Full Length Article

Formation of poly(Azure A)-C_{60} photoactive layer as a novel approach in the heterogeneous photogeneration of singlet oxygen

Agata Blacha-Grzechnik[a],*, Katarzyna Piwowar[a], Tomasz Zdyb[a], Maciej Krzywiecki[b]

[a] Faculty of Chemistry, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland
[b] Institute of Physics – CSE, Silesian University of Technology, Konarskiego 22B, 44-100 Gliwice, Poland

ABSTRACT

Fullerene, C_{60} photosensitizer was incorporated into poly(Azure A) in the process of electrochemical polymerization from the solution of corresponding dye and fullerene. The synthesized organic layer (PAA_C_{60}/ITO) was characterized by means of cyclic voltammetry, UV–Vis, Raman and X-ray photoelectron spectroscopies. It was shown that PAA_C_{60}/ITO exhibits strong absorption in both UV and Vis regions and that both immobilized photosensitizers, i.e. Azure A and C_{60}, retain their photochemical activity towards $^1O_2$ generation under illumination as tested with 2,3,4,5-tetraphenylcyclopentadienone (TPCPD) singlet oxygen quencher. The electro-deposited photoactive layer composed of two photosensitizers was investigated as a source of $^1O_2$ in the process of α-terpinene oxidation.

1. Introduction

Singlet oxygen $^1O_2$, i.e. oxygen in the form without unpaired electrons has been under high research interest since 1963 [1,2]. It has been shown, that this form of oxygen has stronger oxidation properties comparing to triplet oxygen state, which results in its higher reactivity and electrophilicity, but also in its lower stability [3]. Singlet oxygen can be formed in the photoinduction process, where the appropriate photoactive molecule is excited from ground state, S_0, to form lowest excited singlet state S_1 by light illumination generally in one-photon transition. In the next step, the photosensitizer's triplet state with longer lifetime, T_1, is formed in the intersystem crossing process. The photosensitizer being in the triplet state can react either via Type I mechanism, i.e. hydrogen-atom abstraction or electron-transfer with substrates, producing free radicals that in the reaction with oxygen give ROS like superoxide radical anion, or via Type II mechanism, i.e. an energy transfer occurring in the collision of the excited photosensitizer with $^3O_2$ molecules [1]. Many groups of compounds able to generate singlet oxygen are known: dyes and aromatic hydrocarbons, porphirines and tetrapyrroles, transition metals complexes, semiconductors oxides and carbon-based nanostructures, i.e. fullerenes, nanotubes and graphene [3–5]. The photosensitizing abilities of those carbon allotropes have been studied mainly in the bulk, though it has been demonstrated that fullerenes and carbon nanotubes, when deposited from the solution with polystyrene used to increase the adhesion with the solid support are able to generate singlet oxygen molecule upon

illumination [6–8]. The yield of singlet oxygen photogeneration by C_{60} molecule is very high, but its practical use is limited, since it absorbs mainly in UV region. This can be overcome by an introduction of organic moiety absorbing in the lower energy visible region, either in the form of polymeric matrix or covalently attached organic chain [9–11]. When conducting polymers are considered, fullerenes, graphene and carbon nanotubes can be non-covalently incorporated into polymer matrix by electro-co-deposition from the solution of monomer and carbon nanostructures, forming the layer of nanocomposite on the electrode's surface. Such approach has been already reported for polypyrrole or polythiophenes [12–16].

The lifetime of singlet oxygen in the diluted gas phase is relatively long, but due to the molecular interactions it is shortened, for example to about 4 μs in water. Thus, $^1O_2$ has to be generated in situ in the reaction mixture with photosensitizer present in the solution or on the solid support. Since the heterogeneous photocatalysis possesses several advantages over homogenous approach, like ease of operation or easier product separation and purification steps, high attention is paid nowadays on developing methods of photoactive molecules immobilization, so that new solid materials capable of singlet oxygen photogeneration are formed. It is important, that in many cases only thin photoactive layer deposited on the solid support is effective enough to ensure high yield of $^1O_2$ generation in Photodynamic Therapy (PDT), fine chemicals' synthesis or wastewater treatment [3,17–20]. Our group has recently shown that organic thin films of phenothiazine can be immobilized on the solid surface by electrochemical polymerization or

---

* Corresponding author.
  E-mail address: agata.blacha@polsl.pl (A. Blacha-Grzechnik).

electrochemical reduction of the diazonium salts. Such surfaces were able to generate the active singlet oxygen in the reaction mixture, leading to the oxidation of 1,3-diphenylisobenzofuran (DPBF) or phenol [21–23].

In this work, thin photoactive layer containing two types of photosensitizers, i.e. fullerene C_{60} and Azure A, was electro-co-deposited on ITO/glass substrate. The main aim of such approach was to combine the high photosensitizing properties of both C_{60} and AA in order to form heterogeneous photocatalyst that utilizes broader range of light wavelength to produce singlet oxygen molecule. The presence of fullerene and Azure A molecules in the deposited layer is confirmed by means of electrochemical and spectroscopic methods. The singlet oxygen photogeneration by poly(AA)_C_{60} film was investigated with the TPCPD – specific $^1O_2$ – quencher and in the process of α–terpinene oxidation.

2. Experimental

2.1. Materials

Azure A (AA) (purity > 90%) and fullerene C_{60} (purity 99.99%) were purchased from Sigma Aldrich and Across Organics, respectively. Tetrabutylammonium tetrafluoroborate (TBABF$_4$), with or without camphorsulfonic acid (both of purity 99%, Sigma Aldrich) in dichloromethane (HPLC grade, Sigma Aldrich) was used as an electrolyte for the electrochemical deposition and characterization of the photoactive layer. 2,3,4,5-tetraphenylcyclopentadienone (TPCPD) (Acros Organics) in dichloromethane was used as a specific $^1O_2$ quencher. α-Terpinene (TCI, purity 90%) in chloroform (Chempur, distilled prior to use) was employed as a substrate in the photooxidation reaction.

2.2. Electrochemical deposition of PAA_C₆₀ on ITO/glass substrate

The electrochemical measurements were carried out using CHI 660C electrochemical workstation (CH Instruments Inc.). A conventional three-electrode system was employed with the ITO/glass electrode (DELTA Technologies Ltd) acting as a working electrode. The surface of ITO/glass was rinsed with acetone and dichloromethane prior to use. Ag-wire served as a pseudoreference electrode and glassy carbon (GC) rod was applied as a counter electrode. The electrodes mounted in Teflon holder were placed in the electrochemical cell. The electrochemical polymerization of AA was conducted by means of cyclic voltammetry (CV) within the potential range (0; 1.2) V at the scan rate 0.1 V/s. The process was carried out in 0.2 M TBABF$_4$/dichloromethane solution with camphorsulfonic acid (0.1 mM) acting as a source of protons. The concentration of AA and C_{60} was equal to 1 mM and 0.1 mM, respectively.

2.3. Electrochemical and spectroscopic characterization of PAA_C₆₀ layer deposited on ITO/glass substrate

Electrochemical response of the deposited layers was tested in the pure electrolyte solution (purged with Ar for 15 min before measurements) using CHI 660C electrochemical workstation (CH Instruments Inc.) and a conventional three-electrode system.

UV–Vis spectra of ITO electrode modified with PAA_C_{60}/ITO were collected using Hewlett Packard 8452A UV–Vis spectrometer. Comparatively, UV–Vis spectra of 0.1 mM C_{60} solution in dichloromethane and PAA/ITO film were recorded.

Raman spectra of the freshly prepared layers and solid C_{60} were collected by means of Renishaw inVia Raman Microsope (Renishaw, Inc., New Mills, UK) that was equipped with diode excitation laser with the wavelength of 514 nm and 2400-lines grating. All Raman spectra were subjected to smoothing and baseline subtraction procedures using Renishaw software.

X-ray photoelectron spectroscopy (XPS) investigations utilized PREVAC EA15 hemispherical electron energy analyzer with 2D multi-channel plate detector. The samples were irradiated with an energy of 1486.60 eV provided by an Al-Kα X-ray source (PREVAC dual-anode XR-40B source). The system base pressure was 5×10^{-8} Pa. 200 eV pass energy was set for survey spectra (scanning step 0.9 eV) while 100 eV pass energy was set (scanning step 0.05 eV) for particular energy regions. All of the spectra were taken with normal take-off angle.

The energy scale of the analyzer was calibrated to Au 4f$_{7/2}$ (84.0 eV) [24] and fitted utilizing CASA XPS® embedded algorithms and relative sensitivity factors. For background subtraction the Shirley function was used. If not specified in text, the components were represented by a product of Gaussian (70%) and Lorentzian (30%) lines.

2.4. Singlet oxygen photogeneration

Singlet oxygen photogeneration by the deposited PAA_C_{60}/ITO layer was investigated using 0.05 mM solution 2,3,4,5-tetraphenylcyclopentadienone (TPCPD) specific $^1O_2$ chemical quencher in dichloromethane [25]. The progress of the reaction, given as a drop in the absorbance of TPCPD at 500 nm, was monitored by means of Hewlett Packard 8452A UV–Vis spectrometer. The standard 10 mm x 4 mm quartz cuvette (Hellma Analytics) applied in these measurements was arranged as a thin layer cell possessing a cavity of 10 mm pathlength and thickness of 2 mm. This cavity was created between the cuvette wall and the modified ITO electrode, which was fitting the size of the cuvette. 100 W xenon lamp was employed as an excitation light source. The set up was arranged in the same way as in our previous works [26]. Prior to measurements the modified ITO/glass substrates were immersed in chloroform for 15 min in order to remove any unbound photoactive species.

2.5. Photooxidation of α-terpinene

Freshly prepared photoactive layer was then applied as a source of singlet oxygen in the oxidation of α-terpinene (TER) in chloroform, resulting in the formation of ascaridole, i.e. commonly used anthelmintic drug (Fig. 1).

The progress of the reaction was monitored similarly as in the case of TPCPD. 100 W xenon lamp, with or without optical filters (350 nm or 600 nm) was employed as an excitation light source. The yield of photooxidation reaction, thus the singlet oxygen generation, was determined based on the decrease in the absorption of α-terpinene at 270 nm. The initial concentration of TER was 0.05 mM. Since the oxidation of TER with singlet oxygen is selective [27,28], any decrease in the bulk concentration of α-terpinene is a result of its reaction with singlet oxygen, the photooxidation kinetics have been investigated [28]. The concentration of α-terpinene at the given time was found applying Lambert-Beer's law for the absorption maximum at 270 nm ($\varepsilon_{terpinene} = 21900 \ M^{-1}cm^{-1}$ in chloroform). Additionally, the yield of singlet oxygen photogeneration by Azure A and C_{60} present in the solution was determined.
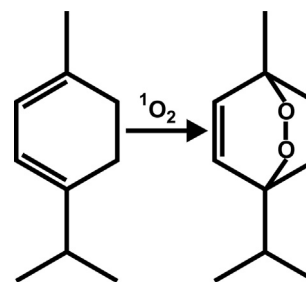

Fig. 1. Scheme of α-terpinene photooxidation by singlet oxygen.