ELECTROCHEMISTRYAND ELECTROCATALYSIS OF FULLERENES AND SURFACTANT DDAB FILMS IN AN AQUEOUS SOLUTION

Meixian Li*, Jianxiu Wang, Nanqiang Li , Zhennan Gu
* Corresponding author
College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

Electrochemical studies of fullerene films have been very rich in nonaqueous solution [1]; however, in an aqueous solution electrochemistry of fullerene films has been very limited [2]. In recent years, our research group has investigated electrochemistry of supramolecular complex films of fullerenes with cyclodextrins and calixarenes in solution containing water [3]. Nakashima *et al* reported electrochemistry of C_{60} and surfactant films in an aqueous solution [4-7]. In this work, electrochemistry of fullerenes (C_{60}, C_{70} or Gd@C_{82})/DDAB (didodecyldimethylammonium bromide) films was studied in an aqueous solution; furthermore, electrocatalysis of some biomacromolecules at the films was investigated.

The films were prepared by dropping a few microliters of toluene solution of mixed fullerenes (C_{60}, C_{70} or Gd@C_{82}) and DDAB onto GC disk and air-dried. The cyclic voltammograms for the C_{60}/DDAB films or C_{70}/DDAB films in KCl solution in the potential range from 0 to –1.0 V exhibit two pairs of redox peaks, and two redox couples correspond to C_{60}/C_{60}^- or C_{70}/C_{70}^-, C_{60}^-/C_{60}^{2-} or C_{70}^-/C_{70}^{2-}, respectively. Furthermore, the cathodic currents for two redox couples have a linear relationship with the square root of the scan rate in the range of 0.05-0.5 V/s, indicating that the voltammograms are diffusion-controlled waves. Whereas cyclic voltammogram for the Gd@C_{82}/DDAB films in 0.1 M Bu_4NBr solution exhibits three reduction peaks and two oxidation peaks. Based on the experimental results, we deduce that the oxidation of Gd@C_{82} is an overlap of two one-electron transfers and the reduction of Gd@C_{82} is two-electron process, and the oxidation and reduction for Gd@C_{82}/DDAB films might correspond to Gd@C_{82}/ Gd@C_{82}^{2+} and Gd@C_{82}/Gd@C_{82}^{2-}, respectively. Furthermore, the anodic current for the oxidation peak and the cathodic current for the reduction peak have a linear relationship with the square root of the scan rate in the range of 0.01-0.3 V/s, indicating that both the oxidation peak and the reduction peak are diffusion-controlled waves. SEM experiment indicates that there might be a structural rearrangement in the fullerenes/DDAB films after electrochemical scan. Moreover, the fullerenes/DDAB films have good stability and reproducibility.

The experiments showed an increase in the height of the second reduction peak current and a decrease in the second oxidation peak current for C_{60}/DDAB films in 0.50 mol L^{-1} KCl with added myoglobin, hemoglobin or cytochrome c between –0.60 and –1.0 V, with no change in the peak potentials. CVs obtained for C_{70}/DDAB films showed an increase of the first reduction peak current and a decrease of the first oxidation peak current with added hemoglobin between 0 and –0.60 V in 0.4 mol dm^{-3} KCl solution, with no change in the potentials of the two electrode processes. Whereas CVs obtained for Gd@C_{82}/DDAB films with added myoglobin or cytochrome c between –0.4 and –1.0 V showed an increase in the height of the reduction and oxidation peak currents for Gd@C_{82}/DDAB films, with no change in the potentials of the two electrode processes. These suggest electrocatalysis of some biomacromolecules at fullerenes/DDAB films, indicating that fullerenes/DDAB films are capable of mediating the electron transfer rate of some biomacromolecules and the embedded fullerenes are electron transfer mediators. This provides a possibility for developing biosensors.

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