

Introduction

Photosynthetic reaction center protein (RC, Fig. 1) converts light energy into chemical potential in the photosynthetic membrane assuring conditions for carbon reduction in cells [1]. Although it is developed in nanometer scale, and is working in nanoscopic power, this is the protein that assures the energy input practically for the whole biosphere. The extremely large quantum yield of the primary charge separation (close to 100 %, [2]) offers a big challenge to use it in optoelectronic nano-devices. The key questions of researches these days are as follows: new applications, reproducibility of the measurements and stability – mainly that of the biological component. Results of optical and electro-chemical investigations on RC/ITO bio-nanocomposite materials will be presented here.

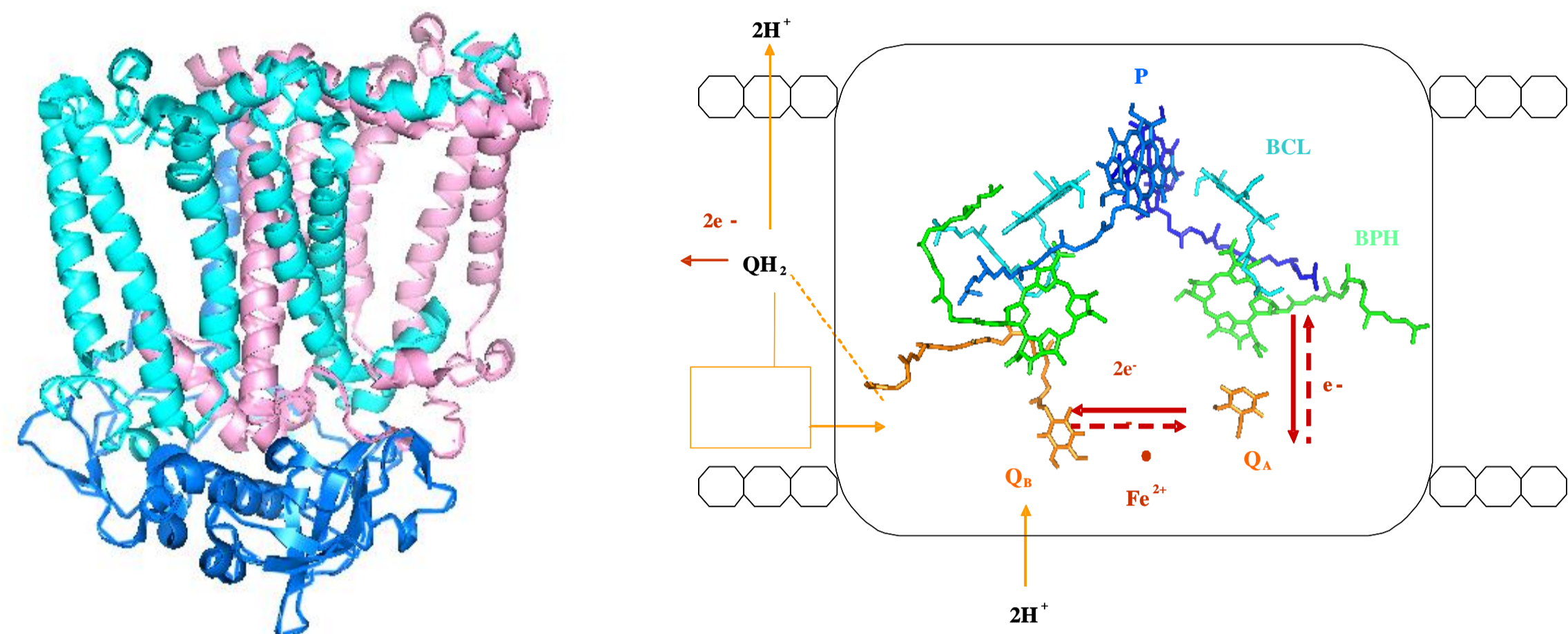


Figure 1. The protein subunits (left) and cofactors (right) of the photosynthetic reaction centers. The helix structures indicate the membrane spanning region of the protein. P: primary electron donor bacteriochlorophyll dimer; BCL: bacteriochlorophyll monomer; BPH: bacteriopheophytin; Q_A: primary quinone; Q_B: secondary quinone; QH: reduced quinone in the membrane pool.

Aims

There are several indications that RCs can be attached to nano-systems in which they largely and retain their activity [3]. Our aim is to bind RCs to ITO and to show that this composite is able to convert light energy, the conductivity is changed in dried system and photocurrent is generated in electrochemical cell.

Experimental

Sample preparation

RCs were prepared by detergent solubilization and purified by ammonium sulfate precipitation, followed by anion-exchange chromatography. Calculated amount of RCs were dried on the surface of ITO or bound through multiwalled carbon nanotubes (MWNT) and poly(3-thiophene acetic acid, PTAA (Fig. 2).

Measurements

Flash-induced absorption change was measured by a single-beam kinetic spectrophotometer of local design. The redox changes of the primary bacteriochlorophyll dimer, the electrochromic response of the absorption of bacteriopheophytins were detected at 860 or 771 nm, respectively [3,4].

Light induced change in the conductivity of RC film deposited on ITO surface was measured by a Keithley 2400s multimeter (7 digits, 4 points connection). 10 mA current was set and the voltage was measured. Data are represented in electric resistance in ohms. Measurement was regulated through the USB port by using the home developed software (<http://www.noise.physx.u-szeged.hu/>).

Special electrochemical cell with three electrodes was designed in our laboratory. The two parts of the cell was separated by a membrane with a 10 kDa cut-off. The working, the counter and the reference electrode was ITO, platinum and Ag/AgCl, respectively. The RC concentration was 6 μM and horse heart cytochrome c and UQ-0 were used as mediators (Fig. 3).

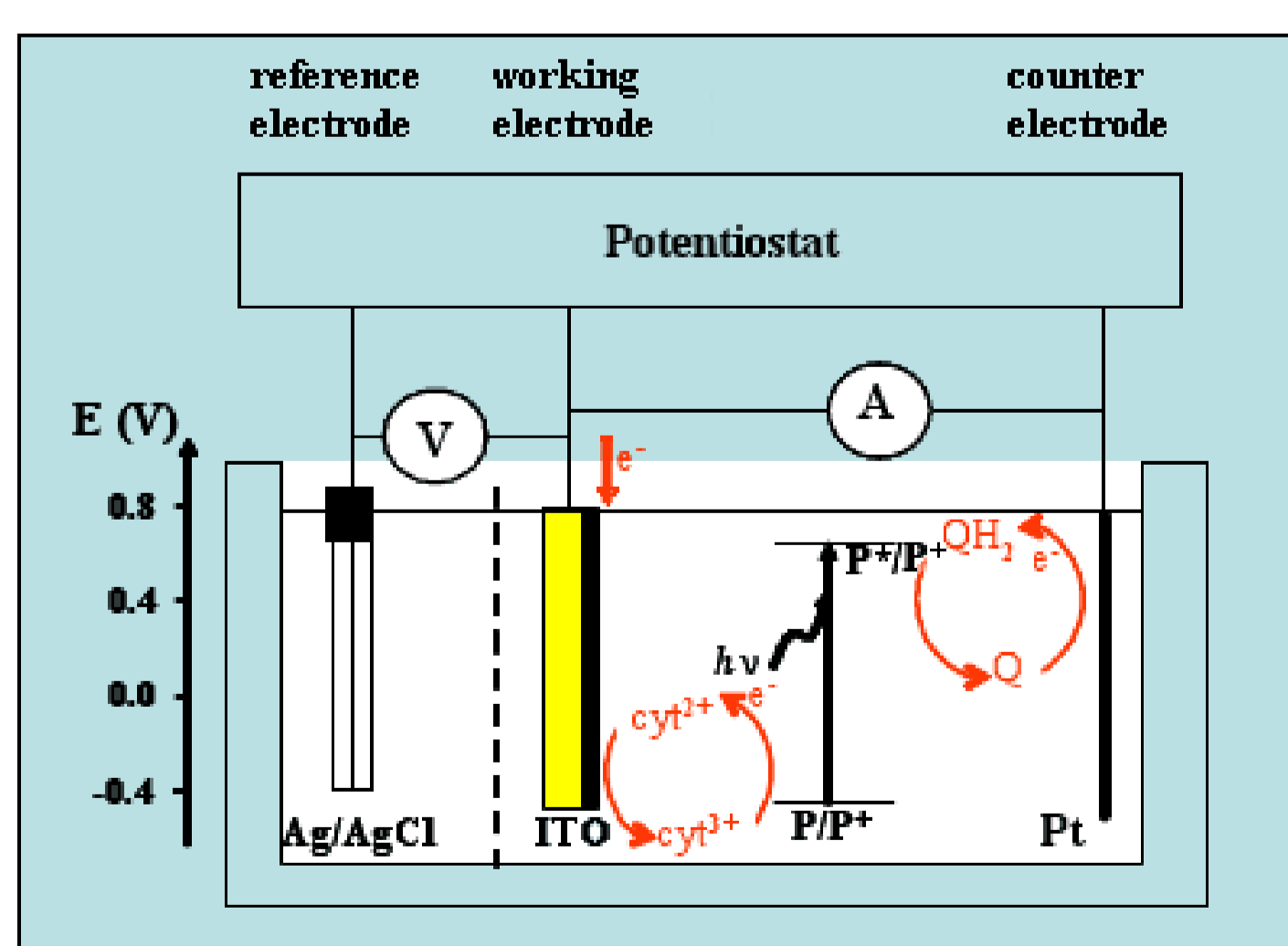


Figure 3. The scheme for the electrochemical cell

Results and discussions

RCs photoactivity dried on ITO

Figures 4-5 show that there is an electric interaction between the RCs and the conductive ITO layer. The electric resistance decreases if the pure ITO is illuminated. The decrease is smaller if RCs are deposited on the surface and reaches a saturation level by increasing the RC concentration. After reaching the saturation, i.e. multiple layers are formed, the resistance increases mainly due to heat dissipation. If the photochemically inactive BChl was deposited the resistance increases linearly with the concentration indicating only the temperature effect.

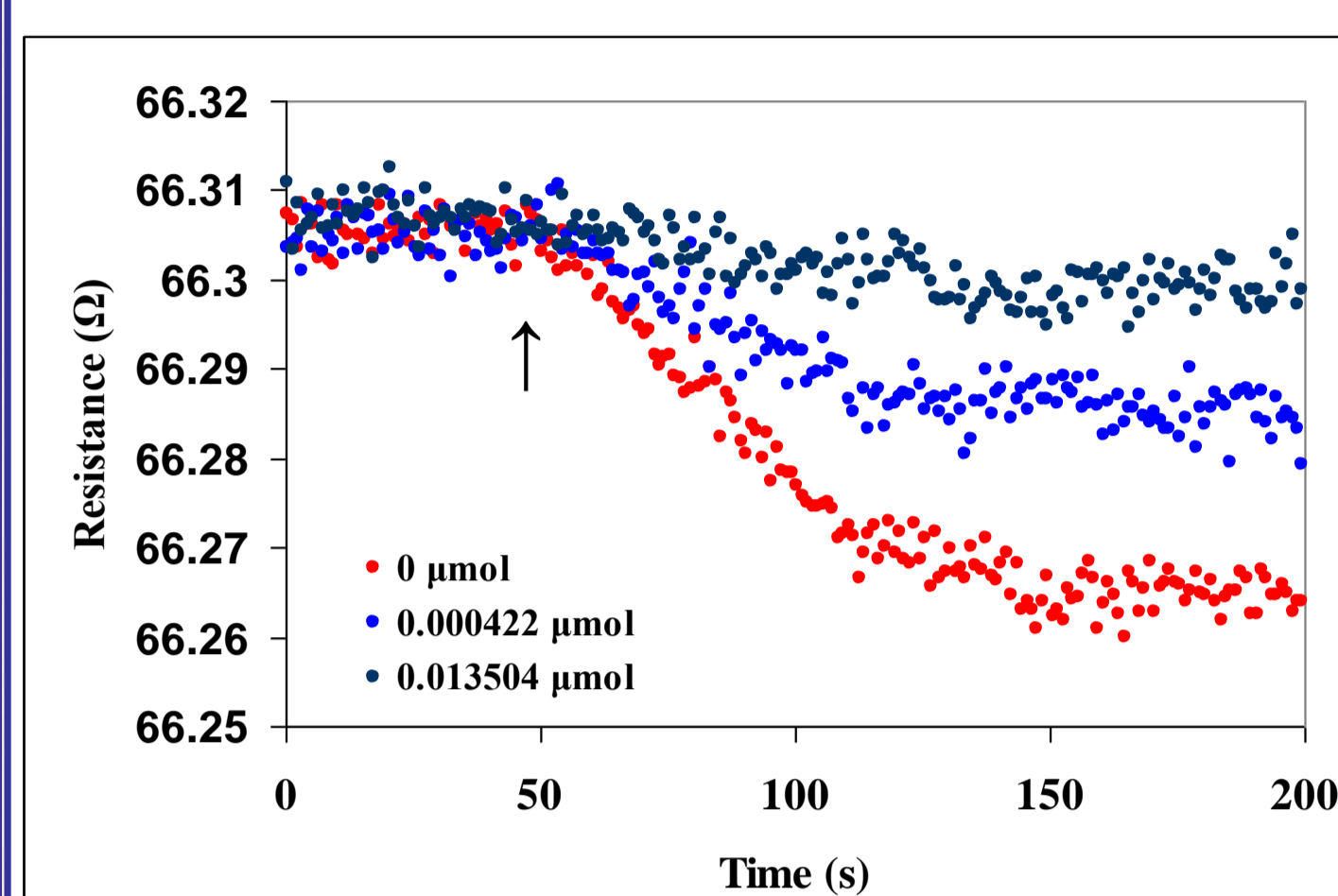


Figure 4. Resistance of ITO with or without RCs as a function of time under light excitation. The concentration of RCs and the time when the light was switched on are indicated.

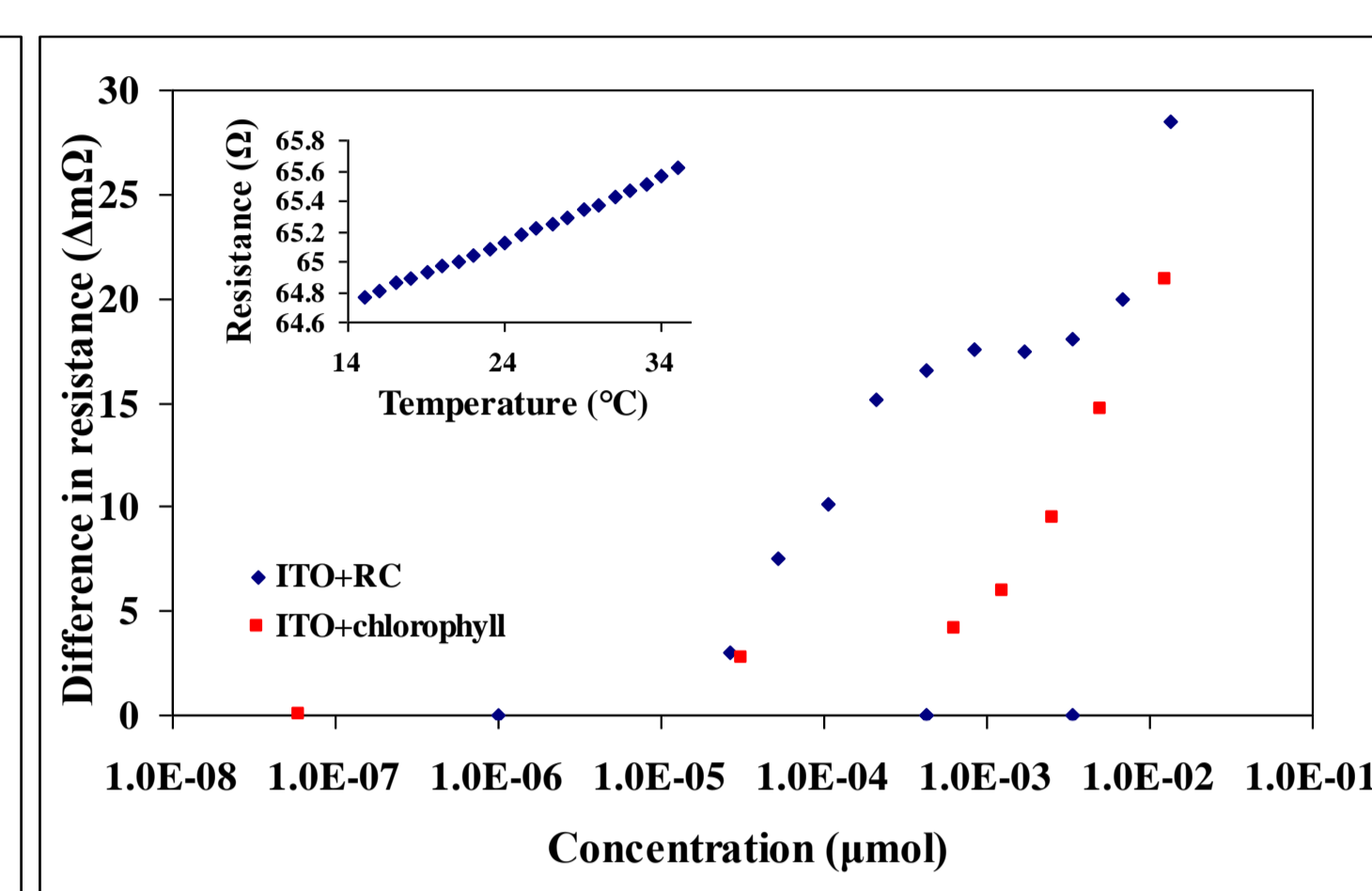


Figure 5. Change of the resistance of ITO as a function of the RC (blue) and bacterio-chlorophyll (red) concentration. Insert shows the resistance of ITO as a function of the temperature.

The photo-electrochemistry of MWNT-PTAA-RC complex on ITO surface

All measurements were done at the dark equilibrium open circuit potential. After the system has reached its equilibrium it was illuminated with tungsten lamp. Figures 6-8 show the photoactivity of the PTAA polymer, PTAA-RC complex and MWNT-PTAA-RC complex, respectively. It seems that UQ 0 mediator affects on the photocurrent.

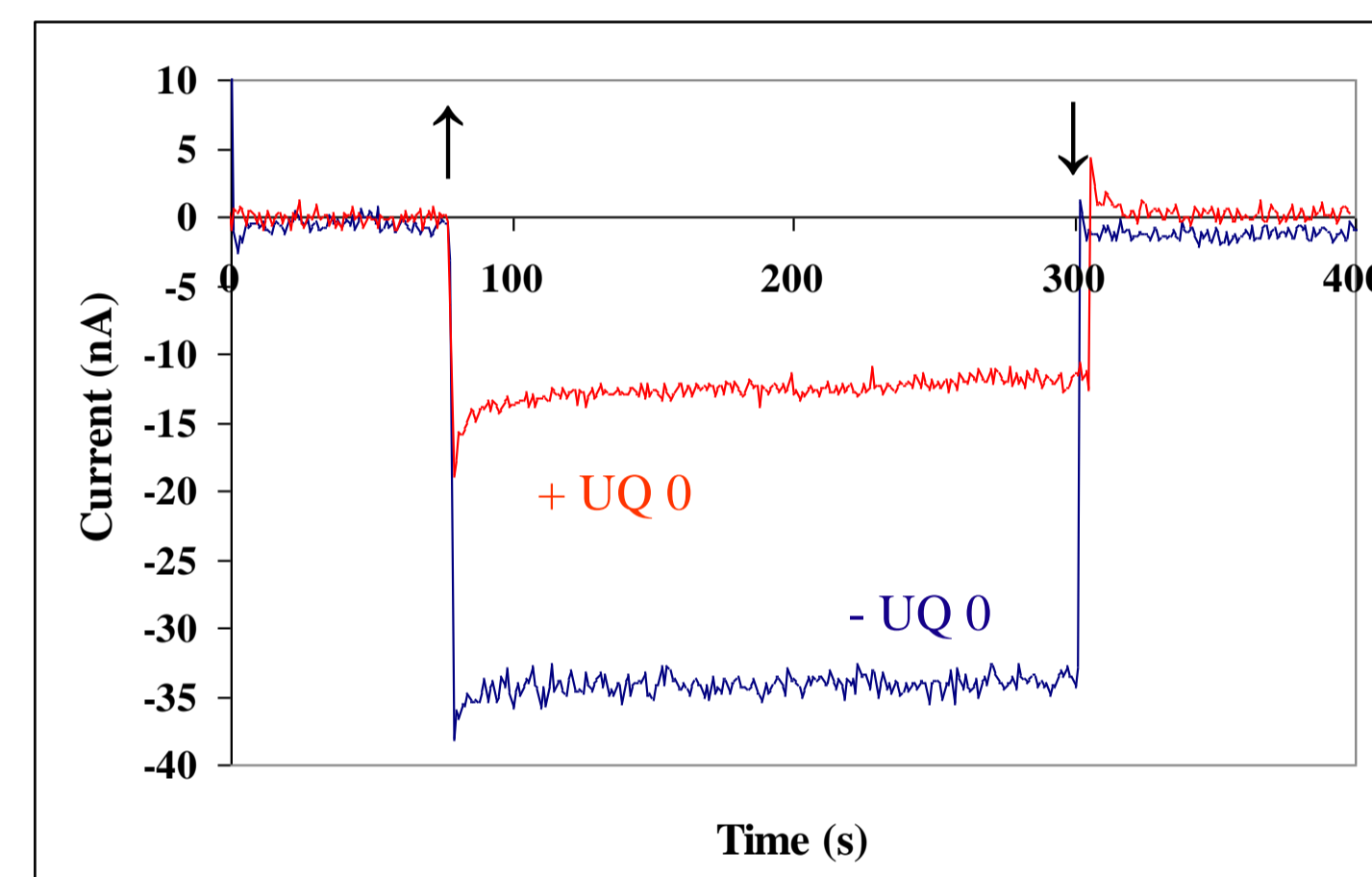


Figure 6. Light induced photocurrent of the electrochemical cell using PTAA covered ITO working electrode without (blue) and with quinone (UQ 0) mediator (red). The time when the light was switched on (↑) and off (↓) are indicated.

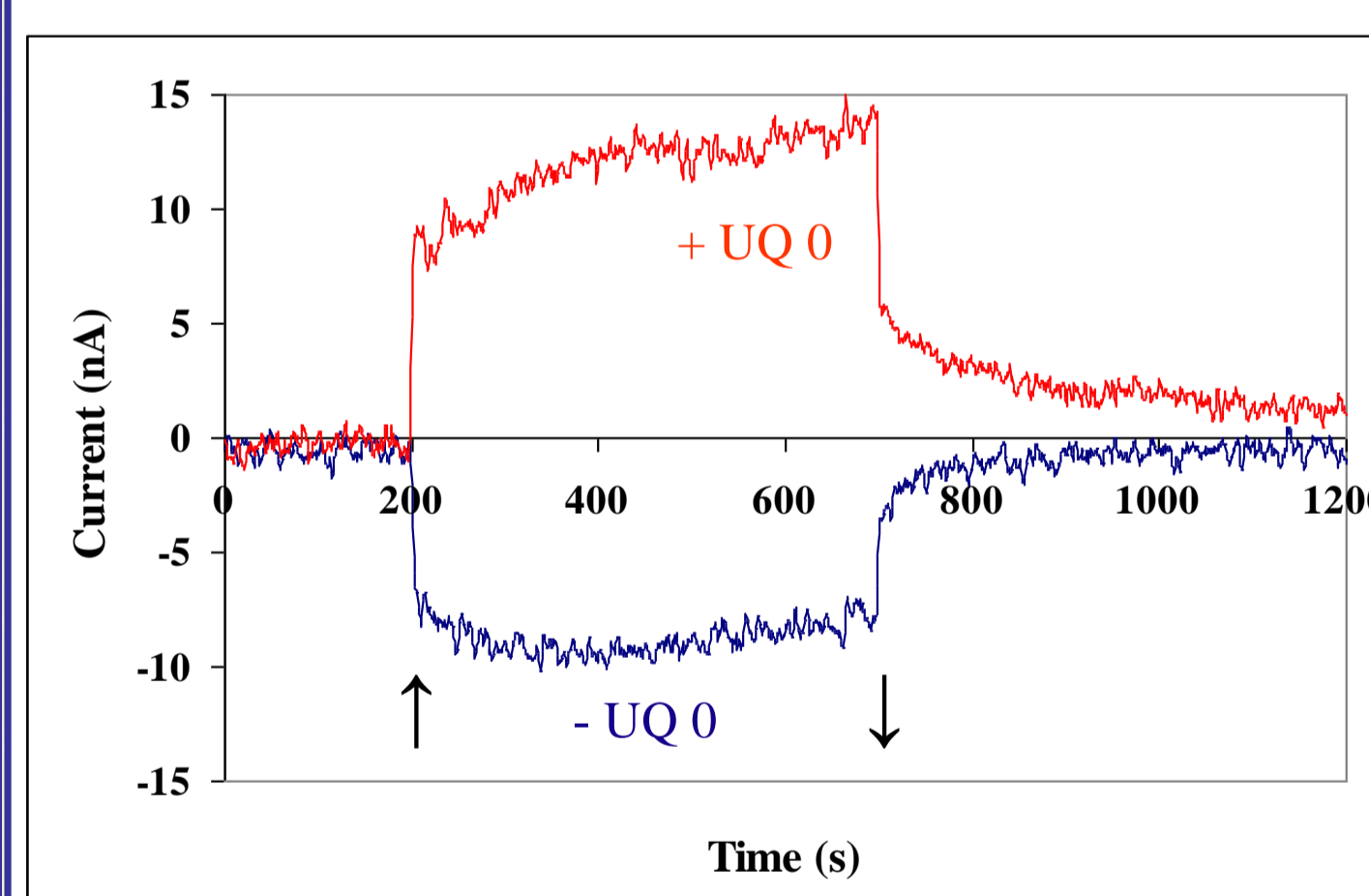


Figure 7. Light induced photocurrent of the electrochemical cell using PTAA and RC covered ITO electrode without (blue) and with quinon mediator (red). The time when the light was switched on (↑) and off (↓) are indicated.

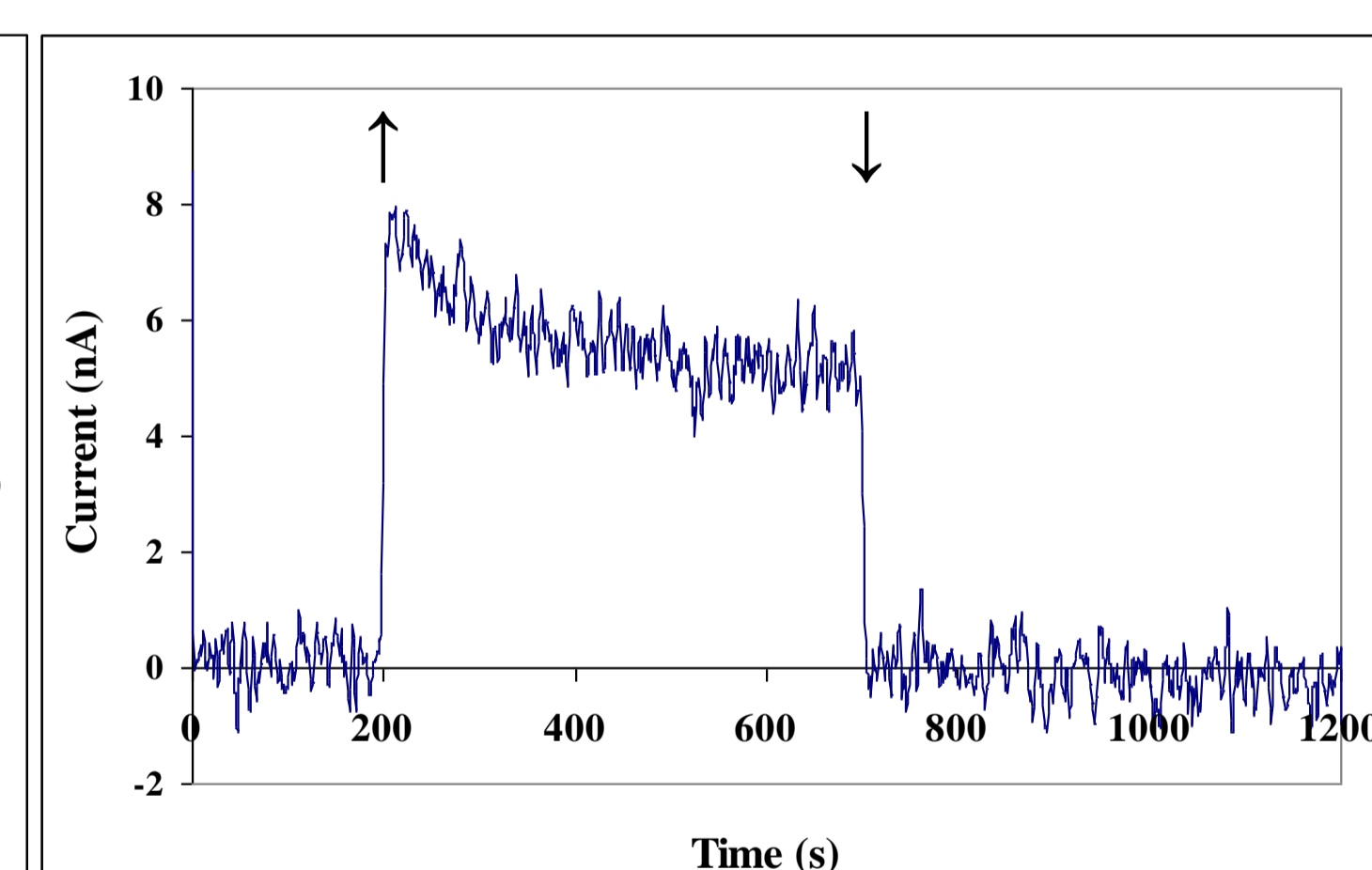


Figure 8. Light induced photocurrent of the electrochemical cell using ITO working electrode covered by MWNT-PTAA-RC complex. The time when the light was switched on (↑) and off (↓) are indicated.

Summary

Our results indicate that
-Resistivity measurements on dried samples indicate that there is a direct electric connection between the RCs and the ITO due to the local electrostatics, which was further confirmed by optical investigations.
-A direct and mediator assisted photocurrent was measured in electrochemical cell containing RCs, MWNT and PTAA. The direction of the photocurrent depends on the donor or the acceptor side reconstitution.

Bibliography

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