Development of an autonomous electrical biosensing device for a colon-rectal cancer protein marker

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Dye-sensitized solar cells (DSSCs) are electrochemical devices capable of transforming photo-energy into electricity. It consists of a porous nanocrystalline semiconductor, titanium dioxide (TiO_2), film with dye adsorbed in the surface acting as photoanode, a counter electrode (CE) coated with a catalytic material (platinum) and an iodide/triiodide redox couple-based electrolyte connecting both electrodes that are linked through an external circuit. When the DSSC is illuminated, the sensitizer adsorbs photons and the photoexcited dye injects an electron in the TiO_2 conduction band leaving the sensitizer oxidized; the electron travels through the semiconductor, external circuit and reaches the cathode where it reduces the electrolyte. In turn, the redox couple at the electrolyte regenerates the sensitizer, completing the circuit (Figure 1).

The DSSC developed herein is to act as an autonomous transducer of an electrochemical biosensor by modifying the counter-electrode with a biorecognition element. Biosensors have two components: a biorecognition element (bioreceptor) and a transducer. When the bioreceptor interacts with the target analyte, this interaction is monitored by the transducer and it changes the energy required to oxidation and that change correlates with the analyte concentration.

The TiO_2 was deposited in the transparent conductive oxide (TCO) coated glass by doctor blade technique, imprinting a circular area of 0.2 cm^2. It was annealed at 450 ºC for 30 min in a furnace and immersed in different dye solutions. The cathode was made by spin-coating a platinum salt, which was after modified by surface imprinting to build a molecularly imprinted polymer (MIP) for carcinoembryonic antigen (CEA) on the CE. A monolayer of the template protein was adsorbed on the Pt/FTO surface and surface imprinting was performed by electro-polymerizing phenol red at 0.8 V vs Ag/AgCl. Different electro-polymerization times were tested to control film thickness in order to prevent overlay the template protein and sterically hinder its removal for creating the negative imprinted sites. Film thicknesses were controlled by the charge passed through the electrode. The template protein was removed from the imprinted sites by potential sweep in acidic medium.

Charge transfer resistance increased with CEA concentration between the limits defined by the charge transfer resistance, before and after template removal. After a concentration of 2.5ng/mL, the biosensor started to saturate, possibly indicating that nearly 100 % of the created cavities available for rebinding were occupied (Figure 2). The linear EIS response showed that the biosensor responded from concentrations as low as 0.05 ng/mL, up to 2.5 ng/mL (slope= 0.21). After this concentration, the biosensor started to saturate and the sensitivity decreased by a factor of ~3 (slope= 0.08). The concentration limit for the presence of a colon-rectal cancer is 2.5 ng/mL for non-smokers and 5.0 ng/mL for smokers, indicating that the biosensor showed a good response in the concentration range of interest.

Figures

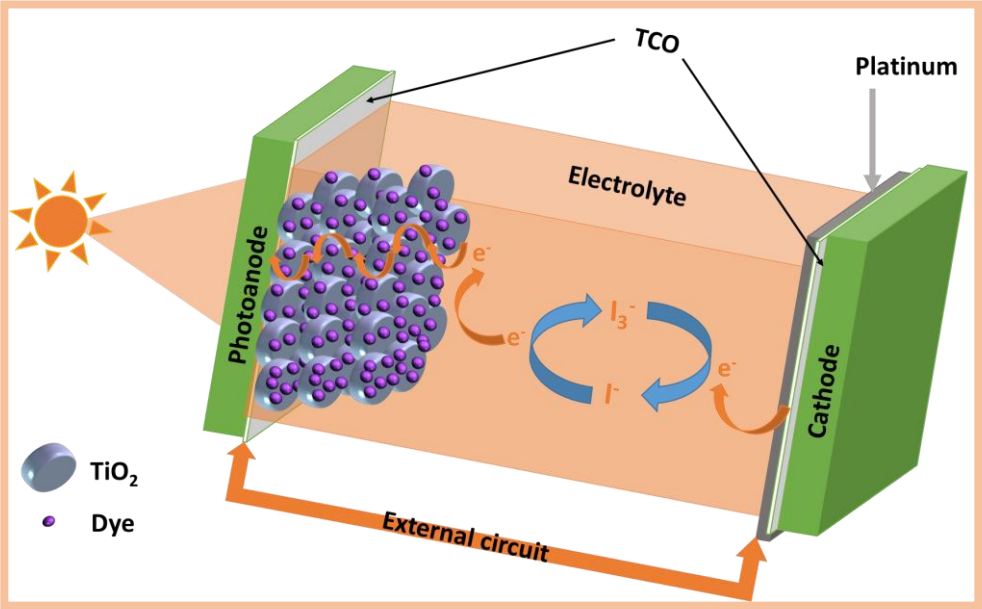

Figure 1. Schematic representation of a DSSC

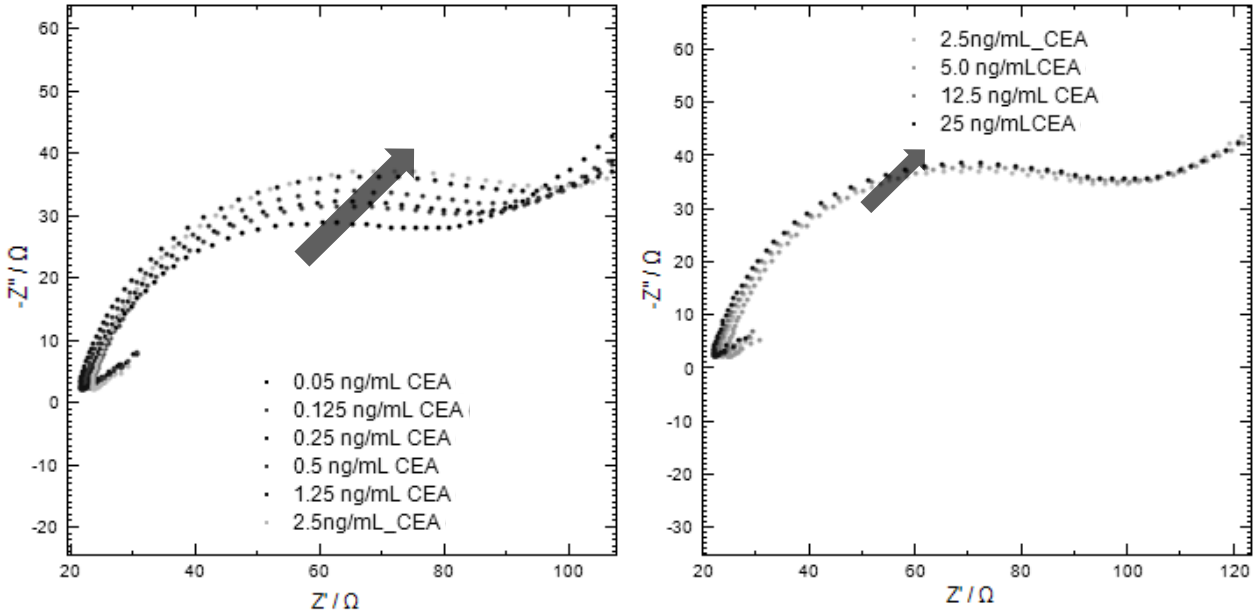

Figure 2. Nyquist plots of the EIS experiments performed on the Pt/FTO MIP modified surface using iodide in PBS as electrolyte during calibration of the CEA biosensor. Left: lower CEA concentration range; Right: higher CEA concentration range

Acknowledgments

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