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Spectroelectrochemical evidence of the role of viologen moiety as an electron transfer mediator from ITO substrate to a Pt complex acting as a confined molecular catalyst for hydrogen evolution reaction

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ABSTRACT Spectroelectrochemical measurements at indium tin oxide (ITO) electrode modified with viologen monolayer showed two redox peaks corresponding to viologen dication/radical cation ($V^{2+}/V^{+\bullet}$) and viologen radical cation/neutral form ($V^{+\bullet}/V^0$) in cyclic voltammogram (CV), and stable spectra corresponding to radical cation ($V^{+\bullet}$) and neutral form (V^0) of viologen at potentials between $V^{2+}/V^{+\bullet}$ and $V^{+\bullet}/V^0$ redox peaks and those more negative than $V^{+\bullet}/V^0$ redox peak, respectively. On the other hand, at viologen monolayer modified ITO electrode with Pt complex confined within the monolayer by ion exchange reaction, no redox peaks but large current due to hydrogen evolution reaction (HER) were observed in CV and no absorption peaks corresponding to $V^{+\bullet}$ or V^0 was observed in the UV/visible spectra obtained during the potential scan. Time-resolved spectroelectrochemical measurements, however, showed that $V^{+\bullet}$ is formed upon the potentials step to the potentials more negative than $V^{2+}/V^{+\bullet}$ redox potential and disappeared within ca. 1 ms, showing that electron is transferred from ITO electrode to proton to form hydrogen via viologen moiety and Pt complex.

Keywords: Spectroelectrochemistry, viologen monolayer, confined molecular catalyst, hydrogen evolution reaction.

1. Introduction

Catalyst is the key to realize chemical and electrochemical processes with high efficiency and selectivity [1-3]. Precious metal and rare elements are often used as essential components of many catalysts. Because of high cost and limited resources, many efforts have been made to develop non-precious metal catalyst and maximize the utilization of these elements. Although molecular and single atom catalysts are expected to have 100% atom efficiency [4-8], both have difficulties in practical use. Molecular catalysts are usually used as homogeneous catalyst in solution and are difficult to be separated from reactants and products after the reaction. It is very difficult to prepare single atom catalysts and to maintain their structures from aggregation without proper supports [9]. We have recently proposed that these problems can be overcome by confining a metal complex on and within molecular layers forming “confined molecular catalyst”, which acts as heterogeneous catalysts, and reported that a Pt complex confined within viologen layer constructed on Si(111) electrode can act as electrocatalysts for both hydrogen evolution [10, 11] and CO₂ reduction [12], demonstrating the effectiveness of the “confined molecular catalyst”. We suggested that covalently attached viologen molecules and a Pt complex act as an electron relay and a catalyst, respectively, but there was no direct evidence that electron is transferred via viologen moiety and the Pt complex. If electron is transferred via viologen moiety, there is a possibility that viologen radical cation (V^{•+}), which is formed by one electron reduction of viologen di-cation (V²⁺) and has a unique absorption in UV/vis spectra around 600 nm [13-15], can be detected spectroelectrochemically as an intermediate state upon potential step to negative potential where hydrogen evolution reaction (HER) takes place.

In the present study, we constructed a viologen monolayer on indium tin oxide (ITO), which is a transparent electrode, so that the electron transfer steps at the Pt complex/viologen monolayer system in the HER process can be clarified by monitoring the electrochemically generated viologen species spectroelectrochemically in UV/vis region upon potential step to HER region.

2. Experimental

2.1 Materials and preparation of viologen monolayer on ITO

ITO (Furuuchi) substrate (2.0 x 2.0 cm², 10 Ω/sq) in a 11-Bromoundecyltrichlorosilane (BUDCS) (Gelest) (1% vol.) toluene (98% Wako Pure Chemicals) solution for 6 h to yield alkylbromide-terminated ITO (Br-ITO) monolayer. Then, the Br-ITO substrate was kept at 70°C for 12 h in benzene (98% Wako Pure Chemicals) solution saturated with 4,4'-bipyridine (99.9% Wako Pure Chemicals) to yield bipyridine terminated monolayer (bpy-ITO), and refluxed in 1-bromobutane (95% Wako Pure Chemicals) solution for 12 h to yield viologen modified monolayer on ITO (1LV-ITO). Finally, Br⁻ was replaced by PtCl₄²⁻ by ion exchange reaction by keeping the 1LV-ITO substrate in 10 mM K₂PtCl₄ (99.9% Wako Pure Chemicals) aqueous solution for 20 min at room temperature to yield 1LV-ITO/Pt_{complex} surfaces.

2.3 Spectroelectrochemical measurements

The spectroelectrochemical measurements were carried out in a three-electrode spectroelectrochemical cell using a potentiostat (Toho Technical Research, Model 2000) and a function generator (Hokuto Denko, HB-111) coupled with a UV-vis spectrometer (Shimadzu, UV-2600). A Ag/AgCl (NaCl sat.) and a Pt wire were used as a reference

and a counter electrode, respectively. A 0.1 M Na₂SO₄ aqueous solution (pH 5.8) was used as an electrolyte solution in all experiments, which were carried out at room temperature. The electrolyte solution was rigorously deaerated by passing Ar gas for at least 15 min as a small amount of residual oxygen might interfere with the viologen electrochemistry [16].

For time-resolved spectroelectrochemical measurements, a fast response function generator (Agilent, 33120A) combined with the potentiostat was used to provide potential step and to measure the transient current. To monitor the transient absorbance, a Xe-lamp (Ushio, UXL-500D) equipped with a monochromator (Ritsu Oyo Kogaku, MC-20N) was used to provide monochromatized light, which was split into 50:50 using a beam splitter, and the transmitted light through the spectroelectrochemical cell (signal: I) and the reflected light by the beam splitter (reference: I₀) were simultaneously detected by two Si photodetectors (Hamamatsu, S1227-1010BQ) and the absorbance, A, was calculated as $A = -\log_{10}(I/I_0)$.

3. Results and Discussion

Figure 1 shows (a) current and simultaneously recorded absorbance at (b) 400 nm and (c) 600 nm of bare ITO (black), 1LV-ITO (red) and 1LV-ITO/Pt_{complex} (blue) electrodes when potential was scanned from 0.1 to -1.5, -1.1, and -0.9 V, respectively, and then positively to 0.1 V with scan rate of 10 mV/s in the 0.1 M Na₂SO₄ aqueous solution.

At the bare ITO electrode, only very small current and no significant changes in the absorbance at 400 and 600 nm were observed within this potential range.

At the 1LV-ITO electrode, two pairs of well-resolved current peaks were observed at -0.42 V/-0.38 V and -0.90 V/-0.74 V. The absorbance both at 400 and 600 nm increased

as cathodic current of the first cathodic peak started to flow and reached steady values between the two cathodic peaks. While the absorbance at 600 nm started to decrease, that at 400 nm further increased as cathodic current of the second cathodic peak started to flow. Electrochemistry of viologen has been studied for long time [17-20] and it is well known that viologen dication (V^{2+}) is subject to the two step electrochemical reduction to yield the neutral form of viologen, V^0 , via radical cation form of viologen, $V^{+\bullet}$. UV/vis spectra of the 1LV-ITO electrode at various potentials are shown in Figure 2(a) and the spectra obtained at potentials between two redox peaks and those at potentials more negative than the second reduction peak are of $V^{+\bullet}$ and V^0 , respectively. Since V^{2+} is colorless with an absorption peak at 260 nm [21] and ITO glass substrate absorbs UV light lower than 300 nm, absorption spectrum of V^{2+} was not able to be obtained in the present experimental conditions. Thus, two redox peaks should correspond to the reversible one-electron redox reactions of $V^{2+}/V^{+\bullet}$ and $V^{+\bullet}/V^0$. The number of viologen moiety on the surface is estimated from the charge of the first cathodic peak, ca. $53 \mu\text{C}/\text{cm}^2$, as ca. $5.5 \times 10^{-10} \text{ mol}/\text{cm}^2$, which is in good agreement with the previously reported value from our group [20].

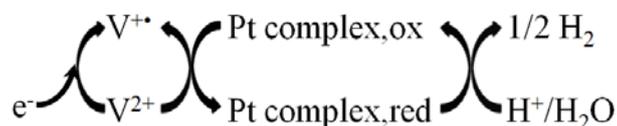
At the 1LV-ITO/ $\text{Pt}_{\text{complex}}$ electrode, no current peak was observed as at the bare ITO electrode but cathodic current due to HER became significant at much more positive potential (ca. -0.72 V) than at the bare ITO electrode. Note the current scale for the 1LV-ITO/ $\text{Pt}_{\text{complex}}$ electrode is 20 times of that for the bare ITO and the 1LV-ITO electrode. This result clearly shows that the confinement of the Pt complex accelerates HER significantly as observed before at Si(111) electrode [11]. No significant changes in the absorbance at 400 and 600 nm were observed within this potential range (Figures 1 (b) and (c)) and no peaks were observed in the UV/vis spectra at all potentials as

shown in Figure 2(b), suggesting that the viologen moiety in the monolayer in steady state is V^{2+} at all potentials. This suggests that as soon as $V^{+\bullet}$ or V^0 is formed, electron is transferred to the Pt complex, which in turn transfers electron to H^+ to generate hydrogen as we suggested before [11].

To see if viologen moiety acts as an electron transfer mediator, i. e., $V^{+\bullet}$ is formed as an intermediate in the electron transfer steps, time resolved measurements of current and absorbance upon the application of double potential step were carried out. Figure 3 shows results obtained when the potential was stepped from 0 to -0.72 V for 20 ms and back to 0 V as the sequence of the potential application is shown in Figure 3 (a). Figure 3(b) shows the current responses to the potential step at both the 1LV-ITO (black) and 1LV-ITO/ Pt_{complex} (red) electrodes.

At the 1LV-ITO electrode, cathodic and anodic spikes were observed upon negative (0 to -0.72 V) and positive (-0.72 to 0 V) potential steps, respectively, and no steady current flowed at -0.72 V. Figure 3 (c), (d), and (e) show the absorbance response at 375 (black), 400 (red), 550 (green), and 600 nm (blue) to the potential steps, contour of the absorbance as functions of probe wavelength and time after the potential step, and time-resolved spectra at -0.5 (black), 0 (red), 1 (green), 5 (blue), and 10 ms (light blue) after the potential step, respectively, at the 1LV-ITO electrode. As soon as the potential was stepped from 0 to -0.72 V, absorbance at all wavelength increased instantly and remained constant until potential was step back to 0 V, upon which the absorbance at all wavelength returned to 0 as shown in Figure 3 (c). All the spectra captured at -0.72 V (Figure 3 (e)) are the same and match well with the steady state spectra at -0.8 V ($V^{+\bullet}$) shown in Figure 2 (a). These results show that the conversions of V^{2+} to $V^{+\bullet}$ is very fast.

At the 1LV-ITO/Pt_{complex} electrode, in addition to the cathodic spike observed upon negative (0 to -0.72 V) potential step, steady state but gradually declining cathodic current due to HER flowed at -0.72 V. Figures 3 (f), (g), and (h) show the absorbance response of the initial 5 ms to the potential step at 375 (black), 400 (red), 550 (green), and 600 nm (blue), contour of the absorbance as functions of probe wavelength and time (initial 5 ms) after the potential step, and (e) time-resolved spectra at -0.5 (black), 0 (red), 0.1 (green), 0.2 (blue), 0.5 (light blue), and 2 ms (pink) after the potential step at the 1LV-ITO/Pt_{complex} electrode. Absorbance transients of various wavelength and transient spectra at various times show that V^{+•} species were formed within the first 0.1 ms after potential was stepped to -0.72 V and then disappeared with half-life of ca. 0.3 ms. No absorption was observed after 1 ms in whole wavelength region as is the steady state spectra, showing viologen is in V²⁺ state. This shows that V^{+•} is generated immediately after the potential is stepped to the potential more negative than the V^{+•} formation potential but its concentration decreases as electron is transferred from V^{+•} to the Pt complex and V^{+•} is converted to V²⁺, which again accepts electron to become V^{+•}. The reduced state of the Pt complex is consumed by reducing H⁺ and/or water to hydrogen and the oxidized state of the Pt complex is regenerated to accept electron from V^{+•} as schematically shown below.



4. Conclusion

Spectroelectrochemical measurements at the bare and viologen monolayer/Pt_{complex} modified ITO electrodes directly prove that electron is transferred from ITO to Pt

complex via viologen moiety during HER. More detailed measurements at various potentials and quantitative analysis are under way to clarify the electron transfer steps from ITO to H⁺ and/or water via viologen and Pt complex during HER at a wide range of potentials.

Acknowledgments

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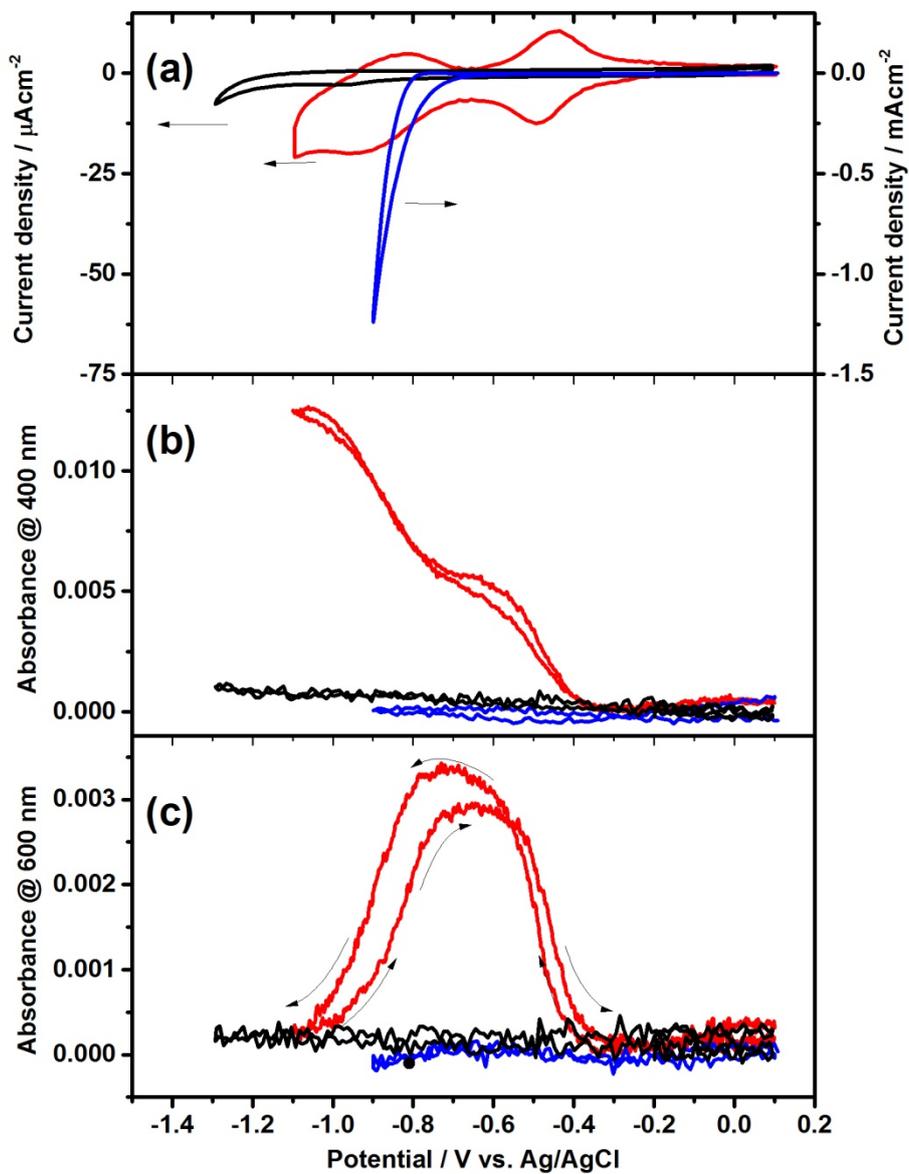


Figure 1. (a) Current, and absorbance at (b) 400 nm and (c) 600 nm at bare ITO (black), 1LV-ITO (red) and 1LV-ITO/ $\text{Pt}_{\text{complex}}$ (blue) when potential was scanned from 0.1 to -1.5 V, -1.1, and -0.9 V, respectively, and then positively to 0.1 V with the scan rate of 10 mV/s in 0.1 M Na_2SO_4 aqueous solution.

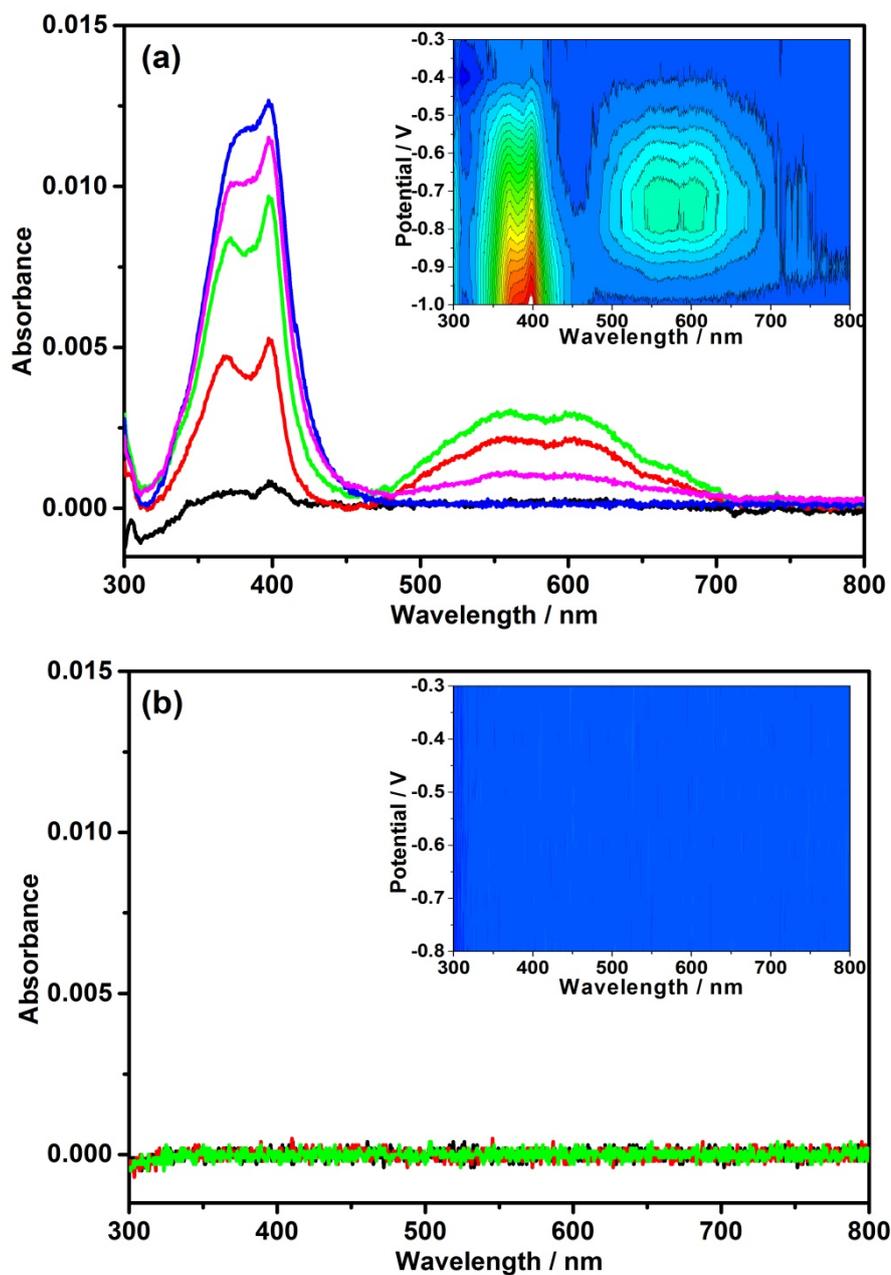


Figure 2. Steady state absorbance spectra of (a) 1LV-ITO and (b) 1LV-ITO/Pt_{complex} electrodes at -0.4 (black), -0.6 (red), -0.8 (green), -0.9 (pink) and -1.0 V (only for 1LV-ITO; blue). Inset: Contour map of steady state UV/vis spectra as a function of potential obtained from -0.3 to -1.0 V for 1LV-ITO and -0.3 to -0.8 V for 1LV-ITO/Pt_{complex} obtained every 0.1 V.

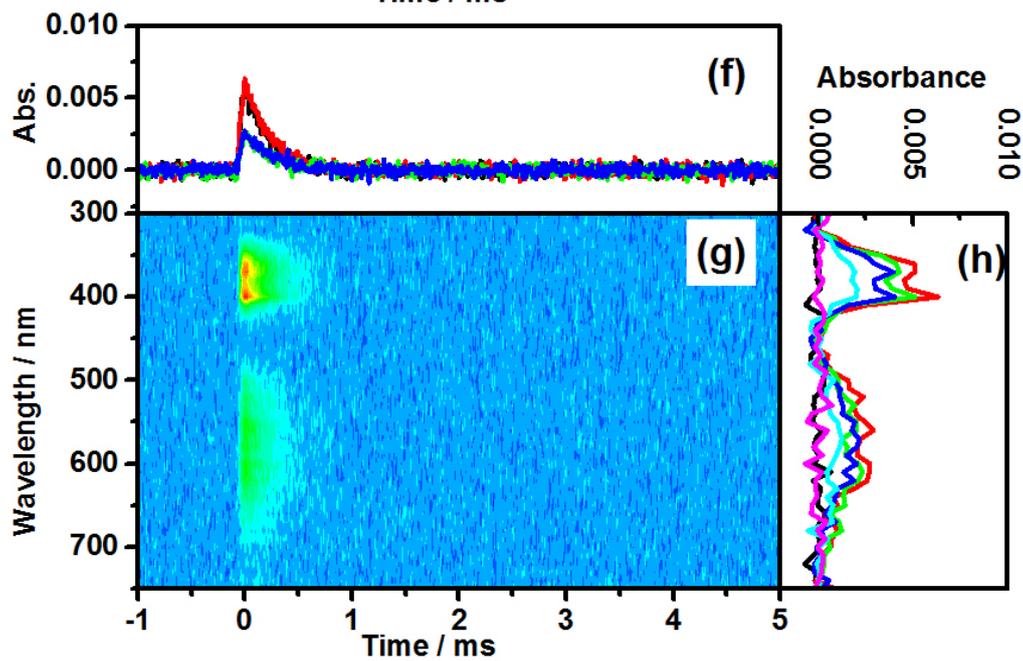
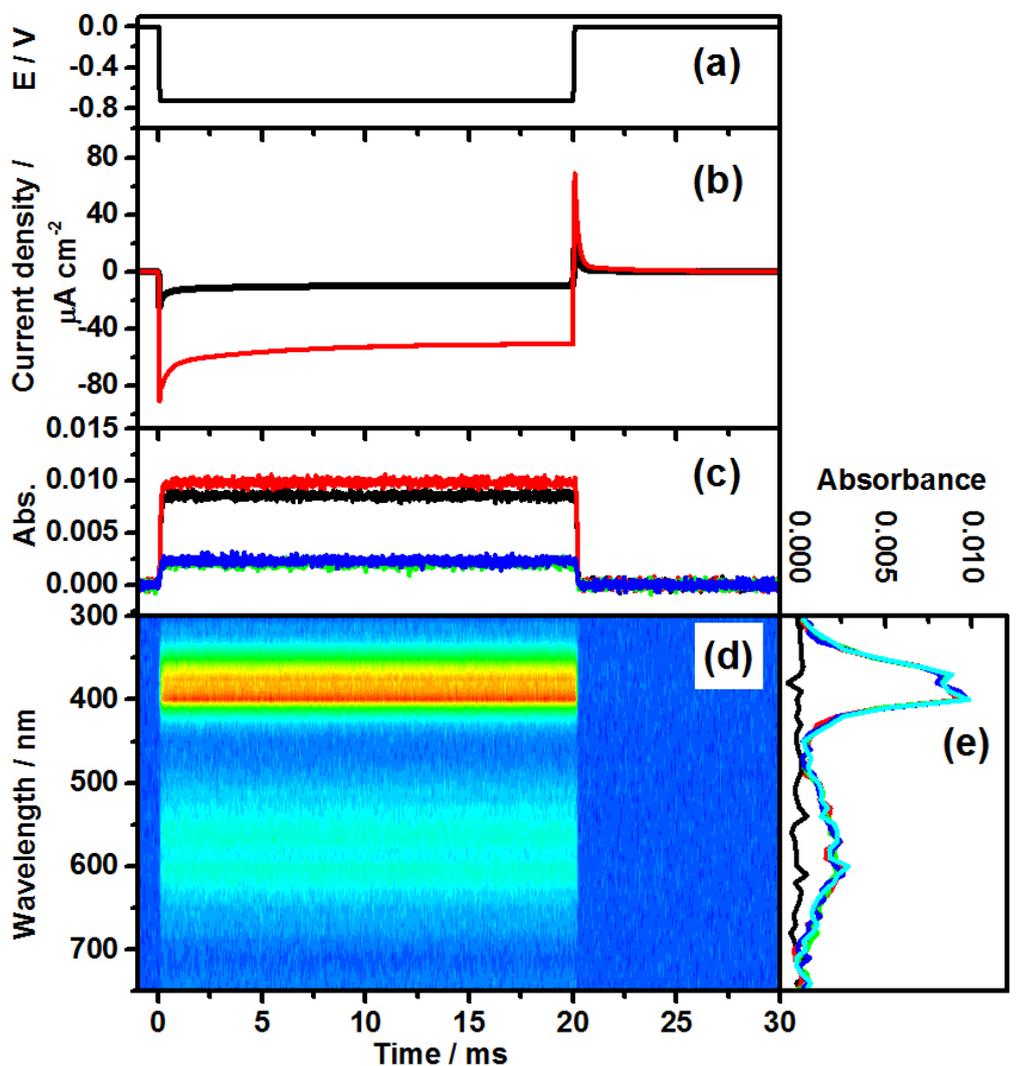


Figure 3. (a) Sequence of potential step from 0 to -0.72 V and (b) the corresponding current response at both the 1LV-ITO (black line) and 1LV-ITO/Pt_{complex} (red line) electrodes. (c) Corresponding absorbance response at 375 (black line), 400 (red line), 550 (green line), and 600 nm (blue line), (d) contour of the absorbance as functions of probe wavelength and time after the potential step, and (e) time resolved spectra at -0.5 (black line), 0 (red line), 1 (green line), 5 (blue line), and 10 ms (light blue line) after the potential step of 1LV-ITO. (f) Absorbance response of the initial 5ms to the potential step at 375 (black), 400 (red), 550 (green), and 600 nm (blue), (g) contour of the absorbance as functions of probe wavelength and time (initial 5 ms) after the potential step, and (h) time resolved spectra at -0.5 (black), 0 (red), 0.1 (green), 0.2 (blue), 0.5 (light blue) and 2 ms (pink) after the potential step of 1LV-ITO/Pt_{complex}.