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Gold Nanoparticle Linking to Polypyrrole and Polythiophene: Monolayers and Multilayers

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The interaction between gold nanoparticles in apolar solvents and polypyrrole or polythiophene films of varous types is investigated. Regular and full monolayers and multilayers are produced via solution processing using gold nanoparticles and soluble polypyrrole or poly(3,4-ethylenedioxythiophene). The new layered materials, characterized by cyclic voltammetry, UV−vis spectroscopy, AFM, and conductivity, are uniform, stable, and mechanically robust. Gold/polymer multilayer conductivities ($3-6 \times 10^{-2}$ S cm^{-1}) are comparable with those previously reported for other multilayered gold nanoparticles of the same size.

1. Introduction

Hybrid materials containing inorganic nanoparticles and π-conjugated polymers[1] have unique properties, and their application in electronic and optoelectronic devices (such as solar cells, light emitting diodes, electronic memories, etc.) is being explored intensively.[2] In particular, for fabrication of flexible light-emitting diodes, a high surface contact with the polymeric emitter results in lower turn-on voltage and higher quantum efficiency. Many of these devices involve understanding and controlling the electron transfer at the interface between conjugated polymer and metal electrodes. Thus, the interfacial phenomena between conducting polymers and metals are an area of intense research for fabricating efficient devices.

Among nanoparticles, gold nanoparticles (AuNPs) are particularly investigated.[3] Simple methods are known for the production of AuNPs with narrow size distributions, and stable solutions of particles can be produced.[4] The unique catalytic properties of AuNPs for carbon monoxide and methanol oxidation have recently attracted considerable interest, and the electrocatalytic activity for methanol oxidation reaction at the anode in methanol oxidation fuel cells has recently been explored.[5]

Conducting polymers (CPs) may be practical materials for such catalysts in fuel cells since they provide both the required electrical conduction and the mechanical support. Among CPs, polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDT) are excellent for synthesis of nanostructured materials and devices since they exhibit electrical, electronic, magnetic, and optical properties similar to metals or semiconductors while keeping flexibility, ease of processing, and modifiable electrical conductivity. Moreover, air stability in the doped conducting state is a very appreciated peculiar property.

PPy/AuNPs composites have recently been prepared electrochemicallly in water solutions of pyrrole and citrate-stabilized 5-nm gold nanoparticles,[6] and analogous composites have previously been prepared chemically,[7] but no compound of definite composition has been reported yet. More recently,[8] a polymer memory device based on a conjugated polymer (poly(3-hexylthiophene)) and gold nanoparticles has been produced. The polymer may interact electrostatically with gold nanoparticles by means of substituents, such as in the case of a poly(fluorene-*co*-1,4-phenylene) sulfonate used for stabilization of AuNPs via anion interaction of the sulfonate ends with the gold surface.[9]

Yet in all the reported cases, no specific interaction between gold and the polymer conjugated backbone has been considered. After our recent discovery that pyrrole- and thiophene-based oligomers are strong aggregating agents of

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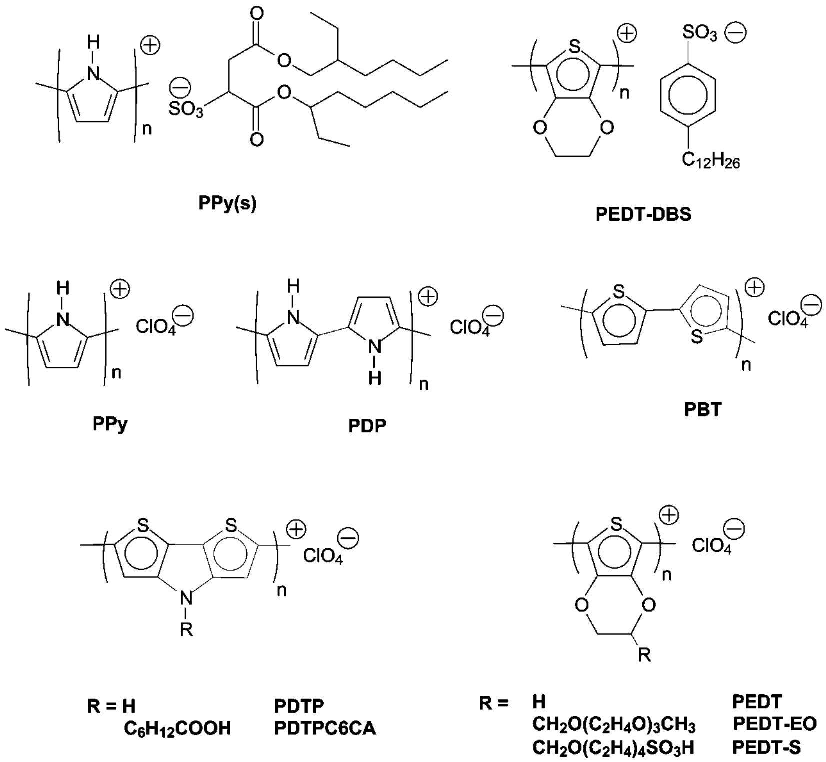
Chart 1



AuNPs in apolar solvents,[10] we have undertaken a study of the interactions between AuNPs with films of polypyrroles and polythiophenes with the purpose of producing new and clearly defined structures. The polymers, shown in Chart 1, are soluble PPy and PEDT for solution coating and a series of insoluble polypyrroles and polythiophenes, as such or with substituents, for electrochemical deposition. The new materials have been produced in the form of mono- and multilayers on electrode surfaces and characterized by cyclic voltammetry, UV−vis spectroscopy, atomic force microscopy (AFM), and conductivity.

2. Experimental Section

2.1. Chemicals and Reagents. Toluene solutions of gold nanoparticles (AuNPs) stabilized by 0.05 M tetraoctylammonium bromide (TOABr) were prepared in 10^{-2} M gold concentration according to Schiffrin.[11] On the basis of TEM analysis, the average particle size of the Au clusters is 5 ± 1 nm. AuNPs were routinely used in 10^{-3} M gold concentration in toluene (or CH_2Cl_2 when required) in the presence of 0.05 M TOABr as stabilizer.

Nafion (5% solution in lower aliphatic alcohols + 10% water, 1200 equiv weight, from Aldrich) was diluted in EtOH to a concentration of 1%.

Soluble polypyrrole di(ethylhexyl)sulfosuccinate (PPy(s)), with a conductivity of 10^{-4} S cm^{-1}, was prepared according to the literature,[12] and dispersions used for monolayer formation were 0.1% in $CHCl_3$ and 0.01% in acetone. Soluble poly(3,4-ethylenedioxythiophene) dodecylbenzenesulfonate (PEDT−DBS) was prepared as described below, and dispersions used for monolayer formation were 0.1% in $CHCl_3$. Soluble poly(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}-2,3-dihydrothieno-[3,4-*b*][1,4]dioxine) (PEDT-EO),[13] poly(4-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-2-ylmethoxy)-butane-1-sulfonic acid) sodium salt (PEDT-S),[14] and 6-ferrocenyl hexanethiol[15] were produced according to the literature.

Acetonitrile was reagent grade (Uvasol, Merck) with a water content of <0.01%. The supporting electrolyte, tetrabutylammonium perchlorate (Bu_4NClO_4), and all other chemicals were purchased from Fluka.

Synthesis of Poly(3,4-ethylenedioxythiophene) Dodecylbenzenesulfonate (PEDT−DBS). A 140 mg portion of 3,4-ethylenedioxythiophene (EDT, 1 mmol) and 640 mg of dodecylbenzenesulfonic acid (DBSA, 2 mmol) are dissolved in 20 mL of methanol. Then a solution of 1.7 g of ferric toluenesulfonate (2.5 mmol) in 20 mL of methanol is added, and the resulting dark blue solution is allowed to react for 2 days. The solvent is then evaporated, and the solid is washed several times with water (to remove iron salts and excess DBSA), dried, and dissolved in chloroform. The solution is filtered from insoluble polymer tosylate, and the solvent, evaporated. Then the solid is washed again with water and dried under vacuum, yielding ~50 mg of chloroform-soluble polymer.

2.2. Substrates and Film Deposition. Transparent gold-coated electrodes were prepared from ITO/glass electrodes (20 Ω sq^{-1} from Merck-Balzers) by treatment with 3-mercaptopropyl trimethoxysilane (MTS),[16] which provides on both sides a surface bearing free thiol groups, and subsequently with 10^{-3} M toluene solution of AuNPs for 18 h, which deposited a monolayer of them on the thiol surface.

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ITO layers of ∼100 nm thickness were vacuum-deposited on KBr disks following a previously published procedure.[17]

Gold electrodes were 1 × 4 cm sheets. They were treated for 1 min with hot sulfochromic acid ($K_2Cr_2O_7$ in 96% H_2SO_4), then carefully washed with Milli-Q water and dried.[18]

Poly(3,4-ethylenedioxythiophene) (PEDT),[19] poly(bithiophene) (PBT),[20] poly(pyrrole) (PPy),[21] poly(dipyrrole) (PDP),[22] poly(dithienopyrrole) (PDTP), poly(*N*-carboxyhexyldithienopyrrole), PDTPC6CA[23] films were electrodeposited as the perchlorate salt according to the literature. Typical polymer thin films were electrodeposited from 0.01 M monomer (0.1 M for Py and EDT; 0.001 M for DP) in acetonitrile plus 0.1 M Bu_4NClO_4 by CV cycling up to the relevant oxidation potential until the passage of the required charge. Then the electrode was carefully washed, and the CV was analyzed in a monomer-free solution at a scan rate of 0.1 V s^{-1}, extracted in the oxidized form, washed, and dried.

The build-up of multilayers was performed according to the methodology introduced by Decher,[24,25] that is, by dipping the electrodes alternately into the solutions of the two components. Dipping times were 5 min for polymer dispersions and 15 min (unless differently stated) for gold nanoparticle solutions. After each immersion step, the substrate was carefully washed and dried in air. The layer build-up was monitored by UV−vis spectroscopy and cyclic voltammetry.

2.3. Apparatus and Procedure. *Electrochemistry and Spectroscopy.* Experiments were performed at room temperature under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrodes were 0.8 × 2.5 cm indium−tin oxide (ITO) sheets (∼20 Ω/square resistance, from Balzers, Liechtenstein).

Electronic spectra were obtained from a Perkin-Elmer Lambda 15 spectrometer. FTIR spectra were taken on a Perkin-Elmer 2000 FTIR spectrometer.

AFM and Prophilometry. AFM was performed in noncontact mode in air at room temperature using a DME DS 95-200 Dualscope STM equipped with noncontact mode silicon tips. Multilayer thicknesses were determined with an Alphas-step IQ prophilometer from KLA Tencor.

Conductivity. Measurements of the sheet resistance of the multilayers were performed on the float-glass side of the substrate with the four-probe technique using a Kuliche-Soffa head (U.K.) with a Keithley 220 programmable current source and a Keithley 195A digital multimeter.

3. Results and Discussion

3.1. New Polymers and Substrates. *Synthesis and Characterization of PEDT−DBS.* The literature reports fully undoped soluble oligo(3,4-ethylenedioxythiophene) (in fact, the hexamer as average) prepared from Ni(0) reaction with the 2,5-dibromo monomer.[26] A soluble conducting poly(3,4-ethylenedioxythiophene) has also been prepared following an easier route as the DBS salt using methanol and ferric toluenesulfonate as solvent and oxidizing agent, respectively, in the presence of excess DBSA.[27] Unfortunately, the characteristics of the polymer, such as UV−vis spectral properties, average degree of polymerization (DP), and DBS content, were not given. For this reason, we have established a detailed procedure for the preparation of a soluble polymer of this type by the ferric chloride route, as reported in the Experimental Section, and here, we give its characterization.

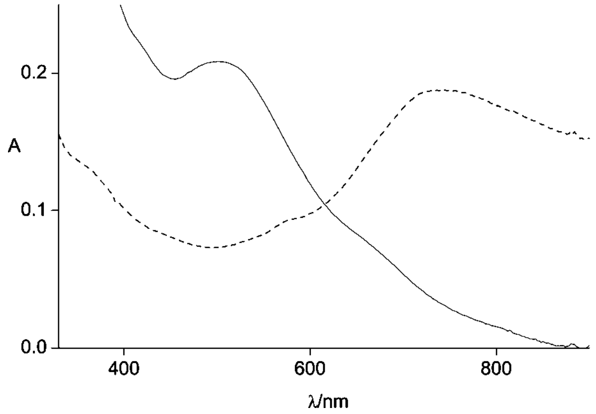

Figure 1. UV−vis spectra of PEDT−DBS dispersion in $CHCl_3$ (- - -) before and (—) after reduction with hydrazine.

NMR spectra of the polymer in $CHCl_3$ could not be run, since the samples are strongly paramagnetic (due to the polymer radical cation form), but FTIR, UV−vis, electrochemistry, and conductivity were performed successfully.

FTIR of the polymer agrees with oligo-EDT cations with DBS as counter anion. The spectrum in the KBr pellet, in addition to the strong sulfonate band at 1200 cm^{-1}, is dominated by the strong bands of the ethylenedioxy moieties (C−O−C stretching mode) at 1060 cm^{-1}[28] and the methylene stretching band at 2930 cm^{-1} of the dodecyl chains of the anion (DBS) and acid (DBSA). From the intensity of the latter bands and calibration with a dodecylthiol/EDT 1:1 molar mixture, the (DBS + DBSA)/EDT molar ratio was calculated as 1.5. Assuming for PEDT a regular doping level of 0.35,[29] the analysis indicates the presence of roughly one DBSA molecule per EDT unit in the polymer. The DBSA component constitutes a lipophilic shell of the polymer chains, which gives them the observed solubility in chloroform.

The blue $CHCl_3$ dispersion of the as-prepared (oxidized) polymer (Figure 1) is reduced with hydrazine to violet (λ_{max} = 510 nm). From this value, the linear relationship of energy

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and inverse of DP obtained for a series of EDT oligomers[30] allows the evaluation of DP = 9 for the average oligomeric mixture. Regarding this point, it must be pointed out that, due to the ferric salt used in this synthesis, methanol may not be an innocent solvent, possibly controlling oligomer formation and DP through end-capping reactions.

Dissolved in acetonitrile/CH_2Cl_2 + 0.1 M Bu_4NClO_4, the oligomeric mixture is reversibly reduced at $E^0 = \sim -0.3$ V (close to the value for PEDT), therefore confirming the electroactivity of the polymer and, hence, its integrity.

Bulk PEDT−DBS displays a conductivity of 5×10^{-6} S cm^{-1}. This value is very low compared with that of the usual forms of PEDT (e.g., 400−450 S cm^{-1} for PEDT-tosylate[31]), but may be easily accounted for by the high DBSA content of the material.

Nafion Monolayers on ITO Electrodes. For this investigation, ITO electrodes were used either bare or treated with Nafion solutions, which form a strongly adsorbed polyanionic monolayer apt to graft the positively charged CPs chains. In fact, we have recently reported[32] that very strongly bound and uniform Nafion monolayers are formed from a 1% ethanol solution on bare gold and platinum surfaces, with a surface mass of 1.0 ± 0.1 μg cm^{-2}. Following the reported procedure, a Nafion monolayer is similarly formed on ITO, as evidenced by the subsequent adsorption of iron phenanthroline complex from acetonitrile solution and by FTIR. When the Nafion-treated ITO electrode is dipped into 10^{-3} M $Fe(o\text{-}phen)_3^{2+}$ perchlorate in acetonitrile for 15 min, the surface is covered with a pink layer. From the absorbance at 510 nm (0.005 au for two sides) and the extinction coefficient of 12 000 M^{-1} cm^{-1}, a coverage of 2×10^{-10} mol cm^{-2}, corresponding to a dense monolayer, was calculated. No similar adsorption is detected on bare ITO under the same conditions.

To determine the thickness of the Nafion film, transmission FTIR analysis was performed on an ITO layer vacuum-deposited on a KBr crystal disk. After dipping the ITO side for 5 min in 1% Nafion solution and washing, the spectrum displays the strong and dominating band at 1220 cm^{-1} due to the antisymmetrical stretching mode of Nafion−CF_2− moieties[33] with an absorbance of 0.006 au. By comparison with a film of known thickness, a monolayer of 1.1 μg cm^{-2} was calculated; that is, in practice, the same coverage obtained previously on gold and platinum surfaces.

3.2. Gold Nanoparticles on Polypyrrole Layers. A previous investigation of AuNPs aggregation in solution has clearly indicated that oligopyrroles are the best polyconjugated aggregating agents for gold nanoparticles.[10] Thus, it was expected that efficient monolayering of AuNPs could be obtained on polypyrrole layers. The layers were characterized by CV in acetonitrile + 0.1 M Bu_4NClO_4 for the CP component and by SP spectroscopy for the AuNPs component. The results are reported below, and the obtained electrochemical and optical parameters are summarized in Table 1.

Table 1. CP Redox Charges, Q_r, and Gold SP Absorbance A[a] for Different AuNP-Modified ITO/Polymer Surfaces

polymer	Q_r/mC cm^{-2}	*A*/a.u.
Nafion/PPy(s)	0.04	0.10
PDP	0.20	0.10
Nafion/PPy	1.0	0.04
Nafion/PEDT−DBS	0.03	0.10
PEDT	0.30	0.05
PDTP	0.30	0.02
PDTPC6CA	0.30	0.02
PBT	0.30	0.05
PEDT-EO	0.03	<0.01
Nafion/PEDT-S	0.03	<0.01

[a] Two-side absorbance after 15 min exposition.

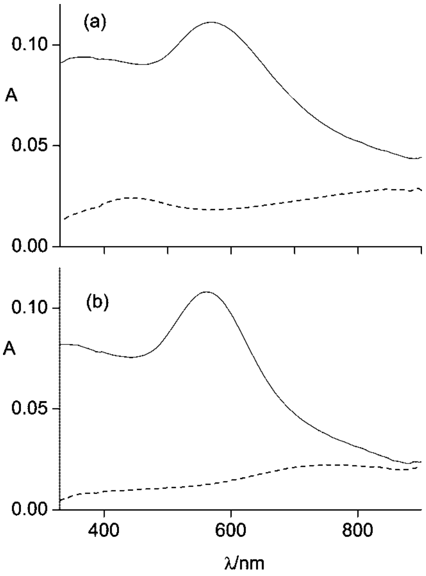

Figure 2. UV−vis spectra of (a) PPy(s) and (b) PEDT−DBS monolayer on ITO/Nafion (- - -) before and (—) after AuNPs adsorption.

Polypyrrole Monolayers from Soluble Polypyrrole (PPy(s)). A Nafion monolayer on ITO has been used for adsorption of polypyrrole from dispersion. We have confirmed that PPy monolayers on ITO/Nafion are formed from soluble PPy (i.e., PPy(s)), as previously found on gold and platinum surfaces.[32] Such ITO/Nafion/PPy(s) monolayers display the CV of PPy with a reversible charge of 40 μC cm^{-2}, which is the same measured on Nafion-modified Au or Pt surfaces[32] and corresponds to a full monolayer.

AuNPs dissolved in CH_2Cl_2 are self-assembled on the ITO/Nafion/PPy(s) monolayer. In fact, the almost colorless film becomes blue and shows an additional absorption at ~570 nm (Figure 2a) due to the surface plasmon (SP) absorption of gold nanoparticles. A SP absorbance of 0.1 au is obtained after 15 min of exposure, corresponding to an optically evaluated AuNP coverage of $\sim 4 \times 10^{12}$ particles cm^{-2}. No such adsorption is observed on a PPy-free ITO/Nafion surface.

Polypyrrole Films from Dipyrrole (PDP). Films were electrodeposited with the passage of 2.5 mC cm^{-2}. The reversible charge involved in the CV cycle of the film from −1.0 to 0.0 V is ~200 μC cm^{-2}. This value is that for a thin film, ~5 times thicker than one monolayer (see above).

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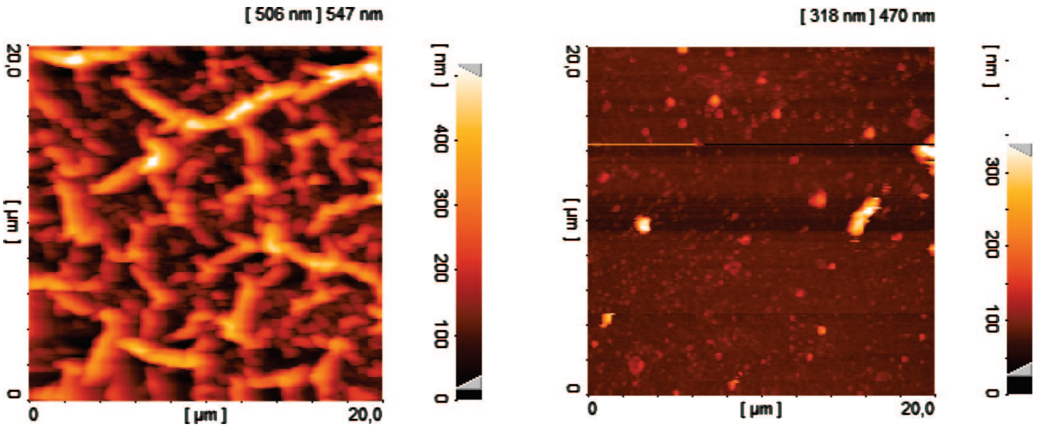

Figure 3. AFM topography images of (left) ITO/PPy and (right) ITO/PDP surfaces.

This PDP thin film on ITO after treatment with AuNPs solution in CH_2Cl_2 becomes blue and shows the SP band of gold nanoparticles at ~610 nm, which is similar to the monolayer above. The bathochromic shift of the band (from 570 to 610 nm) may be attributable to the thicker polypyrrole ground. The same gold treatment using a toluene solution does not cause any adsorption of AuNPs, which points to a dissociative step of the PDP perchlorate or of the TOABr layer on the AuNPs as a prerequisite for adsorption.

Polypyrrole Films from Pyrrole (PPy). Deposited with 5 mC cm^{-2}, the PPy films store a reversible charge of ~1 mC cm^{-2}. We were quite surprised that in this case, no significant AuNPs adsorption was observed. This result may be attributed to a strong inhomogeneity of polymer deposition on the bare ITO surface, in contrast with the behavior of a platinum surface and similar to that reported for anodic polymerization of aniline on ITO.[34] Atomic force microscopy measurements (Figure 3) clearly reveal the difference in surface morphology between PPy and PDP films electrodeposited on ITO. The ITO substrate is covered with a uniform PDP film, whereas a PPy film shows a regular, rod-like surface structure extending over the whole substrate. In fact, it has been clearly shown in the literature[35] that during electrochemical polymerization of pyrrole on ITO anodes, wrinkles are formed. This means that the polymer mass is concentrated in closed structures rather than disposed evenly over the electrode surface, and this accounts for the strongly decreased ability to coordinate gold nanoparticles.

The previously observed ability of alkyl chains on surface to promote polypyrrole deposition from pyrrole[36] has suggested that the use of a lipophilic monolayer would overcome the problem. As a matter of fact, if the ITO surface is primed with Nafion (i.e., a well-known hydrophobic polymer) before PPy electrodeposition, AuNPs are adsorbed regularly on the PPy film, showing the SP band with a noticeable intensity superimposed over the broad absorption of oxidized PPy.

3.3. Gold Nanoparticles on Polythiophene Layers. From the aggregation phenomena observed in solution,[10] it was clear that also thiophenes, such as terthiophene, 3,4-ethylenedioxythiophene, and dithienopyrrole, are good aggregating agents for gold nanoparticles. Thus, it was expected that efficient monolayering of AuNPs could be obtained on layers formed by polymers of such monomers. On the contrary, the presence of substituents is adverse to the aggregation process[10] so that gold nanoparticles should not link to PEDT-EO or PEDT-S layers.

We have also found that the use of CH_2Cl_2 instead of toluene for gold priming of the polymer layers, necessary for polypyrrole, is not required by the generality of polythiophenes so that both solvents may be used for adsorption with no significant difference. The results are reported below, and the obtained parameters are also summarized in Table 1.

PEDT−DBS Monolayers. The Nafion monolayer on ITO has been used for surface adsorption of PEDT−DBS. Monolayers are formed and display the same CV previously shown by a PEDT polysulfonate, such asPEDT-PSS,[31] with a reversible charge of 30 μC cm^{-2}.

The PEDT−DBS monolayer was treated with a TOABr-stabilized AuNP solution in toluene. After 15 min of exposure, the polymer monolayer becomes blue and shows an additional absorption at ~560 nm (Figure 2b) due to the SP absorption, with an absorbance value of ~0.1 au. The situation is very close to that of the PPy monolayer described above.

PEDT-EO and PEDT-S Monolayers. PEDT-EO monolayers are formed on bare ITO according to a published procedure[13] from a 0.1% dispersion of the polymer in CH_2Cl_2. Similarly, PEDT-S[14] forms monolayers on ITO/Nafion surfaces from a 0.1% dispersion of the polymer in water. The CVs of both store the same reversible charge Q_r = 30 μC cm^{-2}, which is comparable with the polypyrrole monolayers (see above).

The PEDT-EO and PEDT-S monolayers after treatment with AuNPs do show an additional absorption at ~550 nm, but the absorbance increase is modest (maximum values lower than 0.01 au). It is therefore confirmed that substituents at the EDT unit hinders to a great extent adsorption of gold nanoparticles.

Polythiophene Films. Differently from pyrrole, the electropolymerization of EDT as the perchlorate salt on ITO

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(either unmodified or Nafion-modified) produces films with a homogeneous surface morphology. A similar homogeneity is produced in the electropolymerization on unmodified ITO of other thiophenes, such as DTP, DTPC6CA, and BT.

Polymer films were deposited with the passage of a charge of 5 mC cm^{-2} (PBT requires a lower deposition charge, 1.5 mC cm^{-2}). The reversible charge involved in the CV cycles of the films from −1.0 to 0.4 V for PEDT, from −0.7 to 0.4 V for the DTP-based polymers, and from 0.0 to 0.9 V for PBT, is ~300 μC cm^{-2}, corresponding to the thickness of roughly 10 monolayers.

When exposed to AuNP solution, the PEDT film turns blue, showing the additional SP absorption of gold at ~570 nm. Similarly, the PDTP and PDTPC6CA films, with absorption maxima at 540 nm, and the PBT film, with absorption at 480 nm, upon treatment with AuNPs show enhancement of their blue color attributable to an additional absorption due to the SP band of adsorbed gold.

3.4. Kinetics of Gold Nanoparticle Adsorption on CPs Layers. It has been previously shown[10] that the presence of additional coordinating heteroatoms (such as oxygen or nitrogen) increases the adsorption ability of thiophene or pyrrole rings toward gold, therefore suggesting that heteroatom coordination is responsible for the heterocycle linkage. Only recently has the ability of gold(I) to activate inert alkenes[37] and 1,3-dienes[38] been evidenced and the formation of a gold(I)-diene complex been observed.[38] It is therefore conceivable that a similar interaction contributes to the formation of bonding between the gold particles and the conjugated diene moieties of the polypyrrole or polythiophene chains.

The results reported previously from solution[10] and here above on films (summarized in Table 1) show that among the investigated polyconjugated polymers, PPy and PEDT are the strongest ligands for AuNPs. To clarify the mechanism of gold adsorption, we have undertaken a kinetic analysis of monolayer formation between gold nanoparticles and these polymers in the soluble form.

First of all, we have found that the formation of a PPy or PEDT monolayer on an AuNPs-primed surface, such as ITO/MTS/AuNPs, is much faster than its inverse; namely, the adsorption of AuNPs on the polymer surface (see below). In practice, a limiting adsorption of the polymer is achieved in less than 2 min exposure. A convincing explanation is that the gold surface, exposed to a TOABr-free polymer dispersion, is not capped any longer by TOABr and, therefore, is much more reactive than the gold nanoparticles in a TOABr solution.

The adsorption of AuNPs on a polymer monolayer has been followed by spectral analysis of the SP maximum absorbance with time (see, for example, Figure 4) The adsorbance A follows a law of exponential saturation:

$$A = A_L[1 - \exp(-kt)] \qquad (1)$$

For AuNPs in toluene on a ITO/Nafion/PEDT−DBS monolayer, $k = 0.035$ min^{-1}, comparable with that obtained under the same conditions for a thiol-primed surface.[39] A limiting value of absorbance A_L of 0.1 is achieved. If we change the AuNPs solvent from toluene to CH_2Cl_2, which has a higher dielectric constant (2.4 for toluene vs 8.9 for CH_2Cl_2), the rate increases to $k = 0.10$ min^{-1}, which points to an ion dissociative process as the rate-determining step of the surface aggregation rate.

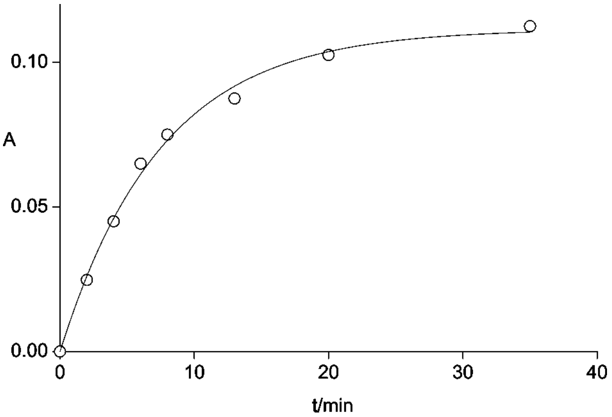

Figure 4. UV−vis kinetics (λ = 570 nm) of AuNPs adsorption on ITO/Nafion/PPy(s) monolayer.

AuNPs in CH_2Cl_2 are self-assembled on the ITO/Nafion/PPy(s) monolayer with a rate constant $k = 0.13$ min^{-1} and a limiting value of absorbance A_L of 0.1 (Figure 4). Since on a PDP film the process occurs at a comparable rate ($k = 0.15$ min^{-1}), it appears that the ion dissociative step concerns the TOABr shell rather than the counter anions (sulfonate or perchlorate) of the polymer layer.

It must be noted that the use of CH_2Cl_2 instead of toluene for gold decoration of CP surfaces is required only for polypyrroles, which indicates in H-bridging at the NH moiety the reason for the stronger linkage of the counter anion to the positively charged polymer.[40]

3.5. Stability and Reactivity of AuNPs Monolayers on CPs. The stability of the linkages between the heterocyclic rings of CPs and the gold nanoparticles has been tested using the substitution ability of alkylthiols. The polymer used for such tests was PPy(s). Thus, the ITO/Nafion/PPy(s)/AuNPs monolayer, exposed for 20 min to a 10^{-3} M solution of hexadecanethiol in EtOH and subsequently washed with EtOH and chloroform, after an initial ~10% loss of weakly bound particles does not show further losses. For comparison, the behavior of an ITO/MTS/AuNPs monolayer is the same. These results indicate that the gold nanoparticles are bound to the PPy substrate strongly enough that substitution by thiols does not take place.

In any case, extra thiol ligands are adsorbed onto the gold nanoparticles, and the amount of additional adsorption has been measured using a ferrocene-substituted thiol. CV of the ITO/Nafion/PPy(s)/AuNP monolayer, after exposure for 60 min to a 10^{-3} M 6-ferrocenyl hexanethiol solution in EtOH, shows in acetonitrile the reversible redox process of the ferrocene ends at $E^0 = 0.05$ V with a redox charge of 80 μC cm^{-2}. For comparison, the ITO/MTS/AuNPs monolayer,

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Table 2. Redox-Charge Increase per Layer, ΔQ_r; SP Absorbance Increase per Layer, ΔA;[a] and Conductivity, σ, for Different AuNPs/Polymer Multilayers at Different AuNP Deposition Times

polymer	dep time/min	$\Delta Q_r/\mu$C cm $^{-2}$	ΔA/a.u.	σ/S cm $^{-1}$
PPy(s)	15	80	0.10	
PPy(s)	60	120	0.18	6×10^{-2}
PEDT−DBS	15	100	0.10	
PEDT−DBS	60	120	0.16	3×10^{-2}

[a] Two-side absorbance.

with the same gold coverage and after the same treatment, shows the same ferrocene redox charge. These results indicate that the gold nanoparticles linked to the polypyrrole layer expose the same active area as a thiol-bound AuNPs monolayer.

3.6. Multilayers of Gold Nanoparticles and CPs. As reported above, PPy and PEDT display the strongest ability to coordinate AuNPs. Through alternation of these polymers in the soluble form and AuNPs on ITO/Nafion supports, regular multilayers have been built, whereas as expected, PEDT-EO and PEDT-S do not present any multilayer formation at all. Given the different rates of monolayer formation for polymer and nanoparticles (see above), multilayering has been performed at short times (5 min) for polymer adsorption and long times (15 or 60 min, unless differently stated) for AuNP adsorption.

Redox-charge increase per layer, ΔQ_r; SP absorbance increase per layer, ΔA; and conductivity, σ for different AuNPs-CPs multilayers at different AuNPs deposition times are summarized in Table 2.

PPy(s)/AuNPs and PEDT/AuNPs Multilayering. Through alternation of PPy(s) and AuNPs in CH_2Cl_2 (15 min), multilayers are regularly built. The progressive CVs and UV−vis spectra are displayed for the first three bilayers in Figure 5. A linear increase of PPy reversible charge (80 μC cm^{-2} per PPy layer) and SP intensity (0.1 au per AuNPs layer) is observed. The first monolayer of PPy stores a charge of 40 μC cm^{-2}, whereas the subsequent layers grow at a faster rate as a consequence of the increased roughness introduced by the gold particles.

If the deposition time of the AuNPs is increased from 15 to 60 min, which allows the maximum gold coverage, the rate of SP intensity is increased to 0.18 au per AuNP layer, and the rate of PPy reversible charge reaches 120 μC cm^{-2} per PPy layer; similarly, alternation of PEDT−DBS and AuNPs (in toluene) on ITO/Nafion for regular multilayers. A linear increase of SP intensity with the number of layers is observed, and the SP maximum shifts progressively from 560 to 610 nm. Also in this case, the first monolayer of PEDT stores a charge, which increases in subsequent layers (from 30 to 100−120 μC cm^{-2} per PEDT layer).

AFM imaging of the ITO/Nafion/(PPy(s)/AuNPs)$_5$ and ITO/Nafion/(PEDT−DBS/AuNPs)$_5$ multilayers, produced with 15 min exposure to AuNPs, displays uniform surfaces with a roughness of 8−10 nm. Domains are 100 and 80 nm wide, respectively. Both structures are robust enough to stand a standard sticky-tape test with no appreciable loss.

Anion Intercalation in Multilayering. During multilayer buildup, the counter anion compensating the positive charges of the PPy layers could, in principle, be sulfosuccinate from the PPy(s) dispersions or bromide from the AuNPs solution. To clarify this point, we have performed the CV analysis of the building process in a step-by-step fashion, looking at the presence and amount of the bromide anion, which displays an irreversible one-electron oxidation at $E_p = 0.40$ V under the used conditions.

The results of this analysis, shown in Figure 6, evidence that some bromide is present only after the AuNP treatment, the subsequent treatment with PPy(s) displacing it completely. Moreover, the amount of bromide, measured from its oxidation charge, is the same after any AuNP step and corresponds to ~5% of the PPy monolayer reversible charge

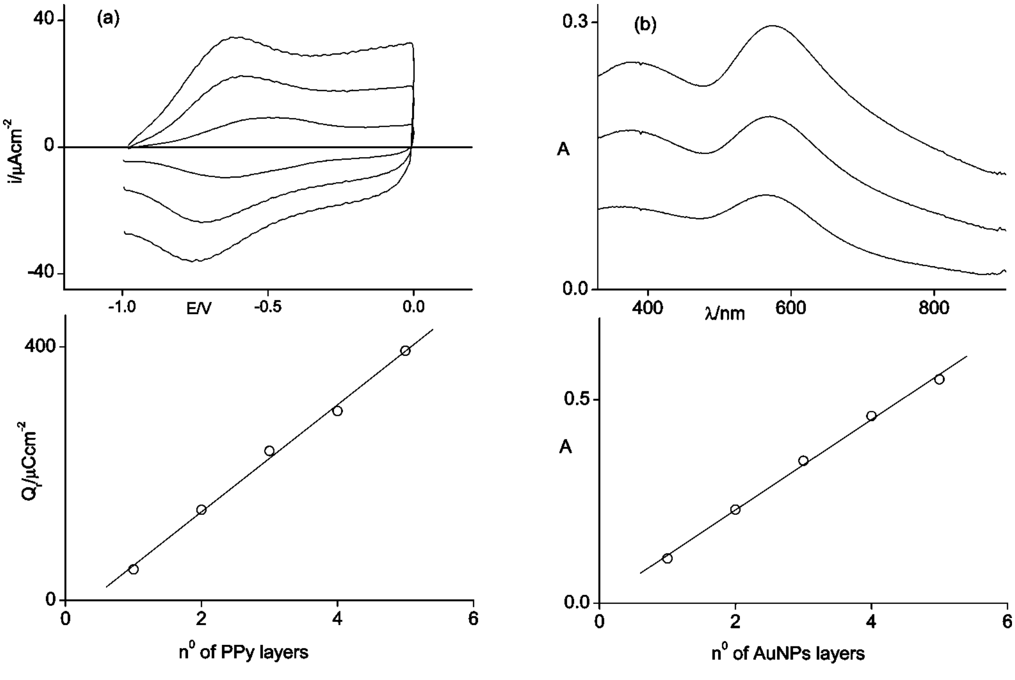

Figure 5. ITO/Nafion/(PPy(s)/AuNPs)$_n$ multilayers. Upper: (a) cyclic voltammograms and (b) UV−vis spectra for $n = 1−3$. Lower: (a) PPy(s) reversible charge and (b) SP absorbance at 570 nm as a function of n. CVs in acetonitrile + 0.1 M Bu_4NClO_4 at 0.1 V s^{-1}.

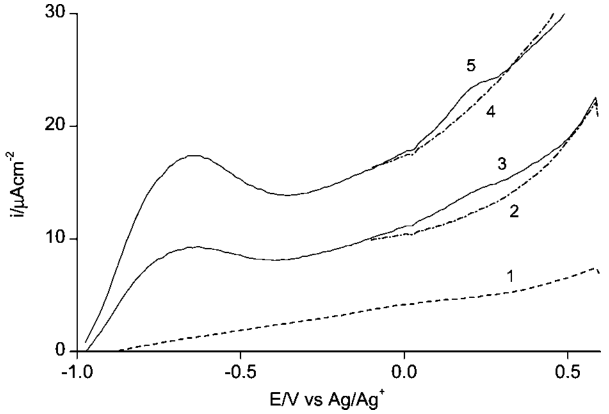

Figure 6. Linear-sweep voltammograms of (1) Pt/Nafion; (2) Pt/Nafion/PPy(s); (3) Pt/Nafion/PPy(s)/AuNPs; (4) Pt/Nafion/PPy(s)/AuNPs/PPy(s), and (5) Pt/Nafion/(PPy(s)/AuNPs)$_2$.

only. Moreover, since the charge of PPy measured at a switching potential of 0.6 V corresponds to ~0.50 electrons (pyrrole ring)$^{-1}$,[32] it is clear that the bromide participation is limited and confined on the outer layer facing the solution, probably associated with the exposed surface of the gold nanoparticles. It is therefore established that the intercalating anion in the PPy multilayer is sulfosuccinate. It is likely that in the PEDT multilayers, the corresponding sulfonate anion DBS covers the same role.

3.7. Conductivity of CPs/AuNPs Multilayers. Four-probe conductivity measurements on ITO/Nafion/(PPy(s)/AuNPs)$_5$ and ITO/Nafion/(PEDT−DBS/AuNPs)$_5$ structures, produced with 60 min of exposure to AuNPs, give surface resistivities of 4×10^6 and 9×10^6 Ω sq^{-1}, respectively. From the corresponding thicknesses of 40 and 45 nm, the bulk conductivities are 6×10^{-2} and 3×10^{-2} S cm^{-1}, respectively.

The corresponding MP4/AuNPs multilayer, where MP4 is the short nonconjugated tetrathiol pentaerythritol tetrakis(3-mercaptopropionate), displays a bulk conductivity of 5×10^{-2} S cm^{-1} [10]; that is, in practice, the same conductivity. This means that the presence of conjugation and even the oxidation state of the conjugated material do not influence the conductivity of these structures.

Considering that, for example, bulk PPy(s) displays a conductivity of 10^{-4} S cm^{-1}, the gold particles increase electron transport, but a limit of around 10^{-1} S cm^{-1} is somehow imposed on the conductivity, independently from the polymeric material linking the particles.

In a series of recent papers[41] the conductivity in polymer/AuNPs has been extensively treated. The conductivity values of the polymer-crossed clusters do not overcome values of 8×10^{-2} to 1×10^{-1} S cm^{-1}. After all these results, a limiting value of 10^{-1} S cm^{-1} for the conductivity appears to be operating not only in dithiol-linked but also in CPs-linked gold clusters.

Conclusions

Polypyrroles and polythiophenes are strongly aggregating agents of gold nanoparticles in apolar solvents so that new and clearly defined 2D structures (mono- and multilayers) have been obtained successfully.

Monolayers of gold nanoparticles on polypyrrole and polythiophene layers are as chemically stable and reactive as those formed on thiolated surfaces. Multilayers built from the two components by the layer-by-layer technique are regular and mechanically robust. The conductivity of these polymer-crossed gold clusters, around 5×10^{-2} S cm^{-1}, is high but essentially the same as clusters with nonconjugated organic linkers. Thus, the presence of a polyconjugated (either insulating or conductive, undoped or doped) linker does not modify electron transport, which appears to be controlled by the gold-polymer contacts. In any case, the realization of these structures has highlighted the possibility of using gold-(conducting polymer) nanostructured materials for the successful preparation of conducting surfaces as nanoelectric components.

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