



# Photogeneration of singlet oxygen by the phenothiazine derivatives covalently bound to the surface-modified glassy carbon



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## ABSTRACT

The selected group of four amine-derivatives of phenothiazine was covalently grafted to the glassy carbon surface in the four-step procedure consisting of the electrochemical reduction of the diazonium salt followed by the electrochemical and chemical post-modification steps. The proposed strategy involves the bonding of linker molecule to which the photosensitizer is attached. The synthesized organic layers were characterized by means of cyclic voltammetry, XPS and Raman Spectroscopy. It was shown that the phenothiazines immobilized *via* proposed strategy retain their photochemical properties and are able to generate  $^1\text{O}_2$  when activated by the laser radiation. The effectiveness of *in situ* singlet oxygen generation by those new solid photoactive materials was determined by means of UVVis spectroscopy. The reported, covalently modified solid surfaces may find their application as the singlet oxygen photogenerators in the fine chemicals' synthesis or in the wastewater treatment.

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## 1. Introduction

Oxygen in the form without unpaired electrons, *i.e.* singlet oxygen  $^1\text{O}_2$  [1], and its possible applications in the areas of fine chemicals' synthesis [1], antibacterial surfaces [2] and wastewater treatment [3] gained increasing research interest in the last years. This reactive molecule is formed in the photoinduction process, in which, under illumination the photoactive compound, *i.e.* photosensitizer, transfers its excessive energy to the atmospheric triplet oxygen [1]. Several groups of photosensitizers are known in this area-aromatic hydrocarbons [4], porphyrins [5], phthalocyanines [6], transition metals complexes [7], semiconductors oxides [8] or phenothiazines [9]. The latter are characterized by the considerable photosensitizing efficiency and the attractive physiochemical properties [10].

Since the  $^1\text{O}_2$  lifetime is in the range of microseconds, its photogeneration *in situ* is considered as the only option for the possible applications. Thus, the extensive research on the synthesis of solids with photoactive surfaces are carried out recently. These materials are believed to possess several distinctive features, like ease of operation in the oxidation process and simple purification of

the process' products or, as shown lately, better stability against oligomerization/aggregation and higher photostability [11].

The photoactive solid surfaces are usually synthesized *via* non-covalent incorporation of the photosensitizer into the polymer matrix (*e.g.* cellulose acetate) [12], or *via* covalent binding of the photosensitizer molecules to the support [13]. The photoactive materials obtained by the first approach are usually characterized by the low stability of the photosensitizers on the surface, due to the photosensitizer molecules outflow, thus the lower stability and the polymer matrix destruction by the free radicals [14]. In the second strategy the higher stability is ensured by the covalent bond that is formed between the photoactive molecule and the solid support, either the polymer matrix (*e.g.* polystyrene, polyamide) [11] or the inorganic substrate [15,16]. Generally, two approaches for the covalent bonding of the molecule to the surface are commonly distinguished-one based on the support's surface modification and its further reaction with the unmodified photoactive molecule, or the alternative based on the conversion of photosensitizer's molecule to another form that may be easily bound to the solid surface. The latter can be accomplished by various chemical, photochemical or electrochemical methods, generally known as *grafting*, leading to the formation of covalently bound organic layers [17,18]. Among them the electrochemical reduction of diazonium salts is still considered as the most perspective one [19,20]. Since rather gentle conditions are required for that electrografting process, a

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variety of conductive surfaces (carbon [21], semiconductor [22], metals [23]) can be covered with the numerous organic compounds [24,25], including phenothiazines [26,27].

Our group has recently shown that by simple electrochemical methods *i.e.* electrochemical polymerization [15] or electrografting [16], a group of electroactive photosensitizers – phenothiazines may be immobilized on the solid surfaces by conversion of the photosensitizer's molecules to other chemical form. In this work, the alternative route is presented, in which four modification steps are conducted on glassy carbon used here as a model surface, including electrochemical and chemical steps, yielding the molecular layer capable of bonding of the basic phenothiazine derivatives possessing an amine group in their structure. The substantial difference in the proposed route is the bonding of the linker molecule, which allows to easily attach the photosensitizer. Although the presented approach is more complicated than the previously reported strategy, it can also be successively applied for the covalent immobilization of the photosensitizer molecule. Azure A (AA), Azure C (AC), Toluidine Blue O (TBO) and Thionine (Th), were covalently immobilized on the solid surface *via* the four-step process consisting of the diazonium salts electrografting and the post-modification of the resulting layer. The effectiveness of such organic layers activated by the laser radiation in the photogeneration process, was monitored in the solution phase with the 1,3-diphenylisobenzofuran (DPBF), which is commonly used as the  $^1\text{O}_2$  trap [28].

## 2. Experimental

### 2.1. Materials

Four amine-derivative phenothiazines were selected for their covalent immobilization on the solid surface (Scheme 1). The group included Azure A (AA), Azure C (AC), Toluidine Blue O (TBO) and Thionine (Th). AA (purity >90%) and TBO (purity >88%) were purchased from Sigma Aldrich, AC (purity >90%) was obtained from Fluka and Th (purity >90%) were purchased from Across Organics.

4-nitroaniline, used to synthesize the respective diazonium salt, was obtained from POCh, Poland, while the terephthaloyl chloride (TC, purity >99%), used as a linker molecule, was purchased from Sigma Aldrich. Tetrafluoroboric acid, sodium nitrate and triethylamine, each from POCh, Poland, were of an analytical grade. The singlet oxygen traps, 1,3-diphenylisobenzofuran (DPBF, purity >97%) and sodium azide (99%) were obtained from Across Organics and Alfa Aesar, respectively.

Tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) (purity = 99%, Sigma Aldrich) in acetonitrile (HPLC grade, Sigma Aldrich), KCl in the water/ethanol solution (all analytical grade POCh), sulfuric acid (analytical grade, POCh, Poland) were used for the surface modification, while the buffer solution at pH 4.00 (analytical grade, POCh, Poland) was used as the electrolyte solution for the covalently bound phenothiazines identification. Other organic solvents, tetrahydrofuran (analytical grade) and methanol (purity >97%) were obtained from Across Organics, while deuterated solvents (methanol – d<sub>4</sub> and DMSO – d<sub>6</sub>) from Sigma Aldrich.

### 2.2. Apparatus

The electrochemical measurements were carried out using the CHI 660C electrochemical workstation (CH Instruments Inc.). A conventional three-electrode system was employed with the glassy carbon disc electrode (GC, EDAQ, 1 mm dia.) or the glassy carbon plate (1 cm<sup>2</sup>) as a working electrode. The substrate surface was polished with an emery paper (grit 2000) and with 1 μm alumina (Buehler), then ultrasonicated in deionized water and finally rinsed

with isopropanol. Ag-wire served as a pseudoreference electrode for the aprotic medium, while Ag/AgCl (sat. KCl) was used as a reference electrode for an aqueous solutions, the GC rod was applied as a counter electrode. The electrodes mounted in Teflon holder were placed in the conical electrochemical cell.

The XPS spectra were collected using a SPECS XPS spectrometer (background pressure  $\sim 10^{-7}$  Pa), equipped with the X-ray source (AlK $\alpha$  1486.6 eV; XR-50 Model) and a hemispherical concentric analyzer (PHOIBOS-100 Model). The pass energy was set at 90 eV for the survey spectra and 20 eV for the high-resolution scans. All of the obtained binding energy (BE) data were calibrated using Au 4f<sub>7/2</sub> peak at 83.8 eV. The data were then analyzed by the SDP v7.0 software.

Raman spectra were recorded *ex-situ* for each freshly prepared layer and after the test for singlet oxygen generation. All spectra were collected by Renishaw inVia Raman Microscope (Renishaw, Inc., New Mills, UK) that was equipped with a diode excitation laser with 50 mW maximum power at the wavelength 633 nm. The laser intensity was then reduced to 1–5% of its power by using a set of neutral density filters at the exit of the objective. The acquisition time was 10 s and the spectral resolution was 2 cm<sup>-1</sup>. The raw spectra were subjected to procedures of smoothing and baseline subtraction using Renishaw software.

The effectiveness of singlet oxygen photogeneration was determined by monitoring of absorption spectra of DPBF using Hewlett Packard 8452A UVVis spectrometer. The standard 10 × 4 mm quartz cuvette (Hellma Analytics) applied in these measurements was arranged as a thin layer cell possessing a cavity of 10 mm path-length and thickness of 2 mm. This cavity was created between the cuvette wall and the GC electrode, which was fitting the size of the cuvette. The diode laser (Oxxius 150 mW model LBX-638-150-ELL-PP) with emission wavelength of 638 nm and laser power adjusted to 20 mW was employed as an excitation light source. The set up was arranged in the same way as in our previous works [15,16].

### 2.3. Procedures

#### 2.3.1. 4-Nitrobenzenediazonium tetrafluoroborate (4-NBDS) synthesis

The procedure of diazonium salts' synthesis was in accordance to that reported previously [29]. The identity and purity of the product was confirmed by means of <sup>1</sup>H NMR spectroscopy. The spectra were collected with Varian UNITY INOVA 300 apparatus (300 MHz resolution) with DMSO-d<sub>6</sub> used as a solvent. (4NBDS): <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 8.72 (d, 2H, *J* = 0.02 Hz, H<sup>3,5</sup>), 8.93 (d, 2H, *J* = 0.02 Hz, H<sup>2,6</sup>).

#### 2.3.2. Phenothiazines covalent immobilization on the glassy carbon surface

The phenothiazine derivatives were bound to the glassy carbon surface in the multi-step process, depicted in the Scheme 2. In the first step the electrochemical reduction of the synthesized 4-nitrobenzenediazonium salt was conducted in the aprotic medium by means of cyclic voltammetry at the scan rate of 0.1 V/s using 3 scan cycles. In the second step, the electrografted aromatic nitro group (NO<sub>2</sub>/GC) was post-modified by electrochemical reduction in the 1 M H<sub>2</sub>SO<sub>4(aq)</sub> solution under the potentiostatic conditions at –0.6 V for 5 min. In the third step, the TC linker molecule was reacted with the aromatic amine group present on the surface (NH<sub>2</sub>/GC) in 0.1 M TC/THF solution with the few drops of triethylamine, for 24 h. The phenothiazines were bound to the resulting surface (linker-NH/GC) in 0.1 M phenothiazine/THF solution with few drops of triethylamine, for 24 h. The synthesized phenothiazine-linker-NH/GC materials were copiously rinsed with water and methanol to remove any phenothiazines weakly adsorbed on the GC surface.

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