In Situ Spectroelectrochemistry and Electrochemical Quartz Crystal Microbalance (EQCM) Characterization of C_{60} Embedded in a Tetraoctylammonium Bromide Film in Aqueous Solution

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The electrochemical behavior of C_{60} embedded in tetraoctylammonium bromide (TOAB) films deposited on glassy carbon, quartz crystal microbalance (QCM) gold crystals, and indium tin oxide (ITO) electrodes was investigated in detail. Three reversible redox peaks were observed in aqueous solution. The first reduction peak for a C_{60}–TOAB film in aqueous solution was found to be much more positive (500 mV shift) than that reported for C_{60} in nonaqueous solution. In situ Vis/NIR spectra were recorded to monitor the electrochemical processes of C_{60}–TOAB on the electrode surfaces. The results provide the first direct evidence for the generation of discrete monoanions and dianions of C_{60} in the TOAB film in aqueous solution. The electrode processes were also monitored using electrochemical quartz crystal microbalance (EQCM) in different supporting electrolytes. Pronounced anionic effects due to diffusion into or out from the C_{60}–TOAB films were also observed for first time.

Introduction

The electrochemistry of fullerenes has received much attention, because it provides direct information about the multiple redox states and properties of these compounds.[1] It is well-known that C_{60} in solution is readily reduced electrochemically, with up to six reversible, one-electron reductions.[1–5] Many spectroscopic techniques have been used to characterize the processes and products of the electrochemical reductions of fullerenes in solution.[6] Kadish et al.[3] reported the spectroelectrochemical study of C_{60} and C_{70} fullerenes and their monoanions, dianions, trianions, and tetranions. UV/Vis/NIR spectra provided clear evidence for the anions and/or cations of the fullerenes at different potentials.[6–11]

The electrochemistry of fullerene films has also been explored, because such films could be potentially good electrode materials for many applications.[12] However, the electrochemical behavior of C_{60} films on electrodes is much more complicated than that of C_{60} in solution.[13,14] Electrochemical quartz crystal microbalance (EQCM) and scanning electrochemical microscopy have been employed to study the electrochemical processes of C_{60} films.[14–19] Self-assembled monolayer films of C_{60} on electrode surfaces have been reported.[20–23] Most of the studies of the electrochemistry of fullerene films are reported in nonaqueous solutions.[13] The electrochemistry of fullerene films in aqueous solutions has been limited, because of the insolubility of fullerene in water and the irreversibility of both reduction and oxidation processes. Recent studies have revealed the potential utility of fullerenes and their derivatives in biological systems, such as in HIV treatment and in photodynamic therapy.[24–26] This has generated interest in characterizing the redox properties of fullerenes in aqueous media. To improve the solubility of fullerenes in water, one of the methods reported is to form cyclodextrin inclusion complexes.[27,28] Boulas et al.[29] reported the preparation of a water-soluble magenta γ-cyclo-

dextrin inclusion complex of C_{60} (γ-CD/C_{60}). The spectroelectrochemical results indicated that the electrogenerated γ-CD/C_{60}^- radical monoanion was stable in water.

It is well-known that the electrochemical behavior of C_{60} films is completely irreversible in aqueous solution and it is very difficult to get well-defined cyclic voltammograms (CVs) of C_{60} films on electrodes in aqueous solution.[30–33] Recently, Nakashima et al. published a series of articles showing the reversible electrochemical behavior of C_{60} in lipid films on electrode surfaces in aqueous solution.[34–40] They employed an unconventional lipid organic–electrolyte (dimethylditetradecyl-ammonium poly(styrene sulfonate)) in the thin film, to improve electron transfer and observed reversible CVs for C_{60}.[34,35] Szucs et al.[31–33] reported the irreversible electrochemical reaction and the cationic effects on the voltammetric behavior of C_{60} film electrodes in aqueous solution. To the best of our knowledge, no spectroelectrochemical characterization of the anions of C_{60} in film-modified electrodes in aqueous solution has been reported. In the present work, the electrochemical behavior of C_{60} in tetraoctylammonium bromide (TOAB) film was investigated in aqueous solutions.

Experimental Section

Chemicals. C_{60} (SES Research, Houston, TX) was directly used without further purification. TOAB was purchased from Fluka Chemika. Toluene (HPLC grade) was purchased from Fisher Scientific. KCl, NaCl, LiCl, KBr, NaI, NaF, Na_2SO_4, $LiClO_4$, $KClO_3$, KNO_3, $NaBrO_3$, CH_3COONa, and tetraethyl-ammonium chloride (TEAC) were reagent grade and directly used as received. All solutions were prepared with deionized water (Barnstead Nanopure, 18 MΩ).

Instrumentation. All the electrochemical and quartz crystal microbalance (QCM) measurements were performed with the CHI 440 electrochemical workstation (CH Instruments Inc., Austin, TX). A single-compartment, three-electrode cell configuration was used in this work, with a 0.5 M supporting

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electrolyte pre-degassed at least 10 min with argon before use. Platinum wire was employed as the counter electrode. All the potentials in this work were referenced relative to Ag/AgCl (3 M NaCl). In situ spectroelectrochemical experiments were conducted using a 3101-PC UV−Vis−NIR spectrometer (Shimadzu, Japan) in combination with the CHI 440 electrochemical workstation.

Preparation of the C$_{60}$−TOAB Film on Electrodes. Glassy carbon electrodes (GCEs) (CHI, 3 mm in diameter) were polished with 1.0 and 0.3 μm aluminum paste and ultrasonicated in deionized water and acetone. AT-cut QCM crystal coated with a gold disk (CHI, area of 0.205 cm^2) was treated with Piranha solution (a mixture of 30% H$_2$O$_2$ and 70% concentrated H$_2$SO$_4$) and rinsed with deionized water. Indium tin oxide (ITO) was rinsed with ethanol and acetone. All the electrodes were dried under a nitrogen stream before they were used for the preparation of the C$_{60}$−TOAB film. A solution-cast method was used in this work. The cast solution for the C$_{60}$−TOAB film was a 1 mM C$_{60}$ toluene solution containing 10 mM TOAB (the ratio of C$_{60}$:TOAB was 1:10). Nakashima et al. used a 1:19 ratio of C$_{60}$ to dimethylditetradecylammonium poly(styrene sulfonate).[34] We tried different C$_{60}$:TOAB ratios, ranging between 1:10 and 1:19. There was no significant difference in the voltammetric response of the resultant films. However, we found that 1:10 was the best ratio for the EQCM experiments. As control experiments, 1 mM C$_{60}$ and 10 mM TOAB were also separately prepared in toluene and their films were analyzed. Several microliters of the solutions were deposited on the GCE or QCM gold electrode surfaces. The electrodes were dried in air for at least 4 h. For the spectroelectrochemical measurements, 15−30 μL of solution was deposited dropwise on the ITO electrode and dried for 24 h in air. After further drying under a nitrogen stream, the C$_{60}$−TOAB film was used for the electrochemical investigation. All experiments were performed at room temperature (20 ± 2 °C).

Results and Discussion

Electrochemical Behavior of C$_{60}$−TOAB Film in Aqueous Solution. The C$_{60}$−TOAB film on the GCE was dried in air and under a nitrogen stream before electrochemical analysis. As shown in Figure 1, the typical CV of C$_{60}$−TOAB/GCE in a 0.5 M TEAC aqueous solution shows three reversible redox couples (called peaks I, II, and III in the following discussion). There are virtually no current peaks observed in the background (dotted line) in the same potential range. This indicates that all the peaks result from the C$_{60}$, not from the TOAB. For simplicity, only the initial three cycles are presented in Figure 1. The peak currents increased sequentially during the first five cycles and reached a maximum after ~10 cycles, followed by very slow subsequent decreases. The cathodic and anodic peak potentials are $E_{pc}(I) = -0.15$, $E_{pa}(I) = -0.06$ V for peak I; $E_{pc}(II) = -0.65$ V, $E_{pa}(II) = -0.58$ V for peak II; and $E_{pc}(III) = -1.28$ V, $E_{pa}(III) = -1.22$ V for peak III. After the peak currents reached their maxima, the CV of the C$_{60}$−TOAB film electrode was recorded at different scan rates. Experimental results showed that the peak currents were proportional to the square root of the scan rate in the range of 20−500 mV/s for all three peaks (data not shown). This observation indicates that the electrochemical reaction at the C$_{60}$−TOAB film electrode is a diffusion-controlled process. Similar electrochemical behavior was described for the C$_{60}$ and tetraoctylphosphonium bromide-modified basal pyrolytic graphite (BPG) electrode by Nakashima.[37] It is important to note and compare the pronounced differences between the first and second CV potential
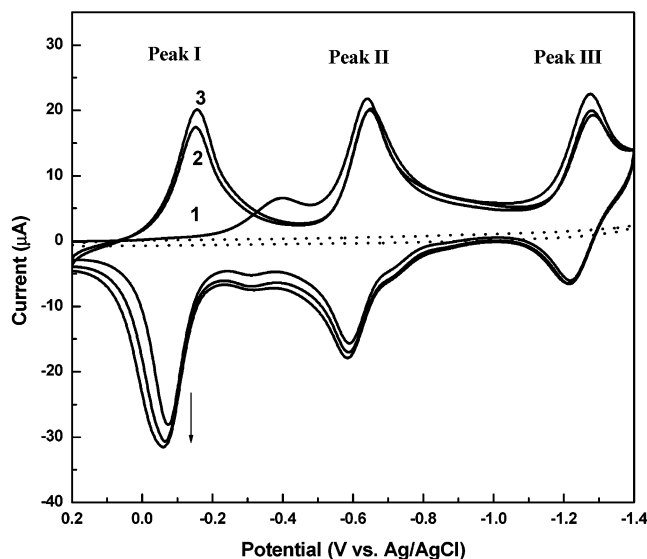

Figure 1. Typical cyclic voltammogram (CV) of C$_{60}$−TOAB film on the GCE in a 0.5 M tetraoctylammonium chloride (TEAC) aqueous solution. Dotted line represents the CV of TOAB film on the GCE. Scan rate: 100 mV/s.

scans. In the first scan, a small peak at approximately −0.4 V is observed, whereas no obvious peak appeared at −0.15 V. However, in the second and subsequent scans, the peak at −0.4 V disappeared completely, whereas a new sharp peak appeared at −0.15 V (peak I). The increase in peak current for peak I was much more significant than that for peaks II and III in the following 10 cycles. In addition, the corresponding oxidation peak current for peak I was larger than those for peaks II and III. Very similar results were obtained for the GCE covered with C$_{60}$−TOAB film in 0.5 M LiCl, NaCl, KCl, NaF, CH$_3$-COONa, and Na$_2$SO$_4$ solutions. Detailed comparisons are discussed in the EQCM section (see below).

There are two interesting observations that can be derived from the electrochemical properties of the C$_{60}$−TOAB films: (i) the pronounced differences between the first and second scans, especially for peak I, and (2) the ease of reduction of C$_{60}$ in the C$_{60}$−TOAB film on the surface of the electrode (−0.15 V), compared to that in organic solutions (−0.6 V vs Ag/AgCl). Related to these observations is the question of how many electrons per C$_{60}$ molecule are being transferred during each process. These observations and questions were addressed independently.

To understand the difference in peak I between the first and second scan, CVs were recorded using different potential scan ranges, and these results are shown in Figure 2. If the potential was scanned positive of −0.4 V, which corresponds to the small peak (in the first scan in Figure 1) (see curve A in Figure 2), the current at approximately −0.1 V was very small and no significant increase in the current after three cycles was observed. When the potential was cathodically scanned past the small peak at −0.4 V but before peak II, a small peak can be observed at −0.4 V in the first reduction scan, which disappeared in the second and third scans (curve B in Figure 2). We can clearly see the oxidative and reductive peaks that correspond to peak I only after the first scan past −0.4 V. This indicates that peak I was transformed from the small peak at −0.4 V when the C$_{60}$−TOAB film was reduced. By further extending the cathodic potential scan to −0.9 V (past peak II), as shown in curve C in Figure 2, we can see the appearance of a large peak I and the disappearance of the peak at −0.4 V. Peak II appears at −0.62 V (formal potential). After scanning beyond

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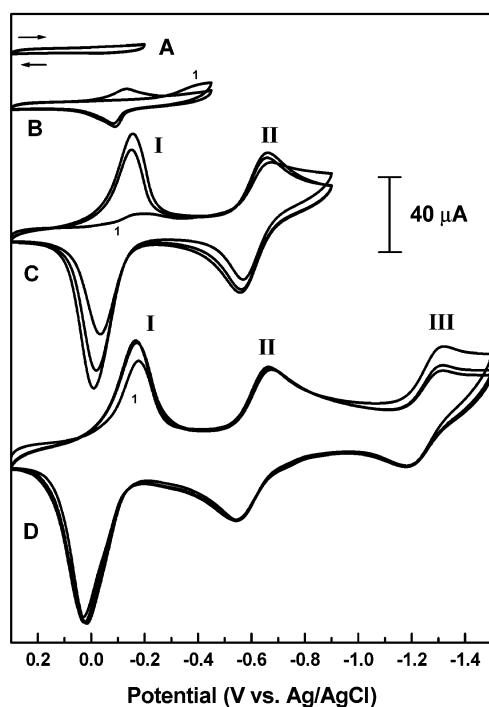
Figure 2. CVs of a C_{60}–TOAB film on the GCE in a 0.5 M TEAC aqueous solution under different potential ranges ((A) +0.3 to −0.2 V, (B) +0.3 to −0.45 V, (C) +0.3 to −0.9 V, and (D) +0.3 to −1.5 V). Scan rate: 100 mV/s.

peak II, the peak current for peak I became much larger than that in curve B in Figure 2 and increased significantly in subsequent cycles. When the potential was scanned past peak III (curve D in Figure 2), there was no significant change in the peak currents of peak I or II; however, the oxidation peak potentials shifted anodically by ∼20 mV. These results indicate that peak I evolves from the initial small peak at −0.4 V and is closely related to peak II.

The voltammetric behavior of C_{60}–TOAB on the gold electrodes is very similar to that on the GCE, except that the peak currents decreased faster than those on the GCE when the potential was scanned to −1.4 V. This is possibly due to the reductive evolution of hydrogen on the gold electrode surface. Therefore, the potential was controlled to less than −1.0 V vs Ag/AgCl in the EQCM experiments, and these are reproducible and reliable.

It is well-known that the first reduction peak for C_{60} in organic solvents occurs at approximately −1.0 V vs Fc/Fc⁺. The reduction potentials of fullerenes are dependent on the nature of the supporting electrolytes, the solvents, and the temperatures.[41] Kadish et al. investigated the effect of tetraalkylammonium cations on the electrochemical behavior of C_{60} in different aprotic organic solvents, and they found a positive shift of the half-wave potential for the first and second reduction peaks with increasing alkyl chain length.[41,42] The first reduction peak of the C_{60}–TOAB film in aqueous solution occurs at −0.55 V vs Fc/Fc⁺ (−0.15 V vs Ag/AgCl), which is considerably more positive than that for C_{60} in organic solvents. As reported by Bard, Kadish, and Oyama,[12−16,18] the returning oxidation peak potentials (E_{pa}) of the reduced C_{60} in the films in organic solution are more positive than those of C_{60} in organic solution. Kadish et al. reported that the E_{pa} value for peak I was −0.57 V vs Fc/Fc⁺ (−0.22 V vs SCE) for a C_{60} film on a QCM gold electrode in acetonitrile solution.[16] Bard et al.[12] reported the first electrochemical study of C_{60} films in acetonitrile solution, and the potentials for the first and second anodic peaks were

found to be −0.5 and −1.0 V vs Fc/Fc⁺. These are relatively close to the peak potentials observed in this work for the C_{60}–TOAB film in aqueous solution, indicating that C_{60} in films has similar voltammetric behavior in both nonaqueous and aqueous solutions. This is possibly due to the strong aggregation of C_{60} in the films, on the basis of observations made for solution-coated films (multilayers) and self-assembled monolayer (SAM) films. Mirkin et al. reported SAMs of fullerene derivatives on electrode surfaces and found that the first reduction of C_{60} in the film occurred at approximately −1.2 V vs Fc/Fc⁺, which is close to that (−1.0 V) for C_{60} in organic solution.[21,22] Echegoyen et al. reported the electrochemical behavior of fullerenes in the SAM films and found that their reduction/oxidation potentials (−1.1 V vs Fc/Fc⁺) are the same as those for the same compounds in organic solutions.[23,43] However, for the C_{60} coated films (multilayer), the E_{pa} value for the first peak was −0.5 V vs Fc/Fc⁺, which is much more positive than that for the C_{60} in organic solvents and in a SAM film. It seems reasonable to attribute the positive potential shift to the three-dimensional aggregation effect of C_{60} in the solution-coated film.

Reversible redox behavior was obtained for the C_{60}–TOAB film in aqueous solution when TOAB was added into the film, whereas a large potential separation (∼500 mV) is observed between the first reduction and the reoxidation process of C_{60} for a pure C_{60} film. Large structural rearrangements of the surface films following the initial electron-transfer process were invoked to explain the large splitting that was observed.[12,13] In the present work, the peak-to-peak separations for peak I (ΔE) was 95 mV and 130−150 mV in Figure 1 and curves C and D in Figure 2, respectively, which are larger than those for peaks II and III. These results indicate that a more drastic reorganization of the C_{60} in the film occurs when C_{60} is reduced from the neutral to the monoanion (peak I) than when it is reduced from the monoanion to the dianion (peak II) and subsequently to the trianion (peak III). Furthermore, a remarkable difference was found for peak I between the first and second scans. This indicates that the structure of the C_{60}–TOAB film before electrochemical reduction might be quite different from that after the first reduction. A significant difference is usually obtained between the first and subsequent scans during voltammetric experiments for drop-coated films.[12−14,18] Kadish et al. reported a big difference between the first and subsequent scans, which is typical for thin films with high resistance.[17]

Nakashima et al. found that the formal potentials of C_{60} embedded in cast films of ammonium-based lipids exhibit a strong dependence on the lipid chemical structure.[34−36] They reported that there is a tendency for the formal potential to be shifted positively, because of the strong coulomb-coupled binding of the anions of C_{60} with the ammonium cations.[38−40] In addition, there should be some electrostatic repulsion between the C_{60} anions in the film. The electrostatic repulsion interaction would be especially strong for the pure C_{60} film, because of aggregation. Thus, a relatively high activation energy, i.e., more negative potential, is necessary for the electrochemical reduction of C_{60} to C_{60}^- and C_{60}^{2-} on the surface. As reported by Bard et al.,[12] the first reduction potential for the C_{60} film without TOAB was approximately −1.1 V vs Fc/Fc⁺ (−0.7 V vs Ag/AgCl) in acetonitrile. However, if positively charged cations such as tetrabutylammonium (TBA⁺) and tetraoctylammonium (TOA⁺) are incorporated into the film, it favors the generation of the negatively charged anions of C_{60} in the film, because of favorable electrostatic interactions. That way, aggregation is inhibited to some extent by the addition of surfactant TOAB
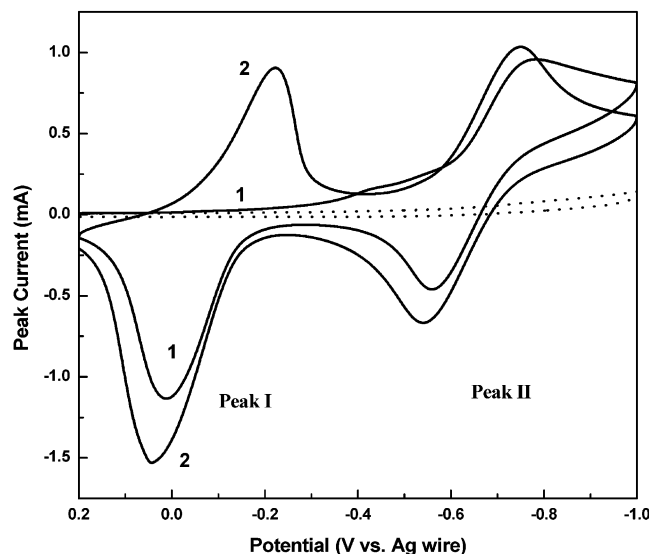
Figure 3. Typical CV of C_{60}−TOAB film on an ITO electrode in a 0.5 M KCl solution. Dotted line represents the CV of TOAB film on the ITO electrode. Scan rate: 100 mV/s.

during the preparation of the films. This is why reversible redox peaks were obtained and the reduction peak potentials are less negative for the C_{60}−TOAB film in aqueous solution than those for the C_{60} film without TOAB and C_{60} in organic solution.

In Situ Spectroelectrochemical Study of C_{60}−TOAB Film on ITO in Aqueous Solution. The electrochemical behavior of C_{60}−TOAB films on ITO electrodes was investigated to select the proper potentials for in situ spectroelectrochemical analysis. Figure 3 shows the typical CV of a C_{60}−TOAB film on ITO, which was obtained in a 0.5 M KCl solution. The dotted line represents the background CV of a plain TOAB film on an ITO electrode. The peak-to-peak separation for both peaks I and II of C_{60} is bigger than that on GCE or gold electrodes. This is probably due to the higher resistance of the ITO electrode. Another possible reason is that the film on the ITO is thicker, because of the larger solution volumes deposited, to obtain stronger spectral signals. For the very thin C_{60}−TOAB film on ITO (data not shown), the peak-to-peak separation was smaller and comparable to those on GCE and QCM gold electrodes.

To follow the electrochemical processes of C_{60} in the film, five different potentials were selected and applied while the Vis-NIR spectrum was recorded after 60 s of applying each potential. Figure 4 shows the experimental results obtained at different applied potentials. As can be seen, at +0.2 V, the spectrum is identical to that obtained for the original film, indicating that neutral C_{60} is stable in the film. At −0.2 V, a new absorption peak was observed at 1080 nm (Figure 4), although no obvious reduction peak was observed (see Figure 3). When the potential was changed to −0.4 V, corresponding to a small voltammetric peak (only in the first scan), the spectrum obtained was similar to that recorded at −0.2 V, except slightly more intense. Thus, the same species is formed at these different potentials. According to the literature,[6,10] the absorption band at 1075 nm corresponds to the C_{60} monoanion in organic solution. Fukuzumi et al.[44−46] and Rapta et al.[11] reported the NIR band of the C_{60} monoanion in organic media at 1080 nm. It is thus reasonable to assign the 1080 nm absorption band to the C_{60} anion. At a potential of −0.85 V, the peak at 1080 nm decreased significantly, whereas a new peak was observed at 950 nm. An absorption band for the C_{60}^{2-} dianion in organic solution was reported at exactly the same wavelength,[6,8,11,47] so the absorption
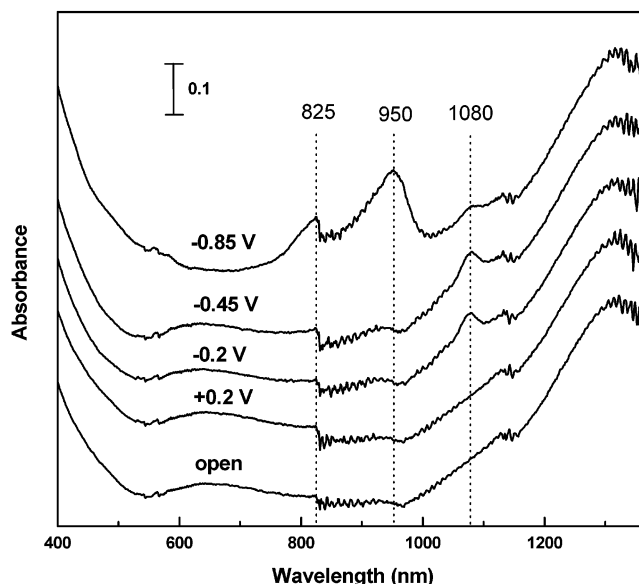
Figure 4. Vis/NIR spectra of C_{60}−TOAB film on ITO at different potentials before potential scan in a 0.5 M KCl solution. Applied potential is labeled on the curves.
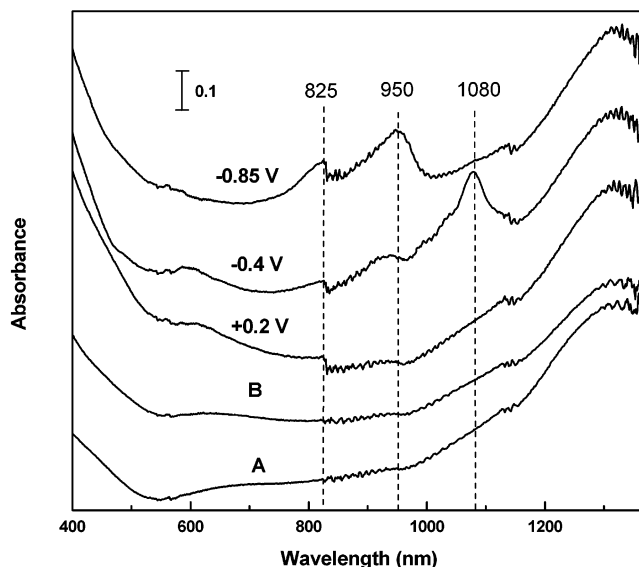

Figure 5. Vis/NIR spectra of C_{60}−TOAB film on ITO at different potentials after potential scan in a 0.5 M KCl solution. Applied potential is labeled on the curves. Curves A and B represent the background spectrum of a pure TOAB and pure C_{60} film on an ITO, respectively.

band at 950 nm is due to the formation of the C_{60} dianion. Therefore, in situ spectroelectrochemical results clearly demonstrate the formation of the monoanions and dianions of C_{60} in the film.

Repeated switching of the applied potential between +0.2, −0.4, and −0.85 V showed that the process of film reduction is fully reversible (see Figure 5). At +0.2 V, the bands at 950 and 1080 nm disappear, whereas returning the potential to −0.4 and −0.85 V causes the bands at 1080 and 950 nm to reappear, respectively.

On the other hand, a film containing only C_{60} on an ITO electrode did not show significant spectral changes at different applied potentials. Only the neutral C_{60} spectral characteristics were observed, even at −0.85 V (curve B in Figure 5). These results are completely consistent with the CV results, i.e., almost no electroreduction of the pure C_{60} film was detected in aqueous solution in the studied potential range. All spectroelectrochemi-
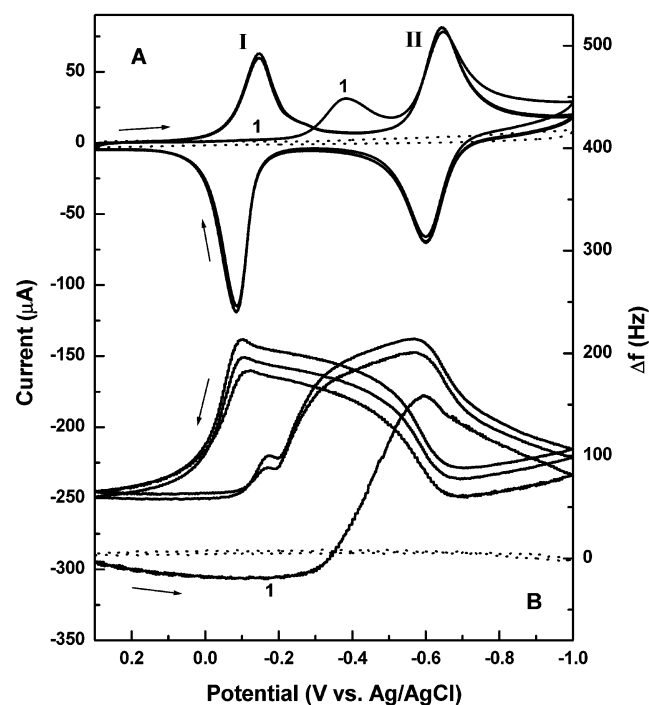
Figure 6. EQCM response of C_{60}−TOAB films in a 0.5 M KCl solution ((A) voltammetric response and (B) QCM response). Dotted lines represent the background responses of the pure TOAB film. Scan rate: 100 mV/s.

cal experiments were repeated at least twice on different ITO electrodes, and they were perfectly reproducible. Results clearly demonstrate that a C_{60} film cannot be readily reduced electrochemically in aqueous solution, whereas a C_{60}−TOAB film can be easily reduced and reoxidized electrochemically and the redox process is very reversible in aqueous solution. C_{60}^- and C_{60}^{2-} anions were generated on the electrode surface by one-electron reduction at peaks I and II, respectively.

Electrochemical Quartz Crystal Microbalance Study of C_{60}−TOAB Film. Electrochemical quartz crystal microbalance (EQCM) is very useful and informative to probe electrode surface reactions.[48−50] Bard, Kadish, and Oyama applied the EQCM technique to study fullerene films in organic solvents.[15−18] The measurements of mass-transport processes within fullerene films during electrochemical reactions showed the incorporation/ expulsion of TBA$^+$ into/out from the film after the first and second peaks and the dissolution/deposition of fullerene films after the third peak.[13]

Figure 6 displays the simultaneously recorded CV (Figure 6A) and QCM response (Figure 6B) of a C_{60}−TOAB film on a QCM gold electrode in 0.5 M KCl solution. The voltammetric behavior (Figure 6A) is very similar to that on the GCE shown in Figure 1 in the range of +0.2 to −1.0 V. By integrating the oxidation peak area of peak I and assuming that it corresponds to a one-electron process, it was found that ∼50% of the total C_{60} incorporated in the C_{60}−TOAB film was electroactive in aqueous solution. At present, it is not clear why only ∼50% of the total C_{60} cast on the film electrode remained electroactive. Nakashima et al. reported that only 63% (measured by similar electrochemical means) of C_{60} cast on the film electrodes was electroactive.[37] There is no significant frequency change (Δf) before the small peak at −0.4 V, and, after that, a frequency increase (mass decrease) was observed upon reduction of the film during the first cathodic process. After peak II, the frequency decreased. A reversible QCM response was obtained in the reverse potential scan (anodic process); i.e., the mass

decreased at peak II and instantly increased after peak I. In the second cathodic scan, the mass decreased after peak I, followed by a short, constant-mass range at approximately −0.18 V, and another increase to a constant value at the start of peak II. After peak II, the frequency decreased, similar to the behavior observed during the first cycle. In the reverse scan, the opposite frequency change was obtained, and the frequency returned almost exactly to the original value. There was no significant net frequency change in the second and third cycles. Both the CV and QCM responses demonstrate that the electrochemical redox reactions of the C_{60}−TOAB film are perfectly reversible after the first cycle in aqueous solution.

According to the Vis/NIR results, peaks I and II are attributed to the first and second one-electron reductions, respectively. Therefore, in the first cathodic scan, C_{60}^- anions form after the small peak at −0.4 V. There are two possible ways to compensate the negative charge of C_{60}^- anions in the film: (1) Br$^-$ anions present in the C_{60}−TOAB film could diffuse into the bulk aqueous solution, which would cause a frequency increase, or (2) K$^+$ cations could diffuse into the film, in which case the frequency would decrease. Another possibility would be for C_{60}^- anions to diffuse into the water phase; however, repeated cycles showed no irreversible loss of the fullerene, ruling out this possibility. On the basis of the fact that the frequency increased, the small peak at −0.4 V is probably the result of the expulsion of Br$^-$ anions from the film. After peak II, K$^+$ cations are incorporated into the film to further compensate for the additional negative charge resulting from C_{60}^{2-} formation, and thus, the frequency decreased. In the reverse scan (anodic process), when C_{60}^{2-} was oxidized to C_{60}^-, K$^+$ cations must diffuse outward from the film and, thus, the frequency increases. When C_{60}^- was further oxidized to neutral C_{60}, Cl$^-$ anions possibly diffused into the film to compensate for the excess of positively charged TOA$^+$ cations and, thus, the frequency decreased. The EQCM responses directly monitor the diffusion of anions and cations into or out from the C_{60}−TOAB film during the electrochemical reactions in aqueous solution.

To further probe and try to understand the anionic effect on the EQCM response, we measured EQCM responses of the C_{60}−TOAB film electrodes in a 0.5 M Na$_2$SO$_4$ solution. Figure 7 shows the simultaneously recorded CV (Figure 7A) and QCM response (Figure 7B) of a C_{60}−TOAB film in a 0.5 M Na$_2$SO$_4$ solution. It can be seen that the CV is similar to that obtained in a 0.5 M KCl solution (Figure 6A), except that the peak potentials shifted 70−110 mV positively (see the $E_{1/2}$ values in Table 1). The first reduction peak appeared at approximately −0.3 V, and it disappeared completely in the second reduction scan. The reduction peak at −0.3 V in the first scan is even more well-defined than peak I in subsequent scans. The first scan may cause the formation of C_{60} populations in the film with a distribution of formal potentials, and this is why peak I is broad, compared to the voltammograms in the KCl electrolyte, and why there is a shoulder peak at −0.1 V. The frequency started to increase at −0.22 V during the first reduction scan. This can be attributed to the diffusion of Br$^-$ anions into the bulk solution, as already described. After peak II, when C_{60}^- is reduced to C_{60}^{2-}, more Br$^-$ anions diffused away from the film (possibly some Na$^+$ cations were simultaneously incorporated into the C_{60}−TOAB film; the mobility order is Br$^-$ > K$^+$ > Na$^+$), which led to an additional decrease in mass. In the reverse scan, SO$_4^{2-}$ must be incorporated into the film to compensate for the excess positive charge of the TOA$^+$ cation. When C_{60}^- was oxidized to the neutral C_{60} after the anodic peak I, more SO$_4^{2-}$ anions were incorporated into the film. In the second
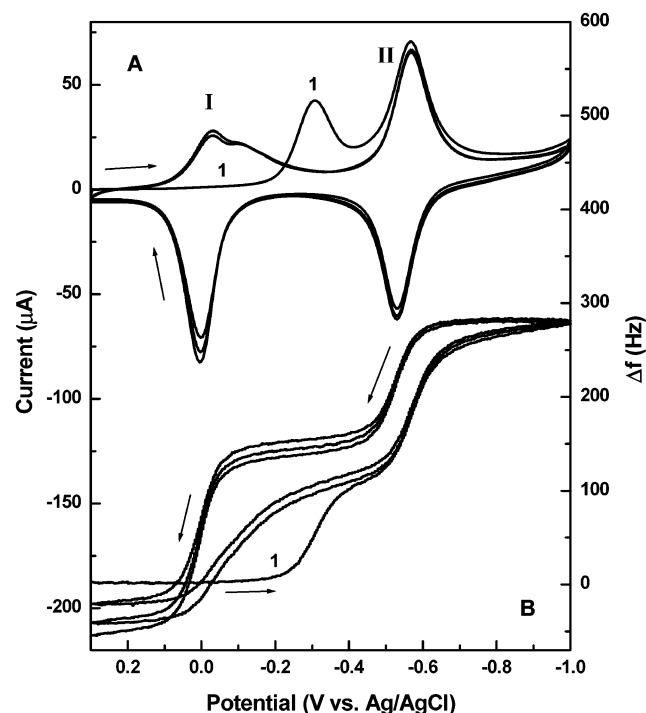
Figure 7. EQCM response of C_{60}–TOAB films in a 0.5 M Na_2SO_4 solution ((A) voltammetric response and (B) QCM response). Scan rate: 100 mV/s.

TABLE 1. EQCM Data Obtained for C_{60}–TOAB Films in Aqueous Solution

		Peak I potentials[a]			Peak II potentials[a]		
solution	$\Delta f(I)$ (Hz)	$E_{pa}(I)$	$E_{pc}(I)$	$E_{1/2}(I)^b$	$E_{pa}(II)$	$E_{pc}(II)$	$E_{1/2}(II)^b$
TEAC	120	−0.072	−0.142	−0.107	−0.586	−0.648	−0.617
KCl	120	−0.086	−0.147	−0.116	−0.601	−0.643	−0.622
NaCl	130	−0.075	−0.140	−0.107	−0.600	−0.638	−0.619
LiCl	130	−0.067	−0.132	−0.100	−0.586	−0.632	−0.609
Na_2SO_4	170	0.020	−0.030	−0.005	−0.528	−0.570	−0.549
NaAc^c	140	0.021	−0.058	−0.019	−0.491	−0.540	−0.516
NaF^c	150	0.020	−0.050	−0.015	−0.460	−0.510	−0.485

^{a} Given in units of V vs Ag/AgCl. ^{b} $E_{1/2} = (E_{pa} + E_{pc})/2$. ^{c} The potentials are not very stable (shifted slowly).

and third cathodic scans, the generation of C_{60}^- and C_{60}^{2-} anions were correlated with the expulsion of the SO_4^{2-} anion into and out from the film.

Comparing Figures 6 and 7, there is a clear effect of the electrolyte on the behavior of the first couple (peak I). The shape of the reverse oxidation process of peak I is strongly influenced by the nature of the electrolyte. The frequency change before and after the first scan seems to be complex and varied with the nature of the electrolytes used, the preparation method of the films, the amount of entrapped solvents from the solution coating, and the surface structure of the film, as well as with the QCM gold substrate. However, after the first scan, the

EQCM response is dependent mainly on the nature of the supporting electrolyte. Therefore, the EQCM responses of the C_{60}–TOAB film-modified electrodes were investigated in different supporting electrolytes, and the results after the first scan are listed in Table 1. It can be seen that there was no significant difference both in the frequency changes (Δf) and in the peak potentials when the cation was changed from TEA^+ to Li^+, Na^+, or K^+, which indicates that the electroneutrality condition during film redox processes is not cation dependent. However, when the anion was changed from Cl^- to SO_4^{2-}, Ac^-, and F^-, as listed in Table 1, the peak potentials became more positive, although the frequency change did not vary very much. The order of the peak potential ($E_{1/2}$) is $F^- > Ac^- > SO_4^{2-} > Cl^-$, which is consistent with their order of hydrophilicity. According to the Hofmeister series,[51] the hydrophilicity of the anions is $F^- > Ac^- > SO_4^{2-} > Cl^- > Br^- > NO_3^- > ClO_3^- > I^- > SCN^- > ClO_4^-$.[52] We studied the EQCM response of the C_{60}–TOAB film in other electrolytes (the anions were changed), including KBr, NaI, KNO_3, $NaBrO_3$, $KClO_3$, and $LiClO_4$. No obvious current peaks in their CVs or significant frequency changes (Δf) in their QCM response were observed. This is possibly related to their lipophilicities. These anions are more lipophilic than Cl^-, so they tend to remain in the film. These results demonstrate that the electrochemical reactions of C_{60}–TOAB films in aqueous solution are closely associated with the nature of the anions in the supporting solution where the CVs were conducted.

Processes during the Electrochemical Reaction of C_{60}–TOAB Films in Aqueous Solution. On the basis of the EQCM and spectroelectrochemistry results, we propose a mechanism for the electrochemical process of peak I for the C_{60}–OAB film-modified electrode in aqueous solution (see Scheme 1). A and B in Scheme 1 represent two different structural forms of the film. X^- represents the anion present in the solution. Form A is the original state of the C_{60}–TOAB film, where C_{60} is heavily aggregated and more difficult to reduce. At approximately −0.4 V, the aggregated C_{60} is irreversibly reduced and it gradually transforms to form B. The C_{60} anions in form B are relatively better dispersed, because of the electrostatic repulsion between the charged fullerenes and electrostatic stabilization by the TOA^+ cations in the film. Therefore, form B is more stable after the film is reduced. When the potential was scanned back to +0.2 V, an anodic peak was obtained at approximately −0.1 V. This peak corresponded to the oxidation of anionic C_{60} to neutral C_{60} in form B and the anions (X^-) present in solution diffused into the film to balance the positively charged TOA^+ cations. Peak I, which is associated with the insertion or expulsion of X^- from the film, was obtained in subsequent scans. The small peak at −0.4 V disappeared completely, because no C_{60} existed in form A. However, the neutral C_{60} in form B slowly transformed to the aggregated form A. When C_{60} in form B was kept in solution without an applied potential for a period of time (>5 min), a small peak or shoulder was

SCHEME 1
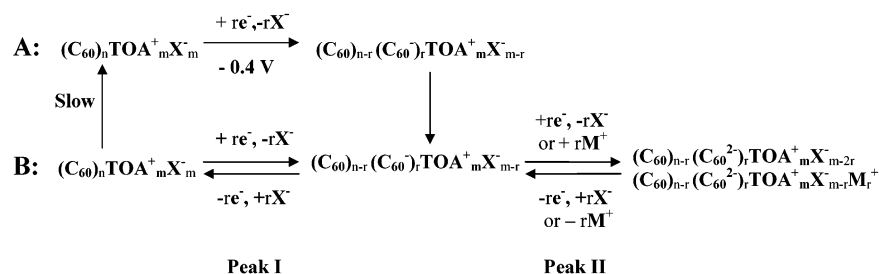
observed after peak I in the first reduction scan, which was attributed to the reduction of some C_{60} in form A. If the transformation of C_{60} from form B to form A was fast, the small peak at -0.4 V would always be observed, and this is not the case. Extending the potential scan past peak II, C_{60}^- was further reduced to C_{60}^{2-} in form B, and X^- was expelled from the film or M^+ cations in solution were incorporated into the film. If X^- expulsion dominates the process, a frequency increase is observed, as shown in Figure 7. In contrast, a frequency decrease is obtained (as shown in Figure 6) if the incorporation of M^+ cations into the film dominates this process. Likewise, a similar mechanism would be involved for peak III, i.e., one-electron reduction of C_{60}^{2-} associated with the incorporation of M^+ or X^- expulsion.

Conclusions

The results indicate that deliberate addition of a surfactant (tetraoctylammonium bromide, TOAB) into the C_{60} film improved the electrochemical behavior of C_{60} in the film in aqueous solution, and thus, three reversible redox cyclic voltammetric peaks were obtained. The first spectroelectrochemical evidence for the successive one-electron reduction of C_{60} in a film in aqueous solution was obtained and presented. The first reduction peak is associated with a large structure reorganization of the C_{60}-TOAB films. The electrochemical behavior of C_{60} and mass transport into and out from the films were related to the nature of the anions present in solution. Anion diffusion into and out from the films associated with the electrochemical reactions were observed clearly using electrochemical quartz crystal microbalance (EQCM) for the first time.

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