Chem. Pharm. Bull. **42**(9) 1870—1873 (1994) Vol. 42, No. 9

Direct Covalent Modification of Glassy Carbon Surfaces with 1-Alkanols by Electrochemical Oxidation

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Received March 9, 1994; accepted April 20, 1994

The modification of a glassy carbon (GC) electrode with an alkanol by electrochemical oxidation was examined. When a GC electrode was oxidized by multiple potential sweep between 0 and 2.0 V *vs.* Ag wire in 1-octanol containing H_2SO_4 (1 M), the electrode was modified with octanol, probably through an ether linkage, as judged from the voltammetric behavior of $Fe(CN)_6^{3-}$ and catechol at the treated electrode, which closely resembled that at a long-chain alkanethiol-modified gold electrode. In the modification, the potential range and the sweep rate affected the extent of linking of the alcohol to the surface, and a potential sweep at 10 mV/s from 0 to 2.0 V gave a GC electrode tightly covered with the alcohol. The membrane thus formed on the GC electrode was stable not only to applied potential bias over the range from −0.5 to 1.5 V *vs.* SCE (saturated calomel electrode) in 0.1 M aqueous NaCl solution but also to sonication in H_2O and MeOH. *n*-Alkanols of various chain lengths were also used to modify a GC electrode. The depression of the electrode process of $Fe(CN)_6^{3-}$ at the modified electrodes was enhanced as the carbon number in the modifiers increased.

Keywords covalent modification; glassy carbon surface; anodic oxidation; alkanol; cyclic voltammetry; modified carbon electrode

A carbon electrode subjected to anodic surface oxidation in an aqueous medium is known to show high electrochemical performance for some species.[1] The phenomena observed at an anodized carbon electrode can be ascribed to oxygen functionalities formed on the carbon surface, though the mechanism that brings about such surface conditions is not clear.[2] One possibility is that carbocations formed by the oxidation of the electrode surface itself are attacked by H_2O molecules in the medium, creating hydroxy group sites on the surface, some of which are further oxidized to carbonyl and carboxyl groups. If this is the case, anodic treatment of a carbon electrode in the presence of 1-alkanol instead of H_2O will directly introduce the alkyl group *via* an ether-linkage to the surface. This hypothesis is very attractive not only because covalent modification of carbon surfaces has been attracting great attention in the fields of electrochemistry[3] and material science,[4] but also because general methods to modify carbon surfaces with alkyl groups *via* an ether linkage require at least two-step reactions, which consist of the oxidative formation of hydroxyl groups on the surfaces followed by their alkylation.[5] Herein, we report a direct covalent modification method of a glassy carbon (GC) surface with alkanols.

Results and Discussion

As reported,[6] a cycled potential method, that is, cyclic voltammetry (CV) was employed to examine the possibility of modifying a GC electrode anodically with an alkanol. When a mechanically polished GC disk electrode was subjected to CV in 1-octanol containing H_2SO_4 (1 M) with a potential sweep rate of 10 mV/s between 0 and 2.0 V *vs.* Ag wire, an irreversible voltammetric peak appeared at 1.85 V, which contracted upon successive potential sweeps (Fig. 1A). However, the origin of the peak is not clear. In order to probe what had happened to the GC surface, CV of $Fe(CN)_6^{3-}$ in 0.1 M aqueous NaCl was performed at the GC electrode treated anodically in 1-octanol (C8-GC electrode). Before the CV measurements, the modified GC electrode was treated cathodically by sweeping between 0 and −0.5 V *vs.* saturated calomel electrode (SCE) in 0.1 M aqueous NaCl, five times. This procedure confirmed that the background current at the C8-GC electrode was stable. As is apparent from Fig. 1B, the electrode process of $Fe(CN)_6^{3-}$ at the C8-GC electrode was depressed as the number of sweeps in the anodic treatment was increased, and was extremely retarded after the fifth sweep.

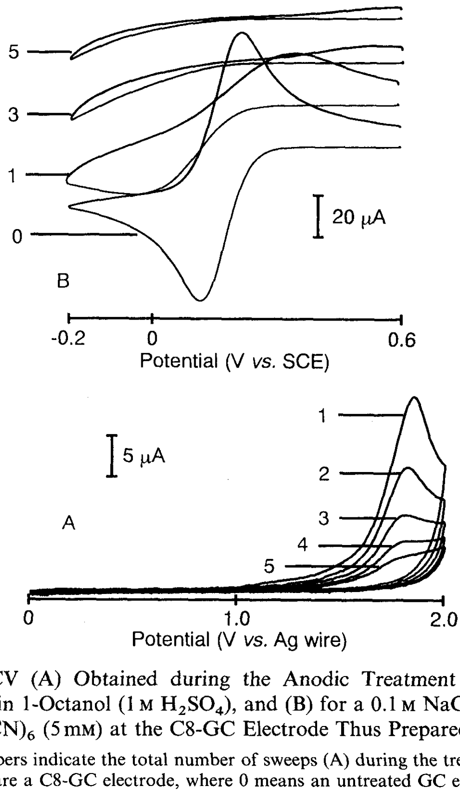

Fig. 1. CV (A) Obtained during the Anodic Treatment of a GC Electrode in 1-Octanol (1 M H_2SO_4), and (B) for a 0.1 M NaCl Solution of $K_3Fe(CN)_6$ (5 mM) at the C8-GC Electrode Thus Prepared

The numbers indicate the total number of sweeps (A) during the treatment and (B) to prepare a C8-GC electrode, where 0 means an untreated GC electrode.

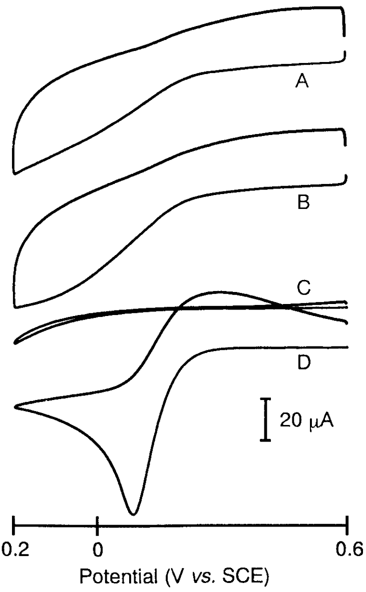

Fig. 2. Voltammograms for a 0.1 M NaCl Solution of $K_3Fe(CN)_6$ (5 mM)

(A) and (B) at a GC electrode anodized in 1 M aqueous H_2SO_4; (C) and (D) at a C8-GC electrode; (B) and (D) in the presence of trimethyldodecylammonium bromide (100 μM); voltages sweep rate, 100 mV/s.

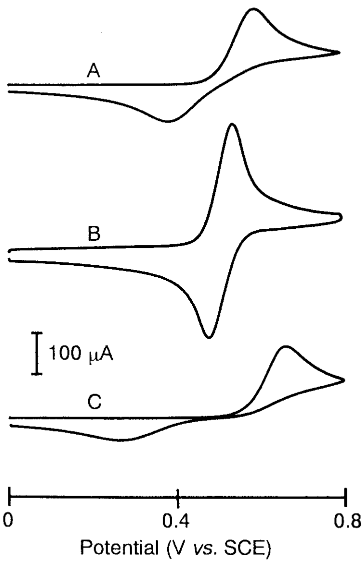

Fig. 3. Voltammograms for a 0.1 M H_2SO_4 Solution of Catechol (5 mM)

(A) at a bare GC electrode; (B) at a GC electrode anodized in 1 M aqueous H_2SO_4; (C) at a C8-GC electrode; voltage sweep rate, 100 mV/s.

The electrochemical performance of the C8-GC electrode was then compared with that of a GC electrode anodized in 1 M aqueous H_2SO_4 according to essentially the same procedure, including the cathodic post-treatment, mentioned above. As shown in Fig. 2A, the electrode process of $Fe(CN)_6^{3-}$ was depressed at the latter electrode as well, but the residual currents were about ten times those at a C8-GC electrode (*cf.* Fig. 2A, C). It is of great interest that the redox wave of $Fe(CN)_6^{3-}$ depressed at the C8-GC electrode was restored by the addition of a surfactant, trimethyldodecylammonium ion (100 μM) (Fig. 2D), while the additive had essentially no effect on the voltammogram of the marker ion at the GC electrode anodized in aqueous H_2SO_4 (Fig. 2B). Similar effects of surfactants have been noted at an electrode covered with a hydrophobic membrane, that is, a gold electrode modified with long-chain alkanethiols.[7,8] The observed behavior was fully reproducible: the same CV curves for the marker ion were obtained repeatedly when the solution in the absence or in the presence of the surfactant was subjected to CV measurements at the C8-GC electrode.

When a solution of catechol (5 mM) in 0.1 M aqueous H_2SO_4 was subjected to CV at both GC electrodes, an intriguing difference was observed on the voltammograms (Fig. 3). As previously reported,[9] at a GC electrode anodized in aqueous H_2SO_4, the redox wave of catechol was remarkably sharpened with the anodic and cathodic peak currents increased in comparison with the wave at a bare GC electrode (Fig. 3B and A). On the other hand, the electrode reaction of catechol was depressed at the C8-GC electrode as in the case of $Fe(CN)_6^{3-}$, although the extent was smaller than that in the latter case and the redox wave was still recognized (*cf.* Fig. 2C, 3C). These phenomena are again reminiscent of a gold electrode covered with a long-chain alkanethiol: a small hydrophobic molecule such as catechol and benzoquinone can permeate the membrane on the gold electrode and exhibit the redox wave to some extent.

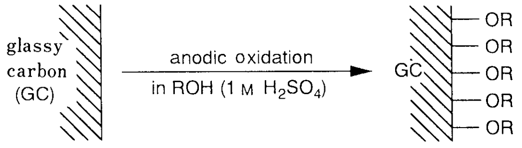

Chart 1

From the results described so far, the electrochemical performance of the C8-GC electrode is rather similar to that of a long-chain alkane thiol-modified gold electrode, but different from that of a GC electrode anodized in 1 M aqueous H_2SO_4. Thus, it can be assumed that through the electrochemical treatment of a GC electrode in 1-octanol, the alcohol is anchored onto the surface probably *via* an ether linkage, leading to the formation of a hydrophobic membrane as shown in Chart 1.

The effects of the potential range and the sweep rate in the preparation of the C8-GC electrode upon the extent of fixation of 1-octanol on the GC surface were examined. In the CV of $Fe(CN)_6^{3-}$ at the modified electrode, the reduction current of the marker ion at its voltammetric peak or at 0 V, when no peak was recognized, was measured (see Fig. 1B), since the depression of the current can be regarded as reflecting the degree of 1-octanol coverage of the electrode surface. The results are summarized in Table I. The potential range has been proved to be crucial for the preparation of a C8-GC electrode and the potential sweep from 0 to 2.0 V was required to obtain a GC electrode tightly covered with the alkanol. The sweep rate was also found to be one of the important factors governing successful modification. When the modification was carried out at a sweep rate higher than 50 mV/s, the hydrophobic membrane appeared to become less well packed as judged from the observed cathodic current of $Fe(CN)_6^{3-}$. Thus, in order to obtain a C8-GC electrode, of which the electrochemical performance is comparable to that of a gold electrode covered

Table I. Effects of Modification Conditions upon the Voltammetric Behavior of $Fe(CN)_6^{3-}$ at a 1-Octanol-Modified GC Electrode[a]

Potential range (V *vs.* Ag wire)[b]	Cathodic currents of $Fe(CN)_6^{3-}$ (μA)[c]	Sweep rate (mV/s)[d]	Cathodic currents of $Fe(CN)_6^{3-}$ (μA)[c]
0—1.0	74 (0.14 V)[e]	100	31
1.2	72 (0.12 V)[e]	50	25
1.4	69 (0.13 V)[e]	20	7
1.6	54 (0.11 V)[e]	10	3
1.8	13	5	3
2.0	3		
2.2	3		

a) For details, see the text: the number of sweep repetitions was five. *b*) Sweep rate was set at 10 mV/s. *c*) Obtained at 0 V *vs.* SCE because no peak was observed on CV. *d*) Potential sweep was carried out over 0—2.0 V *vs.* Ag wire. *e*) Obtained as a peak current at the potential shown in parentheses.

with a self-assembled alkane thiol membrane, the conditions for the potential sweep method are very simple: five repeated sweeps at 10 mV/s between 0 and 2.0 V.

The potential limits, to which a modified electrode can be operated without damage or with good reproducibility, will be an important factor defining the utility of the electrode for analytical purposes. The stability of the membrane formed on a C8-GC electrode with respect to the applied potential was assessed by the following procedure: (1) the C8-GC electrode was subjected to a potential sweep from 0 V *vs.* SCE in both anodic and cathodic directions in an aqueous solution of NaCl (0.1 M); (2) CV of $Fe(CN)_6^{3-}$ was performed at the treated electrode in the absence and in the presence of trimethyl dodecyl ammonium bromide; (3) the extents of the depression of the electrode process of the marker ion and its restoration by the surfactant (see Fig. 2C, D) were estimated. The results are shown in Fig. 4. When the cathodic sweep in (1) was extended to a potential more negative than −0.5 V, the reduction current of the marker ion was gradually increased and reached almost the same value as that observed at a bare GC electrode. On the other hand, the peak current of the marker ion in the presence of the surfactant remained unchanged by the cathodic treatments, indicating that the observed decrease in the depression of the electrode process of $Fe(CN)_6^{3-}$ induced by the application of negative potentials can be simply ascribed to reductive detachment of the modifier from the electrode surface, that is, cathodic C–O bond cleavage resulting in the liberation of the alkoxy moiety.

Regarding the potential sweep in (1) toward a positive direction, the electrode process of the marker ion was still depressed even when the potential limit was expanded to 2.0 V, as if the hydrophobic membrane on the C8-GC electrode remained intact. However, the restoration by the surfactant was sharply suppressed as the anodic limit was set at more positive values than 1.5 V, and eventually became negligible beyond the potential limit of 2.0 V. Accordingly, the hydrophobic membrane on the C8-GC electrode seems to be destroyed by exposure to a potential higher than 1.5 V, leading to disintegration of the surface. Thus, the potential limits of a C8-GC electrode have been shown to be 1.5 and −0.5 V.

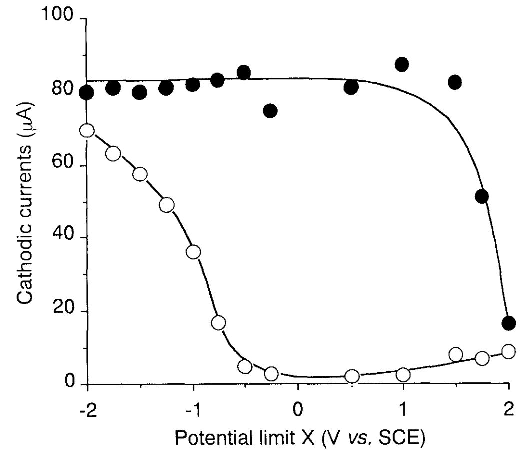

Fig. 4. The Voltammetric Response of $K_3Fe(CN)_6$ in 0.1 M NaCl in the Absence (Open Circles) and the Presence (Closed Circles) of Trimethyldodecylammonium Bromide (100 μM) at a C8-GC Electrode Treated by Sweeping the Potential Five Times between 0 and X (V *vs.* SCE)

The cathodic currents were obtained at the peak or at 0 V *vs.* SCE when no peak was recognized; voltage sweep rate, 100 mV/s.

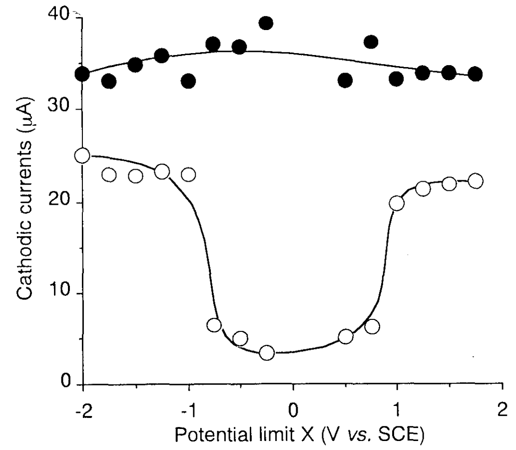

Fig. 5. The Voltammetric Response of $K_3Fe(CN)_6$ in 0.1 M NaCl in the Absence (Open Circles) and the Presence (Closed Circles) of Trimethyldodecylammonium Bromide (100 μM) at an Octanethiol-Modified Gold Electrode Treated by Sweeping the Potential Five Times between 0 and X (V *vs.* SCE)

The cathodic currences were obtained at the peak or at 0 V *vs.* SCE when no peak was recognized; voltage sweep rate, 100 mV/s.

The influence of the applied potential upon the electrochemical performance of a gold electrode covered with octane thiol was also examined in the same way. As shown in Fig. 5, the potential window of the gold electrode is 0.75 to −0.75, which is narrower than that for a C8-GC electrode. These results imply that a GC electrode modified with alcohols by the present method may find wider application in electrochemical analysis than an alkane thiol-modified gold electrode.

A C8-GC electrode exhibits excellent physical stability: the electrochemical performance of a C8-GC electrode was not affected at all by sonication in H_2O and MeOH, again implying that the alkanol may be fixed on the surface not by chemisorption but *via* covalent ether linkages. The mechanism of the fixation is assumed to be similar to that proposed for methoxylation of aromatic compounds by anodic oxidation in MeOH, where an aromatic ring is first oxidized to a radical cation followed by nucleophilic attack

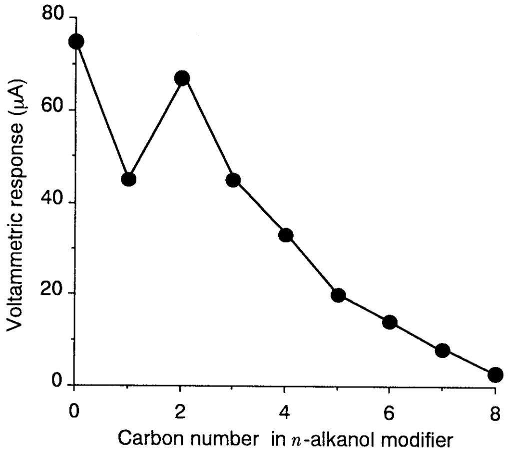

Fig. 6. Effects of the Number of Carbons in *n*-Alkanol upon the Voltammetric Response of $Fe(CN)_6{}^{3-}$ at an *n*-Alkanol-Modified GC Electrode

The responses were obtained as the cathodic peak currents at the peak (for carbon number 0—3) or at 0 V *vs.* SCE (for carbon number 4—8) on CV of a solution of $K_3Fe(CN)_6$ (5 mM) in 0.1 M aqueous NaCl, where the carbon number of 0 denotes the response at a bare GC electrode; voltage sweep rate, 100 mV/s.

of MeOH, further oxidation, and reaction with another molecule of MeOH.[10] The surface of a GC electrode can be compared with an aromatic ring.

Modification of a GC electrode by other *n*-alkanols with carbon number from one to eight was attempted. Figure 6 shows the electrochemical performance of the alkanol-modified GC electrodes with $Fe(CN)_6^{3-}$ as a probe. As can be expected, the depression of the electrode reaction of the marker ion became greater as the number of carbon atoms in the *n*-alkanol increased, which is in line with the results reported for a gold electrode modified with alkanethiols of different chain lengths.[8,11,12] This observation is also considered to confirm that the present method gives an alkanol-modified GC electrode (Chart 1).

The proposed surface structure was further supported by the following experiments: A GC electrode was modified with *p*-nitrophenethyl alcohol by a constant potential method (see Experimental). When CH_3CN containing only $NaClO_4$ (0.1 M) was subjected to CV at the modified GC electrode, a cathodic peak was observed at −1.10 V. The wave was attributed to the reduction of the nitrobenzene moiety, because at a bare GC electrode a CH_3CN solution of *p*-nitrotoluene gave a peak at −1.13 V. These results indicate the existence of *p*-nitrophenethyl alcohol residue on the modified GC surface. The same argument has been put forward in the reductive method to prepare a carbon electrode modified with diazonium salts.[13]

The present method affords a convenient and straightforward access to a GC electrode covalently modified with an alkanol, which is electrochemically and physically stable enough to be applicable to electrochemical analysis. Since alkanols with various functional groups are commercially available, it is expected that the method will furnish carbon electrodes with various properties effective for electrochemical analysis and chemical sensors, including hydrophobicity, charge type, steric effects, molecular-recognition ability, and so on.

Experimental

Methanol, ethanol, 1-propanol, 1-butanol, and 1-heptanol were distilled after the addition of an appropriate amount of Na. Deionized and distilled water was utilized throughout. All other chemicals were of reagent grade, and were used without further purification. CV was performed with the combination of a Huso model 312 polarograph and a Watanabe WX 4421 X–Y recorder. Voltammograms were obtained with a three-electrode system consisting of a bare electrode, a modified GC disk (3 mm i.d.), or an octanethiol-modified gold disk (2 mm i.d.) working electrode, a platinum wire counter electrode, and an SCE as the reference electrode. For the modification of a GC electrode, Ag wire was used as the reference electrode instead of an SCE. The fabrication of GC and gold electrodes has been described previously.[14] GC disks were obtained from Tokai Carbon Co. Ltd. (GC 30, 3 mm i.d. × 100 mm).

General Procedure for the Modification of GC Surfaces with 1-Alkanol A GC disk electrode was polished mechanically with a polishing paper (♯1200) followed by alumina powder (0.05 μm) on a polishing cloth, sonicated in deionized water for 5 min, washed with water and MeOH, dried by a stream of nitrogen, and subjected to CV in 1-alkanol (5 ml) containing 1 M H_2SO_4 (270 μl) with five repetitive sweeps between 0 and 2.0 V at 10 mV/s. After the treatment, the modified electrode was washed with MeOH and water, and treated by CV in 0.1 M aqueous NaCl with five repetitive sweeps between 0 and −0.5 V.

Preparation of a Gold Electrode Modified with Octanethiol A gold disk electrode polished mechanically with alumina powder (0.05 μm) was treated by multiple triangular potential sweeps between −0.2—1.8 V *vs.* Ag/AgCl at 1.0 V/s in 1 M H_2SO_4 for 30 min. The electrode was rinsed with water and MeOH, dried by a stream of nitrogen, immersed in a stirred solution of octanethiol (5 mM) in EtOH for 5 min and washed with EtOH and water.

Preparation of a GC Electrode Modified with *p*-Nitrophenethyl Alcohol and Its CV Measurement A GC disk electrode polished in the same manner as described above was anodized by controlled potential electrolysis in a tetrahydrofuran (THF, 5 ml) solution almost saturated with *p*-nitrophenethyl alcohol (*ca.* 2 g) at 2.0 V in a one-compartment cell equipped with a platinum foil cathode and an Ag wire reference electrode, until 300 mC of electricity had been consumed. After the electrolysis, the modified GC electrode was washed with MeOH, water, and CH_3CN, dried *in vacuo*, and used as a working electrode for CV in CH_3CN solution containing 0.1 M $NaClO_4$, which had been deoxygenated by bubbling N_2 for 20 min.

Acknowledgment This work was supported in part by funds from Takeda Science Foundation.

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