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Redox-active films formed by electrochemical reduction of solutions of C_{60} and platinum complexes

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Electroreduction of a toluene–acetonitrile (4 : 1 v/v) solution of C_{60} and *cis*-$Pt(py)_2Cl_2$ in the presence of 0.10 M tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte produces a black, redox active film that coats the electrode surface. This film retains its redox activity when transferred to an acetonitrile solution that contains only the supporting electrolyte, 0.10 M tetra(*n*-butyl)ammonium perchlorate. The film has been characterized by infrared spectroscopy, laser desorption mass spectrometry, and XPS spectroscopy. The formation of this film is dependent on the platinum complex used as precursor and on the potential range utilized during film growth. No film growth is observed when $Pt(bipy)Cl_2$, $Pt(py)_2I_2$, *cis*-$Pt(PPh_3)_2Cl_2$ or *trans*-$Pt(py)_2Cl_2$ are used as precursors, but $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$ is a useful precursor which allows film growth at less negative potentials. Chemically prepared $C_{60}Pt_1$ is also electrochemically active when precipitated on a platinum electrode. The formation of an electroactive film from the electroreduction of C_{70} and *cis*-$Pt(py)_2Cl_2$ is also reported.

Introduction

Recent work from this laboratory has shown that the electrochemical reduction of fullerenes under specific conditions can lead to the deposition of redox-active films that adhere to the electrode surface and are insoluble in common organic solvents. Monitoring the electrochemical reduction of C_{60} in solution by cyclic voltammetry produces up to six, reversible, one-electron waves under optimal conditions.[1,2] These six waves, which are evenly spaced by *ca.* 400 mV, result from the stepwise filling of the triply degenerate t_{1u} orbital of C_{60}. Many covalent adducts of C_{60} have been observed to undergo successive one-electron reductions at potentials that are somewhat more negative than those of C_{60} itself.[3,4] However, the electrochemistry of one covalent adduct, $C_{60}O$, is remarkable because there is an additional wave at potentials in the vicinity of the second one-electron reduction of C_{60} itself.[5] With multiple redox cycles that scan through this added wave, there is continuous growth of the current and the formation of a brown film on the electrode surface.[6] This film is not soluble in common organic solvents, and strongly adheres to a number of different electrodes (gold, platinum, pyrolytic graphite, conducting tin oxide). The film formed by electrochemical deposition from $C_{60}O$ solutions has been shown to have the ability to store up to eight electrons per C_{60} unit.[7] A related film is formed when C_{60} (or C_{70}) is electrochemically reduced in toluene–acetonitrile (4 : 1 v/v) in the presence of a small amount of dioxygen.[8]

Two-component, redox active films are formed when toluene–acetonitrile solutions of C_{60} are electroreduced in the presence of transition metal complexes including: $Pd(NCPh)_2Cl_2$, $\{Pd(OAc)_2\}_3$, $Rh_2(O_2CCF_3)_4$, and $Ir(CO)_2Cl(p\text{-}NH_2C_6H_4CH_3)$.[9] Again these films are insoluble in common organic solvents and adhere to the electrode surfaces. Spectroscopic studies, particularly infrared absorption studies, show that intact C_{60} moieties are present in the films along with a transition metal component (Pd atoms, $Ir(CO)_2$ units, or $Rh_2(O_2CCF_3)_4$ molecules). The films generated from C_{60} and $Pd(NCPh)_2Cl_2$ (or $\{Pd(OAc)_2\}_3$) retain nearly-reversible redox activity when transferred to a solution that contains only supporting electrolyte. Studies of the effect of solvent and supporting electrolyte on the redox characteristics of this $C_{60}Pd_n$ film have shown that reduction of the layer is accompanied by migration of cations into the film and the re-oxidation results in the expulsion of cations from the films.[10–12] The basic $C_{60}Pd_n$ film itself is believed to consist of a network of $\cdots C_{60}Pd(C_{60}Pd)_nC_{60}Pd\cdots$ units in which the palladium centers are covalently bound to the fullerenes in η^2-fashion. Coordination of metal complexes in η^2-fashion is the most common means of covalent attachment to fullerenes.[13] Additional palladium atoms can form cross links between these chains, but the film must remain permeable to the entrance and exit of cations during redox cycling of the film. Treatment of the $C_{60}Pd_n$ films with triphenylphosphine in dichloromethane solution results in its dissolution and the formation of the well-characterized complex, $(\eta^2\text{-}C_{60})Pd(PPh_3)_2$.[14] Related $C_{60}Pd_n$ materials, also proposed to contain a $\cdots C_{60}Pd(C_{60}Pd)_nC_{60}Pd\cdots$ framework, have been prepared chemically by the reaction of C_{60} with $Pd_2(dba)_3$ (dba is dibenzylideneacetone).[15,16] Depending on reaction stoichiometry and subsequent thermal treatment, the composition of these materials is $C_{60}Pd_n$ where n ranges from 1 to 7.

Here we describe studies designed to obtain analogous $C_{60}Pt_n$ films through electrochemical deposition. Since platinum complexes are generally more robust than their palladium counterparts, we anticipated that such a $C_{60}Pt_n$ film would also display greater stability. Additionally, since $C_{60}Pt_n$, as an amorphous black solid, had been previously prepared by the reaction of C_{60} with $Pt(dba)_2$ in solution; there was ample precedent for the construction of such a film.[17,18] However, we found that the selection of a suitable platinum containing precursor complex was particularly important and that the resulting films were less stable than their palladium counterparts.

Results

Electrochemical studies of the formation and characterization of $C_{60}Pt_n$ films

Fig. 1 shows the results of cyclic voltammetric studies in 4 : 1 toluene–acetonitrile with tetra(*n*-butyl)ammonium perchlorate

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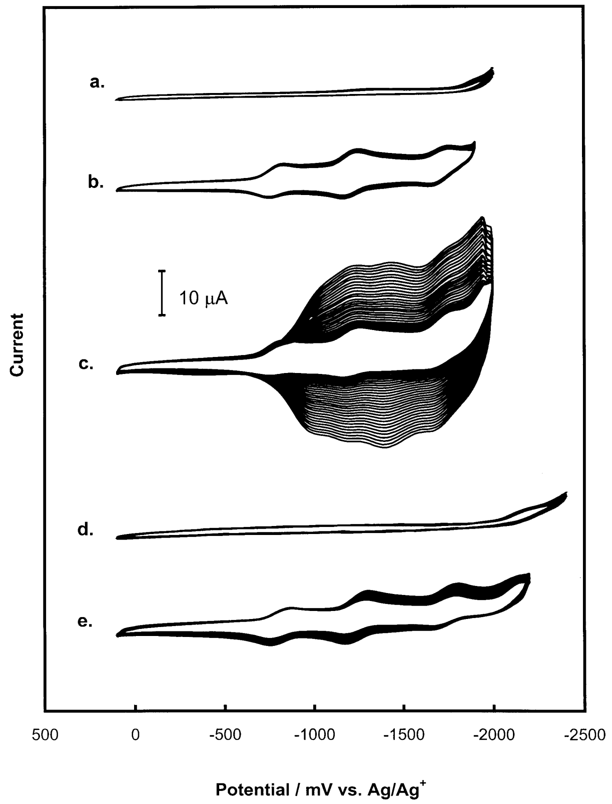

Fig. 1 Multicyclic voltammograms obtained for: a, 0.83 mM *cis*-Pt(py)$_2$Cl$_2$ (10 cycles); b, 0.35 mM C$_{60}$ (30 cycles); c, 0.35 mM C$_{60}$ and 0.83 mM *cis*-Pt(py)$_2$Cl$_2$ (30 cycles) with sweep termination at −2000 mV; d, 0.83 mM *trans*-Pt(py)$_2$Cl$_2$ (10 cycles); e, 0.35 mM C$_{60}$ and 0.83 mM *trans*-Pt(py)$_2$Cl$_2$ (30 cycles). All data acquired at a platinum electrode in an acetonitrile–toluene mixture (1 : 4 v/v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate. The sweep rate was 250 mV s^{-1}.

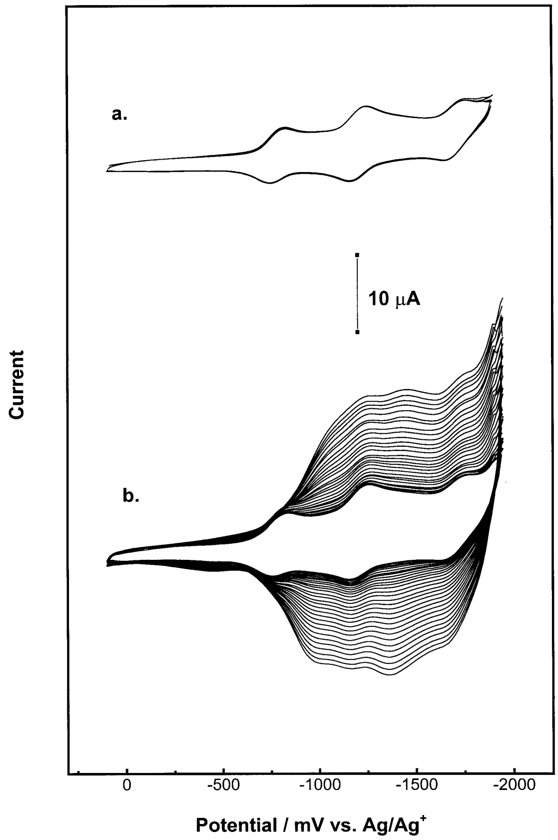

Fig. 2 Multicyclic voltammograms obtained for a solution of 0.35 mM C$_{60}$ and 0.83 mM *cis*-Pt(py)$_2$Cl$_2$ (30 cycles) with sweep termination at: a, −1950 mV; and b, −2000 mV. All data acquired at a platinum electrode in an acetonitrile–toluene mixture (1 : 4 v/v) containing 0.10 M tetra(*n*-butyl)ammonium perchlorate. The sweep rate was 250 mV s^{-1}.

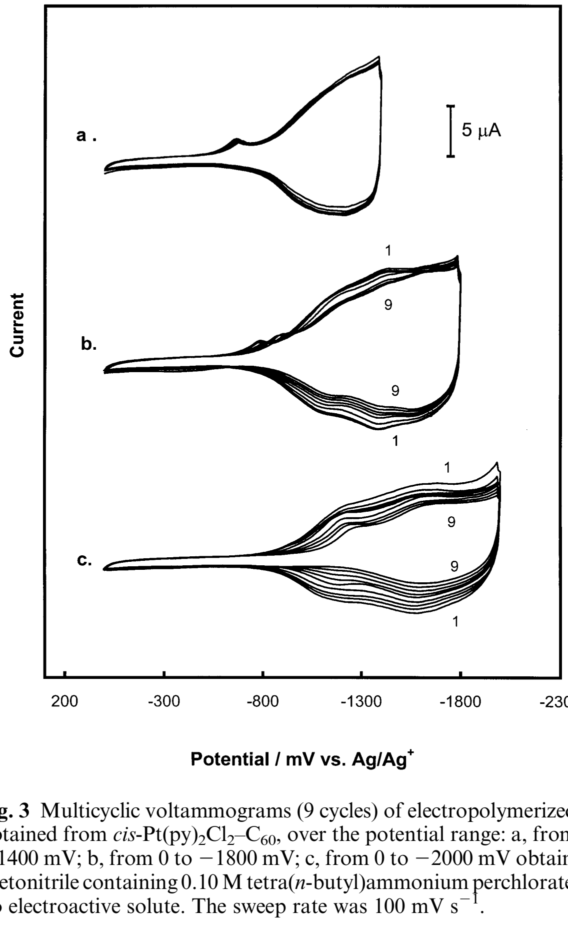

Fig. 3 Multicyclic voltammograms (9 cycles) of electropolymerized film obtained from *cis*-Pt(py)$_2$Cl$_2$–C$_{60}$, over the potential range: a, from 0 to −1400 mV; b, from 0 to −1800 mV; c, from 0 to −2000 mV obtained in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate with no electroactive solute. The sweep rate was 100 mV s^{-1}.

as supporting electrolyte which lead to the formation of a redox-active C$_{60}$Pt$_n$ film. Trace a shows the multicyclic voltammetry for a 0.83 mM solution of *cis*-Pt(py)$_2$Cl$_2$ over the potential range +100 to −2000 mV. At very negative potentials a wave due to the deposition of platinum metal is observed. Trace b shows a multicyclic voltammogram for a solution of 0.35 mM of C$_{60}$. In this situation only the three reversible redox waves for C$_{60}$ are observed. No film formation is seen. Trace c shows the multicyclic voltammogram for a solution containing 0.35 mM of C$_{60}$ and 0.83 mM of *cis*-Pt(py)$_2$Cl$_2$ over the potential range +100 to −2000 mV. Under these conditions successive cycles show steady growth in the current which is indicative of film formation. Inspection of the electrode at the end of the multicyclic process reveals that a black deposit is present on the electrode.

The growth of the film is dependent on the potential range over which the film is deposited as is seen in Fig. 2. Trace a of Fig. 2 shows that no film is deposited when a solution containing 0.35 mM of C$_{60}$ and 0.83 mM of *cis*-Pt(py)$_2$Cl$_2$ is scanned over the potential range +100 to −1950 mV. However, when the switching potential is shifted 50 mV more negatively, film growth is observed as seen in trace b of Fig. 2.

The C$_{60}$Pt$_n$ film prepared by electrochemical deposition from solutions of *cis*-Pt(py)$_2$Cl$_2$ and C$_{60}$ retains electrochemical activity in acetonitrile solution that contains only the supporting electrolyte, tetra(*n*-butyl)ammonium perchlorate. Relevant data are shown in Fig. 3. Traces a, b, and c show data for nine cycles for the C$_{60}$Pt$_n$ film over the potential ranges; 0 to −1400, 0 to −1800 and 0 to −2000 mV, respectively. The film is redox active and stable over the 0 to −1400 mV range as seen in trace a. Note that a large, non-faradaic residual current is observed at the end of the reductive potential scan. This effect is also seen for the $C_{60}Pd_n$ films and is generally associated with double layers of static charge that form during doping of the film although faradaic redox processes may be involved as well.[19–21] Similar effects are also observed for redox active films formed by electrochemical polymerization of polypyrrole, polyaniline or polythiophene.[22] When the scan is extended to −1800 mV, a progressive decrease in the current is observed on successive cycles. This decrease in current is caused by the loss of redox active material from the layer. When the scan is extended to −2000 mV, the extent of decay of current is even greater and loss of particulate material from the electrode surface can be detected visually.

During reduction of the film doping occurs to obtain charge compensation. The doping of the layer by cations from the supporting electrolyte (C^+A^-) can be described by one of the following processes:[23]

$$\{C_{60}Pt_n\ (C^+A^-)_m\} + xe^- + xC^+ \rightarrow \{C_{60}{}^{x-}Pt_n/xC^+,\ (C^+A^-)_m\} \qquad (1)$$

$$\{C_{60}Pt_n\ (C^+A^-)_m\} + xe^- \rightarrow \{C_{60}{}^{x-}Pt_n/xC^+,\ (C^+A-)_{m-x}\} + x\,A^- \qquad (2)$$

In the cation charge transfer process (eqn. (1)), cations, C^+, move from the bulk electrolyte through the double layer and into reduced sites within the film. In the second process (eqn. (2)), anions, A^-, which are already present in the double layer near the film-covered electrode, depart from the double layer while cations move into the film. In order to discover which process is occurring with the film, the electrochemical response of the film has been examined in solutions with different supporting electrolytes. Fig. 4 shows data for the $C_{60}Pt_n$ film-covered electrode in acetonitrile solution with different supporting electrolytes. Comparison of traces a and b, which were obtained with 0.10 M tetra(*n*-butyl)ammonium hexafluorophosphate and 0.10 M tetra(*n*-butyl)ammonium perchlorate, respectively, shows that the voltammograms are similar. Additionally voltammograms obtained in solutions of tetra(*n*-butyl)ammonium tetrafluoroborate, and tetra(*n*-butyl)ammonium bromide as supporting electrolytes have the same shape but are not shown. Thus the redox activity of the film is not influenced by the specific anion present in the supporting electrolyte. However, the redox activity is influenced by the cation in the supporting electrolyte. Comparison of trace d of Fig. 4, which was obtained with 0.10 M tetra(*n*-hexyl)ammonium perchlorate as supporting electrolyte, with trace c, which was obtained with 0.10 M tetra(ethyl)ammonium perchlorate as supporting electrolyte, reveals a substantial difference with the larger cation resulting in a diminished current. These data are consistent with cation transport in and out of the film accompanying the reduction of the $C_{60}Pt_n$ film.

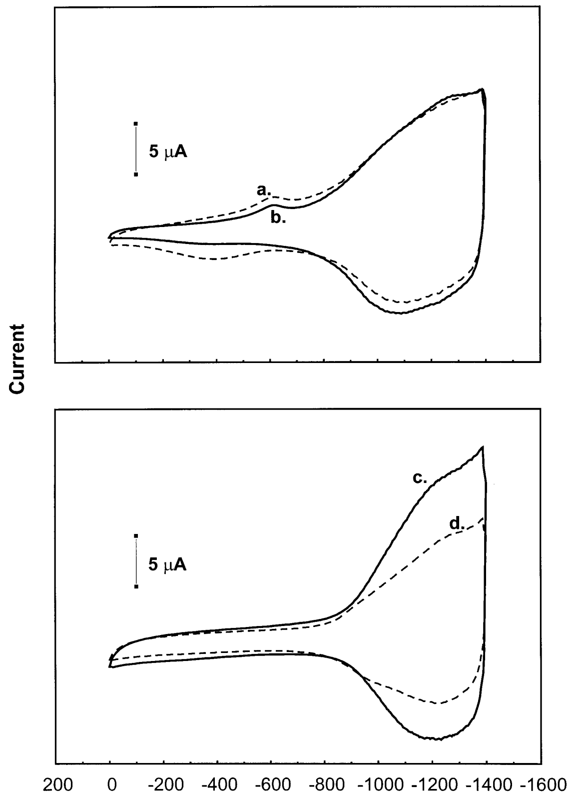

Fig. 4 Cyclic voltammograms of electropolymerized $C_{60}Pt_n$ films obtained in: a, 0.10 M tetra(*n*-butyl)ammonium hexafluorophosphate; b, 0.10 M tetra(*n*-butyl)ammonium perchlorate; c, 0.10 M tetra(ethyl)ammonium perchlorate; d, 0.10 M tetra(*n*-hexyl)ammonium perchlorate. The sweep rate was 100 mV s^{-1}.

The formation of the $C_{60}Pt_n$ film is also critically dependent on the choice of starting platinum complex. For example, trace d of Fig. 1 shows a multicyclic voltammogram for a solution of 0.83 mM of *trans*-$Pt(py)_2Cl_2$. Deposition of platinum is seen at a more negative potential than for the *cis* isomer (compare with trace a). Trace e shows the multicyclic voltammetry of a solution of 0.83 mM *trans*-$Pt(py)_2Cl_2$ and 0.35 mM C_{60} over the potential range +100 to −2200 mV. Some variation in the current is observed in successive cycles but little evidence of film formation is seen. Attempts to grow a $C_{60}Pt_n$ film by electroreduction of solutions of C_{60} and $Pt(bipy)Cl_2$, $Pt(py)_2I_2$, and *cis*-$Pt(PPh_3)_2Cl_2$ under similar conditions were unsuccessful. Each of these complexes alone displayed a reduction potential more negative than −2000 mV, potentials at which film formation and film degradation compete. In order to facilitate film deposition, we sought a platinum complex that is

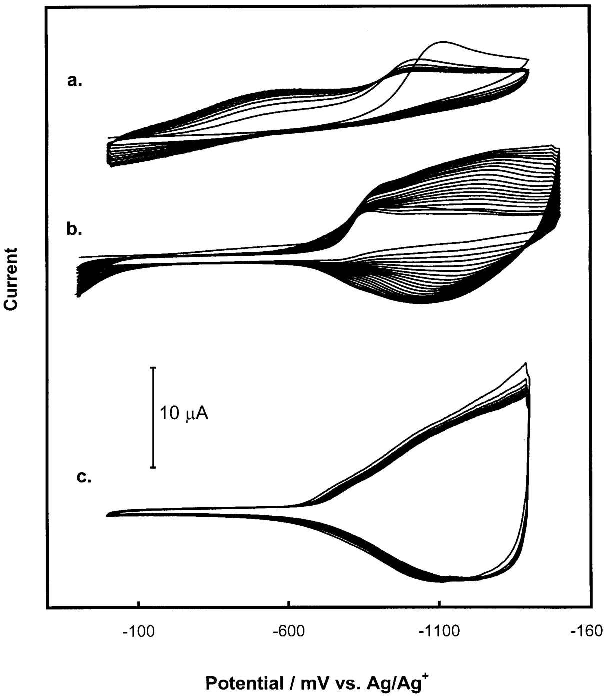

Fig. 5 Multicyclic voltammograms obtained for: a, 1.11 mM $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$ (10 cycles); b, 0.32 mM C_{60} and 0.80 mM $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$ (20 cycles) with sweep termination at −1500 mV; c, Multicyclic voltammograms (9 cycles) for an electropolymerized film formed from $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$ and transferred to an acetonitrile solution containing 0.10 M tetra(*n*-butyl)ammonium perchlorate with no electroactive solute. The sweep rate was 100 mV s^{-1}.

reduced at less negative potentials and has a greater solubility than *cis*-Pt(py)$_2$Cl$_2$.

Fig. 5 shows cyclic voltammograms using just such a complex, {Pt(μ-Cl)Cl(C$_2$H$_4$)}$_2$. Trace a of this figure shows that the wave due to the deposition of platinum metal is observed at a significantly less negative potential than that observed with *cis*-Pt(py)$_2$Cl$_2$. Trace b shows the multicyclic voltammogram for a solution containing 0.32 mM of C$_{60}$ and 0.80 mM of {Pt(μ-Cl)Cl(C$_2$H$_4$)}$_2$ over the potential range +100 to −1500 mV. Successive cycles show film formation as noted in the steady growth in the current and the presence of a black deposit on the electrode. As seen in trace c the film retains its redox activity over the 0 to −1400 mV range when transferred into an acetonitrile solution that contains only the supporting electrolyte. The shape of the resulting voltammogram is very similar to that of the film prepared from *cis*-Pt(py)$_2$Cl$_2$.

Electrochemical studies of chemically produced of C$_{60}$Pt$_1$ films

The electrochemical behavior of a layer of C$_{60}$Pt$_1$ that was prepared by precipitation from a toluene solution containing C$_{60}$ and Pt(dba)$_2$ is shown in Fig. 6. It can be seen in trace a that the film is electroactive by the way its response to cycling in an acetonitrile solution containing only supporting electrolyte (0.10 M tetra(*n*-butyl)ammonium perchlorate) varies during the first cycles. These variations are a consequence of structural modifications that occur in the film as a consequence of film doping that is necessary to obtain charge compensation. However, after ten cycles the electrochemical response is stable as shown in trace b, and that response is notably similar to the voltammetric behavior of electrochemically prepared films as seen in trace a of Fig. 3 and trace c of Fig. 5. Trace c of Fig. 6 shows the response of the film to extending the switching potential in the cyclic voltammetry to −1800 mV. Under these conditions the film, like the electrochemically prepared film is unstable and the current diminishes with increasing cycling. This behavior also results in the loss of the coating from the surface of the electrode.

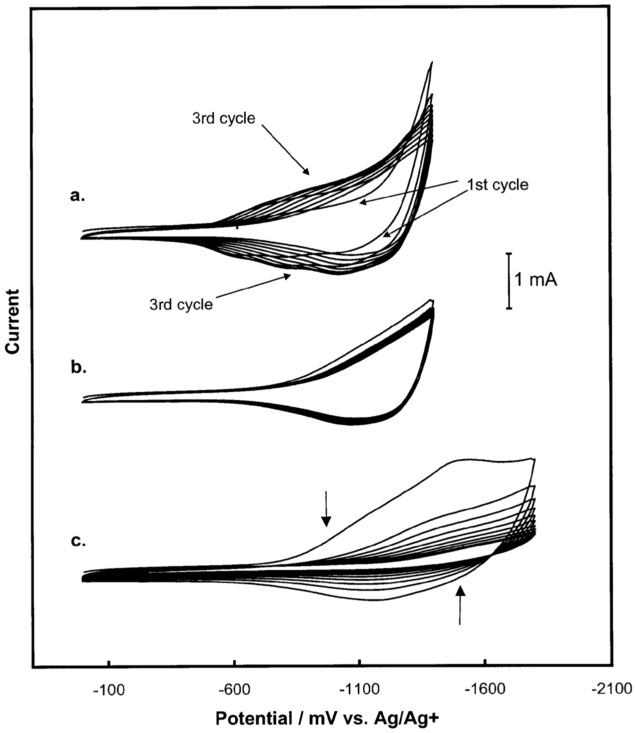

Fig. 6 Multicyclic voltammograms showing redox activity of chemically prepared C$_{60}$Pt$_1$. C$_{60}$Pt$_1$ was deposited on a Pt disk electrode (diameter = 1 cm) by precipitation from a toluene solution containing of C$_{60}$ and Pt(dba)$_2$. The C$_{60}$Pt$_1$-covered electrode was subsequently transferred to a solution of acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate. a, first 10 cycles; b, second 10 cycles over the range from 0 to −1400 mV. c, 10 cycles over the range from 0 to −1800 mV. The sweep rate was 100 mV s^{-1}.

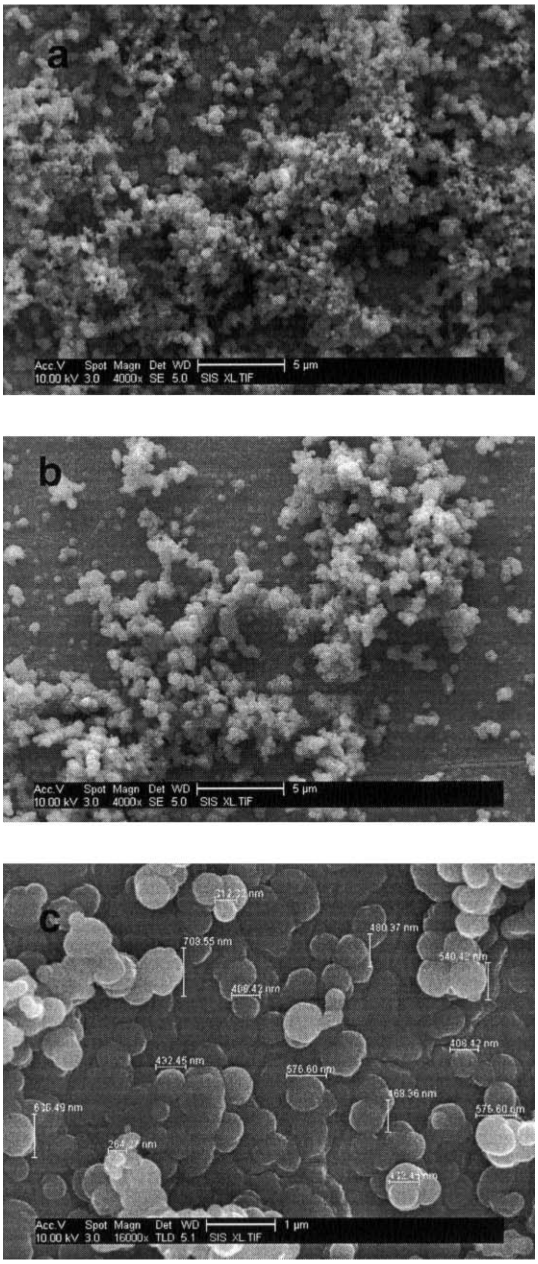

Fig. 7 SEM images of C$_{60}$Pt$_n$ films formed on gold foil under cyclic voltammetry conditions (10 cycles) in an acetonitrile–toluene mixture containing 0.32 mM C$_{60}$, 0.10 M tetra(*n*-butyl)ammonium perchlorate and a, 0.83 mM *cis*-Pt(py)$_2$Cl$_2$ (over the potential range −100 to −2000 mV); b, 0.80 mM {Pt(μ-Cl)Cl(C$_2$H$_4$)}$_2$ (over the potential range −100 to −1500 mV). Part c shows a magnified image of the film shown in b.

SEM studies of the film surfaces

Fig. 7 shows SEM images of a gold electrode after the deposition of the C$_{60}$Pt$_n$ films. The films were grown under cyclic voltammetric conditions in an acetonitrile–toluene mixture containing 0.32 mM C$_{60}$ and 0.10 M tetra(*n*-butyl)ammonium perchlorate. The image in part a of Fig. 7 shows the film grown with *cis*-Pt(py)$_2$Cl$_2$ as a precursor (over the potential range −100 to −2000 mV) while the image in part b shows the film prepared from {Pt(μ-Cl)Cl(C$_2$H$_4$)}$_2$ (over the potential range −100 to −1500 mV). In both cases the electrode is covered with

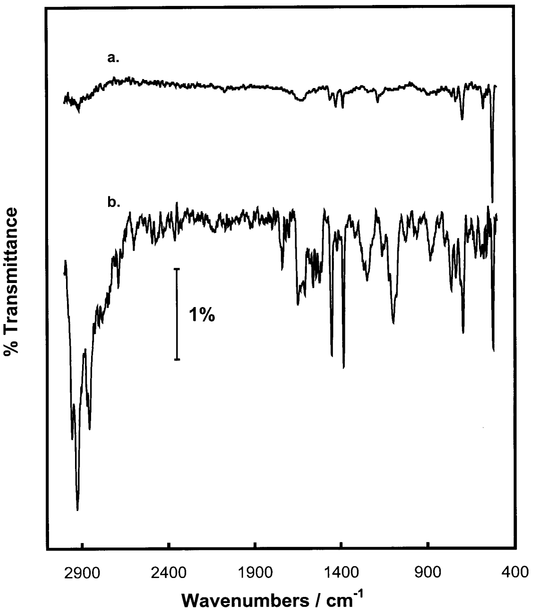

Fig. 8 Infrared spectra of a, chemically prepared sample of $C_{60}Pt_1$; b, electrochemically generated $C_{60}Pt_n$ film prepared from *cis*-$Pt(py)_2Cl_2$.

a uniform film that has spherical outcroppings. Part c shows a magnified image of the film shown in b. Notice the relatively uniform coverage with spherical outcroppings. These particles range in diameter from 300 to 700 nm.

Spectroscopic characterization of the $C_{60}Pt_n$ film

Trace a of Fig. 8 shows the infrared spectrum of chemically prepared $C_{60}Pt_1$. Trace b of Fig. 8 shows the transmission infrared spectra of electrochemically grown $C_{60}Pt_n$ film obtained from *cis*-$Pt(py)_2Cl_2$. Absorption bands in the regions 1440–2420, 1190–1160, 560–570, and 525 cm^{-1} are indicative of the presence of C_{60} units within the film. Bands at 2958, 2929, and 2860 cm^{-1} are attributed to tetra(*n*-butyl)ammonium cations that are trapped within the film. A broad band at *ca.* 1093 cm^{-1} is a feature that is generally observed for a variety of electrochemically prepared C_{60} films and appears to be characteristic of the polyfullerene network that is formed.[8,9] Comparison of traces a and b reveals that the infrared spectra in regions where fullerene features are expected are similar. These similarities suggest that a common $\cdots PtC_{60}PtC_{60}PtC_{60}\cdots$ unit is present in both materials.

Photoelectron spectroscopy was used to qualitatively evaluate the elements present in the $C_{60}Pt_n$ film. The photoelectron spectrum of the film reveals peaks at 79.9 eV for Pt $4f_{7/2}$ and 76.8 eV for Pt $4f_{5/2}$, a strong peak at 289.3 eV due to C 1s and a peak at 536.9 eV due to O 1s. The latter is probably due to contamination of the film by atmospheric exposure during transfer from the sample preparation chamber to the spectrometer.

The $C_{60}Pt_n$ film is insoluble in common organic solvents like toluene, acetonitrile, dichloromethane, and chloroform. However, in the presence of an excess of triphenylphosphine it does dissolve in toluene to produce a green solution. The UV/Vis absorption spectrum of this solution shows bands at 424 and 584 nm. This spectrum matches that of the well characterized complex, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$.[24] Thus, addition of triphenylphosphine to the film disrupts the polymeric network and allows covalently bonded $\eta^2\text{-}C_{60}Pt$ units within the film to be extracted as the stable complex, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$. Similarly, addition of phosphines to chemically prepared $C_{60}Pt_n$ results in the formation of the complexes, $(\eta^2\text{-}C_{60})Pt(PR_3)_2$.[17,18]

Laser ablation mass spectrometric studies have been conducted on this film as reported elsewhere.[25] Desorption with a 340 nm N_2 laser produces a positive ion mode mass spectrum in which the base peak corresponds to $[C_{60}]^+$. This is, of course, consistent with the presence of intact fullerene molecules in the film. Additionally, as reported previously, the mass spectrum shows a cluster of peaks at 903.9 amu which is indicative of the formation of $[C_{59}Pt]^+$ which we have surmised to have a platinum atom replacing one of the carbon atoms within the fullerene cage.[22] We believe that $[C_{59}Pt]^+$ is formed during the laser ablation process since high laser power is necessary to observe this species. It is unlikely that $C_{59}Pt$ is a component of the film itself.

Formation and characterization of a film obtained from C_{70} and *cis*-$Pt(py)_2Cl_2$

Fig. 9 shows the results of cyclic voltammetric studies that lead to the formation of a redox-active film containing C_{70}. Trace a shows the multicyclic voltammetry (30 cycles) for a solution of 0.35 mM C_{70} and 0.83 mM *cis*-$Pt(py)_2Cl_2$ in the potential region from +100 to −2000 mV. Under these conditions, successive cycles show steady growth in the current which is indicative of film formation. Visual inspection of the electrode after electrolysis reveals that a black deposit is present on the electrode. The $C_{70}Pt_n$ film retains its electrochemical activity in acetonitrile solution that contains only the supporting electrolyte, tetra(*n*-butyl)ammonium perchlorate as seen in trace b of Fig. 9. The film is redox active and stable over the 0 to −1600 mV range, although scanning to more negative potentials (not shown) does result in loss of redox activity due to removal of the film from the electrode. Note that a large,

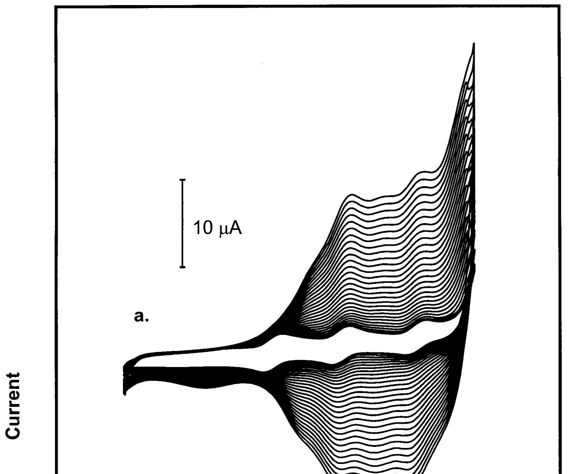

Fig. 9 a, Multicyclic voltammograms (30 cycles) for a solution of 0.35 mM C_{70} and 0.83 mM *cis*-$Pt(py)_2Cl_2$ in the potential region from +100 to −2000 mV. The sweep rate was 250 mV s^{-1}. b, Multicyclic voltammograms (9 cycles) for an electropolymerized film formed from *cis*-$Pt(py)_2Cl_2$–C_{70} obtained in acetonitrile containing 0.10 M tetra(*n*-butyl)ammonium perchlorate with no electroactive solute in the potential region from 0 to −1600 mV. The sweep rate was 100 mV s^{-1}.

non-faradaic residual current is observed in trace b at the end of the negative going potential scan. This effect is also seen for the $C_{60}Pt_n$ film and is associated with double layers of static charge that form during doping of the film.

Discussion

The electrochemical results indicate that a redox active $C_{60}Pt_n$ film can be prepared and that a similar $C_{70}Pt_n$ film also can be made. However, the process of electrochemical deposition of the $C_{60}Pt_n$ film is dependent on the nature of the platinum precursor. The analogous $C_{60}Pd_n$ film can be prepared from a number of precursors, and the film properties do not appear to depend on the precursor.[9,10] In contrast, we have found that *cis*-$Pt(py)_2Cl_2$ and $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$ are the only useful precursors for electrochemical formation of the $C_{60}Pt_n$ film. It appears that reduction of the metal complex itself is required to form both the $C_{60}Pt_n$ and the $C_{60}Pd_n$ films.[26] A number of other platinum(II) complexes, $Pt(bipy)Cl_2$, $Pt(py)_2I_2$, *cis*-$Pt(PPh_3)_2Cl_2$ or *trans*-$Pt(py)_2Cl_2$, are not suitable precursors because their reductions occur in a potential range where the film is unstable.

With *cis*-$Pt(py)_2Cl_2$ it is necessary to reach −2000 mV in order to form the $C_{60}Pt_n$ film as seen in Fig. 2. At this potential C_{60} is reduced to $[C_{60}]^{3-}$, and *cis*-$Pt(py)_2Cl_2$ itself undergoes reduction to platinum metal. As seen in trace c of Fig. 3, the film is inherently unstable at the very negative potentials that are necessary for its growth. Since removal of the film from the electrode surface competes with film deposition, it is difficult to deposit much of the $C_{60}Pt_n$ material on the electrode. The reasons for the instability of these two-component films at negative potentials, which has also been observed for the $C_{60}Pd_n$ films, have been discussed previously.[9–12] At highly negative potentials, the fullerene units within the $C_{60}Pt_n$ film repel one another due to the increasingly higher charges they must bear, and mechanical strain is placed on the film by the influx of cations. Additionally, fullerene reduction also weakens the covalent Pt–C_{60} bonding within the film. The covalent Pt–C_{60} bonding appears to require significant metal ligand back bonding for stability, since it has been shown that reduction of discrete complexes like, $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$, results in more facile dissociation of the fullerene from the platinum complex.[4] Reduction of each of the platinum complexes, $Pt(bipy)Cl_2$, $Pt(py)_2I_2$, *cis*-$Pt(PPh_3)_2Cl_2$ or *trans*-$Pt(py)_2Cl_2$, which do not serve as film precursors, occurs at potentials more negative than −2000 mV. At such negative potentials it appears that film stability is sufficiently low so that no growth occurs with these precursors. Moreover, the solubility of *cis*-$Pt(py)_2Cl_2$ is limited, and the film preparations from this complex have had to be done with solutions that are nearly saturated with *cis*-$Pt(py)_2Cl_2$. The dimer, $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$, is more soluble than *cis*-$Pt(py)_2Cl_2$, and its reduction occurs at a less negative potential than *cis*-$Pt(py)_2Cl_2$. Thus, $\{Pt(\mu\text{-}Cl)Cl(C_2H_4)\}_2$ is a better precursor for the electrochemical deposition of $C_{60}Pt_n$ films.

Structurally, the electrochemically prepared $C_{60}Pt_n$ film, like the $C_{60}Pd_n$ film, is believed to consist of a series of $\cdots C_{60}Pt(C_{60}Pt)_nC_{60}P\cdots$ units in which the platinum centers are covalently bound to the fullerenes in η^2-fashion. This framework must be sufficiently porous to allow access of cations into the film, since the film retains redox activity in acetonitrile solution with only supporting electrolyte present. The insolubility of the material is consistent with the presence of a polymeric network, and the ability of triphenylphosphine to form $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ from the film is evidence that covalent $(\eta^2\text{-}C_{60})Pt$ units are present within the film.

The results in Fig. 6 show that chemically prepared $C_{60}Pt_1$ is redox active and that this film displays a cyclic voltammetric response similar to that of the electrochemically deposited film. However, the electrochemically prepared film adheres more strongly to the electrode surface than does the chemically prepared film which is simply precipitated onto the electrode. Nevertheless, the results reported here form a link between the chemically prepared and the electrochemically deposited materials.

The $C_{60}Pt_n$ film serves as a precursor to the formation of novel fullerenes that contain platinum atoms as part of the fullerene network. Thus the formation of $[C_{59}Pt]^+$ in laser desorption mass spectrometric studies has been reported previously.[22] Ongoing studies have also detected other related species such as $[C_{58}Pt]^-$ and $[C_{57}Pt_2]^-$, which will be discussed elsewhere.[27]

Experimental section

Materials

C_{60} (Southern Chemical Group) and tetra(*n*-butyl)ammonium perchlorate (Fluka, electrochemical grade) were obtained commercially and used as received. Acetonitrile (99.9%) and dichloromethane (99+%), were used as received from Aldrich. Toluene (Aldrich Chemical Co.) was purified by distillation over sodium under argon atmosphere.

Instrumentation

Voltammetric experiments were performed on a BAS CV-50W Electroanalytical System with a three-electrode cell. Platinum disks with a diameter of 1.5 mm (Bioanalytical Systems Inc.) were used as working electrodes. Prior to the experiment the electrodes were polished with fine carborundum paper and then with a 0.5 μm alumina slurry. Subsequently, the electrodes were sonicated in water to remove the traces of alumina from the platinum surface, washed with water, and dried. A silver wire immersed in 0.01 M silver perchlorate and 0.09 M tetra(*n*-butyl)ammonium perchlorate in acetonitrile and separated from the working electrode by a ceramic tip (Bioanalytical Systems Inc.) served as the reference electrode. With this reference electrode and solvent system, the ferrocene–ferrocenium redox couple occurs at +188 mV. The counter electrode was a platinum tab with an area of about 0.5 cm^2. All experiments were performed with 50–80% *iR* compensation.

The infrared spectra were taken with the sample dispersed in a potassium bromide pellet on a Galaxy Series FTIR 300 spectrometer from Mattson Instruments, Inc.

XPS spectra were obtained with a HP 5950A ESCA spectrometer which uses aluminium K-α transition for X-rays; the source was monochromatized at 1486.6 eV.

The SEM images were obtained with the use of an SEM FEI XL30s FEG (Oregon, USA). The accelerating voltage for the electron beam was 10 keV and the average working distance was 5 mm.

Film growth procedure

Films were prepared through electroreduction of an acetonitrile–toluene (1 : 4 v/v) solution that contained both C_{60} (0.35 mM) and *cis*-$Pt(py)_2Cl_2$ (0.83 mM) as well as the supporting electrolyte, 0.10 M tetra(*n*-butyl)ammonium perchlorate. Films were grown by repeated cycling (uniformly 30 cycles for the electrochemical studies reported here) through the potential range of +100 to −2000 mV. After the film was formed, the film-covered electrode was rinsed several times with a fresh acetonitrile–toluene (1 : 4 v/v) mixture. To examine the redox properties of this film, it was placed in a solution of acetonitrile with 0.10 M tetra(*n*-butyl)ammonium perchlorate as supporting electrolyte. The transfer of the electrodes from one solvent to another was accomplished in air without protection from normal atmospheric conditions. The electrodes were allowed to equilibrate for 10 minutes in the new solution before electrochemical measurements were conducted. All solutions were deoxygenated by bubbling argon through the sample prior to electrochemical experimentation.

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