



Short communication

Photogeneration of singlet oxygen by thionine molecular layer grafted on electrode surface from its diazonium salt



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ABSTRACT

Thionine (Th) was electrochemically grafted to the glassy carbon (GC) surface from its corresponding diazonium salt to investigate it as a singlet oxygen source under light excitation. As confirmed by cyclic voltammetry data the Th molecules may form a monolayer structure in the reduction process carried out directly from the diazotization reaction mixture without a time-consuming separation step. It was found that illuminated grafted Th at a level of monolayer coverage on GC surface is able to generate singlet oxygen at a constant rate. To determine efficiency of the photogeneration process a singlet oxygen selective trap, 1,3-diphenylisobenzofuran (DPBF), was employed, which was monitored using UVVis spectroscopy. The progress of the trap decay was determined in terms of its half-life.

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1. Introduction

Photochemically in situ generated singlet oxygen became a primary and versatile oxidant in comprehensive areas such as fine chemical synthesis [1], wastewater treatment [2], photodynamic therapy [3], and formation of antimicrobial surfaces [4]. On the basis of the widespread occurrence of oxygen and easiness of operation with numerous photoactive molecules, the in situ photogeneration of singlet oxygen is usually performed in bulk, homogeneous systems [5]. The currently developed methods of immobilization of organics to solid surfaces might be applied for the photoactive molecules and thus offer new potential possibilities in application of this energy rich oxygen form. Several effective approaches for the immobilization of photosensitizers were recently described, while preserving their capacity to transfer energy from the excited triplet state to oxygen molecules resulting in the formation of singlet oxygen [6,7]. In our previous work [8], the electrochemical methods were applied for the photosensitizers bonding to the solid surface resulting in the polymer-like films capable of singlet oxygen generation.

Since electrografting has become the most remarkable and versatile strategy for the immobilization of various organic layers [9,10], it gained our attention to use it for the immobilization of photoactive molecules. In particular, it allows a stable organic layer to be easily covalently bound to the surface by applying a reductive or oxidative potential [11]. In particular, this method allows binding of aryl groups from

various reagents such as amines, Grignard reagents, diazonium salts and halogenated groups [9,11]. Furthermore, in situ reduction of aryl diazonium salt cation gained a vast interest in the simple grafting of organic compounds to the solid surface due to omission of the complicated product isolation [12].

Among various singlet oxygen generating agents [5], the group of phenothiazines [13] such as Azure A and Toluidine Blue has been already employed in electrografting of respective diazonium salts with application towards NADH sensors [14–17]. Nevertheless, electrochemical grafting of widely explored phenothiazine derivatives has never been applied towards singlet oxygen generation in the heterogeneous systems.

In this study we follow on the last work concerning polymeric form of phenothiazines [8] to explore the effectiveness of singlet oxygen generated by thionine molecular layer. Thionine was bound to the conductive solid surface by electrografting of the respective diazonium salt directly from the diazo reaction mixture. The effectiveness of this molecular layer in the generation of the singlet oxygen induced by xenon lamp equipped with interference filter (550 nm) was monitored by UVVis spectrometry in organic solution containing 1,3-diphenylisobenzofuran (DPBF) used as a selective singlet oxygen trap [18].

2. Experimental

2.1. Chemicals

Thionine as a representative phenothiazine derivative substituted with two amino groups was selected to synthesize its respective

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diazonium salt. Thionine (purity >90%) was obtained from Across Organics and was used as received. Both reagents for the diazotization reaction, 50% tetrafluoroboric acid (Across Organics), and sodium nitrite (POCH) were of analytical grade. The Britton–Robinson (BR) buffer solution of pH 4.45 was used as the electrolyte solution. Other reagents used for the monitoring of singlet oxygen were: 1,3-diphenylisobenzofuran (DPBF, purity >97%), methanol (purity >97%) and carbon tetrachloride (purity ~99.9999%) – these were purchased from Across Organics.

2.2. Apparatus

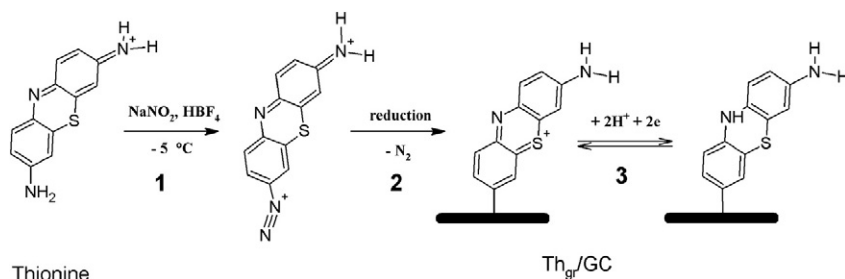
The electrochemical measurements were carried out using the CHI 660C electrochemical workstation. A conventional three-electrode system was employed with a glassy carbon electrode (GC, EDAQ, 1 mm dia.) or GC plate electrode (HTW, polished, 0.81 cm² of exposed surface area) as a working electrode, Ag/AgCl in KCl (sat) as a reference electrode, and GC rod as a counter electrode. The electrodes were mounted in the 2 mL electrochemical cell using a Teflon holder.

The effectiveness of the singlet oxygen generation was determined by controlling the absorption spectra of DPBF using HP 8452A spectrometer. These measurements employed the standard 10 × 4 mm quartz cuvette (Hellma Analytics), which was arranged as a thin layer cell with the cavity volume of 0.2 mL. This cavity was created between the cuvette wall and the GC plate (0.9 × 0.9 cm of active surface area). Excitation of active molecules bound to the GC surface was achieved by the 100 W xenon lamp equipped with interference filters (Carl Zeiss) separating a few nm wide wavelength at half height of the maximum at 550 nm. At that arrangement the spectrophotometer analyzing beam passes along the sample surface, while the lamp beam oriented perpendicularly to the analyzing beam illuminates the active surface without any disruption to the recorded spectra.

2.3. Procedures

• Synthesis and electrochemical grafting of thionine diazonium salt

Diazonium salt was synthesized according to the procedure adopted from the literature [19]. Thionine and HBF₄ were mixed in an ice bath by stirring, while the sodium nitrite aqueous solution was added dropwise into the mixture. After 30 min of stirring at –4 °C, the entire mixture was used for electrochemical grafting process without product purification. The electrochemical reduction of thionine diazonium salt was conducted by means of cyclic voltammetry (CV) within the potential range (–0.6 V to +0.2 V), starting from +0.2 V, at the scan rate 0.05 V/s. All the tests of basic electrochemical properties for resulting monolayer were performed in the pure BR electrolyte solution within the potential range –0.3 V to +0.6 V.



Scheme 1. The schematic representation of thionine diazonium salt synthesis (1), electrografting of diazonium salt onto GC electrode at reductive potential (2) and the redox processes of the resulting thionine molecular layer (Th_{gr}/GC).

• The singlet oxygen photogeneration

Singlet oxygen generation was assayed using the method developed by Cincotta employing the decay of DPBF used as a specific trap [18]. The absorption decrease of DPBF at 416 nm in the mixture of carbon tetrachloride and methanol (v/v; 80:1) at initial concentration of 0.05 mM was observed while singlet oxygen was generated in the system. A bare GC plate was used as a control sample. By assuming that the decay of DPBF is an effect of its reaction with singlet oxygen, the half-time was calculated as a mean efficiency of the photogeneration process.

3. Results and discussion

Thionine is the phenothiazine derivative substituted by two primary amino groups, therefore Th monodiazonium salt is synthesized by preserving the adequate ratio of only one equivalent of diazotization reagent, which is sodium nitrite (Scheme 1, step 1) [11,20]. In our studies, electrografting was performed directly from the reaction mixture without product isolation. Such approach appeared to be especially useful in the case of that highly soluble Th diazonium salt [21]. The course of the related processes is depicted in Scheme 1, in which two Th mesomeric structures are not taken into account for simplicity purposes.

The reduction of Th diazonium salt carried out in the reaction mixture occurs typically for this electrochemical process [14–17], which is illustrated by the CV curves in Fig. 1A. During the first cathodic scan a broad reduction peak appears at potential –0.4 V corresponding to the irreversible reaction occurring on the electrode surface. That peak is characteristic for many diazonium salts [9], thus no additional reaction is observed at this potential [22]. That peak is a response to reductive transfer of electron to diazonium group accompanied by a cleavage of nitrogen molecule and formation of aryl radical (Scheme 1, step 2) [9]. That radical cation creates the covalent bond with the electrode surface causing a progressive blocking of the electrode surface [9,23]. Therefore, in the consecutive cycles, the decrease of the peak's current is observed until flat CV curve is registered. The modified electrode surface may still possess some free space after rinsing, which can be effectively blocked, when repeating the reduction process.

The CV curve recorded in a pure buffer solution for GC surface grafted with thionine (Th_{gr}/GC) is shown in Fig. 1B (a). It is a voltammogram typical for thionine with the well-defined pair of redox peaks at +0.2 V, which come from the immobilized layer (Scheme 1, step 3) [14–17]. Since, the reaction mixture except of thionine monodiazonium salt consists of tetrafluoroborate ion and traces of remaining unconverted thionine, an additional small peak in the cathodic range at –0.05 V is observed, which corresponds to the adsorbed thionine on the GC electrode. Even if the charges assigned to both peaks may slightly vary from one experiment to another [11], the process of Th electrografting is well reproducible. The surface coverage

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