

Formation of poly(Azure A)- C₆₀ photoactive layer as a novel approach in the heterogeneous photogeneration of singlet oxygen

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Abstract

Fullerene, C₆₀ 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_C₆₀/ITO) was characterized by means of cyclic voltammetry, UV-Vis, Raman and X-ray photoelectron spectroscopies. It was shown that PAA_C₆₀/ITO exhibits strong absorption in both UV and Vis regions and that both immobilized photosensitizers, *i.e.* Azure A and C₆₀, retain their photochemical activity towards ¹O₂ generation under illumination as tested with 2,3,4,5-tetraphenylcyclopentadienone (TPCPD) singlet oxygen quencher. The electrodeposited photoactive layer composed of two photosensitizers was investigated as a source of ¹O₂ in the process of α -terpinene oxidation.

Keywords

photoactive layers, singlet oxygen photogeneration, phenothiazines, fullerene, photosensitizers' immobilization

1. Introduction

Singlet oxygen ¹O₂, *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

33 and electrophilicity, but also in its lower stability [3]. Singlet oxygen can be formed in the
34 photoinduction process, where the appropriate photoactive molecule is excited from ground
35 state, S_0 , to form lowest excited singlet state S_1 , by light illumination generally in one-photon
36 transition. In the next step, the photosensitizer's triplet state with longer lifetime, T_1 , is
37 formed in the intersystem crossing process. The photosensitizer being in the triplet state
38 can react either *via* Type I mechanism, *i.e.* hydrogen-atom abstraction or electron-transfer
39 with substrates, producing free radicals that in the reaction with oxygen give ROS like
40 superoxide radical anion, or *via* Type II mechanism, *i.e.* an energy transfer occurring in the
41 collision of the excited photosensitizer with 3O_2 molecules [1]. Many groups of compounds
42 able to generate singlet oxygen are known: dyes and aromatic hydrocarbons, porphyrines
43 and tetrapyrroles, transition metals complexes, semiconductors oxides and carbon-based
44 nanostructures, *i.e.* fullerenes, nanotubes and graphene [3–5]. The photosensitizing abilities
45 of those carbon allotropes have been studied mainly in the bulk, though it has been
46 demonstrated that fullerenes and carbon nanotubes, when deposited from the solution with
47 polystyrene used to increase the adhesion with the solid support are able to generate singlet
48 oxygen molecule upon illumination [6–8]. The yield of singlet oxygen photogeneration by C_{60}
49 molecule is very high, but its practical use is limited, since it absorbs mainly in UV region.
50 This can be overcome by an introduction of organic moiety absorbing in the lower energy
51 visible region, either in the form of polymeric matrix or covalently attached organic chain [9–
52 11]. When conducting polymers are considered, fullerenes, graphene and carbon nanotubes
53 can be non-covalently incorporated into polymer matrix by electro-co-deposition from the
54 solution of monomer and carbon nanostructures, forming the layer of nanocomposite on the
55 electrode's surface. Such approach has been already reported for polypyrrole or
56 polythiophenes [12–16].

57 The lifetime of singlet oxygen in the diluted gas phase is relatively long, but due to the
58 molecular interactions it is shortened, for example to about 4 μs in water. Thus, 1O_2 has to
59 be generated *in situ* in the reaction mixture with photosensitizer present in the solution or
60 on the solid support. Since the heterogeneous photocatalysis possesses several advantages
61 over homogenous approach, like ease of operation or easier product separation and
62 purification steps, high attention is paid nowadays on developing methods of photoactive
63 molecules immobilization, so that new solid materials capable of singlet oxygen

64 photogeneration are formed. It is important, that in many cases only thin photoactive layer
65 deposited on the solid support is effective enough to ensure high yield of $^1\text{O}_2$ generation in
66 Photodynamic Therapy (PDT), fine chemicals' synthesis or wastewater treatment [3,17–20].
67 Our group has recently shown that organic thin films of phenothiazine can be immobilized
68 on the solid surface by electrochemical polymerization or electrochemical reduction of the
69 diazonium salts. Such surfaces were able to generate the active singlet oxygen in the
70 reaction mixture, leading to the oxidation of 1,3-diphenylisobenzofuran (DPBF) or phenol
71 [21–23].

72 In this work, thin photoactive layer containing two types of photosensitizers, *i.e.* fullerene
73 C_{60} and Azure A, was electro-co-deposited on ITO/glass substrate. The main aim of such
74 approach was to combine the high photosensitizing properties of both C_{60} and AA in order to
75 form heterogeneous photocatalyst that utilizes broader range of light wavelength to
76 produce singlet oxygen molecule. The presence of fullerene and Azure A molecules in the
77 deposited layer is confirmed by means of electrochemical and spectroscopic methods. The
78 singlet oxygen photogeneration by poly(AA)- C_{60} film was investigated with the TPCPD –
79 specific $^1\text{O}_2$ - quencher and in the process of α -terpinene oxidation.

80

81 **2. Experimental**

82 **Materials**

83 Azure A (AA) (purity >90%) and fullerene C_{60} (purity 99,99%) were purchased from Sigma
84 Aldrich and Across Organics, respectively. Tetrabutylammonium tetrafluoroborate (TBABF_4),
85 with or without camphorsulfonic acid (both of purity 99%, Sigma Aldrich) in
86 dichloromethane (HPLC grade, Sigma Aldrich) was used as an electrolyte for the
87 electrochemical deposition and characterization of the photoactive layer. 2,3,4,5-
88 tetraphenylcyclopentadienone (TPCPD) (Acros Organics) in dichloromethane was used as a
89 specific $^1\text{O}_2$ quencher. α -Terpinene (TCI, purity 90%) in chloroform (Chempur, distilled prior
90 to use) was employed as a substrate in the photooxidation reaction.

91 **Electrochemical deposition of PAA- C_{60} on ITO/glass substrate**

92 The electrochemical measurements were carried out using CHI 660C electrochemical
93 workstation (CH Instruments Inc.). A conventional three-electrode system was employed
94 with the ITO/glass electrode (DELTA Technologies Ltd) acting as a working electrode. The
95 surface of ITO/glass was rinsed with acetone and dichloromethane prior to use. Ag-wire
96 served as a pseudoreference electrode and glassy carbon (GC) rod was applied as a counter
97 electrode. The electrodes mounted in Teflon holder were placed in the electrochemical cell.
98 The electrochemical polymerization of AA was conducted by means of cyclic voltammetry
99 (CV) within the potential range (0 ; 1.2) V at the scan rate 0.1 V/s. The process was carried
100 out in 0.2 M TBABF₄ / dichloromethane solution with camphorsulfonic acid (0.1 mM) acting
101 as a source of protons. The concentration of AA and C₆₀ was equal to 1 mM and 0.1 mM,
102 respectively.

103 **Electrochemical and spectroscopic characterization of PAA_C₆₀ layer deposited on** 104 **ITO/glass substrate**

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

108
109 UV-Vis spectra of ITO electrode modified with PAA_C₆₀/ITO were collected using Hewlett
110 Packard 8452A UV-Vis spectrometer. Comparatively, UV-Vis spectra of 0.1 mM C₆₀ solution
111 in dichloromethane and PAA/ITO film were recorded.

112
113 Raman spectra of the freshly prepared layers and solid C₆₀ were collected by means of
114 Renishaw inVia Raman Microscope (Renishaw, Inc., New Mills, UK) that was equipped with
115 diode excitation laser with the wavelength of 514 nm and 2400-lines grating. All Raman
116 spectra were subjected to smoothing and baseline subtraction procedures using Renishaw
117 software.

118
119 X-ray photoelectron spectroscopy (XPS) investigations utilized PREVAC EA15 hemispherical
120 electron energy analyzer with 2D multi-channel plate detector. The samples were irradiated
121 with an energy of 1486.60 eV provided by an Al-K α X-ray source (PREVAC dual-anode XR-40B
122 source). The system base pressure was 5x10⁻⁸ Pa. 200 eV pass energy was set for survey

123 spectra (scanning step 0.9 eV) while 100 eV pass energy was set (scanning step 0.05 eV) for
124 particular energy regions. All of the spectra were taken with normal take-off angle.

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

129 **Singlet oxygen photogeneration**

130 Singlet oxygen photogeneration by the deposited PAA_C₆₀/ITO layer was investigated using
131 0.05 mM solution 2,3,4,5-tetraphenylcyclopentadienone (TPCPD) specific ¹O₂ chemical
132 quencher in dichloromethane [25]. The progress of the reaction, given as a drop in the
133 absorbance of TPCPD at 500 nm, was monitored by means of Hewlett Packard 8452A UV-Vis
134 spectrometer. The standard 10 mm x 4 mm quartz cuvette (Hellma Analytics) applied in
135 these measurements was arranged as a thin layer cell possessing a cavity of 10 mm
136 pathlength and thickness of 2 mm. This cavity was created between the cuvette wall and the
137 modified ITO electrode, which was fitting the size of the cuvette. 100 W xenon lamp was
138 employed as an excitation light source. The set up was arranged in the same way as in our
139 previous works [26]. Prior to measurements the modified ITO/glass substrates were
140 immersed in chloroform for 15 minutes in order to remove any unbound photoactive
141 species.

142 **Photooxidation of α-terpinene**

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

146 **Figure 1**

147 The progress of the reaction was monitored similarly as in the case of TPCPD. 100 W xenon
148 lamp, with or without optical filters (350 nm or 600 nm) was employed as an excitation light
149 source. The yield of photooxidation reaction, thus the singlet oxygen generation, was
150 determined based on the decrease in the absorption of α-terpinene at 270 nm. The initial
151 concentration of TER was 0.05 mM. Since the oxidation of TER with singlet oxygen is

152 selective [27,28], any decrease in the bulk concentration of α -terpinene is a result of its
153 reaction with singlet oxygen, the photooxidation kinetics have been investigated [28]. The
154 concentration of α -terpinene at the given time was found applying Lambert-Beer's law for
155 the absorption maximum at 270 nm ($\epsilon_{\text{terpinene}} = 21900 \text{ M}^{-1}\text{cm}^{-1}$ in chloroform). Additionally,
156 the yield of singlet oxygen photogeneration by Azure A and C_{60} present in the solution was
157 determined.

158

159 **3. Results and discussion**

160

161 **3.1. Electrochemical deposition of PAA_ C_{60} layer on ITO/glass substrate**

162 The electrochemical polymerization of phenothiazine derivatives, resulting in the formation
163 of the polymeric layer on the solid surface, have been already widely discussed in the
164 literature. The amine-derivatives of phenothiazine, like Azure A (AA), are commonly
165 electropolymerized from an aqueous solution and it has been shown that, similarly to the
166 mechanism of aniline electropolymerization, the acidity of the solution has strong effect on
167 the forming layer [29,30]. In this work, poly(Azure A) film with embedded C_{60} nanostructures
168 was electrodeposited from the non-aqueous medium with camphorsulfonic acid acting as a
169 source of protons. CV curve recorded for ITO/glass substrate as a working electrode is given
170 in Figure 2. The reversible redox couple characteristic for AA monomer deprotonation
171 (Figure 3 A to B) is observed at around 0.3 V, while its irreversible oxidation (Figure 3 B to C)
172 occurs at 1.2 V [30]. The latter results in the formation of the radical cation and, in
173 consequence, in the elongation of the polymeric chain (Figure 3D)[29,31] that deposits on
174 ITO surface incorporating C_{60} nanostructures. The electro-co-depositing organic layer
175 (PAA_ C_{60}) reveals reversible redox couple centred at 0.4 V characteristic for poly(Azure A)
176 with current increasing in the consecutive scans, which suggests the build-up of the
177 electroactive species on the working electrode surface [29,32].

178 **Figure 2**

179 **Figure 3**

180 **3.2. Electrochemical and spectroscopic characterization of PAA_ C_{60} /ITO**

181 *Cyclic voltammetry*

182 The structure of the electro-co-deposited organic layer was investigated by the
183 electrochemical and spectroscopic techniques. The CV curves recorded for PAA_C₆₀/ITO in
184 the pure electrolyte solution (Figure 4) reveal the presence of three redox couples centred at
185 -0.1 V, -0.7 V and -0.9 V vs. Ag. The first redox couple can be attributed to the reversible
186 reduction of PAA layer (Figure 4 inset). The quasi-reversible redox couples recorded at lower
187 potentials, i.e. at -0.7 and - 0.9 V, comes from the reduction of C₆₀ nanostructures
188 incorporated in the organic matrix to form C₆₀^{•-} and C₆₀²⁻, respectively, and are in agreement
189 with the signals recorded for fullerene solution with bare ITO electrode [33,34].

190 **Figure 4**

191 *UV-Vis spectroscopy*

192 UV-Vis spectra recorded for deposited photoactive layer (PAA_C₆₀/ITO) is given in the Figure
193 5. Three distinctive absorption bands are observed with maxima at 275 nm, 323 nm and 600
194 nm. The incorporation of C₆₀ nanostructures into formed layer is confirmed by the presence
195 of its characteristic band at 323 nm, which is recorded at 329 nm in the C₆₀ solution [35]. The
196 bands at 275 and 600 nm can be attributed to poly(Azure A) film. Since C₆₀ photosensitizer
197 absorbs mainly in the UV region, its incorporation into PAA matrix (which absorbs strongly in
198 visible region [32,36]), should result in better utilization of incident light in the ¹O₂-
199 photogeneration process.

200 **Figure 5**

201 *Raman Spectroscopy*

202 The Raman spectra recorded for the organic coating modifying ITO surface is given in the
203 Figure 6. The signal located at 1460 cm⁻¹ observed for PAA_C₆₀ layer can be attributed to
204 fullerene pentagonal pinch mode [37,38]. The signals arising from PAA polymeric layer are in
205 agreement with those recorded for pure PAA film: the band corresponding to the
206 phenothiazine ring C-C stretching is observed at 1619 cm⁻¹, the signal at 1375 cm⁻¹ arises
207 from symmetric C-N-C stretching vibrations, the band corresponding to C-S-C vibrations in
208 phenothiazine core is observed at 903 cm⁻¹ and the signal of C-N stretching of amine group is
209 located at 1486 cm⁻¹ [39]. Moreover, the presence of the band at 1425 cm⁻¹ arising from the
210 asymmetric stretching vibrations of C=N bond in the central ring, which is characteristic for

211 presence of quinoid ring and at 1476 cm^{-1} , which is attributed to vibrations of C=C in the
212 quinoid rings [40], indicate that poly(Azure A) is in its oxidized form absorbing strongly in
213 visible region, as shown in Figure 5, which should ensure high utilization of light in the
214 process of singlet oxygen photogeneration [26].

215 **Figure 6**

216 *X-ray Photoelectron Spectroscopy*

217 Consecutively, the structure of the deposited organic layer was analyzed by means of XPS.
218 The survey spectra recorded for the bare ITO substrate, PAA/ITO and for PAA_C₆₀/ITO layers
219 are presented in the Figure 7. In the case of the unmodified substrate, signals arising from
220 the indium-tin oxide layer, *i.e.* Sn3p at 715 eV, In3d_{3/2} at 664 eV and O1s at 530 eV, and C1s
221 signal at 285 eV coming from the adventitious carbon, are observed [41–43] After the
222 deposition of polymeric layer with or without carbon nanostructures on ITO substrate,
223 additional N1s and S2p signals appear in the recorded spectrum at 400 eV and 164 eV,
224 respectively. Survey scan registered for PAA/ITO surface revealed lower C1s/N1s signals'
225 ratio, as it was expected due to fullerene contribution in the case of PAA_C₆₀ layer.

226 **Figure 7**

227 **Figure 8**

228 The high-resolution spectra (Figure 8) recorded for PAA_C₆₀/ITO surface provide more
229 details on the structure of the deposited organic layer. The components' full width at half
230 maximum (FWHM) values for the peaks at the same binding energy region were allowed to
231 vary within a narrow range to obtain acceptably low residual values. The estimated
232 uncertainty for components' energy position determination was 0.09 eV.

233 Five components with maxima at 285.2 eV, 286.0 eV, 286.5 eV, 287.0 eV and 289.0 eV can
234 be distinguished in the C1s high-resolution spectrum (Figure 8A) and can be assigned to C-
235 C/C=C, C-S, C-N, C-O and C=O, respectively [44]. The first signal arises from the modifying
236 PAA_C₆₀ layer and partially from attenuated adventitious carbon contribution present on the
237 ITO substrate. C-S and C-N components, which are in stoichiometric 1:3 ratio, comes from
238 poly(Azure A) matrix, while the carbon-oxygen components, C-O and C=O are the residuals
239 from the adventitious contamination layer [42].

240 The presence of the phenothiazine unit on the surface is also confirmed by the appearance
241 of the characteristic N1s signals at 399.7 and 401.8 eV (Figure 8B) coming from N-H and C=N-
242 C bonds present in Azure A molecule [23,45]. Moreover, since in S2p region two components
243 (with their spin-orbit split subcomponents) can be distinguished [46], it may be stated that
244 polymeric matrix in PAA_C₆₀ layer exists in the partially oxidized form after
245 electrodeposition.

246

247 **3.3. Photogeneration of singlet oxygen**

248 *Chemical quenching of singlet oxygen*

249 There are several methods for the detection of singlet oxygen based on the indirect
250 measurements in which chemical traps are applied [25,47]. In this work we have applied
251 2,3,4,5-tetraphenylcyclopentadienone (TPCPD) as specific ¹O₂ chemical quencher, which
252 unlike commonly used 1,3-diphenylisobenzofuran (DPBF) trap is stable under white light
253 illumination. Figure 9 presents the UV-Vis spectra of TCPD in CH₂Cl₂ recorded in time with
254 ITO unmodified or modified with PAA_C₆₀ layer. As it can be seen, clear decrease in the
255 absorption band at 500 nm with time is observed for PAA_C₆₀/ITO layer and no decrease for
256 bare ITO, which indicates photoactivity of the deposited layer towards singlet oxygen
257 photogeneration.

258 *Photooxidation of α-terpinene*

259 In the next step, the photoactive layer composed of Azure A and C₆₀ photosensitizers have
260 been investigated as a source of singlet oxygen in the photooxidation of α-terpinene (Figure
261 1). The progress of this photooxidation reaction can be monitored by UV-Vis spectroscopy as
262 the decrease in α-terpinene absorption at 270 nm [28]. Since PAA and C₆₀ photosensitizers
263 incorporated into PAA_C₆₀ coating absorb in UV or Vis region, respectively, xenon lamp was
264 used as a source of light. Figure 10A shows UV-Vis spectra of α-terpinene recorded in the
265 course of illumination of PAA_C₆₀ layer.

266 **Figure 10**

267 The clear decrease in α-terpinene absorption at 270 nm is observed, indicating drop in its
268 concentration due to the reaction with the singlet oxygen [20,48]. Since almost no drop in

269 the absorption of α -terpinene is observed during illumination of bare ITO (Figure 10B), the
270 self-decomposition of TER is excluded. Importantly, the decrease in the concentration of α -
271 terpinene during 25 minutes of the process is much higher for PAA_C₆₀/ITO than for pure
272 PAA/ITO layer, which confirms the assumed better usage of incident light in the
273 photogeneration process. Additionally, when PAA_C₆₀/ITO coating is illuminated by xenon
274 lamp equipped with either 350 nm or 600 nm filters, the clear drop in TER concentration is
275 observed in time (Figure 10B inset), confirming that both photosensitizers retain their
276 photoactivity after immobilization and are able to generate ¹O₂ in the tested photooxidation
277 reaction.

278 The rate constant of the photooxidation of α -terpinene was determined based on the
279 decrease in its concentration in time. The plot of ($C_{\text{terpinene}} - C_{\text{terpinene, initial}}$) as a function of
280 time gives the straight line, which indicates zero-order reaction under applied conditions
281 [28]. The slope of the line, i.e. the rate constant, determined by the linear regression is equal
282 to $2.50 \cdot 10^{-3} \text{ mM}^{-1} \text{ min}^{-1}$. It was also found that the synthesized organic-C₆₀ layer maintain its
283 photoactivity after usage and can be re-used in the consecutive photooxidation reactions. As
284 it is commonly observed [48,49], the rate of singlet oxygen photogeneration is lower for the
285 immobilized Azure A and C₆₀ photosensitizers, than in the case when they are present in the
286 solution (Figure 10B). However, as already mentioned, for the application in fine chemicals'
287 synthesis the heterogeneous photocatalysis possesses several advantages over homogenous
288 approach [49].

289 4. Conclusions

290 In the presented work, two photosensitizers – Azure A and C₆₀, deposited onto ITO/glass
291 substrates were applied as source of singlet oxygen in the photooxidation of α -terpinene.
292 The proposed straightforward strategy of the electrochemical co-deposition of organic
293 monomer and C₆₀ on the ITO/glass surface results in the stable photoactive layer, which
294 structure was confirmed with electrochemical and spectroscopic measurements. Obtained
295 within presented procedures PAA_C₆₀ layer can be activated by both UV and Vis radiation to
296 generate ¹O₂ molecule in the reaction of α -terpinene oxidation. The deposited two-
297 photosensitizer coating generates singlet oxygen with higher effectiveness than one-
298 component organic layer and thus can be considered as an attractive alternative in the
299 heterogeneous reactions of the fine chemicals' synthesis under daylight illumination.

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