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The First Products of Aniline Oxidation – SERS Spectroelectrochemistry

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There are different opinions on the first products of aniline oxidation throughout the scientific community. While electrochemists basically accept only linear oligomers with repeating units joint in para positions, chemists have proposed formation of various branched and polycyclic oligomers. It was also suggested that one of these structures, N-phenyl-phenazinium cation, is responsible for the adherence of polyaniline films to substrates. In this work, a surface enhanced Raman spectroscopic and spectroelectrochemical analysis of the species adsorbed onto gold surface in aniline-containing solution at pH 1 and 5 is presented. The influence of the pH value on the oligomer structure is declared. The results are discussed in the context of linear and branched/phenazine-like aniline oligomers.

Introduction

Polyaniline (PANI) is a popular conducting polymer due to its ease of preparation, good level of electrical conductivity, redox and ion-exchange properties, and environmental stability.[1,2] Its ability to form thin films and nanostructures enhances the potential field of PANI use even further.[3] Such films are obtained on electrodes by electrochemical polymerization of aniline[4] or by in-situ surface chemical polymerization.[5,6]

Scientists, who work with PANI, fall in two groups that never meet – electrochemists and chemists. Neither meet their views on the PANI films formation. Chemically prepared PANI films are reported to contain a layer of ortho-coupled oligomers (o-AO, Figure 1 a),[7,8] although they sometimes are too thin to detect.[9] Chemists believe these oligomers are necessary for the film formation because they have been observed in every film-formation study[10,11] with only one exception.[12] Here though the conclusion was drawn that the oligomer layer is just too thin to be detected.

Chemical oxidation of aniline is typically started at mildly acidic medium, where ortho-linking is possible.[8,13–15] As reaction proceeds, the pH decreases, and eventually the regime of exclusive para-linking polymer chain growth is reached.[13]
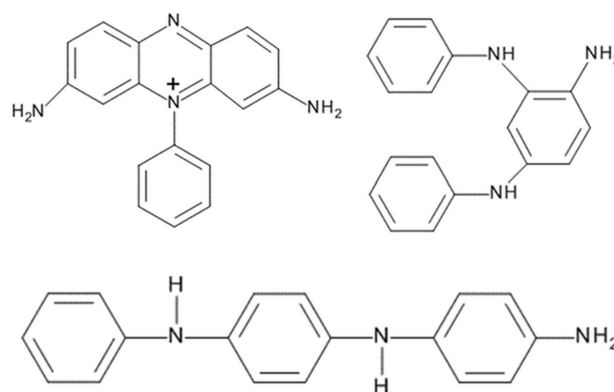

Figure 1. Examples of chemical structures of ortho-linked aniline oligomers (top) and linear para-linked aniline trimer in its leucoemeraldine form (bottom).

Electrochemists, on the other hand, expect only para-linked linear oligomers (p-AO, Figure 1 b) to be formed.[4,16,17] Consequently, only aniline dimerization was found worth studying by the electrochemists.[4,15,16,18–20] For electrochemical aniline oxidation, there is just one paper reporting a Raman spectrum of o-AO.[21] In this case, aniline oxidation was performed in neutral medium and PANI was not obtained.

Properties of the thin layer in direct contact with the substrate are difficult to study but the existence of a different layer between the substrate and the chemically prepared PANI film was proven by ellipsometry, Raman spectroscopy and X-ray photoelectron spectroscopy.[9,11,22] The molecular structure of o-AO is still widely discussed, various branched, quinonoid, benzoquinonoid and phenazine-like structures have been proposed.[7,8] In fact, o-AO is a mixture of species containing the above-mentioned structural units, however, N-phenyl-phenazinium cation based o-AO (Figure 1 a, first structure) are believed to be the ones responsible for film formation.[9]

Spectroscopic study of very thin layers requires a sensitive analytical technique. Surface enhanced Raman spectroscopy

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(SERS) is a logical choice also for its compatibility with electrochemical studies.[23] SERS of PANI has already been conducted on electrochemically prepared films[24,25] but the first products of aniline oxidation have not been studied this way. Bands of o-AO have been reliably distinguished only on PANI films prepared in situ chemically in neutral medium on flat gold substrate.[9]

In this work, we aim to analyze the first products of electrochemical aniline oxidation and prove or disprove the N-phenyl-phenazinium cation theory by searching for the specific N-phenyl phenazinium cation spectral profile under various electrochemically reachable conditions, and by the method previously found effective at detecting them – SERS on gold substrates at 633 nm excitation.

Results and discussion

Adsorption of aniline at pH 1

The SERS electrode was immersed into aqueous solution containing 0.05 mM aniline, 0.1 M sulfuric acid and 0.01 M p-toluene sulfonic acid at pH 1 (electrolyte-1). Just after completing the spectroelectrochemical cell with electrolyte-1, without applying any potential, surface enhanced Raman signal on the SERS electrode was observed (Figure 2 – black spectra, Table 1). (In a corresponding experiment with flat gold electrode, no signal was observed. The SERS substrate may be the source of oxidation in this process.) The spectra correspond to linear aniline oligomers (p-AO) in their emeraldine-like form (Figure 3) formed by coupling of monomers in the para-positions (p-AO are often used in quantum mechanical calculations as model molecules of polyaniline chain[26–31]) and aniline monomer[32] (Table 1).

The formation of linear oligomers manifests itself by the appearance of characteristic bands at 1615, 1335, 1230, 1175, 860, 805, 713, 505, 407 and 370 cm^{-1} in the Raman spectrum of the adsorbed layer excited at 633 nm and at 1625, 1340, 1240, 1190, 880, 820, 725, 527, 430 and 370 cm^{-1} in the Raman spectrum of the adsorbed layer excited at 785 nm.

Only minor changes were observed in the spectrum after washing with distilled water and introduction into aqueous solution of 0.1 M sulfuric acid and 0.01 M p-toluene sulfonic acid at pH 1 (electrolyte-2). The adsorbed material remained the same (Figure 2 – red spectra). The minor changes are most probably due to oxidation of aniline by air and photo-oxidation during the process of washing and electrolyte change.

Photo-oxidation

Oligomers were found on the SERS electrode even before any potential was applied. Aniline could be oxidized either photochemically by the laser irradiation and ambient light, or by a chemical oxidant present in the system – the fresh SERS electrode. The influence of photo-oxidation is important to study also for determination of the influence of laser irradiation on the sample during the experiment. It was investigated at pH 1 for both laser excitations (633 nm and 785 nm). A spot on
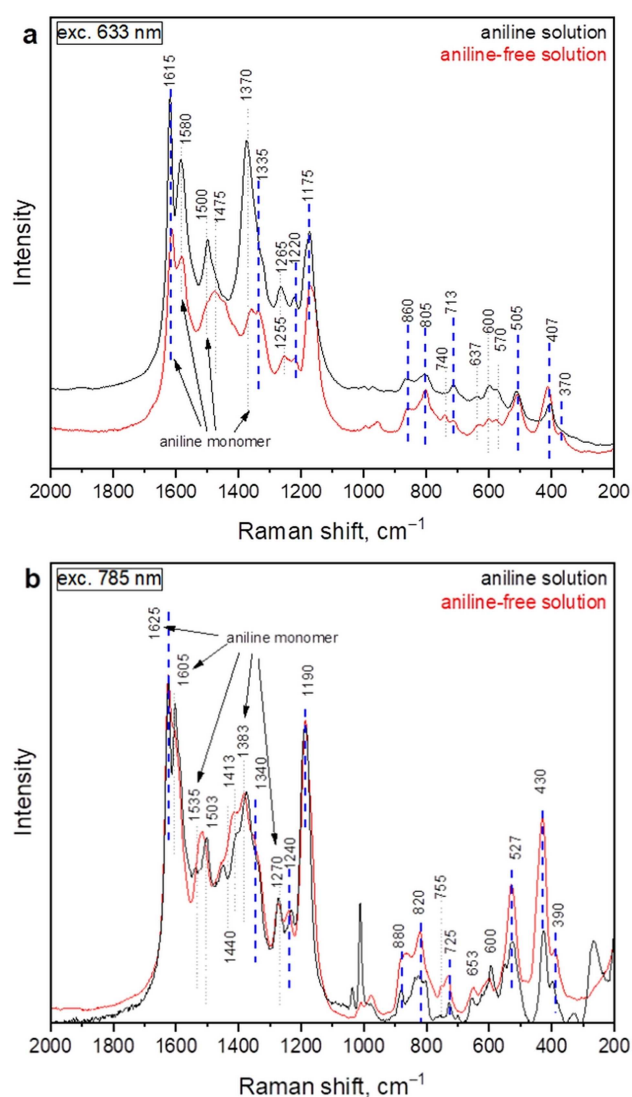
Figure 2. Raman spectra of material adsorbed on gold SERS electrode without application of potential, excited with 633 nm (a) and 785 nm (b) wavelength. Bands typical for p-AO are marked with blue lines.
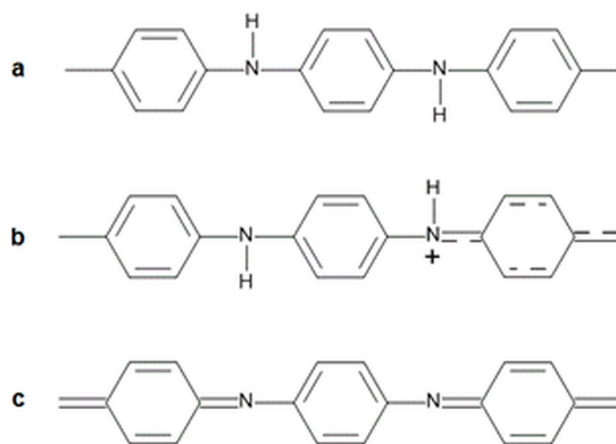
Figure 3. Neutral benzenoid (a), charged semiquinonoid (b) and quinonoid (c) form of p-AO.

Table 1. Summary of Raman band positions (excitation with 785 nm (black) and 633 nm (red) laser lines).

Adsorbed layer — pH 1 at OCP	Adsorbed layer — pH 5 at OCP	Layer adsorbed at pH 1 — Reduced	Layer adsorbed at pH 1 — Oxidized	attribution	references
		Band position [cm⁻¹]			
390	380	–	–	$\gamma(ring)_Q$ (**p-AO**, monomer)	30–32
370	370	–	–		
430	425	425	425	H_2SO_4, $\gamma(C–H)_Q$ (**p-AO**)	30,31,45
407	413	405	402		
–	–	–	–	$\gamma(ring)_{BQ,Q,P}$ (**o-AO**)	37,46–48
–	440	–	445	$\gamma(ring)_{SQ,Q}$, $\tau(C–N–C)$ (**p-AO**)	30,31,46,47
527	530	535	525		
505	530	–	508		
–	–	–	–	H_2SO_4, $\gamma(ring)_P$ (monomer, defects)	45,49
570	560	570	575	$\gamma(ring)_{B,SQ}$ (all structures, **o-AO**)	26–31,50
600, 653	620	–	597		
600, 637	603	605	–		
725	750	–	760	$\delta(C{=}N–C)_Q$ (o-AO, p-AO)	26,27
713	740	–	745		
820	–	813	815	$\delta(ring)_{SQ,Q}$ (p-AO, monomer)	26,27,29–32,39
805	800	–	795		
880	850	880	850	$\delta(N–H)$, $\delta(ring)$ (**p-AO**)	26–28,30,31
860	850	–	850		
1000	1000	1000	1000	H_2SO_4, $\delta(N–H)$, $\delta(ring)_{B,P}$ (**monomer, p-AO**)	27,29,32,45,51
1000	990,950/980	1000	950		
–	–	–	–	H_2SO_4, $\delta(C–H)_Q$ (**o-AO**)	37,45,48,52
–	1155	–	–		
1190	1167	1180	1205, 1182	$\delta(C–H)_{B,SQ,Q}$ (monomer, **p-AO**)	26,27,29–31,38,39
1175	1185	1170	1170		
1240	1233	1235	1233	$\nu(C–N)_B$ (o-AO, p-AO)	26,27,29,39,53
1220	1220	–	1215		
1270	1255	–	1288	$\nu(C–N)_Q$, $\delta(C–H)_B$ (**monomer**, p-AO, o-AO)	26,27,29–32,38
1255/1265	–	1250	1280		
–	1345	1340	1345	$\nu(C{\sim}N)$ L+• (**p-AO**)	29–32,37–39,48,52
1335	1340	1335	1357		
1385	1380	1370	1365	$\nu(C{\sim}N)$ D+• (o-AO, p-AO, **monomer**)	9,37,48,52
1370	1365	1364	–		
1413	–	1405	1405	$\nu(C{\sim}N)$ 2(+•) (o-AO, p-AO)	36,39,44
–	–	–	–		
1440	1450	1450	1455	$\delta(C–H)+\nu(ring)_{B,SQ}$ (o-AO, p-AO)	27,39
–	1450	1445	–		
–	1475	–	–	$\nu(C{=}N)$ (**o-AO**, p-AO in quinonoid form)	26,27,40
1475	1470	1475	1470	$\delta(N–H)$ (o-AO, p-AO, monomer)	26,29–32,38,39
1503, 1535	1507	1505	1495, 1520		
1500	1530	1507	–	$\nu(ring)_{B,Q,SQ}$ (o-AO, p-AO, **monomer**)	26,27,29,30,32,38,39
1605	1595	1595	1595		
1580	1580, 1595	1560, 1595	1555, 1580		
1625	–	–	1625	$\nu(ring)_B$ (B next to Q) (**p-AO, monomer**)	26,27,31,32,39
1615	1620	–	1620		

Abbreviations: BQ – benzoquinone-like rings, B – benzenoid ring, SQ – semiquinonoid ring, Q – quinonoid ring, P – phenazine-like ring, D+• – delocalized polaron, L+• – localized polaron, 2(+•) – pair of polarons, + + – bipolaron, ν – stretching vibration, δ – in-plane deformation vibration, γ – out-of-plane deformation vibration, τ – torsion vibration, ∼ – bond intermediate between single and double bond typical for SQ. Note: Although most of the bands appear in the spectra of more species, their intensities differ. Bands typical for a specific species are noted with bold font.
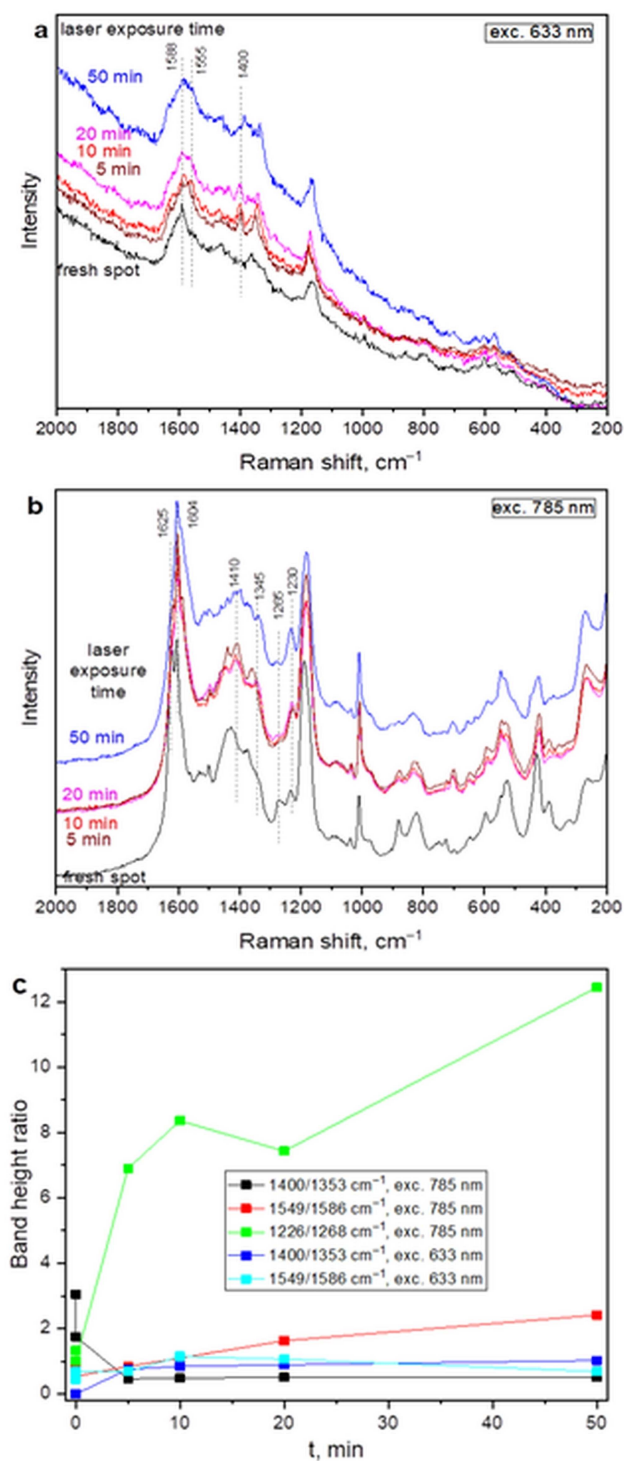
the SERS electrode immersed in electrolyte-1 was irradiated various times without any potential applied (Figure 4). Changes in the spectra (marked in Figure 4. a and b) are due to the oxidation of monomer to *p*-AO in their oxidized state (decrease of bands at 1549 and 1260 cm⁻¹, shift of intensity in the group of bands around 1600 cm⁻¹) and localization of present polarons (decrease of the band at 1353 cm⁻¹ accompanied by increase of the band at 1410 cm⁻¹) (Table 1, Figure 4c). It can be concluded that the photo-oxidation (both by laser irradiation and by ambient light during the electrolyte change) takes place but is not the major reason for the immediate oligomer formation. No sign of formation of azobenzene-based species, known product of photooxidation of aniline,[33] was detected.

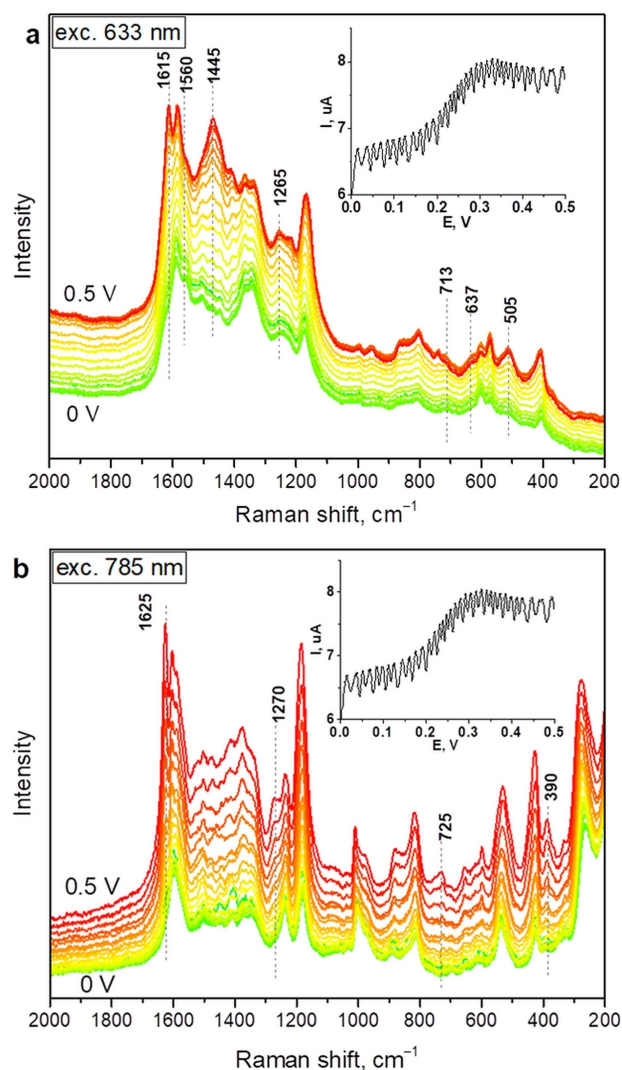## Spectroelectrochemistry of the adsorbed layer

The adsorbed layer was electrochemically reduced (when decreasing the potential from open-circuit voltage (OCP = 0.27 V) to 0 V) and then oxidized by potential sweep to 0.5 V in monomer-free electrolyte (electrolyte-2).

The value of OCP shows that the adsorbed layer is in oxidized state (Figure 3) because of the appearance of the

Figure 5. Raman spectra obtained during oxidation of the oligomer layer adsorbed on SERS electrode in monomer-free solution at pH 1, excited with 633 nm (a) and 785 nm (b) wavelength.

Figure 4. Raman spectra obtained on gold SERS electrode in monomer solution at pH 1 after indicated times of irradiation, excited with 633 nm (a) and 785 nm (b) wavelength and the time dependency of chosen band ratios (c).

oxidation peak at approx. the same potential in the cyclic voltammogram (CV) (Figure 5. Inserts). Desorption was not observed as the material remained strongly adhered to the electrode. However, the oligomer was transformed from its semiquinonoid form (observed at OCP and at higher potentials) to its reduced benzenoid form (observed at lower potentials) (Figure 3).[29,35] Figure 5 shows the transformation of neutral *p*-AO into semiquinonoid form during the oxidation process by appearance of the bands at 1625, 1270, 725, 390 cm^{-1} in the Raman spectrum excited with 785 nm laser line and 1615, 1445, 1265, 713, 637, 505 cm^{-1} and decrease of the band at 1560 cm^{-1} in the Raman spectrum excited with 633 nm laser line.

The connection between these changes represented by the intensity ratio of the quinonoid (1625 resp. 1615 cm^{-1}) and benzenoid (1595 resp. 1580 cm^{-1}) C—C stretching vibration bands and the oxidation peak around 0.3 V is shown in Figure 6. The potential was switched between 0 V and 0.35 V several times and, according to the Raman spectra, the process is reversible.
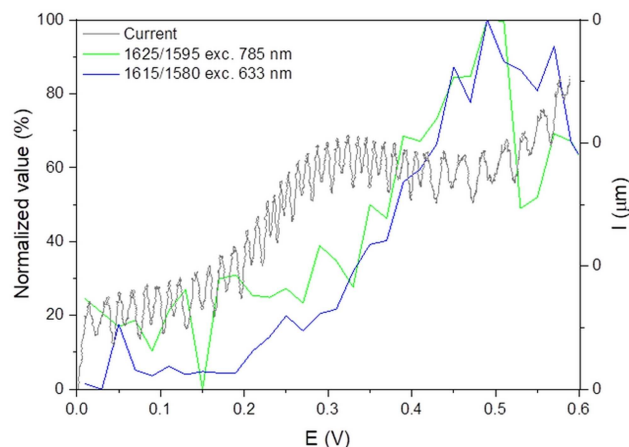
Figure 6. Potential dependence of the ratio of the intensity of the benzenoid-next-to-quinonoid ring stretching vibration band and the benzenoid ring stretching vibration band in leucoemeraldine-like structure.

The adsorbed layer was further oxidized by a potential sweep to 0.8 V in electrolyte-2 (Figure 7). Residual aniline monomer present at the electrode was oxidized as indicated by the appearance of the oxidation peak at 0.7 V in the CV and connected to the p-AO. The spectroscopic features show structural changes connected with oxidation of the adsorbed p-AO. If the monomers are oxidized and form oligomers, the characteristic bands of the aniline monomer (1615, 1270, 1000 cm^{-1}) get weaker, the band at 1000 cm^{-1} disappears completely. At high potentials, degradative over-oxidation of the p-AO layer takes place in addition to the growth of p-AO, as manifested by the appearance of Raman bands of C=N stretching vibration at 1485 cm^{-1}, decrease of the ring-stretching band of the benzenoid rings neighboring to the quinonoid rings at 1615 cm^{-1} together with strong increase of the quinonoid ring stretching band at 1580 cm^{-1} (Figure 5, Figure 6, Table 1), and a change in the baseline shape. This effect is well observed by the 633 nm excitation line due to the resonant enhancement of quinonoid structures (Figure 5 a, Figure 3).

In the electrolyte containing aniline monomer (electrolyte-1), the oxidation of aniline in the solution takes prominent part of the passed current (Figure 8), as can be seen when spectra obtained at the same potential (the plot with same color, shades of red correspond to potential region ca 0.5–0.7 V) in Figures 7 and 8 are compared. The transformation of p-AO to their quinonoid form manifested mainly by the strong band at 1485 cm^{-1} in the spectra excited with 633 nm laser line for the adsorbed layer is observed only as a weak band at 1465 cm^{-1} for oxidation in monomer solution.

Otherwise, the same structural changes connected with oxidation were observed as on adsorbed layer in monomer-free solution (Figure 5 and 7).

The results indicate that the first products of electrochemical oxidation of aniline at pH 1 are p-AO; and the o-AO: 1) do not form in an low pH electrochemical experiment under
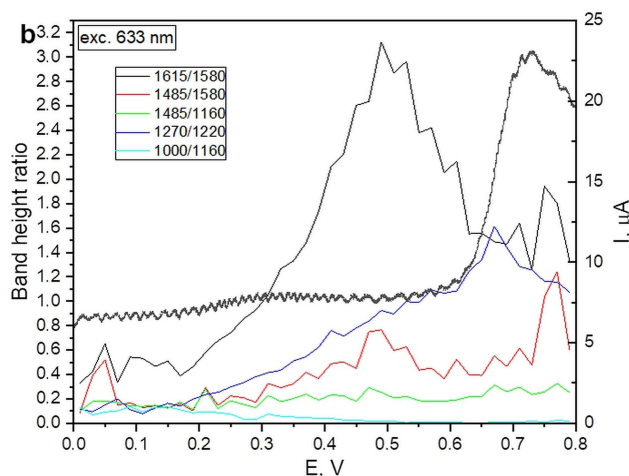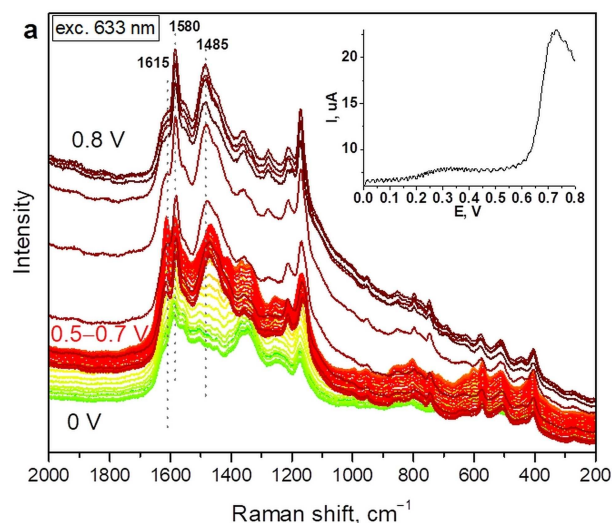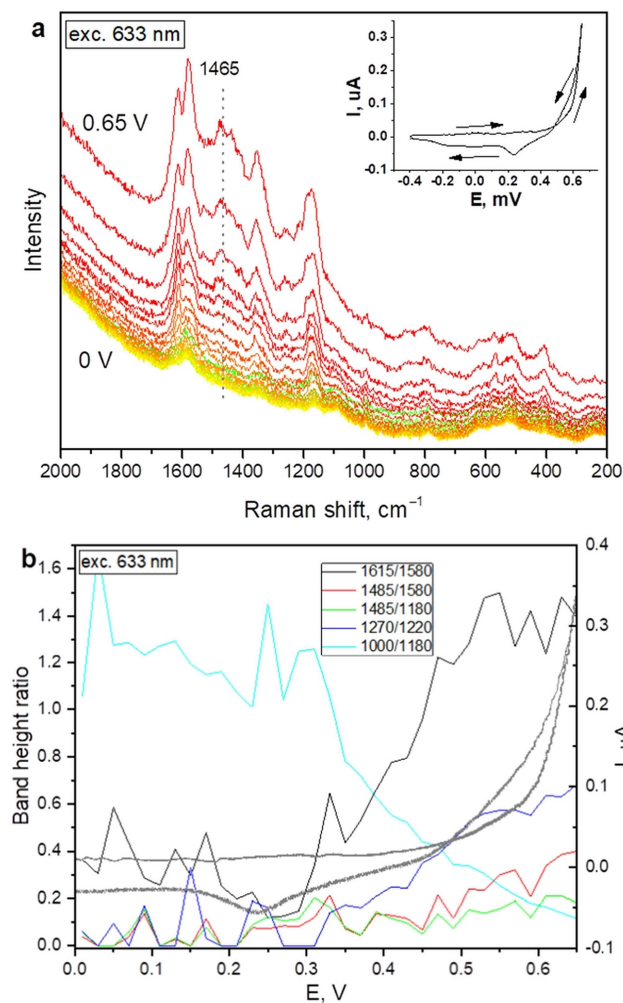

Figure 7. Raman spectra obtained during oxidation of aniline adsorbed on SERS electrode in aniline-free solution at pH 1, excited with 633 nm laser line (a) and the corresponding potential dependencies of selected band-ratios (b). Each spectrum has a fixed color connected with certain potential. Corresponding data obtained with 785 nm laser line can be found in supporting information (Figure S1 in Supporting information).

any potential and 2) are not necessary for PANI film-formation, as was postulated earlier.

Adsorption of aniline at pH 5

An oligomer layer is adsorbed on the electrode also in solution containing aniline, sulfuric acid and sodium hydroxide balanced to pH 5 (electrolyte-3). The typical bands of the o-AO known from chemically prepared PANI films[9] are clearly detected mainly with the 633 nm excitation (strong band of C∼N$^+$ stretching of localized charges at 1360 cm^{-1} dominates the spectrum and bands of medium intensity at 1470 and 600 cm^{-1} are observed) (Figure 9 a, black line), but also the Raman spectra obtained with the 785 nm excitation show similar spectral profile (Figure 9 b, black line). Raman bands of aniline monomer and p-AO are also detected (most typical of the monomer is the N–H bending at 1000 cm^{-1}). This experiment
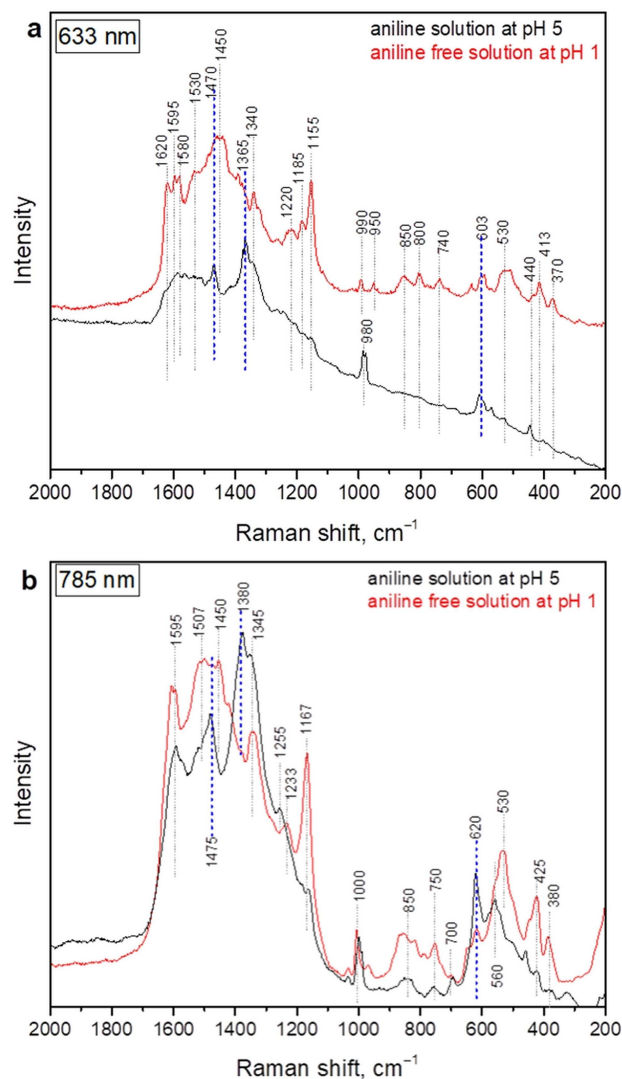
Figure 8. Raman spectra obtained during oxidation in aniline solution on SERS electrode at pH 1, excited with 633 nm laser line (a) and the corresponding potential-dependencies of selected band-ratios (b). Each spectrum has a fixed color connected with certain potential. Corresponding data obtained with 785 nm laser line can be found in supporting information (Figure S2 in Supporting information).

Figure 9. Raman spectra of material adsorbed on gold SERS electrode in monomer solution at pH 5 (electrolyte-3) measured without application of potential and after rinsing with water in electrolyte-2 (pH 1, without monomer), excited with 633 nm (a) and 785 nm (b) wavelength. Raman bands typical for o-AO are marked with blue lines.

proves that at higher pH, o-AO is formed, as in a chemical oxidation of aniline with strong oxidizing agent like persulfate.

After washing the electrode with adsorbed layer with water and introduction into the acidic electrolyte-2 for further analysis, the spectrum changes drastically. The band of $C \sim N^+$ stretching in structures carrying localized polaron[29,36,37] (1370/1375 cm^{-1}) decreases while bands connected with ring stretching[26,27,31,38] ($\sim$1580 cm^{-1}) and C–H deformation vibrations[26,27,29–31,38,39] (1170 cm^{-1}) typical of p-AO appear in the spectra. The band attributed to C≡N stretching in quinonoid structures[27,30,40] (1465 cm^{-1}) is increased. It appears that additional oxidation of available monomer takes place in the acidic medium after washing and p-AO in their semiquinonoid and quinonoid form appear in addition to o-AO.

The absence of o-AO features in the spectrum of the sample prepared at pH 1 (Figure 2) disproves the common

argument that the o-AO are just impurities coming from low-grade aniline reactant.

## The effect of acidity on the first products of aniline oxidation

The o-AO known from chemically prepared PANI films were not observed to participate in the electrochemical oxidation of aniline in acidic medium, even though we were specifically searching for these by a method previously found to be sensitive to them.[9] It can be concluded that o-AO are thus not necessary for the formation of PANI film.

To understand, why at certain conditions the aniline oxidation leads to p-AO and in other to o-AO, theoretical approach has been applied by the chemists.[14,41–43] Most of their

findings are, however, applicable also on the electrochemical oxidation of aniline.

First, aniline or anilinium cation has to be oxidized to aniline cation radical or aniline nitrenium cation.[15] Neutral aniline molecules are reported to be more easily oxidized than anilinium cations.[15] The anilinium cation is the dominant species in strongly acidic medium (pH < 1), in which electrochemical oxidation of aniline is typically conducted (pKa of aniline is 4.6), while significant amount of more reactive neutral aniline is present at pH 2.5 and above.[41–43]

Aniline dimerization was shown to proceed via electrophilic aromatic substitution on aniline or anilinium cation by aniline nitrenium cation or aniline cation radical, leading mainly to 4-aminodiphenylamine[14,16,42,43] (4-ADPA) (Figure 10). The reaction
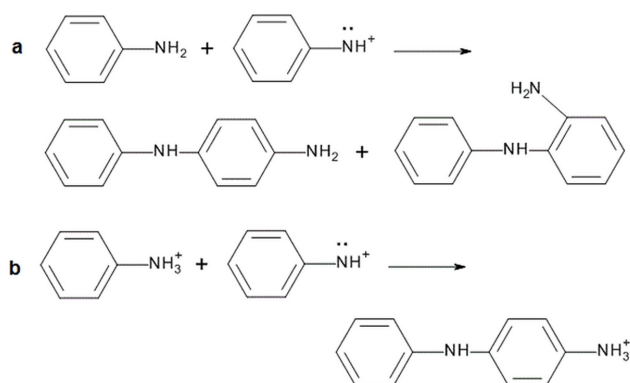
Figure 10. The formation of aniline dimers: (a) reaction of neutral aniline with nitrenium cation leads to both ortho-linked 2-ADPA and linear 4-ADPA; (b) reaction of anilinium cation with aniline nitrenium cation leads only to linear 4-ADPA.

is directed to ortho- and para- positions for neutral aniline, while the substitution at ortho-positions is deactivated by the protonation for anilinium cation[14] (acidic conditions). Nevertheless, even in neutral or alkaline conditions, 4-ADPA strongly dominates.[15]

Similar ortho-position deactivation takes place also for aniline oligomers. In the following step, i.e., trimer formation when the dimer structure reacts with monomer,[14,42,43] both branched and linear trimers are formed at comparable yields from neutral dimers, while only linear trimers form when the dimers are protonated (Figure 11).[14,15] The respective p-AO and o-AO formation is thus determined at the trimer-stage.

From the differences between the reactions of neutral and protonated species follows that the higher the concentration of neutral species, the higher the fraction of ortho-linkages.[8,43] As neutral species are present in higher concentrations at higher pH, the concentration of the ortho-linked structures is dependent on the acidity of the reaction medium in both chemical[8,13–15] and electrochemical oxidation of aniline (Figure 6 and 9) while the nature of the oxidant is of lesser importance. The results indicate that the electrochemical oxidation of aniline is driven by similar rules found for chemical
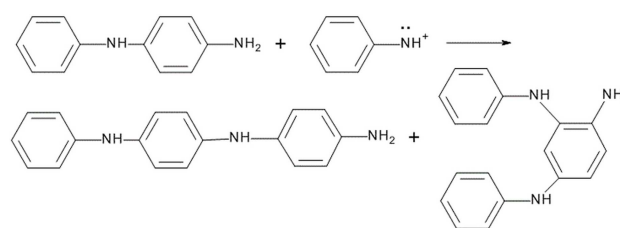
Figure 11. Reaction of neutral ADPA with aniline nitrenium cation leads to both linear and branched aniline trimers.

oxidation with ammonium peroxydisulfate, and the formation of o-AO cannot simply be rejected as never happening in an electrochemical experiment (Figure 8 and 9, Table 1). The formation of linear or branched oligomer structures clearly depends on acidity of the solution.

A PANI film without the o-AO can be obtained also by chemical oxidation of aniline if the substrate is induced into reaction medium when the reaction is already running in the chain-growth mode.[44] Thin films of material linked purely in para-positions are then obtained. However, this observation was previously misinterpreted, and the conclusion, that o-AO forms in "necessary" amount even in low pH, was drawn.[44]

Conclusions

In the strong acidic solution (pH < 1) containing aniline, an adsorbed layer of the monomer aniline molecules and linear aniline oligomers is formed on gold surface. The oligomers are formed by oxidation of the aniline monomers. The aniline molecules are most likely oxidized by the fresh SERS substrate. The formation of linear oligomers manifests itself by the appearance of characteristic bands in the Raman spectrum of the adsorbed layer. Oligomers in the adsorbed layer are in oxidized state. The adsorbed layer can be electrochemically reduced and re-oxidized. According to the Raman spectra, this process is reversible. No desorption of the layer takes place. Furthermore, by application of higher positive potentials, the adsorbed aniline molecules are incorporated into the oligomer molecules.

The first product of electrochemical oxidation of aniline under strong acidic conditions is a linear oligomer, and the linear strictly para-linked structure applies also for higher oligomers. This observation proves that the presence of o-AO is not necessary for the polyaniline film formation as was postulated earlier.

In mildly acidic medium (pH 5), the ortho-coupled oligomers with characteristic Raman bands are detected together with para-coupled ones. Thus, the acidity of the solution plays the same role in the formation of aniline oxidation products in electrochemical oxidation of aniline as is known for chemical aniline oxidation. The first products of electrochemical oxidation of aniline are para-coupled oligomers due to the strong acidic conditions.

Conflict of Interest

The authors declare no conflict of interest.

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