Studies on Metallofullerene ($Dy@C_{82}$) Embedded in a DDAB Film in Aqueous Solution

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The electrochemical behavior of metallofullerene ($Dy@C_{82}$) in didodecyldimethylammonium bromide (DDAB) films deposited on glassy carbon, quartz crystal microbalance (QCM) gold crystals, and indium tin oxide (ITO) electrodes in aqueous solution was investigated in detail. Four pairs of reversible redox peaks were observed, and for the first time, these peaks were characterized by vis/NIR spectroscopy. Different from previous fullerene/cationic lipid modified electrodes, one oxidation and three reduction processes were observed. The stability of $Dy@C_{82}$ and its ions in the film toward air was detected by measuring its cyclic voltammogram after holding the potentials for 10 s, followed by introducing 10 μL of air to the solution. $Dy@C_{82}$ and its first three anions are stable toward air and water, while some chemical reactions take place when the third anion is further reduced in the film. $Dy@C_{82}^{+}$ is less stable than $Dy@C_{82}^{-}$ toward water and air. The electrochemical processes were measured in different electrolytes, which showed pronounced anionic dependence on either its cation or anions. The electrochemical processes were also monitored using electrochemical quartz crystal microbalance (EQCM), and from the result a possible electron-transfer mechanism of a $Dy@C_{82}$/DDAB electrode in aqueous solution was presented. It showed that the anions of $Dy@C_{82}$ were bound to the DDA^{+} cation in the film, while the anions of electrolyte diffused into the film to compensate the positive charges when a cation of $Dy@C_{82}$ was generated.

Introduction

Endohedral metallofullerenes with metal atoms encapsulated inside hollow carbon cages have attracted special interest as new spherical molecules because they have unique properties that are not seen in empty fullerenes.[1,2] Among these properties, their electrochemistry has received much attention because they are good electron donors as well as good electron acceptors as compared with empty fullerenes, showing special electronic properties and reactivity.[3] Suzuki et al. first measured cyclic voltammograms (CVs) on $La@C_{82}$ and found unusual redox properties of the metallofullerene, which differ significantly from those of empty fullerenes.[4] $La@C_{82}$ exhibits five reversible reduction processes and one reversible oxidation process, and the six reversible couples appear to be arranged in sets of two, unlike those of empty fullerenes.[5−7] So far, many lanthanofullerenes $M@C_{82}$ (M = Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu, etc.) have been electrochemically studied.[8−12] Their electrochemical properties are similar. One common feature is that the difference between the first oxidation and the first reduction potentials is very small due to the open-shell electronic structure. Distinguishingly, it has also been shown that the reduction and oxidation of $La@C_{82}$ take place on the carbon cage, leading to a closed-shell electronic structure. As a result, $La@C_{82}^{-}$ and $La@C_{82}^{+}$ are stable toward air and water,[13] opening the possibility of using metallofullerenes in aqueous solution media. This is a significant advantage considering that the applications of C_{60} films in aqueous solutions have been hindered by the poor stability of its ionic forms (e.g., C_{60}^{-} is very sensitive to H_2O, and C_{60}^{2-} reacts rapidly with oxygen).[14]

In view of the unique electrochemical properties of metallofullerenes in practical applications and their heterogeneous electron-transfer characteristics, we have engaged in the preparation of metallofullerene films by a variety of techniques. Some properties of these films have been measured regarding their photoelectrochemistry and electrochemistry.[15−21] We have reported the first study on the electron transfer of the $Dy@C_{82}$(I) film on electrode surfaces in an organic media such as acetonitrile.[21] The electrochemistry of the metallofullerene film was found to be quite different from that of dissolved $Dy@C_{82}$(I). The first two pairs of reduction and reoxidation waves show large splittings because of the attendant structural reorganizations of the species in the solid film. However, a pair of reversible oxidation and rereduction waves was observed, which was not seen in empty fullerene films. On the other hand, considering the promising application potentials of metallofullerenes in the biological area, we have prepared $Dy@C_{82}$ films on a GC electrode by direct solution cast and studied their electrochemical response.[20] We have also encapsulated $Dy@C_{82}$ in membrane films formed with a cationic surfactant didodecyldimethylammonium bromide (DDAB). The electrochemistry of this electrode in the absence and presence of hemoglobin (Hb) has been systematically studied. Such a protein-loaded biomembrane film may provide a good model for the understanding of redox processes in biological systems.[22−24] We have demonstrated the electrocatalysis of $Dy@C_{82}$ reduction by Hb and the role of $Dy@C_{82}$ as an electron-transfer mediator in the film.

On the same line of development, the electrochemistry of $La@C_{82}$ on an artificial lipid film modified electrode has been studied in water,[25] showing redox responses analogous to those of the solution phase. Most recently, Li et al. also reported the electrochemistry of $Gd@C_{82}$/DDAB films in an aqueous solu-

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tion.[26] To the best of our knowledge, no spectroelectrochemical characterization of the redox peaks of metallofullerenes in film-modified electrodes in aqueous solution has been reported, although many of them have been assigned clearly in organic solution.[13,27,28] In view of the promising application potentials of metallofullerenes in the biological area, it is necessary to scrutinize the electrochemistry of metallofullerene films in aqueous solution thoroughly. The present paper is a continuation of our earlier initial work and describes more extensive investigation of the electrochemical behavior of Dy@C_{82} in DDAB film systematically. The bulk of the results including spectroelectrochemical characterization of the redox peaks of Dy@C_{82} in DDAB, the stability of its anions and cation toward water and air, the dependence of its electrochemical process on supporting electrolytes, and a possible mechanism for the electron-transfer based on the electrochemical quartz microbalance (EQCM) result etc. will be reported in this paper.

Experimental Procedures

Materials and Chemicals. High-purity Dy@C_{82} (99.5% as estimated by mass spectrometry) was prepared in our laboratory by a combination of a standard DC arc-discharge method and an isolation method described previously.[29−31] The raw soot from the arc-discharge was subjected to Soxlet extraction with *N*,*N*-dimethylformamide (DMF), followed by HPLC separation using a 5PYE column with toluene being the mobile phase. The identity and purity of the sample were verified by methane DCI negative ion mass spectrometry.

Deionized water (20 ± 1 °C, pH = 7, ρ = 18.3 MΩ cm) was purified by passing through an EASY pure compact ultrapure water system (Barnstead Co.). KCl (Riedel-De Haen AG), tetrabutylammonium bromide (TBAB, 99+%, Acros), tetrabutylammonium chloride (TBAC, 99+%, Acros), KCl (Sigma), NaCl (Sigma), LiCl (Acros), NH_4PF_6 (Acros), and $NaClO_4$ (Acros) were used as received for the preparation of supporting electrolytes. Didodecyldimethylammonium bromide (DDAB, 99%) was purchased from Acros.

Electrode Preparation. A glassy carbon (GC) disk (3 mm diameter) was used as the working electrode. Before use, the surface of the GC electrode was polished with fine emery paper and chamois leather soaked with a Al_2O_3 slurry, then rinsed thoroughly with water in an ultrasonic bath. The Dy@C_{82}-DDAB film electrode was prepared by dropping 10 μL of a toluene solution containing 9.7×10^{-4} mol/L Dy@C_{82} and 0.01 mol/L DDAB on the surface of the GC electrode, the AT-cut QCM crystal coated with a gold disk (CHI, area of 0.196 cm^2) for EQCM measurement, or the ITO electrode (1×1 cm^2) for spectroscopic measurement, followed by drying in a vacuum at ambient temperature for a period of 4 h.

Equipment and Measurements. Cyclic voltammetry (CV) experiments were performed using model 600 Electrochemical Analyzer from CH instruments Inc. in a conventional three-electrode electrochemical cell at ambient temperature. A modified film electrode was used as the working electrode, a Pt wire served as the auxiliary electrode, and a saturated calomel electrode (SCE) was employed as the reference. Simultaneous CV and EQCM were carried out with a model CHI 420 electrochemical workstation (CH Instrument Inc., Austin, TX). An 8 MHz atom (AT)-cut quartz crystal resonator was used. Mass sensitivity of this quartz crystal based on the Sauerbrey equation was 1.4 ng Hz^{-1}. A central 5 mm diameter circular gold spot served as the working electrode. A Pt wire and a KCl saturated Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively. The electrochemical measurements were conducted in an ultrahigh purity N_2 atmosphere (99.995%) at ambient temperature (22 ± 1 °C).

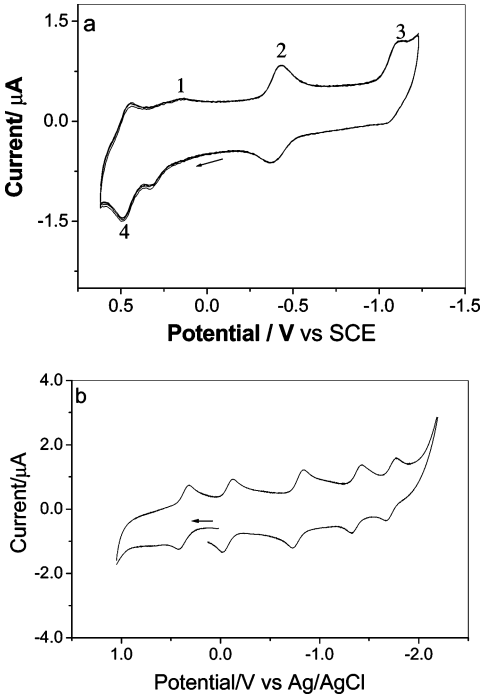


Figure 1. Cyclic voltammograms (CVs) of (a) Dy@C_{82}/DDAB films on a GC electrode in water containing 0.1 M KCl and (b) Dy@C_{82} solution in a toluene/MeCN (4:1, v) solution containing 0.1 M $TBAPF_6$. Scan rate: 50 mV s^{-1}.

The anion and cation of Dy@C_{82} (Dy@C_{82}^- and Dy@C_{82}^+) were obtained on the modified ITO electrode in the water solution containing 0.1 M KCl by setting the applied potentials at −0.1 or +0.6 V, respectively. The extent of electrolysis for a given amount of Dy@C_{82} in a film was monitored by a CV peak of Dy@C_{82}^- to Dy@C_{82} (or Dy@C_{82}^+ to Dy@C_{82}): the electrolysis was continued until the CV peak stopped increasing. The electrolysis time for the full conversion of Dy@C_{82} to Dy@C_{82}^- or Dy@C_{82}^+ in the film was estimated to be 10 s. The ITO with electrogenerated Dy@C_{82} anion or cation in the film was then transferred from the bulk cell to a quartz cuvette. Vis/NIR measurements were carried out with Perkin-Elmer LAMBDA 900 UV−vis−NIR spectrometer.

Results and Discussion

Electrochemical Behavior of Dy@C_{82}/DDAB Film in Aqueous Solution. Figure 1a shows typical cyclic voltammograms (CVs) of a Dy@C_{82}/DDAB film on a GC electrode in water containing 0.1 M KCl. Four reversible redox couples ($E_{1/2}1$= 0.471 V, $E_{1/2}2$ = 0.234 V, $E_{1/2}3$= −0.405 V, and $E_{1/2}4$ = −1.08V) were observed. Obviously, the well-defined redox responses of the Dy@C_{82}/DDAB film are similar to that of Dy@C_{82} dissolved in an organic homogeneous solvent (see Figure 1b) but are a sharp contrast to that of its own film in acetonitrile[21] or in aqueous media.[20] Experimental results showed that the peak currents for all four peaks were proportional to the square root of the scan rate in the range of 10−200 mV/s, which indicates that the electrochemical reaction of the Dy@C_{82}/DDAB film is a diffusion-controlled process.

CVs were carried out using different potential scan ranges. As shown in Figure 2a, when the potential cathodic scan reversal was set at −0.7 V, the reoxidation peak corresponding to that at +0.16 V (shown in Figure 1a) was not detected. Actually, we find that this peak was not observed each time even when

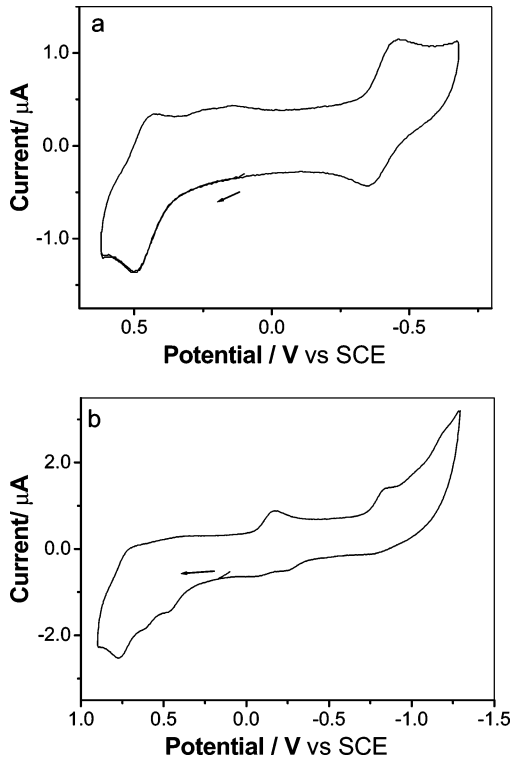


Figure 2. CVs of Dy@C_{82}/DDAB films on a GC electrode in water containing 0.1 M KCl in the potential scan range between +0.6 and −0.70 V (a) and between +0.8 and −1.25 V (b). Scan rate: 50 mV/s.

the scanned potential is between +0.7 and −1.2 V (see EQCM results).[20,25,26] It can be interpreted mostly that this peak overlaps into the next oxidation peak at +0.50 V. However, when the cathodic scan potential reversal was beyond −1.0 V, the reversible reoxidation peaks corresponding to the reductions disappeared, and several small peaks were presented at −0.23, −0.08, +0.04, and +0.62 V, respectively. This suggests that some chemical reactions took place once a reduced ion beyond −1.0 V was generated on the electrode surface.

Spectroelectrochemical Characterization of Dy@C_{82}/DDAB Film on ITO. We have reported the vis/NIR (visible near-infrared) absorption spectra of Dy@C_{82} and its monoanion (Dy@C_{82}^-) and monocation (Dy@C_{82}^+) in organic solution and in its own film.[21] Dy@C_{82} shows characteristic absorption bands at 640, 937, and 1400 nm. For Dy@C_{82}^-, there are two absorption peaks, which are at 650 and 880 nm, respectively. However, only one obvious absorption peak appears at 1210 nm for Dy@C_{82}^+. We have assigned the cathodic peaks at +0.19, −0.43, and −1.11 V, to the first, second, and third reductions of Dy@C_{82}, while the anodic peak at +0.49 V corresponds to its first oxidation according to the characteristics of reductive and oxidative peaks in organic solution[20] (i.e., reversible couples appear to be arranged in sets of two as shown in Figure 1b, which is different from that reported in the literature).[25,26] Here, the stability of Dy@C_{82}^- and Dy@C_{82}^+ to air and water allows us again to confirm the nature of these peaks. As shown in Figure 3, the spectrum of Dy@C_{82}/DDAB (curve a) is identical to that obtained in organic solution, indicating that Dy@C_{82} is stable in a DDAB film. The electrochemical behavior of a Dy@C_{82}/DDAB film on ITO electrodes is similar to that obtained on GC electrodes. When the potential was held at −0.1 V after peak 1 (see Figure 1a) for about 10 s, the characteristic absorption peaks of Dy@C_{82}^- were at 681 and 875 nm, respectively (as shown in Figure 3, curve b). It is thus reasonable to assign peak 1 in Figure 1a at

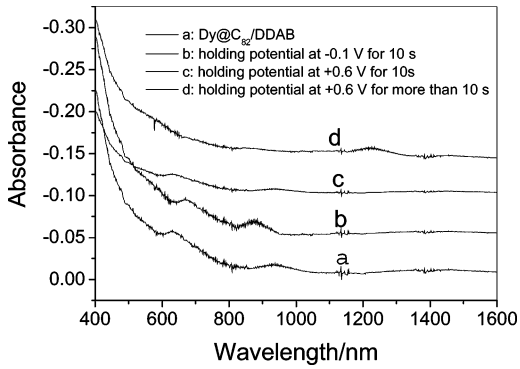


Figure 3. Vis/NIR spectra of a Dy@C_{82}/DDAB film on ITO at different potentials in a 0.1 M KCl solution. Applied potential is labeled in the figure.

+0.19 to the first reduction of Dy@C_{82} in the DDAB film, followed by peak 2 at −0.43 V and peak 3 at −1.11 V that should correspond to the second and third reduction of Dy@C_{82} in the DDAB film, respectively. When the applied potential was changed to +0.6 V after peak 4 for about 10 s, at first the spectrum obtained was similar to that of the neutral Dy@C_{82}/DDAB film (see Figure 3, curve c) except slightly less intense. However, if the electrolyte time was extended to more than 10 s, a new peak at about 1200 nm was observed significantly (Figure 3, curve d), which is completely consistent with the suggestions (i.e., peak 4 is the first oxidation of Dy@C_{82} in DDAB film), and sometimes, the reoxidation of the Dy@C_{82}^- anion overlapped into this peak, like the case shown in Figure 2a or in the literature.[25,26] All spectroelectrochemical experiments were repeated, and they were reproducible. This supports our CV peak assignment of a Dy@C_{82}/DDAB film in aqueous solution because the spectral band and current profile are closely related. The relative peak shifts of the spectrum as compared to Dy@C_{82} in organic solution indicate the interaction of Dy@C_{82} with DDAB.

Stability Study of Dy@C_{82}/DDAB Film. Dy@C_{82} in the DDAB film is stable. Continuous potential scanning between +0.7 and −1.25 V over the first three reduction peaks and the first oxidation peak for more than several hours showed almost no changes in the redox peak shapes or potentials. Even when the electrode coated with Dy@C_{82}/DDAB film was taken away from the solution after measurement and exposed to air for 1 day, the CV behavior of this electrode did not change anymore. This indicates that the DDAB film on the electrode provides favorable microenvironments for Dy@C_{82} and its electrochemical reductions up to the Dy@C_{82}^{3-} anion and the oxidation to the Dy@C_{82}^+ cation as well. Comparing the redox peak potentials for Dy@C_{82} dissolved in a toluene−MeCN organic solution with that of Dy@C_{82} in a DDAB film (Figure 1), the first oxidation peak shifts positively for 0.081 V, while the first, second, and third reduction peaks shift positively at 0.313, 0.407, and 0.32 V, respectively. The larger shift value for the reduction of Dy@C_{82} in DDAB than that for its oxidation implies the stronger binding of Dy@C_{82} anions with the cation in DDAB.

The stability of the electrogenerated Dy@C_{82} ions toward air in the DDAB film was further examined by the holding potential experiment. We conducted this measurement by holding the potentials at −0.1, −0.7, −1.3, and +0.6 V, respectively, for about 10 s, followed by introducing 10 μL of air and then performing its CVs. The results are shown in Figure 4. When the potential was held at −0.1 V, where the first anion was formed (Figure 4a), the peak currents, potentials, or shapes of sequent scanning remained the same as the original scanning,

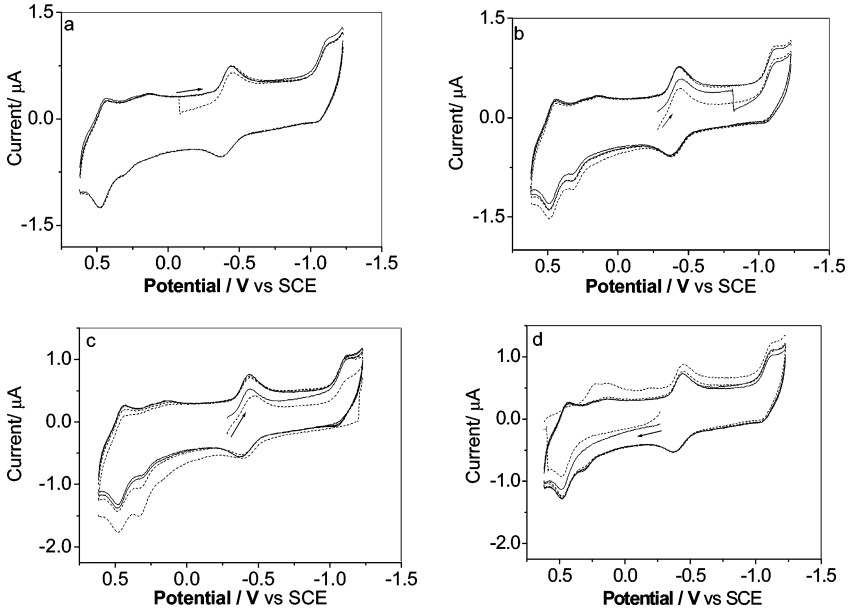


Figure 4. Cyclic voltammograms (CVs) of Dy@C_{82}/DDAB films on a GC electrode in water containing 0.1 M KCl with holding potentials for 10 s at (a) −0.1 V, (b) −0.7 V, (c) −1.3 V, and (d) +0.6 V, then introducing 10 μL of air and performing its CVs. Scan rate: 50 mV s^{-1}.

TABLE 1: Anodic and Cathodic Peak Potentials and Half-Wave Potentials for the First Two Reduction Peaks and the First Oxidation Peak for Dy@C_{82}/DDAB Film on a GC Electrode in Aqueous Solution Containing Various 0.1 mol L^{-1} Electrolytes at a Scan Rate of 50 mV s^{-1}

	Dy@C_{82}^+/Dy@C_{82} (E/V vs SCE)			Dy@C_{82}/Dy@C_{82}^- (E/V vs SCE)			Dy@C_{82}^-/Dy@C_{82}^{2-} (E/V vs SCE)		
electrolyte	E_{pa1}	E_{pc1}	$E_{1/2}$	E_{pc1}	E_{pa1}	$E_{1/2}$	E_{pc2}	E_{pa2}	$E_{1/2}$
LiCl	0.490	0.446	0.468	0.158	0.322	0.240	−0.342	−0.426	−0.384
NaCl	0.491	0.453	0.472	0.164	0.326	0.245	−0.343	−0.437	−0.390
KCl	0.494	0.447	0.470	0.160	0.326	0.243	−0.425	−0.361	−0.393
TBAC	0.489	0.443	0.466	0.157	0.324	0.240	−0.351	−0.290	−0.320
TBAB	0.464	0.383	0.424	0.101	0.297	0.199	−0.464	−0.412	−0.438
$NaClO_4$	0.424	0.368	0.396	0.050	0.250	0.150	−0.501	−0.449	−0.475
NH_4PF_6	0.386	0.320	0.353	-0.048	0.198	0.075	−0.572	−0.487	−0.530

indicating that no new sample is formed and that Dy@C_{82}^- is stable in air. The resemble results were obtained when the holding potentials were set at −0.7 or −1.3 V as shown in Figure 4b,c, which shows that both Dy@C_{82}^{2-} and Dy@C_{82}^{3-} are stable toward air under this condition. This could be interpreted in two ways. As proposed for La@C_{82}, Ce@C_{82}, and Gd@C_{82}, their reduction and oxidation take place on their carbon cage, leading to a closed-shell electronic structure;[13,28] thus, their monoanions are stable in air or water. The electronic properties of Dy@C_{82} are very similar to that of La@C_{82}, that is, the difference between the first oxidation and the reduction potentials is very small (see Figure 1b). It should also have an open-shell electronic structure, meaning that Dy@C_{82}^- is stable in air and water. On the other hand, DDAB may provide a suitable microenvironment for the reduction of Dy@C_{82}. As reported on C_{60} in cationic lipids,[32−34] such as $3C_{12}N^+Br^-$, $4C_8N^+Br^-$, and $4C_8P^+Br^-$, aqueous systems in which strong binding of electrochemically reduced fullerenes with the matrix lipid cation were suggested. Therefore, up to Dy@C_{82}^{3-} can be stable in the DDAB film toward air. In contrast with this result, when the potential was held at +0.6 V (Figure 4d), where the first cation was generated, the peak potential of the corresponding rereduction has a large negative shift from 0.42 to 0.22 V, which indicates that Dy@C_{82}^+ possibly reacts with O_2 and forms a new species. This is consistent with the result that the monocation of metallofullerene is less stable toward air or water than its monoanion.[13] It is also clear, unlike its cations, that the anions in DDAB cannot stabilize the cations of Dy@C_{82} efficiently. In contrast, after the first reduction, the behavior of CV comes back to that of Dy@C_{82} and is stable during sequence continuous cycling, implying that Dy@C_{82} and its anions are stable in a DDAB film.

Electrolyte Dependence. Nakashima[35] and Echgoyen[36] have reported the electrolyte dependence for the electrochemistry of $C_{60}/3C1_2N^+Br^-$ and $C_{60}/4C_8N^+Br^-$ modified electrodes in water containing a variety of electrolytes. It has been shown that the CVs for these two kinds of electrodes have no electrolyte cation dependence but a strong electrolyte anion dependence. Compared with C_{60}, Dy@C_{82} can be not only reduced to its anions but also oxidized to its cation within the same potential window. To understand the electron-transfer mechanism for more details for the Dy@C_{82}/DDAB electrode, we first examined the electrolyte cation dependence at a scan rate of 50 mV s^{-1} in water containing 0.1 mol L^{-1} KCl, NaCl, LiCl, and TBACl. The redox shapes of the films in these supporting electrolytes are similar to each other. From the data obtained, cathodic (E_{pc}) and anodic (E_{pa}) peak potentials and half-wave potentials ($E_{1/2}$) for the first two reduction peaks and the first oxidation peak are listed in Table 1. As expected, the CVs for the Dy@C_{82}/DDAB electrode showed no electrode cation dependence, and there was no significant difference in the peak potentials. Considering these facts together with the results for the stability of Dy@C_{82} anions in the DDAB film described previously, it is proven again that the electrochemically generated Dy@C_{82} anions in the DDAB films are bound not to electrolyte cations but to the ammonium moieties on DDAB. We next selected TBAC, TBAB, $NaClO_4$, and NH_4PF_6 to investigate the electrolyte anion dependence of the Dy@C_{82}/DDAB film. As also

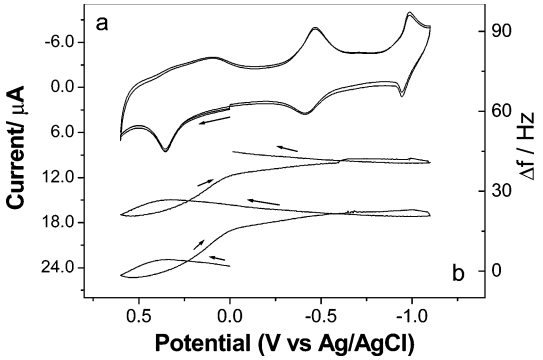
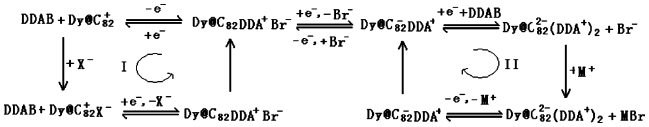


Figure 5. Simultaneous cyclic voltammogram and EQCM response of Dy@C_{82}/DDAB film on a Au/quartz electrode in a 0.1 M KCl solution (panel a: voltammetric response and panel b: QCM response). Scan rate: 50 mV s^{-1}.

listed in Table 1, the peak potential shifts for both the oxidation peak and the reduction peak showed a strong electrolyte anion dependence. With the size increasing from Cl^-, to Br^-, ClO_4^-, and PF_6^-, the peak potential became more negative. For the first oxidation of Dy@C_{82}/DDAB, it is obvious that Dy@C_{82}^+ tends to bind to the anion of the electrolyte but not to that of DDAB, and the anions with a larger size will stabilize Dy@C_{82}^+ much more. For the reduction of Dy@C_{82}/DDAB, the shift of the half-wave potentials should relate to the binding of the electrolyte anions with the cation of DDAB as postulated earlier for the film of $C_{60}/3C_{12}N^+Br^-$ and $C_{60}/4C_8N^+Br^-$.

Figure 5 displays the simultaneously recorded CV (curve a) and EQCM response (curve b) of the Dy@C_{82}/DDAB film on a EQCM gold electrode in a 0.5 M KCl solution. The CV behavior is very similar to that on the GC electrode shown in Figure 1a in the potential range of +0.7 to −1.1 V (vs Ag/AgCl). There is a frequency increase and then a decrease from a +0.0 to +0.7 V positive scan. According to the previous analysis and vis/NIR results, the peak in this range is associated with the overlap of the Dy@C_{82}^-/Dy@C_{82} and Dy@C_{82}/Dy@C_{82}^+ processes. When Dy@C_{82}^- was reoxidized to its neutral Dy@C_{82} form, some species, such as a K^+ cation incorporated into the film in advance (as discussed next), was expulsed from the film, resulting in the frequency increase. Next, while Dy@C_{82} was oxidized to Dy@C_{82}^+, Cl^- must diffuse into the film to compensate for the positive charges; thus, the frequency decreased. In the reverse scan (cathodic process), when Dy@C_{82}^+ was reduced to Dy@C_{82}, Cl^- must be expulsed from the film, accompanying the frequency increase from 0.7 to 0.25 V. While Dy@C_{82} was reduced to Dy@C_{82}^-, which bound to the cations of DDAB, the anion of DDAB (Br^- anion) would diffuse into the solution, resulting in the frequency increase further. There are two possible ways to compensate for the additional negative charge resulting from the Dy@C_{82}^{2-} or Dy@C_{82}^{3-} anions: (1) Br^- present in the DDAB film could continue diffusing into the bulk aqueous solution, which would cause a frequency increase. (2) K^+ could diffuse into the film to compensate for the negative charges caused by additional Br^-, in which case the frequency decreases. On the basis of the fact that the frequency accompanying the Dy@C_{82}^-/Dy@C_{82}^{2-} and Dy@C_{82}^-/Dy@C_{82}^{3-} steps increases slightly, possibly some K^+ was simultaneously incorporated into the film when Br^- was diffusing outward from the film. This also explains that the frequency increased during a subsequent reverse anodic scan from −0.1 to 0.25 V during the Dy@C_{82}^{3-} to Dy@C_{82} processes, which suggests that K^+ diffused outward from the film for the excess of positively charged DDA^+ cations. Noticeably, the frequency difference during each cycle is very small (less than 30 Hz), which indicates that the mass of the film during the whole process did not vary very much.

Processes during the Electrochemical Reaction of Dy@C_{82}/DDAB Films in Aqueous Solution. Considering the spectroelectrochemistry, electrolyte dependence, and EQCM results, we propose a mechanism for the electrochemical process of the first two reductions and the first oxidation of Dy@C_{82}/DDAB in aqueous solution as shown in the following:



Here, M^+ is the electrolyte cation and X^- is the electrolyte anion. When neutral Dy@C_{82} in a DDAB film is oxidized to the Dy@C_{82}^+ cation, the potential cycling will follow path I indicated as the curved arrow I, where anions in the solution, such as Cl^-, will diffuse into the film to balance the positively charged Dy@C_{82}^+ cation, and these anions will diffuse out of the film once Dy@C_{82}^+ is reduced to the original form Dy@C_{82} in the DDAB film. Therefore, path I is associated with the insertion or expulsion of anions in solution to the film. For the reduction process of Dy@C_{82} in the DDAB film, the Dy@C_{82} anions always bind to the large sized cation DDA^+ in the film. When Dy@C_{82} is reduced to the Dy@C_{82}^- anion, the Br^- anion in the film will be ejected from the film. However, if Dy@C_{82}^- is further reduced to Dy@C_{82}^{2-}, Dy@$C_{82}^{2-}(DDA^+)_2$ will be formed. As shown in path II, to compensate the more negatively charged film by excess Br^-, cations of the electrolyte were simultaneously incorporated into the film to bind with Br^- while some Br^- was diffusing outward from the film. These cations would be expulsed from the film when Dy@C_{82}^{2-} is oxidized to Dy@C_{82}^-. Likewise, a similar mechanism will be involved for the process of Dy@C_{82}^{2-}/Dy@C_{82}^{3-}.

It can be seen from this mechanism that the Dy@C_{82} anions in the film, Dy@C_{82}^-, Dy@C_{82}^{2-}, as well as Dy@C_{82}^{3-}, always bind to the large sized cation DDA^+. Hence, they are stable in water or air, whereas when Dy@C_{82}^+ binds to the anion of the electrolyte, it is less stable in air. Furthermore, because of all the ions getting in and out of the film in the whole electroreduction process, including Br^-, and because the electrolyte ions are much smaller than the Dy@C_{82} ions, they can easily get into and out of the film. As such, no structural reorganization, like that of the Dy@C_{82} film, is needed after the electroreaction of the film; hence, the reversible redox process is obtained.

Conclusions

In summary, the electrochemical behavior of metallofullerene (Dy@C_{82}) embeded into the cationic DDAB film on the electrode was investigated in detail. For the first time, the redox peaks of this film were characterized using vis/NIR spectroscopy. Three pairs of reduction peaks and one couple of oxidation peaks can be obtained in the DDAB film in aqueous solution. Most important is that both oxidation and reduction of Dy@C_{82} are obtained in this film, which supplies useful information for studying the interaction between Dy@C_{82} ions and environmental ions involved in DDAB and electrolyte. On the basis of the results of EQCM, it is clear that the Dy@C_{82} anions in the film, Dy@C_{82}^-, Dy@C_{82}^{2-}, as well as Dy@C_{82}^3, always bind to the large sized cation DDA^+, while Dy@C_{82}^+ binds to the anion of the electrolyte. Therefore, these anions are more stable toward water and air. The whole electrochemical process is related to the diffusing out and into the film of the

electrolyte anions, the Br^- anion of DDAB, as well as the electrolyte cation to compensate for the extra negative charge of Br^- in DDAB when $Dy@C_{82}^{2-}$ or $Dy@C_{82}^{3-}$ was generated. Therefore, the electrochemistry for $Dy@C_{82}$/DDAB modified electrodes is electrolyte anion dependent. This should be very useful information for metallofullerene applications in biology.

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References and Notes

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