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Electrogenerated Chemiluminescence. 67. Dependence of Light Emission of the Tris(2,2′)bipyridylruthenium(II)/Tripropylamine System on Electrode Surface Hydrophobicity

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We describe the effect of electrode surface hydrophobicity on the electrochemical behavior and electrogenerated chemiluminescence (ECL) of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridyl)/tripropylamine (TPrA) system. Gold and platinum electrodes were modified with different thiol monolayers. The hydrophobicity of the electrode surfaces changed with different terminal groups of the thiol molecules. The oxidation rate of TPrA was found to be much larger at the modified electrode with a more hydrophobic surface. The adsorption of neutral TPrA species on this kind of surface was assumed to contribute to the faster anodic kinetics. Due to the rapid generation of the highly reducing radical, $TPrA^•$, ECL intensity increased significantly at more hydrophobic electrodes. This electrode surface effect in the ECL analytical system allows one to improve the detection sensitivity at low concentrations of $Ru(bpy)_3^{2+}$. The surfactant effect on the ECL process was also examined and discussed based on the change of electrode hydrophobicity by the adsorption of surfactant species.

There have been extensive studies of electrode surface effects, e.g., surface oxidation and adsorption, on the rates of electrochemical processes.[1] It is becoming apparent that electrode surface effects can also be important in electrogenerated chemiluminescence (ECL), particularly in systems where coreactant oxidation at the electrode plays an important role in the overall observed light emission. ECL has become a highly developed technique with important analytical applications in immunoassay.[2,3] Tris(2,2′)bipyridylruthenium(II), $Ru(bpy)_3^{2+}$, is a commonly used tag molecule, while tripropylamine (TPrA) has been found to be an efficient coreactant.[2] In a previous paper,[4] we described the important role of the direct oxidation of TPrA on light emission at low (submicromolar) concentrations of $Ru(bpy)_3^{2+}$. An increase in the TPrA oxidation reaction rate resulted in a significant enhancement of ECL intensity. In the potential region where ECL occurs, Pt and gold electrodes were covered by anodic oxide layers which were shown to inhibit the direct oxidation of TPrA, and the ECL intensity was lower. When a glassy carbon (GC) electrode was used to generate ECL, however, the light emission intensity was much higher because of the faster TPrA oxidation rate. On the basis of these experimental results, we proposed that the generation of highly reducing species from TPrA at low concentrations (≤1 μM) of $Ru(bpy)_3^{2+}$ is mainly due to the direct anodic oxidation of TPrA at the electrode (eq 2a), while the catalytic TPrA oxidation by electrogenerated $Ru(bpy)_3^{3+}$ (eq 2b) is less important.[4]

$$Ru(bpy)_3^{2+} - e \rightarrow Ru(bpy)_3^{3+} \tag{1}$$

$$TPrA - e \rightarrow TPrA^{+•} \rightarrow TPrA^{•} + H^{+} \tag{2a}$$

$$Ru(bpy)_3^{3+} + TPrA \rightarrow Ru(bpy)_3^{2+} + TPrA^{+•} \rightarrow TPrA^{•} + H^{+} \tag{2b}$$

$$Ru(bpy)_3^{3+} + TPrA^{•} \rightarrow Ru(bpy)_3^{2+*} + \text{products} \tag{3}$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu \tag{4}$$

In this paper, we study the effect of hydrophobicity of the electrode surface on TPrA oxidation as well as the ECL intensity. The modification of gold and platinum electrodes by thiol monolayers with different terminal groups allowed us to control the electrode hydrophobicity. Significant increases in the TPrA oxidation rate and ECL intensity were observed at an alkanethiol-modified electrode, while the influence of the thiol layer with a hydrophilic terminal group on either TPrA oxidation or ECL was much less. The effect of surfactants on the ECL process was also examined and is discussed based on the changes of the electrode surface hydrophobicity.

EXPERIMENTAL SECTION

Chemicals were used as received. $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (minimum 98%) was obtained from Strem Chemicals (Newburyport, MA). Tripropylamine (99+%) from Aldrich (Milwaukee, WI) was dissolved in 0.15 M phosphate buffer solution. The pH value of the solution was adjusted to 7.5 with concentrated NaOH or H$_3$-

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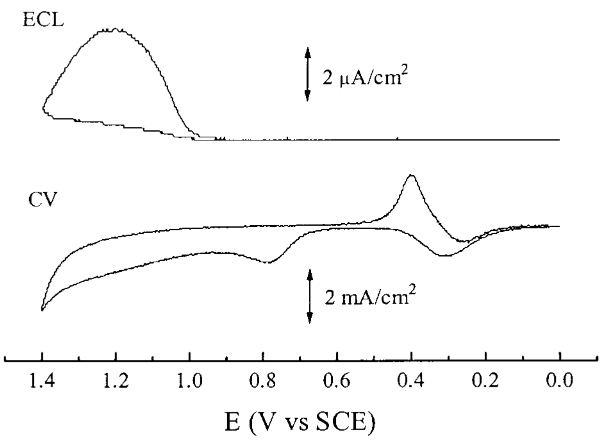

Figure 1. Cyclic voltammogram and ECL curve at a Au electrode in 0.15 M phosphate buffer solution (pH 7.5) containing 100 mM TPrA and 1 μM $Ru(bpy)_3^{2+}$. Potential scan rate, 0.1 V/s.

PO_4. All aqueous solutions were prepared with deionized water (Milli-Q, Millipore). 6-Mercapto-1-hexanol (97%), 1-hexanethiol (95%), 1-butanethiol (99%), and 3-mercapto-1-propanesulfonic acid sodium salt (90%) from Aldrich were dissolved in ethanol. Triton X-100 was purchased from Fluka (Milwaukee, WI).

Cyclic voltammetry was carried out with a homemade potentiostat. Platinum (0.018 cm^2), gold (0.012 cm^2), and glassy carbon (0.07 cm^2) disk electrodes were polished with 0.05-μm alumina to obtain a mirror surface and then were ultrasonicated and thoroughly rinsed with Milli-Q water. The reference electrode was a saturated calomel electrode. A coiled platinum wire was used as the auxiliary electrode. The self-assembled thiol monolayer (SAM) was formed by immersing the gold or Pt electrodes in 5 mM thiol ethanol solution for 12 h, followed by a thorough rinsing with ethanol and water. The ECL signal was measured with a photomultiplier tube (PMT, Hamamatsu R4220p) installed under the electrochemical cell. A voltage of 750 V was supplied to the PMT with high-voltage power supply series 225 (Bertan High Voltage Corp., Hicksville, NY).

The current density and the normalized ECL intensity (PMT output, I_{ecl}) were calculated according to the geometrical surface area of the electrodes.

RESULTS AND DISCUSSION

Electrochemical and ECL Behavior of the $Ru(bpy)_3^{2+}$/TPrA System at Thiol-Modified Electrodes. Cyclic voltammetry (CV) and ECL curves at a bare Au electrode in a $Ru(bpy)_3^{2+}$/TPrA solution are shown in Figure 1. This behavior has been described in a previous paper.[4] The anodic peak at 0.3 V was attributed to the catalytic oxidation of TPrA via some hydrous oxide species at the gold surface. The direct oxidation of TPrA occurred in the potential region more positive than 0.65 V. Following the oxidation of $Ru(bpy)_3^{2+}$ beyond 1.0 V, a main ECL peak with a peak intensity of $\sim$4 μA/cm^2 appeared at $\sim$1.15 V. As discussed previously,[4] the ECL intensity was very sensitive to the electrode materials and was proportional to the oxidation current of TPrA.

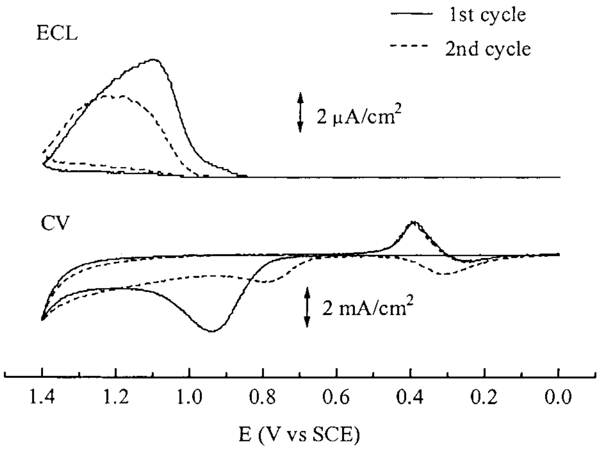

Figure 2. Cyclic voltammograms and ECL curves at a $HO(CH_2)_6$-SH monolayer-coated Au electrode in 0.15 M phosphate buffer solution (pH 7.5) containing 100 mM TPrA and 1 μM $Ru(bpy)_3^{2+}$. Potential scan rate, 0.1 V/s.

Modification of the gold electrode with a SAM alters the surface properties and electrochemical behavior, as has been noted in the literature.[5-11] Figure 2 shows the CV and ECL curves at a $HO(CH_2)_6SH$-derivatized Au electrode. No oxidation peak appeared at $\sim$0.3 V in the first cycle of CV. The thiol monolayer on the gold electrode apparently suppressed the formation of any premonolayer gold oxides at the electrode surface; hence, no catalytic oxidation of TPrA occurred in the low-potential region. When the electrode potential was scanned beyond 0.75 V, an oxidation peak appeared. In this potential region, the thiol monolayer was destroyed due to the oxidative desorption of thiol molecules, e.g.,[12]

$$RCH_2S{-}Au + 14OH^- \rightarrow SO_4^{2-} + RCO_2^- + 8H_2O + 11e + Au \quad (5)$$

This desorption of the thiol layer led to the exposure of electroactive sites. TPrA was oxidized directly, and Au surface oxides were formed at the same time. No significant change of ECL intensity was observed compared to that shown in Figure 1, suggesting that the thiol molecules with an OH terminal group had little influence on the ECL process. In the second cycle, the CV and ECL curves were similar to those obtained at a bare Au electrode. The oxidation peak at 0.3 V appeared, and the initial potential for TPrA oxidation shifted to less positive potentials. Clearly, the thiol monolayer was completely destroyed in the high-potential region during the first scan. This indicates instability of the thiol-modified electrode surface in the ECL system, as also observed in a previous study.[13]

Figure 3 shows the behavior of a $CH_3(CH_2)_5SH$-derivatized Au electrode for the $Ru(bpy)_3^{2+}$/TPrA system. The oxidation current

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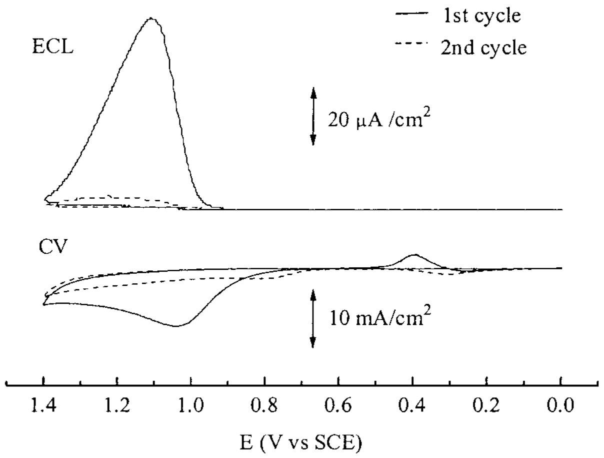

Figure 3. Cyclic voltammograms and ECL curves at $CH_3(CH_2)_5$-SH monolayer coated Au electrode in 0.15 M phosphate buffer solution (pH 7.5) containing 100 mM TPrA and 1 μM $Ru(bpy)_3^{2+}$. Potential scan rate, 0.1 V/s.

Table 1. TPrA Oxidation Current and ECL Peak Intensity of the $Ru(bpy)_3^{2+}$/TPrA System at Bare or Various Thiol-Derivatized Electrodes (Potential Scan Rate, 0.1 V/s)

electrode	i_a (mA/cm^2)[a]	I_{ecl} (μA/cm^2)
bare Au	1.80	4.2
Au/S$(CH_2)_6$OH	1.83	5.9
Au/S$(CH_2)_2SO_3^-$	1.56	3.0
Au/S$(CH_2)_5CH_3$	8.78	65.4
Au/S$(CH_2)_3CH_3$	6.02	47.6
bare Pt	1.25	0.5
Pt/S$(CH_2)_6$OH	1.28	0.7
Pt/S$(CH_2)_5CH_3$	2.38	7.9

[a] Anodic current measured at the potential where the ECL peak appeared. Background current (usually much smaller than the TPrA oxidation current) due to surface oxide formation and thiol monolayer oxidation has not been subtracted.

of TPrA in the potential region more positive than 0.75 V was over 4 times larger than that shown in Figures 1 and 2. Consistent with the larger oxidation rate of TPrA, the ECL intensity increased more than 10 times. A SAM can also be formed at a Pt surface,[14,15] and the same kind of effect on ECL was observed.

Table 1 lists the TPrA oxidation peak current and the ECL peak intensity at thiol-modified gold and platinum electrodes. Clearly, the terminal groups of the thiol molecules affected significantly the electrochemical and ECL behavior of the $Ru(bpy)_3^{2+}$/TPrA system. After the modification with an alkyl chain thiol with a terminal methyl group, the electrode surface was rendered hydrophobic, leading to an increase in the TPrA oxidation rate. When the electrode surface was coated by thiol molecules terminated with a hydrophilic group, however, no significant change of TPrA oxidation current was observed.

In a previous paper,[8] Becka and Miller showed that the electron-transfer kinetics of a given redox species, e.g., $Fe(CN)_6^{3-}$, was very different on the hydroxythiol and alkanethiol monolayer-coated Au electrodes. For the hydrophilic species, $Fe(CN)_6^{3-}$, the reduction rate at the dodecanethiol-derivatized Au electrode was more than 20 times smaller than that at the hydroxythiol monolayer-coated electrode. On the contrary, for a more hydrophobic and less charged molecule, $Fe(bpy)(CN)_4^-$, the reduction rate was considerably faster at the Au electrode modified with the alkanethiol than that coated with hydroxyl thiol. This difference in rates was primarily attributed to the change of the hydrophobicity of the electrode surface. In another report,[9] a similar effect of thiol monolayer hydrophobicity on the electrochemical response of hydrophilic probes was observed. For hydrophobic electroactive species, however, no improvement in electron-transfer kinetics was found following an increase of thiol layer hydrophobicity.

The experiments here were carried out in a phosphate buffer solution at pH 7.5. At this pH, most of the TPrA is in the protonated form ($K_b = 10.4$).[16] As the solution pH value increased, the solubility of TPrA dropped sharply due to the hydrophobicity of the neutral (unprotonated) TPrA molecules. The electrochemical oxidation of TPrA has been studied by several groups,[17−21] and in aqueous solution, neutral TPrA molecules were more readily oxidized compared with protonated ones. When TPrA is oxidized at an electrode surface, the following proton-transfer reaction takes place in the solution near the surface:

$$\mathrm{TPrAH^+ + HPO_3^{2-} \rightarrow TPrA + H_2PO_3^-} \qquad (6)$$

The hydrophobicity of the electrode surface might have several effects on the kinetics of the oxidation of hydrophobic neutral TPrA species. The adsorption free energy of TPrA molecules would be more negative at a hydrophobic surface than at a hydrophilic one. The adsorption of the TPrA species could facilitate the electron-transfer process at the electrode. Although we have no molecular level information on the process, this could occur by changing the conformation of the molecule compared to that in the aqueous medium (i.e., making the N atom more accessible). Desolvation of the protonated TPrA, perhaps with loss of a proton as it adsorbs in the hydrophobic layer, would also promote electron transfer. The alkanethiol-modified electrode surface also might cause some preconcentration of the hydrophobic TPrA molecules, although the amount of preadsorbed TPrA cannot make a significant contribution to the total current passed in the CV wave at these scan rates.

Surfactant Effect on the $Ru(bpy)_3^{2+}$/TPrA System. Although the addition of several nonionic surfactants is known to increase the ECL emission intensity of the $Ru(bpy)_3^{2+}$/TPrA system by severalfold, the mechanism of the surfactant effect is still not quite clear.[22] However, the influence of surfactant molecules on electrochemical reactions has been extensively studied.[23−33] The adsorption of a surfactant at an electrode surface

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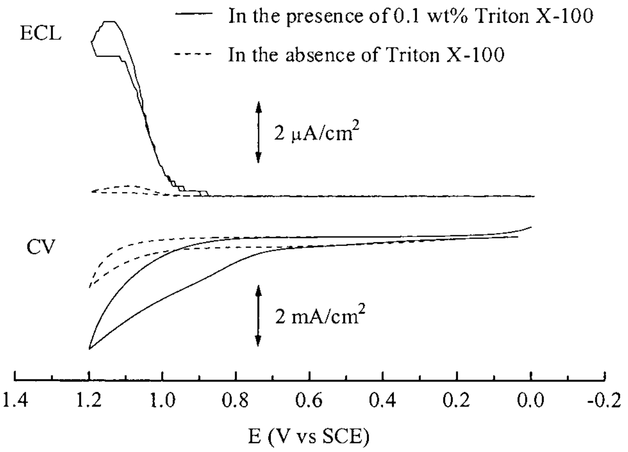

Figure 4. Cyclic voltammograms and ECL curves at a Pt electrode in 0.15 M phosphate buffer solution (pH 7.5) containing 100 mM TPrA and 1 μM $Ru(bpy)_3^{2+}$ in the presence and absence of 0.1 wt % Triton X-100. Potential scan rate, 0.1 V/s.

can affect the interfacial electron-transfer kinetics.[24−26] The interactions occurring between micelles and electroactive species have also been addressed in a number of electrochemical studies in surfactant solutions.[26−31] The effect of surfactants on the ECL of specific systems has been attributed to the strong hydrophobic interaction between the luminescent species and the micellized surfactant.[34,35]

Figure 4 shows the effect of a nonionic surfactant, Triton X-100, on the oxidation of TPrA and ECL of the $Ru(bpy)_3^{2+}$/TPrA system at a platinum electrode. Since the concentration of $Ru(bpy)_3^{2+}$ in our experiment was quite low, the oxidation wave changed little in the presence or absence of $Ru(bpy)_3^{2+}$. Therefore, the anodic current can be mainly attributed to the oxidation of TPrA. In the presence of 0.1 wt % Triton X-100, the oxidation rate of TPrA increased significantly, as was seen with the alkanethiol-modified electrode (Figure 1). A 10-fold increase in ECL intensity was observed after the addition of the surfactant species. The same kind of surfactant effect was also clearly exhibited at a gold electrode.

The increase of TPrA oxidation current can also be due to a hydrophilicity change of the electrode surface. Clean, bare Pt and gold electrode surfaces are quite hydrophilic. As a result of competition between interactions of the functional groups with the metal and with the aqueous phase, the surfactant molecules tend to be oriented with the functional heads toward the electrode surface. Therefore, the alkyl chain oriented toward the solution will tend to make the interface more hydrophobic. This surfactant adsorption layer was similar to the alkanethiol monolayer at Pt or Au electrodes, except the latter showed a bigger effect.

In these experiments, the concentration of Triton X-100 was 0.1 wt %, larger than the critical micelle concentration (cmc ~ 0.01 wt %). The interactions between the micelles and $Ru(bpy)_3^{2+}$ or TPrA can also influence the electrochemical behavior. To confirm the effect of surfactant adsorption at the electrode surface, we immersed a Pt electrode in a 0.1 wt % Triton X-100 solution for 10 min, rinsed it thoroughly with water, and then carried out the CV and ECL measurements. In the first cycle, a response similar to that shown in Figure 4 was obtained. In the subsequent cycles, however, both the oxidation current and the ECL intensity dropped significantly. This result clearly indicated that the effect of surfactant on the electrochemical and ECL behavior of the $Ru(bpy)_3^{2+}$/TPrA system was mainly due to the adsorption of surfactant species at the electrode/solution interface, which led to the change of the hydrophobicity of the electrode surface. In the higher potential region, the increase of surface charge would result in the desorption of surfactant molecules, which diffused into the bulk solution. Therefore, after the first voltammetric cycle, the electrode behaved just like a bare one. However, in the presence of 0.1 wt % Triton X-100 in the solution, the readsorption of surfactant took place in the lower potential region, and the CV and ECL curves remained almost the same in the subsequent cycles.

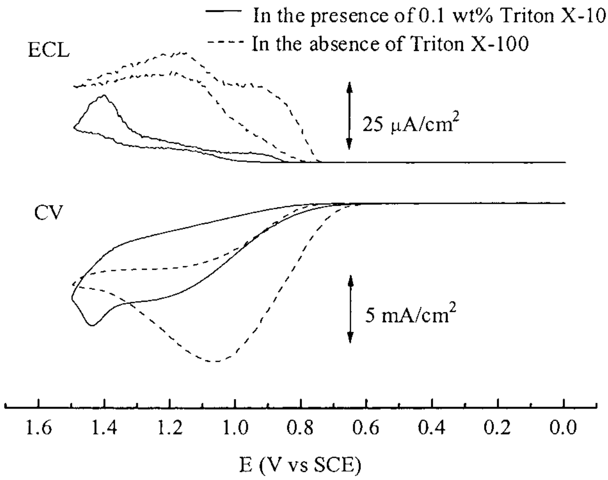

Figure 5. Cyclic voltammograms and ECL curves at a GC electrode in 0.15 M phosphate buffer solution (pH 7.5) containing 100 mM TPrA and 1 μM $Ru(bpy)_3^{2+}$ in the presence and absence of 0.1 wt % Triton X-100. Potential scan rate, 0.1 V/s.

At a GC electrode, however, the presence of Triton X-100 suppressed both TPrA oxidation and ECL intensity, as shown in Figure 5. In the absence of the surfactant species, TPrA oxidation at a GC electrode started at 0.65 V, and a relatively broad anodic current peak appeared at 1.05 V. The ECL curve exhibited two peaks. The first one was below 1.0 V; the mechanism of this ECL process is still unclear. The second one was the usually observed ECL process that was described in eqs 1−4. The oxidation current of TPrA at GC was much larger than that at Pt or Au electrodes. Studies of electrochemical behavior with a GC electrode in contact with aqueous solutions previously showed that, compared to metal electrodes or other carbon electrodes, such as various graphites, glassy carbon exhibited greater inertness to chemical attack.[36,37] At Pt or gold electrode surfaces, however, the formation of oxide layers is much easier in an aqueous solution. Clean Pt and gold

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surfaces and Pt or gold oxide layers are all hydrophilic, leading to a lower oxidation rate of TPrA. On the contrary, GC has a relatively hydrophobic surface that facilitates TPrA oxidation. In the surfactant aqueous solution, head-on interaction of surfactant molecules with a GC surface has also been reported.[33] However, the Triton X-100-modified GC electrode was apparently less active in oxidizing TPrA than the bare GC, and ECL intensity was lower. Thus, for a hydrophobic surface like GC, the adsorption of surfactant does not promote oxidation of the neutral TPrA species. In fact, the surfactant layer at the electrode inhibits the electron-transfer process. A recent paper[22] also demonstrated a large increase in $Ru(bpy)_3^{2+}$ ECL with TPrA coreactant in the presence of Triton X-100 (and other surfactants) at a Pt electrode. These increases were ascribed to improved emission from $Ru(bpy)_3^{2+}$/surfactant or micelle species. The results here, however, seem more consistent with a surface effect.

CONCLUSIONS

TPrA anodic oxidation is very sensitive to the surface condition of the electrode. As shown in a previous paper, the oxidation rate of TPrA is significantly different with different electrode materials. Here, we examined the effect of electrode hydrophobicity on TPrA oxidation as well as on the ECL intensity of the $Ru(bpy)_3^{2+}$/TPrA system. Various thiol molecules were used to modify Pt and Au electrode surfaces. The hydrophobicity of the electrode surface was controlled by the terminal group of the thiol monolayer. On the more hydrophobic surfaces, the kinetics of TPrA anodic oxidation was obviously faster. The larger TPrA oxidation rate resulted in a significant increase in the ECL intensity. The hydrophobic interaction allowed close approach and perhaps reorganization of neutral TPrA molecules to the alkanethiol-modified electrode surface, which could facilitate the electron transfer. Due to the increase of the TPrA oxidation rate, the ECL intensity of the $Ru(bpy)_3^{2+}$/TPrA system was much larger at the hydrophobic modified electrode than at the hydrophilic one. Therefore, the application of an electrode with a hydrophobic surface can increase the analytical ECL sensitivity in the TPrA coreactant system.

The well-known surfactant effect (Triton X-100) on the $Ru(bpy)_3^{2+}$/TPrA system was also examined at Pt, Au, and GC electrodes. Significant enhancement of both the TPrA oxidation current and ECL intensity was observed at Pt and Au electrodes and attributed to the changes of electrode surface hydrophobicity. The adsorption of surfactant species would render the electrode surface more hydrophobic and facilitate TPrA oxidation. However, Triton X-100 suppresses both TPrA oxidation and ECL emission at a hydrophobic GC electrode, indicating that the surfactant effect depends on the electrode material.

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