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ORIGINAL PAPER

# Electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ associated with surfactants on the MWNTs/GC electrode

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**Abstract** The electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ (where bpy = 2,2′-bipyridine, tatp = 1,4,8,9-tetra-aza-triphenylene) on the multi-walled carbon nanotubes-modified glassy carbon electrode (MWNTs/GC) in the presence of anionic and cationic surfactants has been investigated. A diffusion-controlled wave and three prewaves are exhibited on the differential pulse voltammogram of $[Ru(bpy)_2tatp]^{2+}$. The formal potential of the prewaves is found to be much negative than that of the diffusion-controlled wave. An appropriate amount of anionic surfactants including dihexadecyl phosphate (DHP) and deoxyribonucleic acid (DNA) can prompt the assembly of $[Ru(bpy)_2tatp]^{2+}$ on the MWNTs/GC electrode by using the method of repetitive voltammetric sweeping. In contrast, cationic surfactant such as hexadecyl trismethyl ammonium chrolide (HTAC) dispersed on the MWNTs surface is found to inhibit the assembly of $[Ru(bpy)_2tatp]^{2+}$. Meanwhile, the assembled principle of $[Ru(bpy)_2tatp]^{2+}$ on the MWNTs/GC electrode with the participation of surfactants is discussed in detail.

**Keywords** Polypyridyl ruthenium(II) complex · Surfactant · Carbon nanotubes · Assembly · Voltammetry

## 1 Introduction

Polypyridyl ruthenium complexes have emerged as a new kind of applied materials with rich redox activities and well-known photoluminescence properties [1–3]. Recently, some ruthenium complexes have been organized onto electrodes to construct redox systems using Langmuir–Blodgett techniques [4, 5], self-assembled monolayers [6–8], covalent binding [9], and layer-by-layer alternate adsorption methods [10–12], etc. These approaches in surface chemistry are very significant for the construction of artificial molecular devices or innovative sensors.

Carbon nanotubes (CNTs) have attracted enormous interest based on their unique electronic, structural, and mechanical properties [13, 14]. Many efforts have witnessed a marked progress in synthesis, manipulation, functionalization, and application of CNTs [15–17]. Besides their high impact in other fields, the special electronic and structural properties of CNTs make them both interesting in electrochemistry and attractive for practical applications [18–20]. The modification of carbon-based electrodes with CNTs has been extensively applied in the catalytic field from fuel/electrochemical cells to heterogeneous catalysis [21–24]. However, the poor solubility of CNTs in both aqueous and nonaqueous solvents has severely restricted their effective uses and development [25, 26]. In order to disperse adequately CNTs in water and further prepare the carbon-based electrodes with CNTs, a variety of surfactants are added by sonication in solvents such as octylphenol ethoxylate (Triton X-100), sodium dodecylbenzenesulfonate (SDBS) [27], sodium dodecyl sulfate (SDS) [28], dihexadecyl phosphate (DHP) [29], cetyltrimethyl ammonium bromide (CTAB) [30], and deoxyribonucleic acid (DNA) discovered recently [31]. These surfactants mostly possess long and hydrophobic

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chain tail that binds to CNTs and hydrophilic headgroup that mediates the interaction with water.

Synchronously, it has been demonstrated that CNTs can interact with polypyridyl ruthenium compounds by covalent and noncovalent functionalization methods. Dong et al. demonstrated that CNTs/Nafion composite films had the ability to adsorb $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and showed the sensitive electrogenerated chemiluminescence properties with tripropylamine as a coreactant [32, 33]. By using covalent attachment method, $[Ru(bpy)_2(dcbpy)]^{2+}$ (dcbpy = 4,4′-dicarboxy- 2,2′-bipyridine) or $[Ru(bpy)_3]^{2+}$ was interconnected on the multi-walled CNTs (MWNTs) for treating ammonia atmosphere or increasing their persistent photoconductivity [34, 35]. Recently, single-walled carbon nanotubes (SWNTs) with terminal carboxylic acid groups were used as an electron-transfer bridge layer for improving photocurrent of viologen/Ru complex-based photoelectrochemical cells [36]. A ruthenium metallodendrimer was discovered to bind strongly and specifically to the SWNTs [37]. Moreover, Kavan et al. synthesized a kind of polypyridyl ruthenium complexes with amphiphilic surfactant, used as the dispersing reagent of CNTs for their applications in high-energy lithium-ion batteries [38, 39]. However, there are fewer reports on in situ assembly of polypyridyl ruthenium complexes associated with surfactants at CNTs-modified surface. In our previous reports [40], a DNA-prompted assembly technique of $[Ru(bpy)_2IP]^{3+/2+}$ with imidazo[4,5,f] [1, 10] phenanthroline (IP) at an ITO electrode has been developed.

Herein, to further extend the assembled technique of polypyridyl ruthenium complexes on carbon-based electrodes with CNTs, we choose $[Ru(bpy)_2tatp]^{2+}$ (where tatp = 1,4,8,9-tetra-aza-triphenylene) with two uncoordinated N atoms as a research object, exploring its assembly on the MWNTs-modified glassy carbon (GC) electrode with participation of surfactants including DHP, DNA, and hexadecyl trismethyl ammonium chrolide (HTAC). Fortunately, $[Ru(bpy)_2tatp]^{2+}$ can be successfully assembled onto the MWNTs/GC electrode by using the method of progressive voltammetric sweeping. The assembled principle of $[Ru(bpy)_2tatp]^{2+}$ associated with anionic or cationic surfactants on the MWNTs/GC electrode is proposed as depicted in Fig. 1.

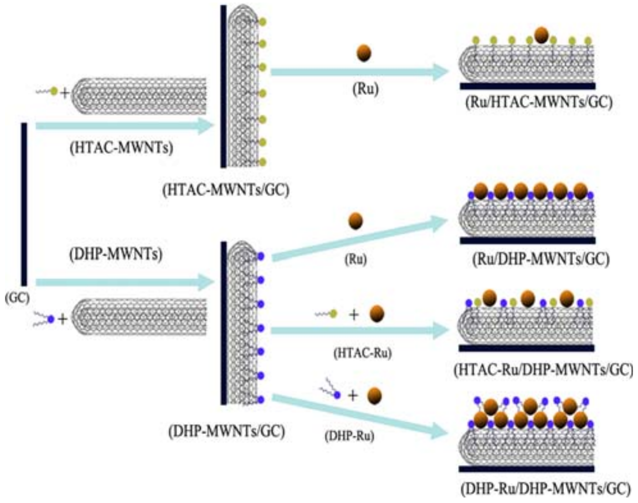

**Fig. 1** Schematic diagram showing the assembled principle of $[Ru(bpy)_2tatp]^{2+}$ (Ru) associated with anionic surfactant DHP and cationic surfactant HTAC on the MWNTs/GC electrode

## 2 Experimental

### 2.1 Chemicals and materials

$[Ru(bpy)_2tatp]Cl_2$ was prepared and purified according to the procedures reported previously [41]. The structure of the complex is shown in Fig. 2. Tris (where Tris is tris(hydroxy methyl)amino-methane) was purchased from Sigma Chemical Company. Calf thymus DNA (Huamei Co.) was used as received. DNA in electrolyte solution gave a UV absorbance ratio at 260–280 nm of 1.89, indicating that the DNA was sufficiently free of protein [42]. After dilution, DNA concentration per nucleotide phosphate, NP, was determined by UV absorbance at 260 nm. The molar absorption coefficient of the DNA at this wavelength was taken as 6,600 $Lmol^{-1}$ $cm^{-1}$ [43]. The DNA stock solutions of 5 mmol $L^{-1}$ were stored at 4 °C and used within 4 days after their preparation. The multi-walled carbon nanotubes (MWNTs) with the inside diameter of 2–5 nm and the length of 10–30 μm were obtained from Chengdu Organic Chemistry Co. Ltd, China. Dihexadecyl phosphate (DHP), hexadecyl trismethyl ammonium chrolide (HTAC), and other reagents were of analytical grade and used as received unless otherwise noted. The electrolyte solution was 10 mmol $L^{-1}$ Tris/50 mmol $L^{-1}$ NaCl at pH of 7.2. Doubly distilled water was used to prepare buffer solutions.

### 2.2 Apparatus

Voltammetric measurements were performed on a CHI660a electrochemical system with a corresponding software package (Shanghai, China). The differential pulse voltammetric test employed the step potential of 4 mV and pulse period of 0.2 s. A regular three-electrode system with test solution of 0.4 mL was used, consisting of a glassy carbon (GC) disk working electrode (Southampton, England, $\Phi = 2$ mm), a platinum-wire auxiliary electrode, and an Ag–AgCl reference electrode with 50 mmol $L^{-1}$ NaCl.

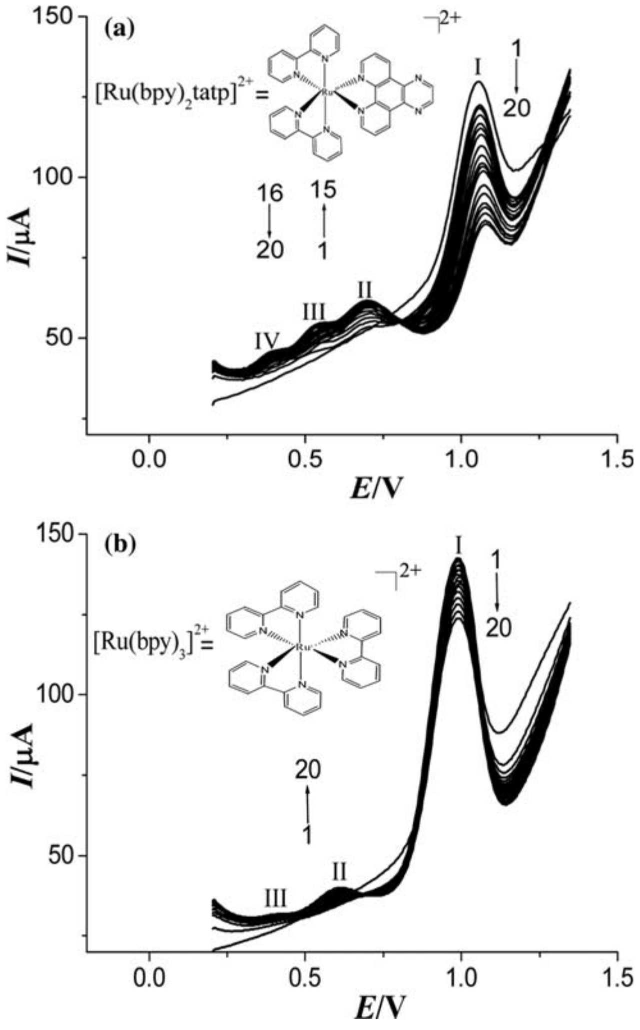

**Fig. 2** Repetitive DPVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ (**a**) or $[Ru(bpy)_3]^{2+}$ (**b**) on the DHP-MWNTs (1.67)/GC electrode (where the value in bracket represents the weight ratio of surfactant to MWNTs). The inset is structures of the complexes

### 2.3 Preparation of MWNTs modified GC electrode

Prior to preparation of MWNTs modified GC electrode (MWNTs/GC), the GC disk electrode was polished with 3 μm and 0.1 μm alumina paste on a polishing cloth (Buehler) and then subjected to ultrasonic cleaning for about 10 min in double distilled water. The MWNTs suspension was prepared by dispersing 3 mg MWNTs in 5 mL water and an appropriate amount of surfactants with the aid of ultrasonic agitation. Next, the modified electrode was prepared by dropping 5-μL suspensions of MWNTs onto the GC electrode surface and then evaporating the solvent under an infrared lamp. The effective area of MWNTs/C electrode was 0.13 $cm^2$, which is determined by a reversible system (4 mmol $L^{-1}$ $K_4[FeCN_6]$ in 1 mol $L^{-1}$ KCl), with the diffusion coefficient of $6.3 \times 10^{-6}$ $cm^2$ $s^{-1}$ [44, 45].

All the experiments were performed at room temperature in the range of 23–25 °C.

## 3 Results and discussion

### 3.1 Electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ on DHP-MWNTs/GC electrode

The differential voltammograms (DPVs) of $[Ru(bpy)_2tatp]^{2+}$ in buffer solutions are shown in Fig. 2a. Starting at 0.2 V and scanning in the positive potential direction, a well-defined redox wave is observed at the peak potential of 1.052 V, taken as the formal potential ($E^{\circ\prime}$). Compared to the result of $[Ru(bpy)_3]^{2+}$ shown in Fig. 2b and combined with our previous reports [40], the wave (peak I) can be assigned to the oxidation of soluble $[Ru(bpy)_2tatp]^{2+}$ to $[Ru(bpy)_2tatp]^{3+}$. According to the cyclic voltammograms (CVs) shown in Fig. 3, peak potentials of the oxidative and reductive waves are 1.125 V and 1.047 V at a scan rate of 0.1 V $s^{-1}$, respectively. The peak separation is 78 mV, and $E^{\circ\prime} = 1.086$ V, taken as the average of oxidative and reductive peak potentials. The oxidative peak I heights increase linearly with the square root of scan rate ($\upsilon^{1/2}$) in the range from 0.02 to 0.30 V $s^{-1}$ (see the inset of Fig. 3). These results show that $[Ru(bpy)_2tatp]^{3+/2+}$ reaction in solution is controlled by the diffusion process, hence peak I is regarded as a diffusion-controlled wave [40].

From the analysis of Fig. 2, it is interesting that another three waves (peaks II, III, and IV) appear at 0.694, 0.543, and 0.399 V except the peak I with increasing voltammetric sweeping times in the potential range from 0.2 to

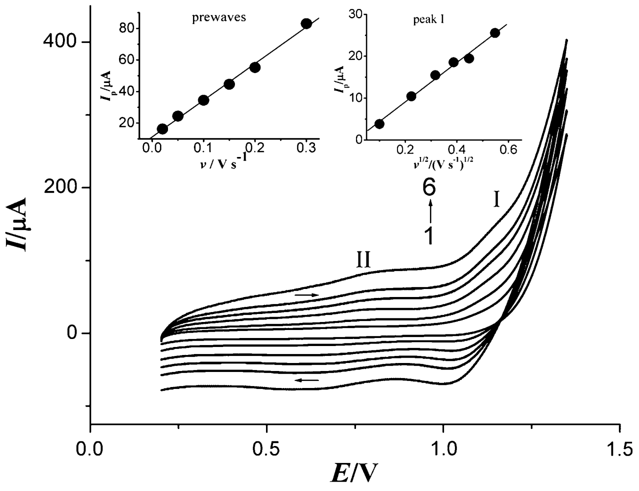

**Fig. 3** CVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ on the DHP-MWNTs (1.67)/GC electrode after repetitive DPVs of 20 cycles at the different scan rate (V $s^{-1}$): (1) 0.02, (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20, and (6) 0.30. The inset is the plot of prewaves currents *vs* scan rate or peak I currents *vs* the square root of scan rate

1.35 V, respectively. These waves are based on the strong adsorption of the oxidized product [46]. The free energy of $[Ru(bpy)_2tatp]^{3+}$ adsorption facilitates the oxidation of $[Ru(bpy)_2tatp]^{2+}$ to form the adsorbed $[Ru(bpy)_2tatp]^{3+}$ on the DHP-MWNTs/GC electrode, therefore, considered as prewaves. It is possible due to the presence of multiple different configurations for the adsorbed $[Ru(bpy)_2tatp]^{2+}$, three prewaves appear on the DPVs. Peak potential values of these prewaves have a negative shift of 0.358–0.653 V compared with that of the diffusion-controlled wave (peak I). As a result, $[Ru(bpy)_2tatp]^{2+}$ is assembled on the DHP-MWNTs/GC electrode by repetitive voltammetric sweeping. Moreover, it is found that repetitive DPVs of $[Ru(bpy)_3]^{2+}$ only exhibit two weak prewaves (peaks II and III) (Fig. 2b), suggesting that the electrochemical assembly of $[Ru(bpy)_3]^{2+}$ on the DHP-MWNTs/GC electrode is mainly based on the $\pi$-$\pi$ conjugation system between CNTs and bpy ligands. Tatp ligand in $[Ru(bpy)_2 tatp]^{2+}$ complex has two uncoordinated N atoms, possibly contributed to the assembly of the complex. On the other hand, cationic surfactant DHP dispersed on the modified electrode may also participate in the electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ from the analysis below.

## 3.2 Electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ prompted by anionic surfactants

When the weight ratio of DHP to MWNTs on the modified electrode is increased twice, as shown in Fig. 4, the repetitive DPVs of $[Ru(bpy)_2tatp]^{2+}$ still show a diffusion-controlled wave and three prewaves. However, the peak currents of prewaves generate an enhancement from 21.4 μA in Fig. 2a to 28.6 μA, implying that an appropriated amount of DHP can facilitate the assembly of $[Ru(bpy)_2tatp]^{2+}$ on the MWNTs surface as shown in Fig. 1. It is possible owing to the electrostatic attraction of $[Ru(bpy)_2tatp]^{2+}$ with DHP.

Moreover, when 0.1 mmol $L^{-1}$ DHP emerges in the test solution, DHP in solution can also prompt the electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ on the modified electrode (Fig. 5). However, while the DHP concentrations become larger, as shown in the inset of Fig. 5, the electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ becomes weak. It is possible due to the binding of anionic DHP micelles in solution to the positively charged complex, as a result, the electrostatic attraction of $[Ru(bpy)_2tatp]^{2+}$ with DHP dispersed on the modified electrode is weakened, and their electrochemical assembly in the presence of high concentration DHP is inhibited.

Interestingly, while synthetic lipid DHP is displaced by natural DNA molecule, as shown in Fig. 6, the observed result is similar to the case in the presence of DHP. A positively charged ruthenium complex, and DNA as a negatively charged counterpart molecule are deposited on the MWNTs modified GC electrode, hence, an appropriated amount of DNA in solution can also prompt the electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ on the MWNTs surface.

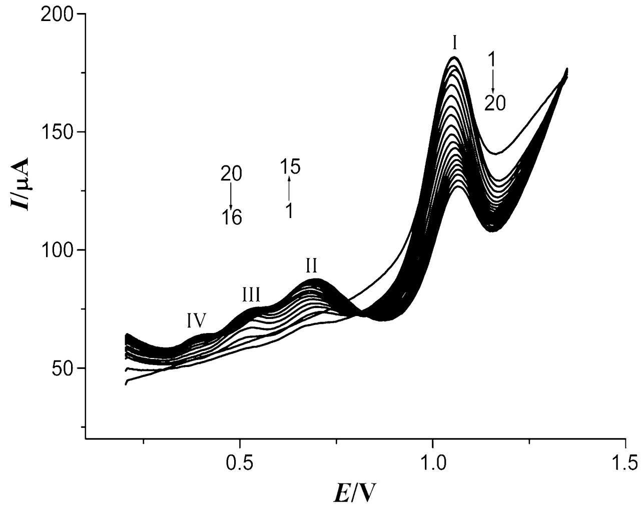

**Fig. 4** Repetitive DPVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ on the DHP-MWNTs (3.40)/GC electrode

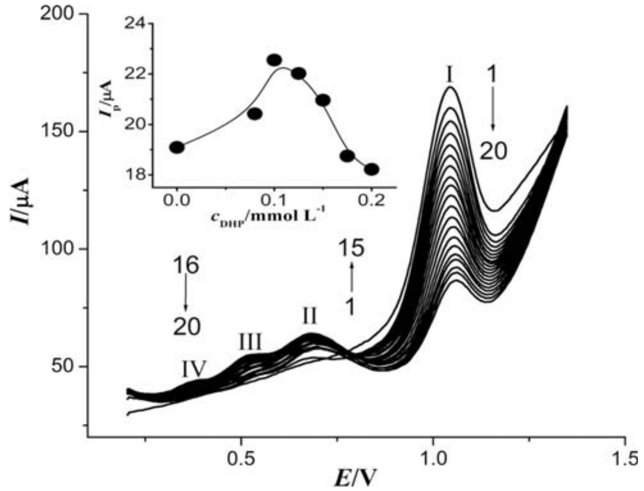

**Fig. 5** Repetitive DPVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ in the presence of 0.1 mmol $L^{-1}$ DHP on the DHP-MWNTs (1.67)/GC electrode. The inset is plot of the prewave currents *vs* DHP concentrations in buffer solution

## 3.3 Electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ inhibited by cationic surfactants

According to the results mentioned above, appropriate DHP or DNA can facilitate the electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ on basis of the contribution from $\pi$-$\pi$ conjugated interaction and electrostatic attraction between

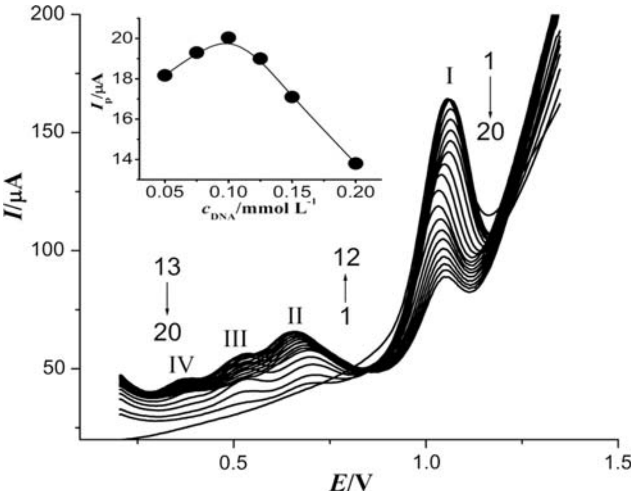

**Fig. 6** Repetitive DPVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ in the presence of 0.1 mmol $L^{-1}$ DNA on the DHP-MWNTs (1.67)/GC electrode. The inset is plot of the prewave currents *vs* DNA concentrations in buffer solution

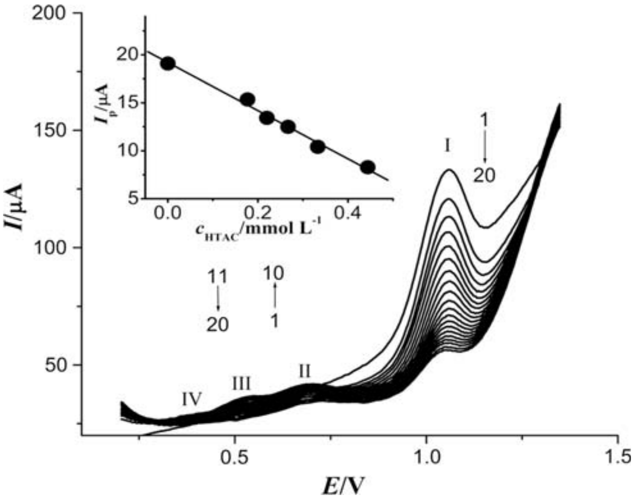

**Fig. 7** Repetitive DPVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ in the presence of 0.1 mmol $L^{-1}$ HTAC on the DHP-MWNTs (1.67)/GC electrode. The inset is plot of the prewave currents *vs* HTAC concentrations in buffer solution

the complex and anionic surfactants. In contrast, can the cationic surfactants counteract the assembly of $[Ru(bpy)_2tatp]^{2+}$ on the DHP-MWNTs/GC electrode? In response to the problem, Fig. 7 gives the progressive DPVs of $[Ru(bpy)_2tatp]^{2+}$ in the presence of 0.1 mmol $L^{-1}$ HTAC. The results imply that although a diffusion-controlled wave and three prewaves are still observed, the peak currents of three prewaves indicate a dramatic decrease compared with that of the complex alone, revealing that the cationic HTAC may partly neutralize the negative charge of the modified electrode. Of course, while the cationic HTAC is immobilized on the MWNTs surface, as the repetitive DPVs shown in Fig. 8, the electrochemical assembly of $[Ru(bpy)_2tatp]^{2+}$ on the MWNTs surface is completely inhibited, only background current is observed. The results imply that a positively charged $[Ru(bpy)_2tatp]^{2+}$ cannot carry out its electrochemical assembly on a positively charged electrode based on the electrostatic repulsions.

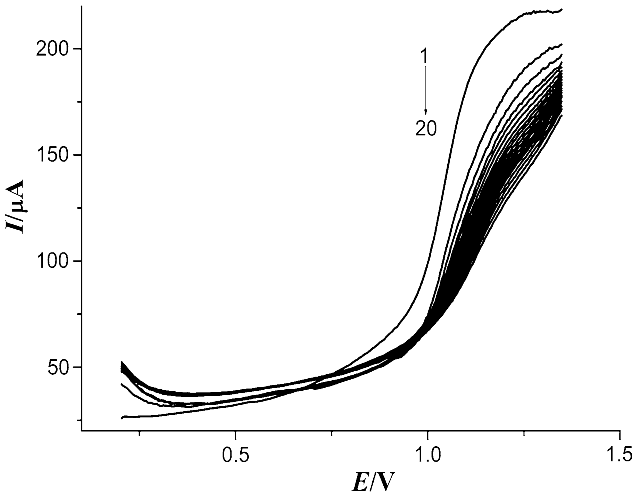

**Fig. 8** Repetitive DPVs of 0.1 mmol $L^{-1}$ $[Ru(bpy)_2tatp]^{2+}$ on the HTAC-MWNTs (1.40)/GC electrode

## 4 Conclusions

A repetitive voltammetric sweeping technique has been developed for controllable assembly of polypyridyl ruthenium complexes on the MWNTs-modified GC electrode with participation of cationic and anionic surfactants. With this technique, a surface-confined redox film associated with surfactants is fabricated. From this study, the following conclusions are derived:

(1) In pH = 7.2 buffer solutions over a scan potential range from 0.2 to1.35 V, a diffusion-controlled wave and three prewaves are observed on the repetitive differential pulse voltammograms of $[Ru(bpy)_2tatp]^{2+}$ at the MWNTs/GC electrode.
(2) An appropriate amount of anionic surfactants including DHP and DNA can prompt the assembly of $[Ru(bpy)_2tatp]^{2+}$ on the MWNTs/GC electrode by using the method of repetitive voltammetric sweeping.
(3) Cationic surfactant HTAC dispersed on the MWNTs surface is proved to inhibit the assembly of $[Ru(bpy)_2tatp]^{2+}$.

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