



Short communication

Visible LED light photoelectrochemical sensor for detection of L-Dopa based on oxygen reduction on TiO₂ sensitized with iron phthalocyanine



Sakae Yotsumoto Neto, Rita de Cássia Silva Luz*, Flávio Santos Damos*

Department of Chemistry, Federal University of Maranhão, 65080-805 São Luís, MA, Brazil

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ABSTRACT

The present work describes the development of a new strategy to photoelectrochemical detection of L-Dopa at low potential based on oxygen reduction on TiO₂ sensitized with iron phthalocyanine (FePc/TiO₂). The FePc/TiO₂ composite shows a photocurrent 10-fold higher than that of pure TiO₂ nanoparticles and it was 4-fold higher than that of FePc exploiting visible light. The band gaps of pure TiO₂ nanoparticles, FePc and FePc/TiO₂, calculated according to the Kubelka–Munk equation, were 3.22 eV, 3.11 eV and 2.82 eV, respectively. The FePc/TiO₂ composite showed a low charge transfer resistance in comparison to the photoelectrode modified with FePc or TiO₂. Under optimized conditions, the photoelectrochemical sensor shows a linear response range from 20 up to 190 μmol L⁻¹ with a sensitivity of 31.8 μA L mmol⁻¹ and limit of detection of 1.5 μmol L⁻¹ for the detection of L-Dopa.

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1. Introduction

In nowadays, the photoelectrochemical sensors have received high attention due to their unique characteristics, including the separation between the source of excitation and detector apparatus resulting in high sensitivity due to the low background signal [1,2]. In addition, the photoelectrochemical sensor is simple and inexpensive in comparison to many optical detection techniques [3].

In this sense, the photoactive nanostructured materials have received high attention in the field of sensors and biosensors in the last decade, including the semiconducting oxide-based structures [4, 5], semiconductor quantum dots [6,7], carbon-based nanomaterials [8] and metal nanoparticles [9] since they show high photoelectrochemical activity and biocompatibility to many molecules. Among them, titanium dioxide is recognized as one of the most efficient photocatalyst since it is photochemically stable, abundant, nontoxic, and cost-effective material [10], which has been exploited in development of photochemical sensors since the pioneering work of Compton's group [11].

However, the use of TiO₂ nanoparticles in photoelectrochemical sensors has some limitations due to its wide band gap of 3.2 eV for anatase form, which limits its photoelectrochemical activity to the ultraviolet region [12]. In this sense, the use of bare TiO₂ nanoparticles in development of sensors and biosensors is very limited, since the most biomolecules are very unstable under UV light. In addition, TiO₂ nanoparticles suffer from rapid recombination of conduction-band electrons and valence-band holes, which occurs faster than the time required for these carriers to react with suitable species [13]. Therefore, a number of

materials have been exploited to improve the visible light response of TiO₂ nanoparticles as well as avoid the carrier recombination, including metal and non-metal doping [10], external dye sensitization [14], or coupling with a narrow band gap semiconductor [15].

Among these sensitizers, phthalocyanine derivatives are particularly attractive due to: (1) their strong absorption in the region of Soret bands around 300–450 nm and in the region of Q bands around 500–700 nm, (2) excellent photoelectrochemical properties, (3) high thermal and chemical stability, and (5) high molar extinction coefficient at the near-IR region [16]. Furthermore, the strong electronic coupling between metallomacrocylic compounds and TiO₂ nanoparticles surface has been observed because of the efficient electron injection from the dye excited single state to the conduction band of the illuminated TiO₂ [17]. Therefore, metallophthalocyanine has attracted high attention for the development of photoelectrochemical sensors and biosensors [18], photoinduced degradation of organic compounds [19], and dye sensitized solar cells [20].

Another recent strategy to change the effective band gap of TiO₂ nanoparticles is attaching biomolecules on its surface exploiting the ability of oxygen-containing substituents to bind to the surface of titanium oxide nanostructures [21]. These biomolecules can adjust the coordination environment giving new hybrid optical properties to these nanostructures. These hybrid properties arise from the ligand-to-metal charge transfer interaction between the ligand and metal surface atoms that further couple with semiconductor electronic properties of the core of the nanostructures.

The pioneering works of Dimitrijevic et al. [22] and Rajh et al. [23] have shown that the modification of TiO₂ nanoparticles with some enediol ligands, such as dopamine, catechol, and ascorbic acid can enable harvesting of visible light and promote more efficient spatial

* Corresponding authors. Tel.: +55 98 3272 9411.

E-mail addresses: rita.luz@ufma.br (R.C.S. Luz), flavio.damos@ufma.br (F.S. Damos).

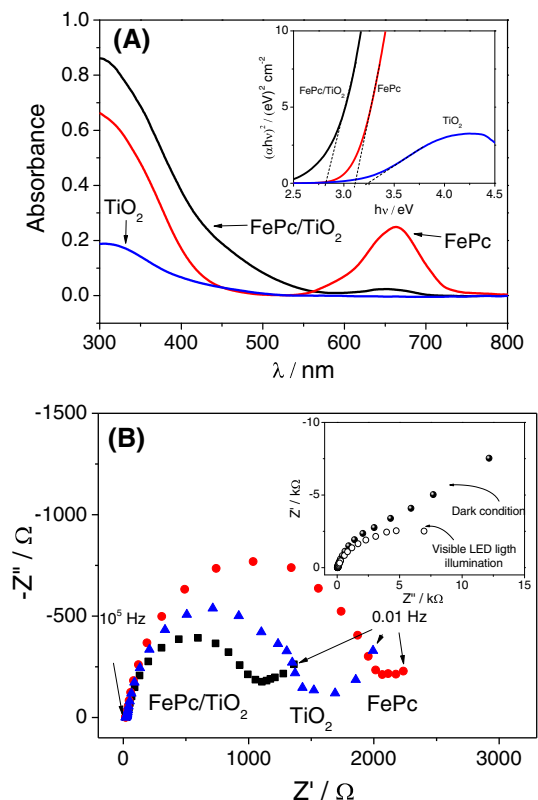


Fig. 1. (A) UV-vis absorption spectra of TiO_2 , FePc, and FePc/ TiO_2 . Inset of Fig. 1A: Plots of $(\alpha h\nu)^2$ versus $h\nu$ of FePc/ TiO_2 composite, TiO_2 , and FePc. (B) Nyquist plots of the substrate photosensor in 0.1 mol L^{-1} KCl solution containing 5 mmol L^{-1} $[\text{Fe}(\text{CN})_6]^{3-/4-}$ modified with FePc/ TiO_2 composite, TiO_2 , and FePc. Inset of Fig. 1(B) shows the Nyquist plots for the FePc/ TiO_2 composite on photoelectrode substrate in 0.1 mol L^{-1} Na_2SO_4 aqueous solution electrolyte recorded at room temperature at open circuit potential in the dark and under visible LED light.

separation of charges. In these charge transfer complexes, the electrons are in the titania lattice while holes are at complexed enediol molecule, which has opening a new field to detection of several molecules [24–27].

The aim of this manuscript is to evaluate the performance of a novel FePc/ TiO_2 composite to determine L-Dopa exploiting the shallow lattice-trapped electrons generated by the charge transfer complex between FePc/ TiO_2 /L-Dopa to improve the reduction of molecular oxygen to form superoxide anions. To the best of our knowledge, this is the first indirect and low potential detection of L-Dopa exploiting its interaction with FePc/ TiO_2 composite under visible LED light.

2. Experimental

All used chemicals were of analytical grade. Photoelectrochemical measurements were carried out with a CompactStat from Ivium (Ivium Technologies, Netherlands) using a three-electrode system composed of samples with an active area of 1.0 cm^2 as a working electrode, a Pt wire as a counter electrode, and an Ag/AgCl (saturated) as reference electrode. All photoelectrochemical measurements were carried out in oxygen saturated solution. The electrochemical impedance spectra were recorded in 0.1 mol L^{-1} KCl solution containing 5 mmol L^{-1} of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in the frequency range of 0.01 Hz – 10^5 Hz under AC amplitude of 10 mV . A commercial 20 W LED light was used as the irradiation energy in photoelectrochemical measurements. UV-visible spectra of all materials were obtained using an AvaSpec-2048 spectrometer from Avantes.

The photoelectrode substrate was firstly polished with $0.3 \mu\text{m}$ alumina slurry and then sonicated in ethanol and water to remove any adsorbed species. A suspension was prepared by mixing 10 mg of TiO_2 nanoparticles and 3 mg iron phthalocyanine in $500 \mu\text{L}$ of dimethyl sulfoxide with the aid of sonication. $15 \mu\text{L}$ of this suspension was placed directly onto the photoelectrode substrate and allowed to dry at 50°C for 1 h to form a FePc/ TiO_2 photoelectrochemical sensor.

3. Results and discussion

3.1. Characterization of the FePc/ TiO_2 composite photoelectrochemical sensor

As can be seen at Fig. 1A (blue line), the TiO_2 nanoparticles show an optical threshold at about 420 nm , which can be attributed to the charge-transfer process from the valence band to the conducting band of TiO_2 nanoparticles. On the other hand, the iron phthalocyanine shows an absorption band at about 320 nm and other in the range of 600 – 700 nm , respectively (Fig. 1A, red line). The former band at 320 nm is assigned to the Soret band of FePc arising from the transition of $a_{2u}(\pi)$ to $e_g^*(\pi)$, and the latter band in the range of 600 – 700 nm is attributed to the Q bands of FePc corresponding to the $a_{1u}(\pi) - e_g^*(\pi)$ transition [28,29]. After the sensitization of the TiO_2 nanoparticles with FePc molecules, the absorption band of the FePc/ TiO_2 composite is extended to visible region and the threshold of the absorption band is red-shifted to 550 nm , which facilitates the strong absorption of visible LED light (Fig. 1A, black line).

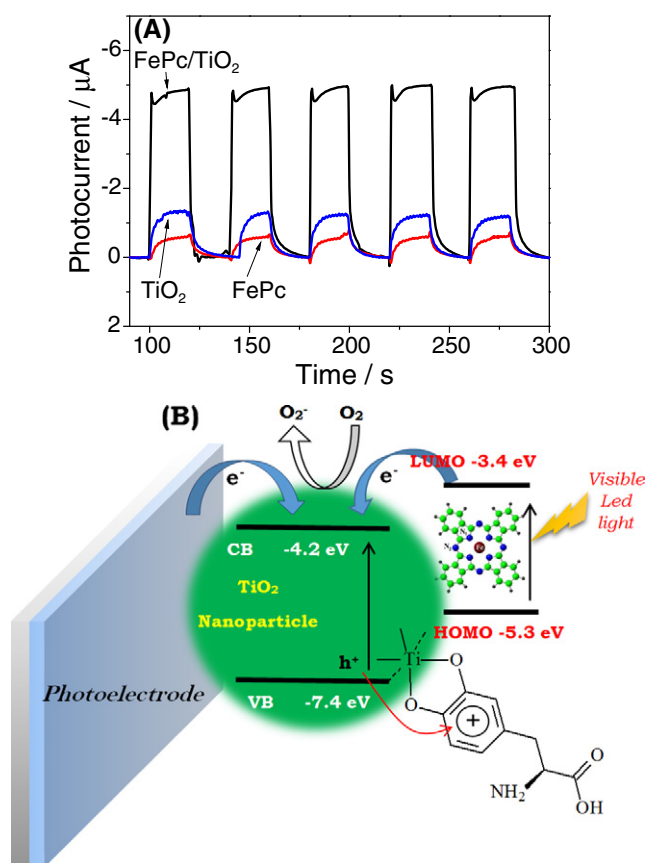


Fig. 2. (A) Photocurrent response of FePc/ TiO_2 , TiO_2 and FePc in 0.1 M Imlvine buffer solution (pH 3.0) containing 5 mmol L^{-1} L-Dopa under applied potential of 0 V vs Ag/AgCl. (B) Possible mechanism for the photoelectrochemical detection of L-Dopa.

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