



Electrochemically-tuned luminescence of a $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ -sensitized TiO_2 anode and its applications to photo-stimulated guanine/ H_2O_2 fuel cells

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ABSTRACT

A phenazine-containing Ru(II) complex $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ (bpy = 2,2'-bipyridine and tstp = 1,4,8,9-tetraaza-triphenylene) is first applied to a modification of the nano- TiO_2 /indium-tin oxide (ITO) electrode by the method of repetitive voltammetric sweeping. The resulting $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ -modified TiO_2 electrode shows two pairs of well-defined redox waves and excellent electrocatalytic activity for the oxidation of guanine. $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ on TiO_2 surfaces exhibits intense absorbance and photoluminescence in visible region, revealed by absorption spectra, emission spectra and fluorescence microscope. While $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ -sensitized TiO_2 is functionalized as an anode to combine with a continuous wave green laser via an optical microscope, the luminescence of Ru(II)-based excited states can be enhanced by the oxidation of guanine. Furthermore, the $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ -sensitized TiO_2 electrode is used as photoanode and hemoglobin-modified single-walled carbon nanotubes (SWCNTs) as cathode for the elaboration of a photo-stimulated guanine/ H_2O_2 fuel cell with a saturated KCl salt-bridge. It becomes evident that the photo-stimulated fuel cell performance depends strongly on the excited states of Ru(II) complex-sensitized anodes as well as the electrocatalytic oxidation of guanine. This study provides an electrochemically-tuned luminescence method for better evaluating contributions of the sensitizer excited states to photo-stimulated fuel cells.

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1. Introduction

Polypyridyl ruthenium(II) complexes have received considerable interest and found applications in many fields due to a series of desirable advantages such as excellent electrochemical or photochemical activity [1,2] and thermal stability [3], tunable emission colors [4] and photo-sensitive properties by varying ligand structure [5,6]. $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) and related complexes have been used as photo-oxidants or electrocatalytic mediators for biochemical and medical analysis [7–9]. Because DNA oxidative damage always leads to the permanent oxidation of guanine, which is the most easily oxidized nitrogenous base, the Ru(II) complexes have been applied to the catalytic oxidation of guanine [10–12]. To date, the oxidative mechanism of guanine using Ru(II) complexes as photo-oxidants or electrocatalytic mediators in solutions has been well-documented, however there have been very few photo-induced electrocatalytic studies of guanine oxidation at a catalyst-modified electrode surface [13,14]. This information would be useful for the design of spectroscopic or electrochemical

DNA biosensors [15]. Recently, a photoelectrochemical DNA sensor has been developed for the rapid detection of DNA damage by the photogenerated Ru(III) complexes [13].

In addition to their use for the oxidation of guanine as photo-oxidants or electro-catalysts, some Ru(II) complexes have served as the sensitizers for photo-electrochemical solar cells [14–16]. The Ru(II)-based sensitizers were usually assembled on the semiconductor electrode surfaces for absorbing ultraviolet or visible light [17–19]. For example, a classical dye-sensitized (Grätzel) solar cell employing Ru(II) complex-sensitized nanocrystalline TiO_2 thin film photo-anodes and I/I_3^- redox electrolytes has been intensively studied [20,21]. In order to simultaneously convert light energy and chemical energy into electricity, a biofuel cell has been combined with photo-electrochemical solar cells, resulting in hybrid photoelectrochemical biofuel cells [22,23]. The Ru(II) complex-sensitized semiconductor electrodes were used as photo-anodes with glucose as typical fuels. The anodic reactions were coupled to cathodic redox ones through an ion-permeable membrane in a two-compartment electrochemical cell [24]. A non-polarizable, highly reversible reference electrode or O_2 reduction catalytic electrode was usually employed as fuel cell cathodes [25,26].

Our laboratory has studied the photoluminescence of $[\text{Ru}(\text{bpy})_2(\text{tstp})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ incorporated in

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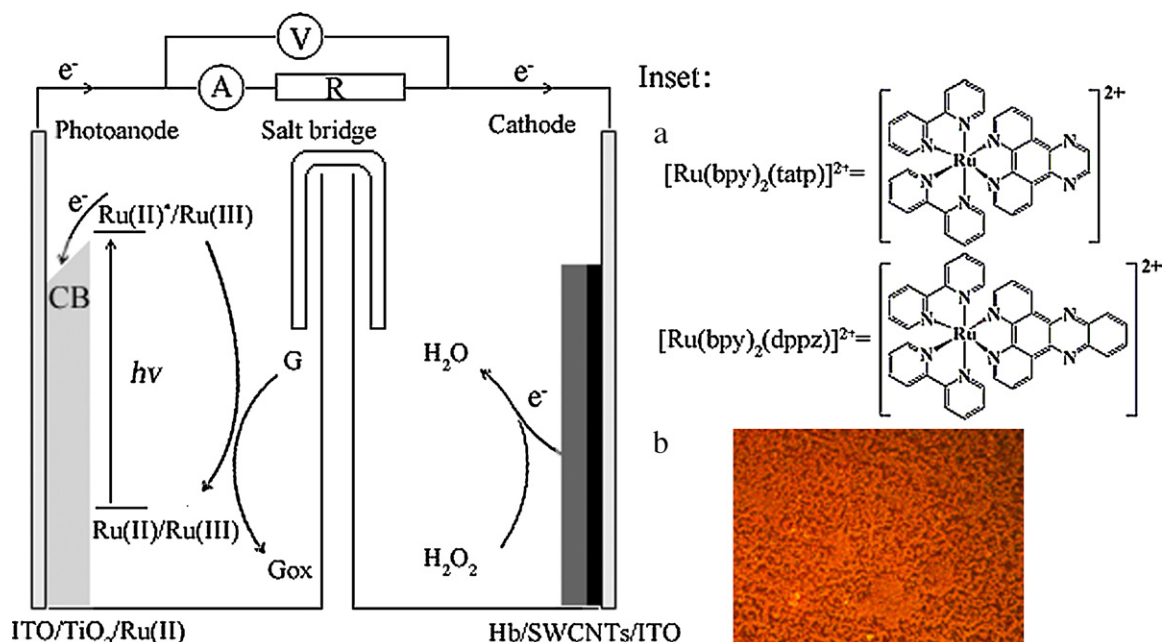


Fig. 1. Schematic configuration of a photo-stimulated guanine/ H_2O_2 fuel cell using Ru(II) complex-sensitized TiO_2 as photoanode and Hb/SWCNT as cathode. The inserted plots a and b show the structures of Ru(II) complexes and fluorescence microscopic image of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$, respectively.

DNA aggregates (bpy = 2,2'-bipyridine, tatp = 1,4,8,9-tetra-aza-triphenylene and dppz = dipyrido[3,2-a:2',3'-c]phenazine) on the electrode surfaces with appropriate applied electrode potentials under the excitation of a continuous wave green laser [27,28]. Interestingly, we have found that the $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ -based luminescence can be enhanced by an anodic potential whereas $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ showed an opposite result. In the current work, an attempt is made to estimate the contributions of both electrochemically-tuned luminescence of Ru(II)-based excited states and electrocatalytic oxidation of guanine to the photo-stimulated guanine/ H_2O_2 fuel cell. The Ru(II)-sensitized anodes possessing the luminescence either quenched by external electric field or enhanced by electrocatalytic oxidation of guanine, may be of value to the fabrication of photo-stimulated fuel cells. To our knowledge, this work for the first time presents an electrochemically-tuned luminescence application in photo-stimulated fuel cells.

2. Experimental

2.1. Chemicals and materials

Tris-hydroxy methyl amino-methane (Tris) from Sigma Chem. Co. St. Louis, Mo, USA was used to prepare buffer solutions. The single-walled carbon nanotubes (SWCNTs) with 2–5 nm inside diameter and 10–30 μm length were obtained from Chengdu Organic Chemistry Co., China. The SWCNTs were dispersed with sodium dodecylsulfate (SDS) from Damao Chem. Co., Tianjin, China. Guanine (Boao Bioscience Tech. Co., Shanghai, China) and hemoglobin (Qiyun Co., Guangzhou, China) were used as received. Unless otherwise noted, the buffer solution was 10 mmol L^{-1} Tris/50 mmol L^{-1} NaCl of pH 7.2, prepared with doubly distilled water. $[\text{Ru}(\text{bpy})_2(\text{tatp})](\text{ClO}_4)_2$ and $[\text{Ru}(\text{bpy})_2(\text{dppz})](\text{ClO}_4)_2$ were synthesized following procedures reported previously [29–31]. The structures of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ were shown in Fig. 1.

2.2. Preparation of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ -sensitized TiO_2 thin layer electrode

An indium tin oxide (ITO)-coated glass (coating 90 nm, sheet resistance = 20 Ω/square , Nanbo Co., Shenzhen, China) was cleaned in an ultrasonic cleaner sequentially with ethanol and de-ionized water for 20 min. A coating of homemade nanoparticulate TiO_2 sol-gel was spread on a piece of ITO-coated glass and dried in a warm box of 100 $^\circ\text{C}$ for 20 min [32]. The TiO_2 thin film was then sintered at 450 $^\circ\text{C}$ within 30 min for adhering strongly to the ITO surface. Subsequently, the $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ sensitizer was assembled onto the TiO_2 electrode surfaces by the method of repetitive voltammetric sweeping (Fig. 2). The resulting electrodes were rinsed with buffer solution for 5 min.

2.3. Preparation of hemoglobin-(Hb) modified SWCNT thin layer electrode

The SWCNT suspensions were first prepared by dispersing 3 mg SWCNTs into 5 mL water containing 5 mg SDS with the aid of ultrasonic agitation (200 W) for ca. 40 min [33]. Next, the SWCNT-modified ITO electrode was prepared by dropping 20 μL of the SWCNT suspensions onto the ITO electrode surface and then evaporating the solvent under an infrared lamp for 30 min. Subsequently, the Hb dissolved in buffer solution was immobilized by placing the Hb solution (2.0 g L^{-1} , 0.4 mL) drop-wise onto the SWCNT/ITO surfaces, followed by solvent evaporation/drying at room temperature. The resulting Hb-modified SWCNT thin layer electrode was also rinsed with buffer solution for 5 min.

2.4. Instruments and experimental conditions

Steady-state emission spectra were recorded using a Hitachi RF-2500 fluorescence spectrophotometer (Hitachi city, Japan). The samples were excited at 450 nm. The fluorescence image was taken using a Nikon Eclipse TS100 inverted fluorescence microscope (Tokyo, Japan), equipped with a 50-W mercury lamp. The images were captured with a Nikon E4500 camera with blue

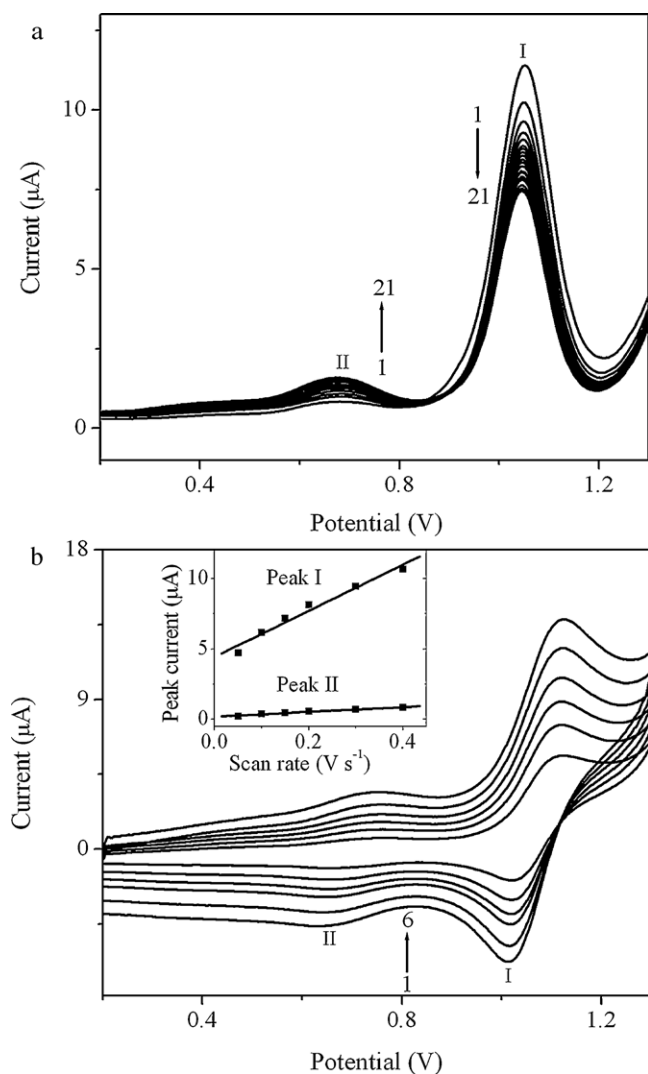


Fig. 2. (a) Repetitive DPVs of $0.1 \text{ mmol L}^{-1} [\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 -modified ITO electrodes and (b) CVs performed after 21 cycles DPVs at different scan rate (V s^{-1}): (1) 0.4, (2) 0.3, (3) 0.2, (4) 0.15, (5) 0.1, (6) 0.05. The inset shows the current values of peak I and peak II as a function of scan rate.

light radiation. Voltammetric measurement was performed on a CHI660a electrochemical system (Chenhua Co., Shanghai, China) in a regular three-electrode cell with 0.4 mL test solution. The electrochemically-tuned emission spectra were recorded using a home-built system similar to that used in our previous report [27]. This system consisted of an optical microscope (Zeiss Axio Observer A1, Oberkochen, Germany), a continuous wave (CW) green laser source (532 nm, Verdi-5, Coherent, Santa Clara, CA, USA) and an electrochemical setup. The electrocatalytic reduction of H_2O_2 on the Hb-modified SWCNT thin layer electrode was performed under nitrogen atmosphere. The platinum sheet was used as counter electrode and saturated calomel electrode (SCE) as the reference. The measurement of photo-stimulated fuel cell performance was performed in a two-compartment cell. An ultraviolet UV lamp (8 W) was as the light source of photo-stimulated fuel cells. The back side (non-conductive, not TiO_2 coated) of the photoanodes faced the excitation beam. The illuminated area was ca. 2.3 cm^2 . The anodic and cathodic compartments were filled with 3 mL buffer solutions containing 0.2 mmol L^{-1} guanine and 1.0 mmol L^{-1} H_2O_2 , respectively. All the experiments were performed at room temperature ($23\text{--}25^\circ\text{C}$).

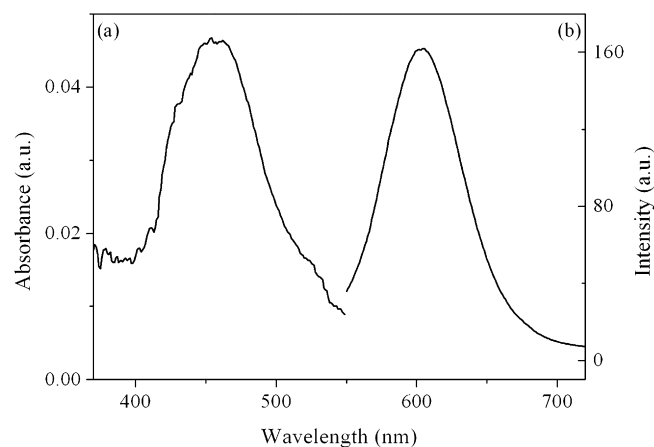


Fig. 3. (a) Electronic absorption spectra and (b) emission spectra of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ immobilized on TiO_2 surfaces.

3. Results and discussion

3.1. Fabrication and characterization of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces

The repetitive differential pulse voltammograms (DPVs) of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces are shown in Fig. 2a. In these figures, an anodic wave at 1.050 V, labeled as wave I, is observed. Since a similar anodic peak was previously reported for $[\text{Ru}(\text{bpy})_3]^{2+}$ [34,35], this anodic wave I is assigned to the oxidation from Ru(II) to Ru(III). With increasing voltammetric sweep number, a new wave II appears at 0.680 V, which is far more negative than that of wave I.

In order to better assign waves I and II, the effect of scan rate on the electrochemical behavior of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2/ITO electrodes was studied. After repetitive differential pulse voltammetric scans of 21 cycles, cyclic voltammograms (CVs) in Fig. 2b shows an anodic ($E_{p,a}$) peak at 1.116 V and a cathodic ($E_{p,c}$) peak at 1.028 V (peak I), with a peak separation, ΔE_p of 88 mV and a formal potential, $E^{\circ'}$ of 1.072 V, taken as the half of the sum of $E_{p,a}$ and $E_{p,c}$. The current ratio of anodic peak to cathodic peak was close to 1.0 for all the scan rates, while the peak currents were proportional to scan rate (ν) over the range from 0.4 to 0.05 V s^{-1} (inset). Similarly to peak I, the peak II currents increase linearly with the rising scan rate. These electrochemical characteristics indicate that $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ has been adsorbed onto TiO_2 surfaces [36]. The peaks I and II are therefore ascribed to the $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{3+/2+}$ reactions adsorbed weakly and strongly on TiO_2 surfaces in the process of voltammetric sweeping, respectively. The free energy of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{3+}$ adsorption arising from interactions between phenazine unit in the tatp ligand and TiO_2 , facilitates the adsorption $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{3+/2+}$ on TiO_2 surfaces by repetitive voltammetric sweeping [37]. The fluorescence image shown in Fig. 1 further illustrates that $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ in buffer solutions can be adsorbed onto TiO_2 surfaces.

Fig. 3 shows absorption spectra and emission spectra of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces. A distinct absorption band at 458 nm is observed, arising from $\text{Ru}(d\pi) \rightarrow \text{bpy}(\pi^*)$ and $\text{Ru}(d\pi) \rightarrow \text{tatp}(\pi^*)$ transitions [38]. An intense emission peak appears at 603 nm. This emission peak is based on the $d\pi \rightarrow \pi^*$ electron transition from Ru(II)-to-ligand [39]. These results imply that $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces possesses excellent photosensitive and luminescent properties.

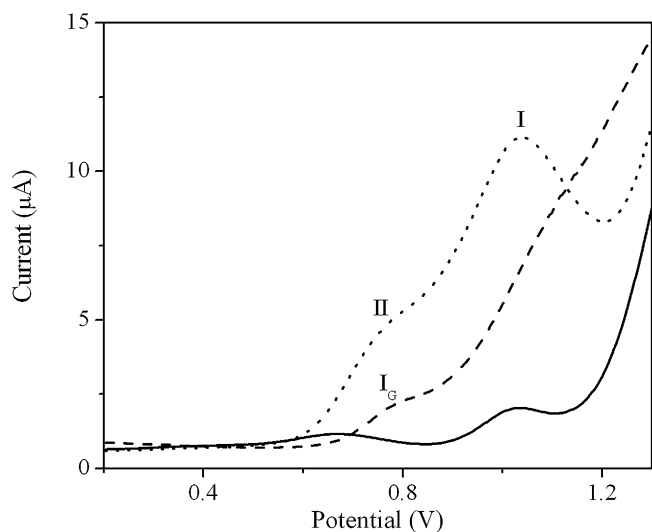


Fig. 4. DPVs of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 -modified ITO electrodes in the absence (solid line) and presence of 0.2 mmol L^{-1} guanine (dotted line). The dashed line shows the DPV of 0.2 mmol L^{-1} guanine.

3.2. Electrocatalytic oxidation of guanine by $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces

As reported before, $[\text{Ru}(\text{bpy})_3]^{2+}$ and related complexes in solutions have the ability to induce the oxidation of guanine [10,11]. It is interesting to know whether $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces could electrochemically catalyze the oxidation of guanine. As shown in Fig. 4, $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces in the absence of guanine shows two well-defined oxidative waves (peaks I and II) at 0.694 V and 1.030 V, assigned to the oxidation of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ to $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{3+}$ adsorbed weakly and strongly on TiO_2 surfaces (solid line), respectively. These observations are in good agreement with the results obtained from cyclic voltammetry. In the presence of 0.2 mmol L^{-1} guanine (dotted line), the peak currents of both oxidative waves have an obvious increase compared with the case of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ alone. For the oxidation (I_G) of guanine alone (dashed line), the broad wave at 0.823 V is considered to be the direct oxidation of guanine on TiO_2 surfaces. Thus, the enhanced currents from the dotted line illustrate that $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ adsorbed weakly and strongly on TiO_2 surfaces can electrochemically catalyze the oxidation of guanine in buffer solutions.

3.3. In-situ electrochemically tuned luminescence of $\text{Ru}(\text{II})$ complex-based anodes

With the encouraging results mentioned above, an attempt was made to study the in situ electrochemically tuned luminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}/\text{TiO}_2$ anodes under the excitation of a continuous wave (CW) green laser. As shown in Fig. 5a, the emission spectra of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces show a broad emission peak at 606 nm under open-circuit conditions. The application of 1.2 V anodic potential did not cause any noticeable shift in the position of emission peak, implying that the species responsible for the excitation are identical and hence the chemical nature of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ is independent of applied external electric fields. However, an applied electrode potential of 1.2 V above the open circuit potential leads to a luminescence enhancement of 58.9%. This finding reveals that the luminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}/\text{TiO}_2$ is influenced by the external electric field. When the green laser is turned off, the application of 1.2 V anodic potential does not lead to a detectable luminescent signal under our experimental

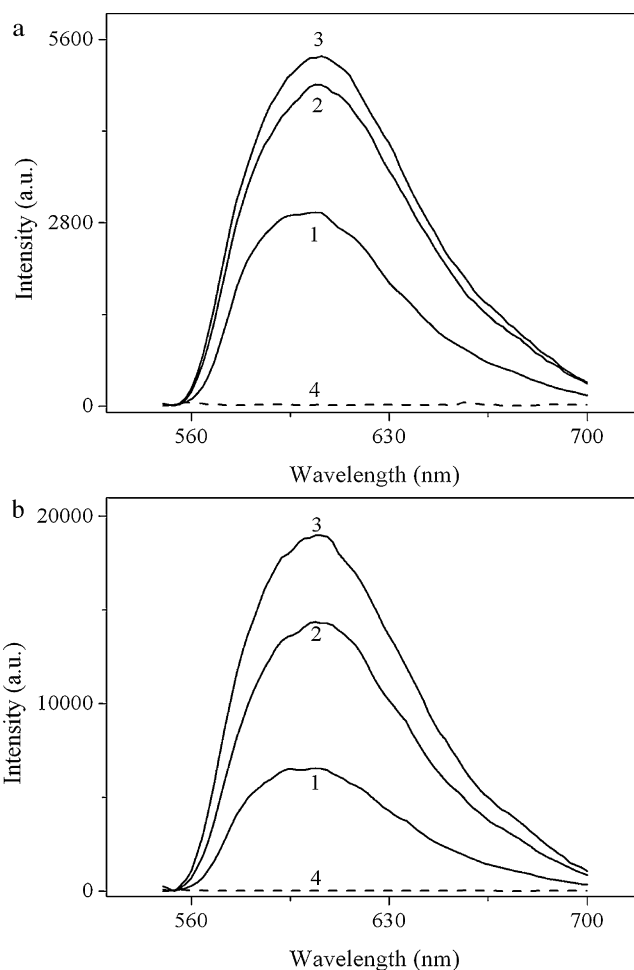


Fig. 5. Emission spectra of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ immobilized on the TiO_2 -modified ITO electrodes in the absence (a) and presence of 0.2 mmol L^{-1} guanine (b) under the excitation of a CW green laser under open-circuit conditions (1) and at 1.2 V anodic potential holding for 1 min (2) or 11 min (3). The dashed line 4 corresponds to the emission spectra in the absence of a CW green laser at 1.2 V anodic potential. PMT biased voltage: -470 V .

conditions, as shown by the dashed line in Fig. 5a. It is clear that the contribution from electroluminescence (or electrochemiluminescence) at 1.2 V applied electrode potential in the absence of laser is too low to be detected by our photo-multiplier tube (PMT). Combined with previous reports [27,28], $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ excited states from laser irradiation can release electrons to recombine with the holes from TiO_2 surfaces. Thus, excitons are formed on $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}/\text{TiO}_2$ anodes, leading to an increase of the luminescence [40,41].

As in our previous reports [28], another classical $\text{Ru}(\text{II})$ complex $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ ($\text{dppz} = \text{dipyrido}[3,2-a:2',3'-c]$ phenazine) was also studied for comparison. Because $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ only emits very weak luminescence in aqueous solutions, the DNA was added to enhance the emission of the complex via a classical intercalation [42]. As shown in Fig. 6, two $\text{Ru}(\text{II})$ complexes intercalated in DNA aggregates on TiO_2 surfaces show a very different change in the luminescence as an external electric field is added. The result reveals that the electrons from $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ excited states can inject into TiO_2/ITO anodes, but the electrons from $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ excited states recombine with holes from TiO_2/ITO anodes to yield excitons. As a result, the introduction of an anodic potential (1.2 V) makes the luminescence of $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ in DNA aggregates at 615 nm quenched by 32.6%, but that of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ at 609 nm increased by 70.5%.

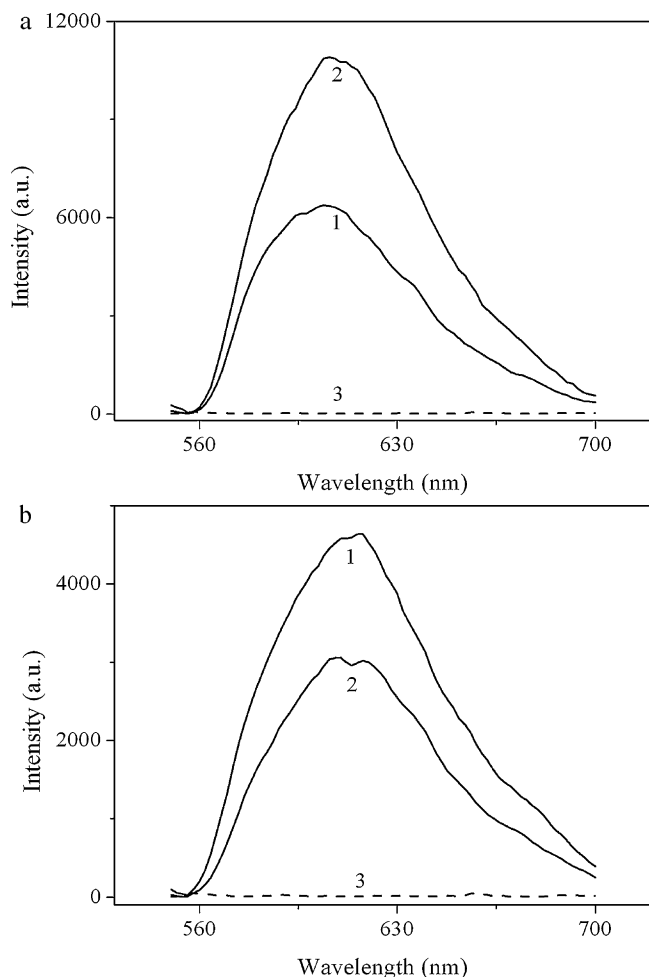


Fig. 6. Emission spectra of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ (a) or $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ (b) in DNA aggregates immobilized on TiO_2 electrodes under the excitation of a CW green laser tuned by anodic potentials (E , V): (1) open circuit potential, (2) 1.2. PMT biased voltage: -470 V. The dashed line 3 corresponds to the emission spectra in the absence of a CW green laser at 1.2 V anodic potential.

This finding may facilitate the fabrication of photo-stimulated fuel cells (as described below).

3.4. Luminescence of Ru(II) complex-based anodes enhanced by guanine oxidation

The results mentioned above show that $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ adsorbed on TiO_2 surfaces can electrochemically catalyze the oxidation of guanine. It is now of interest to know whether the photoluminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ could be enhanced by the electrocatalytic oxidation of guanine.

In the presence of guanine, as depicted in Fig. 5b, the luminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}/\text{TiO}_2$ is stronger than the case without guanine under open-circuit conditions or at 1.2 V anodic potential. When the green laser was turned off, the application of 1.2 V anodic potential did not lead to a detectable luminescence (dashed line), suggesting that the observed luminescence in the presence of guanine is based on the Ru(II)-based excited states under the excitation of a green laser. The presence of guanine can increase the luminescence intensity of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ by 125.2% under open-circuit conditions and by 187.7% at 1.2 V holding for 1 min, respectively. This result reveals that the electrocatalytic oxidation of guanine by $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ may enhance the luminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces under the excitation of a green laser. This proposition is proved by the luminescence change

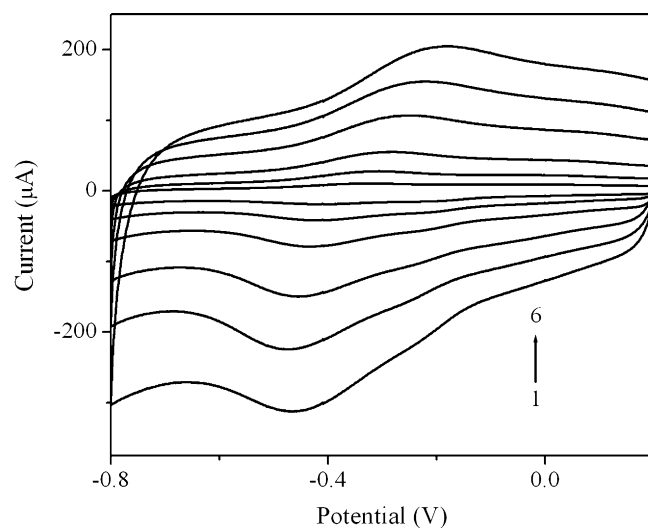


Fig. 7. CVs of the Hb-modified SWCNT electrode in buffer solutions under nitrogen atmosphere at different scan rates (V s^{-1}): (1) 0.4, (2) 0.3, (3) 0.2, (4) 0.15, (5) 0.1, (6) 0.05.

upon increasing the hold time at 1.2 V. When this was 11 min, the luminescence in the presence of guanine showed a larger enhancement (255.5%) in contrast to that without guanine. These results reveal that the photoluminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces can be enhanced by the electrocatalytic oxidation of guanine. Ru(II)-based excited states release electrons to yield Ru(III) species, which oxidizes guanine to regenerate the Ru(II) species. As a result, the photoluminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ on TiO_2 surfaces under laser irradiation at 1.2 V anodic potential is enhanced by the oxidation of guanine.

3.5. Electrocatalytic reduction of Hb-modified SWCNT thin layer electrodes

As is well-known, because the direct electron transfer between hemoglobin (Hb) and electrode is usually difficult due to the deeply embedded redox-active centers [43], single-walled carbon nanotubes (SWCNTs) are employed to improve the redox reversibility and electrocatalytic activity of Hb [44,45]. In order to minimize restrictions of cathodic reactions on the cell performance, the Hb-modified SWCNT thin layer electrode was employed for the electrocatalytic reduction of H_2O_2 . As shown in Fig. 7, CVs of Hb on SWCNT surfaces show a pair of well-defined redox waves, ascribed to Fe(III)/Fe(II) reactions of Hb. In the presence of H_2O_2 , linear sweep voltammograms (LSVs) of the Hb/SWCNT electrode show a larger cathodic current than that of Hb or H_2O_2 alone (Fig. 8), revealing that H_2O_2 can be electrocatalytically reduced on the Hb/SWCNT thin layer electrode.

3.6. Performances of photo-stimulated guanine/ H_2O_2 fuel cell

With the encouraging results mentioned above, we attempt to fabricate a photo-stimulated fuel cell as shown in Fig. 1. Ru(II) complex-sensitized TiO_2 thin layer is functionalized as photoanode, Hb-modified SWCNT thin layer as cathode, guanine/ H_2O_2 as oxidized/reduced fuels, and a U-shaped glass tube filled with saturated KCl gel as salt bridge. Because the Ru(II) complexes adsorbed on TiO_2 surfaces can catalyze the oxidation of guanine in the absence and presence of laser irradiation, Ru(II) complex-sensitized TiO_2 was chosen as photoanode, and guanine as oxidized fuels. In addition, the results described above have shown that the luminescence of $[\text{Ru}(\text{bpy})_2(\text{tatp})]^{2+}$ -based anodes

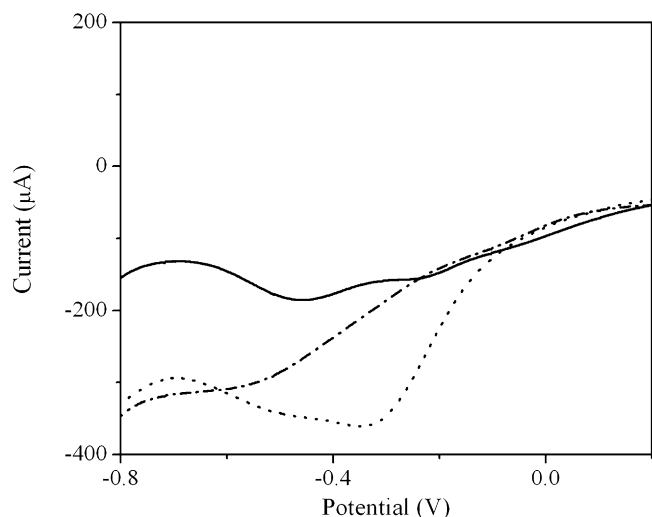


Fig. 8. LSVs of the Hb-modified SWCNT electrode in the absence (solid line) and presence of $1.0 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ (dotted line) under nitrogen atmosphere at 0.05 V s^{-1} scan rate. The dashed line shows the LSV of $1.0 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ on the SWCNT-modified ITO electrode.

is enhanced by the external electric field whereas the luminescence of $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ -based anodes is quenched. We suggest that the photoanode possessing the luminescence quenched by the external electric field should facilitate the electron transfer from excited states to cathodes, resulting in higher efficiencies for photo-stimulated fuel cells. The performance of the fabricated cell proves this point. As shown in Figs. 9 and 10, the cell voltages using $[\text{Ru}(\text{bpy})_2(\text{tatz})]^{2+}$ -sensitized TiO_2 as the anode are -0.304 V in a dark chamber (light off) and -0.681 V under light irradiation (light on), respectively, indicating a negative shift of 0.377 V (solid line). For $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ -sensitized TiO_2 photoanodes (dashed line), the cell voltages show a negative shift of 0.534 V from -0.241 V (off) to -0.775 V (on). These results suggest that the light irradiation can excite the $\text{Ru}(\text{II})$ complex-sensitized TiO_2 anode to generate the excited states of $\text{Ru}(\text{II})$ complexes (Fig. 1), which inject electrons to ITO substrate via the TiO_2 thin layer, resulting in a negative shift of cell voltages. The $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ -sensitized TiO_2 anode can offer more useful contributions to the photo-induced fuel cell compared with the $[\text{Ru}(\text{bpy})_2(\text{tatz})]^{2+}/\text{TiO}_2$ anode. While altering

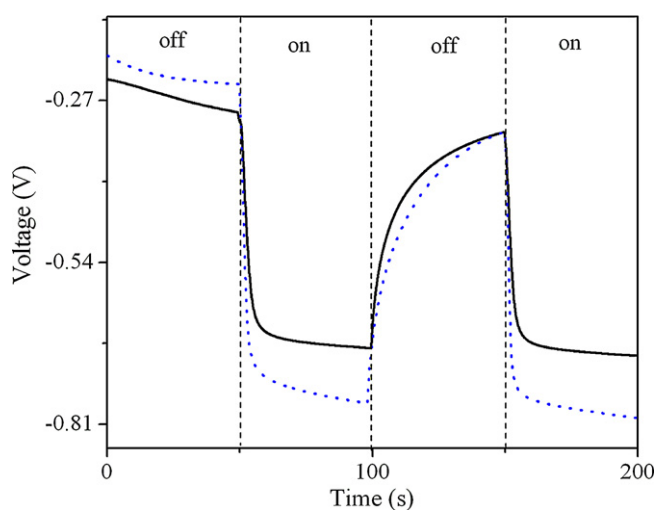


Fig. 9. Effects of UV light (off and on) on cell voltage of 0.2 mmol L^{-1} guanine/ $1.0 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ fuel cells using $[\text{Ru}(\text{bpy})_2(\text{tatz})]^{2+}$ (solid line) or $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ (dotted line) sensitized TiO_2 as anodes and Hb/SWCNT as cathodes.

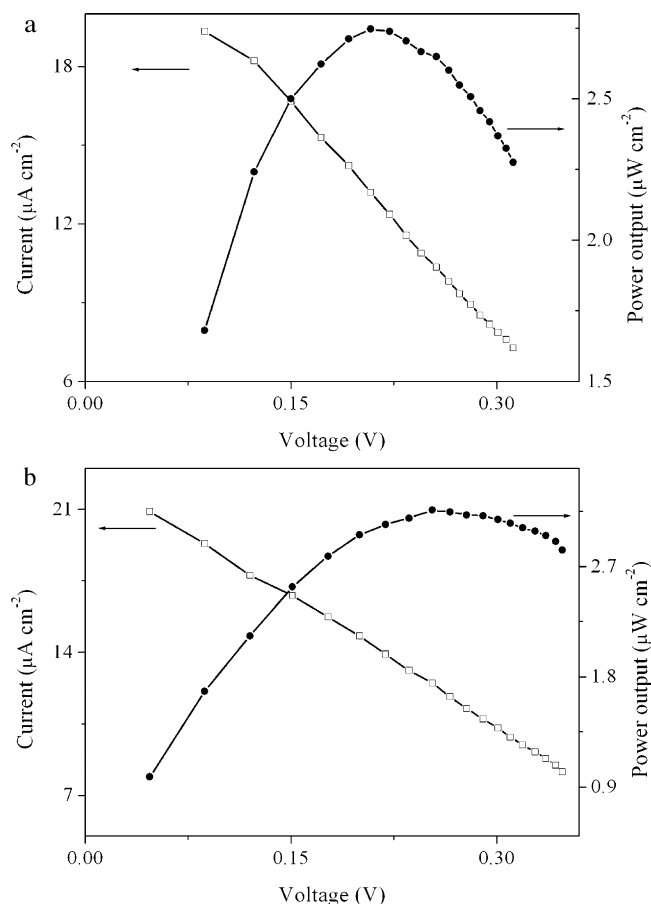


Fig. 10. Cell current and power output from 0.2 mmol L^{-1} guanine/ $1.0 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ fuel cells using (a) $[\text{Ru}(\text{bpy})_2(\text{tatz})]^{2+}$ or (b) $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}$ -sensitized TiO_2 as anodes and Hb/SWCNT as cathodes under the excitation of UV light by altering the external load from 1000Ω to $19,000 \Omega$.

external loads from 1000 to 19000Ω , the cell current and power output under light excitation were shown in Fig. 10. The assembled fuel cell using $[\text{Ru}(\text{bpy})_2(\text{tatz})]^{2+}$ -sensitized TiO_2 as the anode yields a maximum power density of $2.8 \mu\text{W cm}^{-2}$ at a cell voltage of 0.208 V , whereas the maximum power reaches $3.2 \mu\text{W cm}^{-2}$ at 0.253 V using $[\text{Ru}(\text{bpy})_2(\text{dppz})]^{2+}/\text{TiO}_2$ as the anode. These results illustrate that the photosensitizers possessing the luminescence quenched by anodic electrode potentials are suitable for use as the anodes of photo-stimulated fuel cells.

4. Conclusions

A novel electrochemically-tuned luminescence technique has been developed for better evaluating contributions of the sensitizer excited states to photo-stimulated fuel cells. Combined with this technique, the photosensitizers possessing the luminescence quenched by anodic electrode potentials are suitable for use as the anodes of photo-stimulated fuel cells. From this study, the following conclusions are derived.

(1) A phenazine-containing $\text{Ru}(\text{II})$ complex can be adsorbed onto the nano- TiO_2 surfaces by repetitive voltammetric sweeping, showing two pairs of well-defined redox waves.

(2) The $\text{Ru}(\text{II})$ complexes adsorbed on TiO_2 electrodes can catalyze the oxidation of guanine in the absence and presence of light irradiation, which are functionalized as the photoanodes, and guanine as the oxidized fuels.

(3) On the basis of electrochemically-tuned photoluminescence properties of $\text{Ru}(\text{II})$ complex-sensitized TiO_2 anodes followed

by the electrocatalytic oxidation of guanine, a photo-stimulated guanine/H₂O₂ fuel cell has been successfully fabricated.

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References

- [1] L. Bijire, B. Elias, J.P. Souchard, E. Gicquel, C. Moucheron, A.K. Mesmaeker, P. Vicendo, *Bioelectrochemistry* 45 (2006) 6160.
- [2] S. Luukkainen, M. Haukka, E. Eskelinen, T.A. Pakkanen, V. Lehtovuori, J. Kallioinen, P. Myllyperkiö, J. Korppi-Tommola, *Phys. Chem. Chem. Phys.* 3 (2001) 1992.
- [3] P. Wang, C. Klein, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* 127 (2005) 808.
- [4] J. Xu, J. Liang, J. Li, W. Yang, *Langmuir* 26 (2010) 15722.
- [5] A.D. Ryabov, R.L. Lagadec, H. Estevez, R.A. Toscano, S. Hernandez, L. Alexandrova, V.S. Kurova, A. Fischer, C. Sirlin, M. Pfeffer, *Inorg. Chem.* 44 (2005) 1626.
- [6] R.J. Forster, E. Figgemeier, A.C. Lees, J. Hjelm, J.G. Vos, *Langmuir* 16 (2000) 7867.
- [7] D.H. Johnston, K.C. Glasgow, H.H. Thorp, *J. Am. Chem. Soc.* 117 (1995) 8933.
- [8] I.V. Yang, H.H. Thorp, *Inorg. Chem.* 39 (2000) 4969.
- [9] M.F. Sistine, S.J. Codden, G. Heimlich, H.H. Thorp, *J. Am. Chem. Soc.* 122 (2000) 4742.
- [10] M.R. Arkin, E.D.A. Stemp, S.C. Pulver, J.K. Barton, *Chem. Biol.* 4 (1997) 389.
- [11] C.C. Cheng, J.G. Goll, G.A. Neyhart, T.W. Welch, P. Singh, H.H. Thorp, *J. Am. Chem. Soc.* 117 (1995) 2970.
- [12] P.K.L. Fu, P.M. Bradley, D. van Loyen, H. Dürr, S.H. Bossmann, C. Turro, *Inorg. Chem.* 41 (2002) 3808.
- [13] M. Liang, L.H. Guo, *Environ. Sci. Technol.* 41 (2007) 658.
- [14] C.Y. Chen, M. Wang, J. Li, N. Pootrakulchote, L. Alibabaei, C. Ngoc-le, J. Decoppet, J. Tsai, C. Gratzel, C.G. Wu, S.M. Zakeeruddin, M. Grätzel, *ACS Nano* 3 (2009) 3103.
- [15] G. Sauve, M.E. Cass, G. Coia, S.J. Doig, I. Lauerermann, K.E. Pomykal, N.S. Lewis, *J. Phys. Chem. B* 104 (2000) 6821.
- [16] T. Peng, D. Ke, P. Cai, K. Dai, L. Ma, L. Zan, *J. Power Sources* 180 (2008) 498.
- [17] S.H. Bossmann, C. Turro, C. Schnabel, M.R. Pokhrel, L.M. Payawan Jr., B. Baumeister, M. Wörner, *J. Phys. Chem. B* 105 (2001) 5374.
- [18] R. Buscaino, C. Baiocchi, C. Barolo, C. Medana, M. Grätzel, M.K. Nazeeruddin, G. Viscardi, *Inorg. Chim. Acta* 361 (2008) 798.
- [19] C.J. Kleverlaan, M.T. Indelli, C.A. Bignozzi, L. Pavanin, F. Scandola, G.M. Hasselman, G.J. Meyer, *J. Am. Chem. Soc.* 122 (2000) 2840.
- [20] M.K. Nazeeruddin, E. Muller, R. Humphry-Baker, N. Vlachopoulos, M. Grätzel, *J. Chem. Soc.: Dalton Trans.* 23 (1997) 4571.
- [21] T.A. Heimer, E.J. Heilweil, C.A. Bignozzi, G.J. Meyer, *J. Phys. Chem. A* 104 (2000) 4256.
- [22] M. Hambourger, M. Gervaldo, D. Svedruzic, P.W. King, D. Gust, M. Ghirardi, A.L. Moore, T.A. Moore, *J. Am. Chem. Soc.* 130 (2008) 2015.
- [23] L. de la Garza, G. Jeong, P.A. Liddell, T. Sotomura, T.A. Moore, A.L. Moore, D. Gust, *J. Phys. Chem. B* 107 (2003) 10252.
- [24] Z. Dong, S.J. Kennedy, Y. Wu, *J. Power Sources* 196 (2011) 4886.
- [25] Y.J. Kim, W.H. Hong, S.I. Woo, H.K. Lee, *J. Power Sources* 159 (2006) 491.
- [26] J. Herranz, M. Lefèvre, N. Larouche, B. Stansfield, J.P. Dodelet, *J. Phys. Chem. C* 111 (2007) 19033.
- [27] J.Y. Shao, T. Sun, S.B. Ji, H. Li, S. Lan, Z. Xu, *Chem. Phys. Lett.* 492 (2010) 170.
- [28] Q. Guo, J. Shao, H. Liu, H. Li, S. Lan, *Electrochim. Acta* 56 (2011) 1432.
- [29] L.A. Zwellung, S. Michaels, H. Schwartz, P.P. Dobson, K.W. Kohn, *Cancer Res.* 41 (1981) 640.
- [30] A.E. Friedman, J.C. Chambron, J.P. Sauvage, N.J. Turro, J.K. Barton, *J. Am. Chem. Soc.* 112 (1990) 4960.
- [31] R.M. Hartshorn, J.K. Barton, *J. Am. Chem. Soc.* 114 (1992) 5919.
- [32] D.J. Kim, S.H. Hahn, S.H. Oh, E.J. Kim, *Mater. Lett.* 57 (2002) 355.
- [33] T.K. Leeuw, D.A. Tsybolski, P.N. Nikolaev, S.M. Bachilo, S. Arepalli, R.B. Weisman, *Nano Lett.* 8 (2008) 826.
- [34] X.X. Yan, H. Li, Z. Xu, W.S. Li, *Bioelectrochemistry* 74 (2009) 310.
- [35] L. Mao, R. Yuan, Y. Chai, Y. Zhuo, X. Yang, *Sens. Actuators B: Chem.* 149 (2010) 226.
- [36] W. Zou, L. Wang, B. Lu, H. Li, H. Chen, *J. Appl. Electrochem.* 39 (2009) 2015.
- [37] H. Li, Z.H. Xu, D.W. Pang, J.Z. Wu, L.N. Ji, Z.H. Lin, *Electrochim. Acta* 51 (2006) 1996.
- [38] M.J. Han, L.H. Gao, Y.Y. Lü, K.Z. Wang, *J. Phys. Chem. B* 110 (2006) 2364.
- [39] M.K. Brennmann, T.J. Meyer, J.M. Papanikolas, *J. Phys. Chem. A* 108 (2004) 9938.
- [40] L. Hammarström, L.C. Sun, B. Åkermark, S. Styring, *Spectrochim. Acta A* 57 (2001) 2145.
- [41] E. Rajkumar, S. Rajagopal, P. Ramamurthy, M. Vairamani, *Inorg. Chim. Acta* 362 (2009) 1629.
- [42] Y. Jenkins, A.E. Friedman, N.J. Turro, J.K. Barton, *Biochemistry* 31 (1992) 10809.
- [43] J.F. Rusling, *Acc. Chem. Res.* 31 (1998) 363.
- [44] C. Guo, F. Hu, C.M. Li, P.K. Shen, *Biosens. Bioelectron.* 24 (2008) 819.
- [45] S. Chen, R. Yuan, Y. Chai, L. Zhang, N. Wang, X. Li, *Biosens. Bioelectron.* 22 (2007) 1268.