereas with the addition of

NaOH, the spectrum shows absorption at 530 nm (shoulder) and 589 and 641 nm (sharp). The latter two peaks are assigned to the neutral form of PEDOT.<sup>36</sup> The shoulder at 530 nm, associated with plasmon resonance band of AuNPs, is slightly red-shifted, probably due to aggregation occurring in alkaline solution. It is known that PEDOT becomes neutral upon the addition of NaOH<sup>35</sup> and may tend to aggregate in solution. This process is found to be reversible between pH 3.0 to 12.0 for several cycles of the addition of acid and base. A possible explanation might be the color response of PEDOT in the  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite particle to the acid/base environment since oxidized PEDOT is sky blue and turns deep blue on the addition of NaOH. In this context, it is also important to mention a similar observation reported by Shiraishi et al.<sup>37</sup> in the case of gold nanoparticles protected by 3-mercaptopropionic acid (MPA). The color of the dispersion of MPA-Au changed from red to purple by the addition of HCl and returned to red by the addition of NaOH. This reversible response was attributed to synchronized changes between dispersion and assembly of MPA- $\text{Au}_{\text{nano}}$ , governed by a combination of two factors: van der Waals attraction and Coulombic repulsion forces among charged particles and shown by TEM. Applying similar arguments to the case under consideration in the present work, at pH 3.0, PEDOT chains are positively charged and experience Coulombic repulsion. At pH 12, however, PEDOT chains are mostly neutral, and hence, the stabilization due to electrostatic repulsion is weakened and may lead to an ordered aggregated structure of  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite particles. However, in the absence of detailed TEM examination, these aspects remain speculative at this point in time. It can also be deduced that the reversible color change appears to be the effect of acid/base on the properties of PEDOT, as reported by Jang et al.<sup>31</sup> in the case of PEDOT nanorods, in turn changing the environment around the embedded AuNPs.

It is well-known that base treatment of conducting polymers usually leads to lower conductivities.<sup>35,38,39</sup> In the case of PANI and PPy, this reduced conductivity is due to deprotonation of the conducting polymer backbone that leads to dedoping without any change in the oxidation state of the OCP backbone. Li and Qian<sup>40</sup> have extensively reported on the electrochemical aspects of the base treatment of conducting polymers in which they observed counteranion exchange with  $\text{OH}^-$  in the basic solution upon the base treatment of PPy and redox reactions with the basic solution.<sup>41</sup> In the case of thiophene based conducting polymers such as PEDOT, the precise role played by the base is more difficult to rationalize, as there are no acidic (labile) protons available on the polymer backbone. However, like PPy and PANI, base treatment of PEDOT also resulted in an essentially nonconductive state, the mechanism of which remains unclear. While Foot et al.<sup>35</sup> postulated that treatment of polythiophene films with ammonia led to disproportionation of the cation radicals on the polymer backbone, Li and Qian showed that a redox reaction takes place between polythiophene and basic solution that results in the reduction (dedoping) of polythiophene.<sup>41</sup>

The usefulness of the  $\text{Au}_{\text{nano}}\text{-PEDOT/PSS}^-$  nanocomposite in biological applications, however, will require much more than just water solubility. The stability of this nanocomposite in a high ionic strength environment is shown in Figure 8 (inset). The normalized absorption spectra of the  $\sim 6$  nm  $\text{Au}_{\text{nano}}\text{-PEDOT/}$

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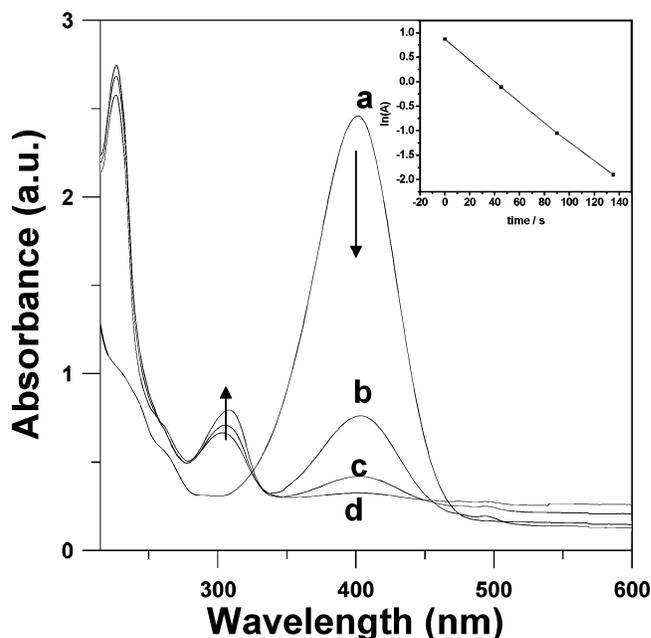
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PSS<sup>-</sup> nanocomposite at various concentrations of NaCl shown in Figure 8 (inset) display the characteristic plasmon band absorption of AuNPs at 525 nm. The spectra recorded up to a NaCl concentration of 3 M are indistinguishable. The same behavior was exhibited in the presence of KCl and NaNO<sub>3</sub> (data not shown). This increased particle stability may arise due to the difficulty of the electrolyte anion in causing detachment of a macromolecular protecting agent<sup>42</sup> like PEDOT/PSS<sup>-</sup> from the particle surface.

Apart from the previous observations, the Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> composite aqueous dispersion was stable in a wide range of pH values from 3 to 12, according to the simple visual observation of the color of the solution and the appearance of the absorption band at 525 nm for over several months. They did not show any color change and signs of aggregation and precipitation. In addition, the dispersions were stable even after vigorous centrifugation at a speed of 6000 rpm. However, on complete removal of water, a violet partially transparent solid was obtained that could be redispersed in water without any change in the adsorption characteristics. This indicates that Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> can be isolated as a solid and redissolved in aqueous solutions without any change.

**(b) Catalytic Activity of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup>.** Having discussed the synthesis and structure of the composite particles, we now turn to explore the catalytic properties of these particles. One of the main objectives in nanoscience is to catalyze reactions or activate chemical bonds that are otherwise not feasible. Catalysis with AuNPs is now an expanding area, and a large number of new catalytic systems for various reactions are now being explored.<sup>43</sup> With this in mind, we have shown the application of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> for the reduction of 4-nitrophenol (4-NP). In this experiment, the absorption peak of 4-NP (0.1 mM) undergoes a red-shift from 317 to 400 nm immediately upon addition of aqueous NaBH<sub>4</sub> solution (15 mM) with an associated color change from light yellow to yellow-green (corresponding to the generation of a 4-nitrophenolate anion). The absorption peak at 400 nm remains unchanged for extended periods of time, showing that even an excess concentration of NaBH<sub>4</sub> is unable to bring about reduction of a 4-nitrophenolate anion. Interestingly, the addition of very small aliquots (10 μL) of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> dispersion (containing 0.5 μg of Au) 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 gradual disappearance of the absorption peak at 400 nm after the addition of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup>, with a concurrent appearance of two new peaks at 300 and 230 nm, corresponding to the formation of 4-aminophenol. A control experiment was performed to ascertain if the reduction is activated by PEDOT/PSS instead of AuNPs in the nanocomposite Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup>. An aliquot of PEDOT-PSS dispersion (Bayer) (20 μL) alone was added to 4-NP (0.1 mM) and NaBH<sub>4</sub> (15 mM) aqueous solution. No change in the color and position of the absorbance was observed. Thus, this clearly demonstrates that the reduction is catalyzed by AuNPs in Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup>. This catalytic activity arises due to access for the reactant to the surface of the AuNPs probably because of the porous nature (hydrogel) of the stabilizing shell around the gold nanoparticles in the nanocomposite. In all these experimental runs, the concentration of NaBH<sub>4</sub> was chosen to exceed the concentration of 4-nitrophenol by far. Thus, the kinetics of the reduction reaction can be treated as pseudo-first-order in the



**Figure 9.** Successive UV-vis spectra of the reduction of 4-nitrophenol by Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> solution, collected at various time intervals after the addition of the gold nanocomposite. (Inset: corresponding plot of ln(A) vs time for the disappearance of 4-nitrophenol absorption at 400 nm upon reduction in the presence of excess borohydride in solution.)

**Table 1. Comparison of Apparent Rate Constants for Reduction of 4-Nitrophenol at Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> with Reported Catalyst Systems and Their Corresponding Hydrodynamic Diameter Values**

composition	hydrodynamic diameter (nm) measured by DLS	apparent rate constant (s <sup>-1</sup> )
PNIPA gels <sup>23</sup>	250 (approximately)	3.5 × 10 <sup>-3</sup>
β-D-glucose network <sup>24</sup>		6.54 × 10 <sup>-3</sup>
PPI-dendrimers <sup>22</sup>	21.0 ± 4.5	13.2 × 10 <sup>-3</sup>
PAMAM-dendrimers <sup>22</sup>	18.2 ± 5.0	3.7 × 10 <sup>-3</sup>
Au <sub>nano</sub> -PEDOT/PSS <sup>-</sup> (this work)	26.3 ± 1.5	4.39 × 10 <sup>-2</sup>

nitrophenol concentration, which simplifies the present analysis. More importantly, the large excess of NaBH<sub>4</sub> takes into account the slow but noticeable hydrolysis of this reagent at pH 10. Because the concentration of Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> particles in the system is very low, the absorption spectra of 4-nitrophenol are not disturbed by the presence of the gold nanocomposite. The process of reduction was monitored by measuring UV-vis absorption recorded at different times, *t*. A good linear relation with time (i.e., ln(A) vs time plot) was obtained (Figure 9, inset). Figure 9 displays a typical example of such an analysis that yields a value for the rate of 4-NP reduction reaction to be 4.39 × 10<sup>-2</sup> s<sup>-1</sup>. This value may be compared with those reported for AuNPs prepared using various encapsulants such as PNIPA gels,<sup>23</sup> β-D-glucose networks,<sup>24</sup> PPI-dendrimers, and PAMAM-dendrimers<sup>22</sup> (Table 1). Aqueous dispersions containing 0.5 μg of Au, prepared using the other stabilizers, also showed catalytic activity, although varying in their rates (Table 2). It is observed from the table that, of all the stabilizers, PEDOT/PSS<sup>-</sup> is associated with a relatively high rate of the reaction, whereas it is least with PVP. Increase of the hydrodynamic diameter of the dispersions clearly shows an increase in the aggregate size. It is appropriate to consider here the results of Esumi et al.<sup>22</sup> on the catalytic activity of dendrimer protected AuNPs, wherein they observed that the rate constant is affected by the size of the dendrimer adsorbing on the gold nanoparticles. The aggregate

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**Table 2. Au-PEDOT Nanocomposites Prepared Using Various Stabilizers, Corresponding Hydrodynamic Diameters in an Aqueous Dispersion, and Apparent Rate Constants for the Reduction of 4-Nitrophenol at 25 °C**

composition	hydrodynamic diameter (nm)	apparent rate constant (s <sup>-1</sup> )
Au <sub>nano</sub> -PEDOT/PSS <sup>-</sup>	26.3 ± 1.5	4.39 × 10 <sup>-2</sup>
Au <sub>nano</sub> -PEDOT/SDS <sup>-</sup>	45.3 ± 3.6	2.26 × 10 <sup>-2</sup>
Au <sub>nano</sub> -PEDOT/PVP	219.9 ± 0.5	1.37 × 10 <sup>-3</sup>

size and morphology are likely to play an important role in deciding the rate of the reaction, and these issues warrant detailed studies.

In our studies, while the gold content of the dispersion (ranging from 0.25 to 1.0 μg) did not show a great influence on the value of the apparent rate constant, the stabilizers showed a variation, dispersion with PVP being the least catalytic among the stabilizers used. Recently, various groups have shown a catalytic activity of metal nanoparticles toward the reduction of 4-nitrophenol.<sup>22–24,44</sup> In all these cases, catalysis of the Au nanoparticles was attributed to the efficient electron transfer from a BH<sub>4</sub><sup>-</sup> ion to nitro compounds mediated by the nanoparticles. An increased driving force for electron transfer may arise due to a shift in the energy level in the presence of electron-injecting species like borohydride.<sup>44</sup> It is interesting to bring here a few examples wherein the polymer supported platinum and rhodium<sup>45,46</sup> and palladium<sup>47,48</sup> catalysts have been used to carry out hydrogenation reactions and fuel cell reactions. Our current work is directed towards the exploration of chemoselective hydrogenation of nitro compounds<sup>49</sup> and reactions with relevance to electrocatalysts for direct methanol and borohydride fuel cells, using Au-PEDOT

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nanocomposites with interfacially present borohydride. Investigations into the role of PEDOT as a support for the catalytic metal nanoparticles vis-à-vis carbon and metal oxides are our ongoing interest.

## Conclusion

In summary, this study is significant for several reasons: (a) we report a one-pot synthesis of highly stable Au nanoparticles using EDOT as a reductant and polystyrenesulfonate (PSS<sup>-</sup>) as a dopant for PEDOT and particle stabilizer. (ii) AuNPs in Au<sub>nano</sub>-PEDOT/PSS<sup>-</sup> are highly catalytic toward the reduction of 4-nitrophenol. It is observed from the table that, of all the stabilizers, PEDOT/PSS<sup>-</sup> is associated with a relatively high rate of the reaction, whereas it is the least with PVP. The hydrodynamic diameter of the nanocomposite estimated from DLS measurements increases in the order PSS < DS < PVP. an increase in the hydrodynamic diameter of the dispersions clearly shows an increase in the aggregate size. (iii) The color of the Au-PEDOT/PSS<sup>-</sup> aqueous dispersion changed reversibly between violet and blue and vice versa on addition of NaOH and HCl, respectively. (4) The nanoparticle dispersion also exhibited very high stability in the presence of 3.0 M NaCl. The nanocomposite presented in this work belongs to the class of polymer supported catalysts for solution-phase synthesis, if extended to other catalytic reactions.

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