Detection of Hydroxyl Radicals Formed on an Anodically Polarized Diamond Electrode Surface in Aqueous Media

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Electrochemically generated hydroxyl radicals at anodically polarized boron-doped diamond electrodes in aqueous media have been suggested to be responsible for their ability to electrochemically incinerate organic waste. In this letter, for the first time, we provide experimental evidence for the generation of hydroxyl radicals by using coumarin followed by the fluorescence detection of its hydroxylated product.

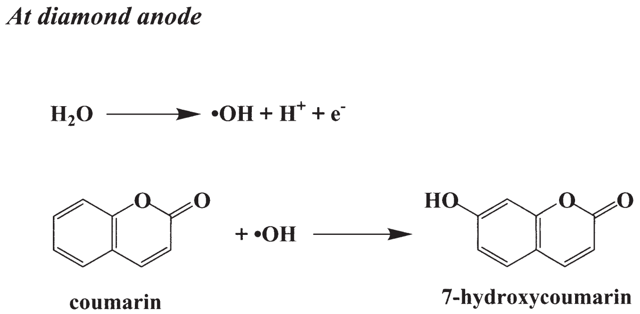
Recently there has been an increasing interest in studying the potential for application of boron-doped diamond (BDD) films, covering an extremely wide range of fields.[1] Electrochemical treatment of waste water using BDD electrode has attracted special attention because of its chemical stability and high overpotential for oxygen evolution. Hydroxyl radicals produced at BDD at high anodic potentials are thought to be responsible for the observed incineration reactions. However, no experimental evidence was provided for the generation of hydroxyl radicals. The hydroxyl radical formation on the anodically polarized BDD electrode has been suggested by Fóti et al.[2] and Koppang et al.[3] However, no experimental evidence of hydroxyl radical formed on an anodically polarized BDD electrode surface exists to the best of our knowledge.

The aim of this study is to detect the hydroxyl radicals produced at the BDD electrode. In this letter, we provide evidence for the hydroxyl radical generation at BDD electrode by using coumarin followed by its fluorescence detection. This method is widely used in radiation chemistry, sonochemistry, biochemistry, and photocatalysis.[4–16]

BDD thin-films were prepared on *p*-Si (100) substrates by use of a microwave plasma-assisted chemical vapor deposition (MPCVD, ASTeX Corp., Woburn, MA). The B/C atomic ratio was 10^4 ppm. The CVD conditions have been explained in detail elsewhere.[9,10] Water was purified with a Milli-Q system (Millipore Co.). Its resistivity was over 17.3 MΩ cm. All other chemicals were of extra pure grade and used as received without further purification.

The potentiostatic electrolysis was made using an HZ-3000 (HOKUTO DENKO Co.) potentiostat. Electrolysis experiments were performed in a two-compartment cell, with carried out in 1 M H_2SO_4 containing coumarin in working electrode (WE) compartment and in 1 M H_2SO_4 in counter electrode (CE) compartment. The CE was a Pt/Pt black plate enclosed by a porous Vycor® glass (Corning, Inc.). The geometrical surface area of the diamond electrode was 6.3 cm^2. The volume for electrolyte solution at each electrode compartment was 1.6 mL. Fluorescence spectrum of electrochemically generated 7-hydroxycoumarin was measured on an F-3010 (Hitachi, Ltd.) fluorescence spectrophotometer.

The expected reaction scheme, when the BDD electrode is anodically polarized at +2.6 V vs Ag/AgCl in an aqueous media, is shown in Scheme 1. Significant levels of hydroxyl radicals generation are not observed at typical metal electrodes, because the four-electron oxidation of water to dioxygen occurs at a potential (+1.1 V vs Ag/AgCl at pH = 0) well below that required for the one-electron oxidation of water to hydroxyl radicals (+2.6 V vs Ag/AgCl at pH = 0). The hydroxyl radicals generated at BDD electrode readily react with coumarin to produce 7-hydroxycoumarin, a highly fluorescent product. Figure 1 shows the fluorescence spectrum of the standard sample 7-hydroxycoumarin and for the coumarin solution before and after electrolysis. As shown in the Figure 1a, the 7-hydroxycoumarin gives strong fluorescence emission at about 453 nm. The electrochemical formation of 7-hydroxycoumarin was identified on the basis of this peak. Coumarin solution alone does not give the peak at 453 nm, but gives a sharp peak at 375 nm in consistent with the previous results.[8] However, after electrolysis a new broad peak appeared at about 455 nm, which is matching with the peak of 7-hydroxycoumarin (Figure 1a). Earlier, Ishibashi et al. found similar spectrum with photocatalytically treated coumarin that produced 7-hydroxycoumarin.[8]



Scheme 1.

The yields of the hydroxyl radicals estimated from the total charge passed during the electrolysis and from the fluorescence intensity of the electrolysis product (Figure 1) are shown in Table 1. Here, the estimated value from the chronoamperogram is on the basis of the assumption that all the charge passed in the electrolysis contributes to the formation of the hydroxyl radicals ($H_2O \rightarrow \cdot OH + H^+ + e^-$). The estimated value from Figure 1 is on the basis of the assumption that all the hydroxyl radicals

Table 1. Comparison of the yields of the hydroxyl radicals determined on the basis of chronoamperogram in electrolysis and Fig. 1

	Chrono-amperometry	Figure 1
·OH yield/M cm^{-2}	1.2×10^{-5}	1.1×10^{-9}

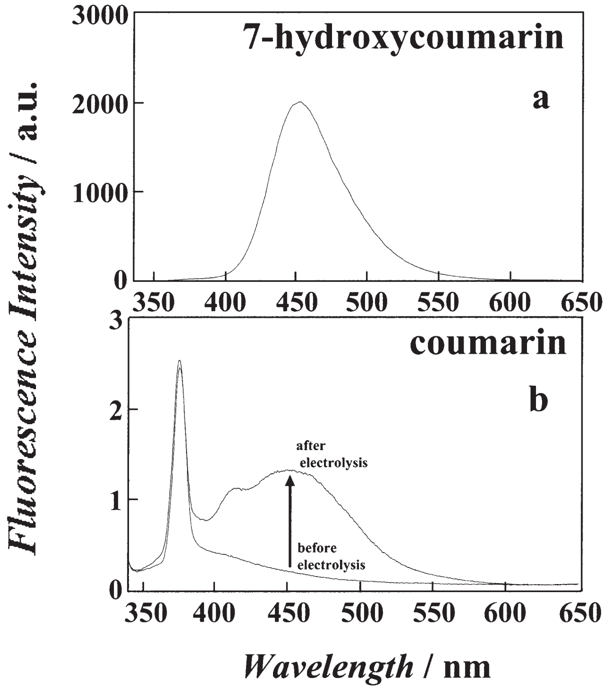


Figure 1. The fluorescence spectrum in 30 min of the potentiostatic electrolysis of (b) 10 mM coumarin in 1 M H_2SO_4 (but 1000 times diluted by Milli-Q ultrapure water) in the WE compartment. Hold potential: +2.6 V vs Ag/AgCl; excitation wavelength: 332 nm. The fluorescence spectrum of 10 mM 7-hydroxycoumarin in 1 M H_2SO_4 is shown in (a).

generated at the electrode are reacted with coumarin to produce 7-hydroxycoumarin according to Scheme 1. The possibility of direct oxidation of coumarin is ignored as no oxidation response of coumarin in electrolyte solution was observed until the positive potential range of +2.8 V vs Ag/AgCl (not shown). Similarly, the possible formation of H_2O_2 from hydroxyl radicals is ignored because the estimated life time (50 ns) of the hydroxyl radical for reaction with coumarin is much shorter than that (26 ms) estimated for H_2O_2 formation on the basis of the hydroxyl radical concentration (Table 1) calculated from the fluorescence intensity. And, at the fluorescence spectrum in Fig. 1b, peak of coumarin around the wavelength of 375 nm is almost not changed in electrolysis. Thus, direct oxidation of coumarin by electrode may not occur. The yield of the hydroxyl radicals estimated from Figure 1 is 9×10^{-5} times lower than that from the electrolysis charge. One obvious reason for the higher values for the electrolysis estimation is that the interference of the oxygen evolution reaction is neglected in this estimation. The other reason may be that not all the hydroxyl radicals produced at the surface contribute to the reaction in Scheme 1. For quantitative considerations, it is necessary to know whether all the hydroxyl radicals are trapped by coumarin or not.

However, these results clearly demonstrate the formation of hydroxyl radicals in the electrolysis using diamond electrode. This may help the elucidation of the mechanisms of O_2 evolution from water and CO_2 evolution from organic compounds in the aqueous media contacted with the BDD electrode. Further studies with other compounds which reacts with hydroxyl radicals to produce fluorescennt products and various electrolysis conditions are in progress.

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