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Raman spectroelectrochemical study of polyaniline at UV, blue, and green laser line excitation in solutions of different pH

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A detailed study on Raman spectroelectrochemistry of polyaniline layer deposited at a gold electrode was performed. Raman spectra were excited by three laser wavelengths: UV line at 325 nm, a blue line at 442 nm, and a green line at 532 nm in solutions of different pH ranging from 1 to 9, and at different electrode potentials ranging from −0.5 V to 0.8 V. UV excitation results in a strong resonance with the reduced leucoemeraldine form of polyaniline that absorbs visible light at a maximum around 315 nm, revealing features characteristic for this form, thus nearly avoiding the possibility to observe the oxidised form and the corresponding electrochemical redox transformations. Both redox forms and their redox interconversions depending on electrode potential and solution acidity were well observed and analysed for green laser line excited Raman spectra. Blue laser line probably appears in resonance with the intermediate polyaniline form that absorbs visible light at a maximum of 420 nm.

1. Introduction

Since the discovery of conducting polymers, Raman spectroscopy has been widely used in elucidation of their structure, properties, doping and oxidation-reduction processes. More than two decades ago, fundamental works on Raman spectroscopy and spectroelectrochemistry of polyaniline and its derivatives were published [1–3]. These early works deal with the detailed analysis of Raman features observed, and their relation to structure of polyaniline and its changes taking place in the redox transformations. Also, some works dealing with polyaniline derivatives like sulfonated polyaniline [4], with conformational changes [5], or electrochemical decomposition [6] were done. At the same time, some fields for potential applications of this novel material were discussed, like corrosion protection [7,8], or analytical applications [9].

More recently, Raman spectroscopy and spectroelectrochemistry has been successfully applied for the study of polyaniline based composite and nanocomposite materials like polyaniline nanofibers [10], or electrodeposited composites with polysulfonic acids [11]. Polyaniline nanocomposites with a clay mineral montmorillonite have been prepared by intercalation procedure, and the formation of oxazine type structures upon heating has been shown to proceed slower with intercalated polyaniline [12]. Optically transparent nanocomposites with exceptional optical and electrical properties composed of polyaniline and graphene have been prepared, and the possibility for tailoring of these composites was shown by Raman spectroscopy [13]. Composite nanowires with a gold core and polyaniline shell were prepared using liquid crystal directing template by a simple chemical reaction [14]. The prepared nanowire composites show good surface enhanced Raman scattering, and good catalytic behaviour for the chemical reduction of organic dye [14]. The stability of a silica sorbent modified with polyaniline has been successively studied at various working conditions by confocal Raman spectroscopy [15].

Next to practically oriented applications, Raman spectroscopy is continually used in elucidation of polymer structure, peculiarities of polymerization and electropolymerization processes, and other aspects. With the use of Raman spectroscopy, a new insight was presented for species, initially formed at electrode during electropolymerization of aniline [16]. With the use of Raman spectroelectrochemical techniques, the formation ordered layers of polyaniline at electrode by the use of a special surface treatment has been evidenced [17].

For successful applications of Raman spectroscopy and spectroelectrochemistry, one important issue should be taken into account. Different forms of polyaniline differ in their light absorption properties depending on the degree of oxidation-reduction, and protonation level. In general, the protonated reduced form of polyaniline, protonated leucoemeraldine, absorbs in a near UV spectral range around 300 − 320 nm, thus appearing lightly yellow in color. Upon its gradual chemical or electrochemical oxidation, this form turns into a half oxidised, emeraldine form, and into a fully oxidised pernigraniline form.

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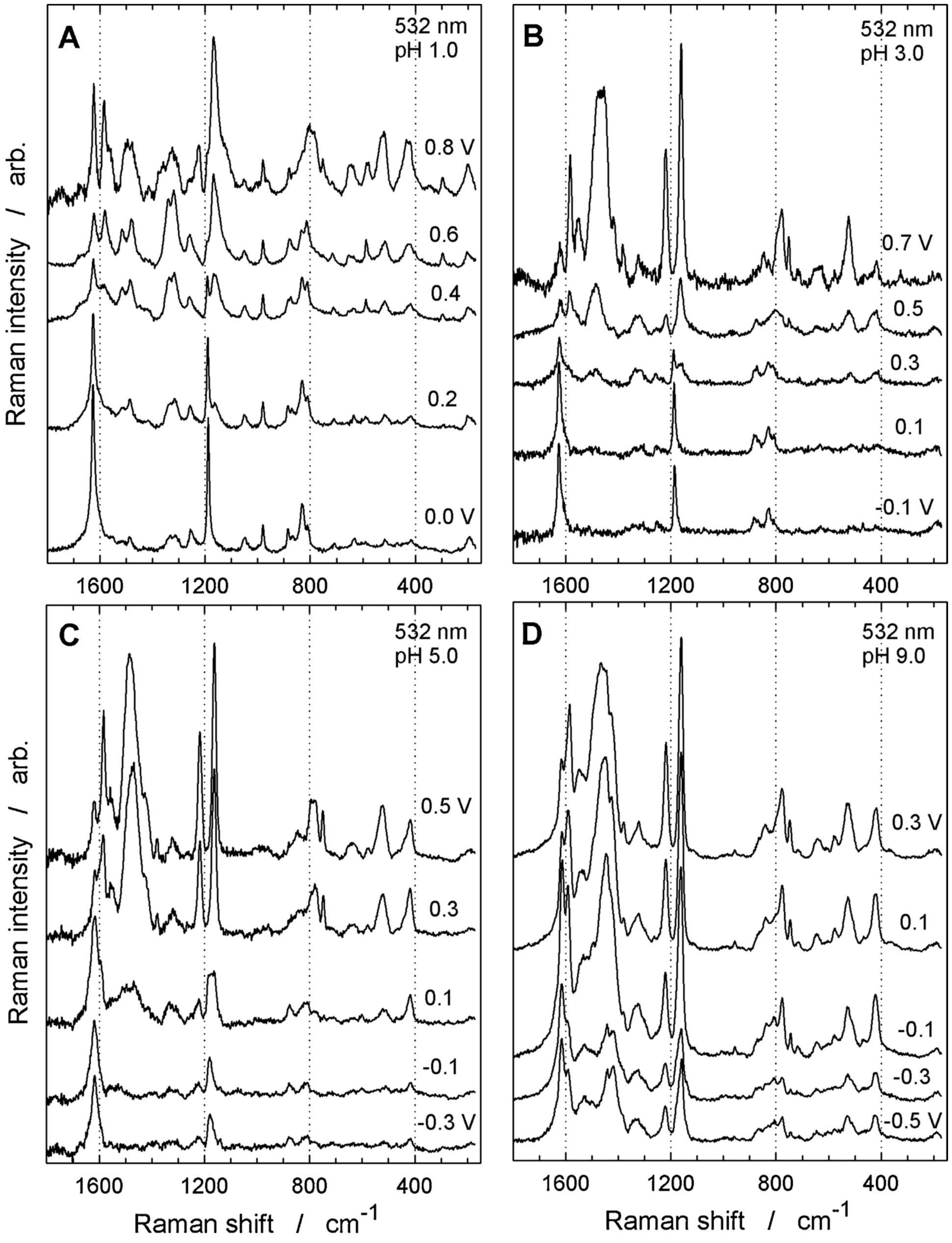

Fig. 1. Raman spectra from a gold electrode containing electrodeposited layer of polyaniline, as obtained at 532 nm laser line excitation in solutions of different pH (A: pH 1.0, B: pH 3.0, C: pH 5.0, and D: pH 9.0) at different electrode potentials ranging from −0.5 to 0.8 V (as indicated).

This gradual redox transformation is followed by the continuous growth of light absorption in the red and NIR ranges of visible spectrum at a maximum beyond 600 nm. Next to this, an intermediate absorbance band around 420 nm is observed, corresponding probably to an intermediate state characterized by isolated polarons [18]. Therefore, different forms of polyaniline are specifically enhanced by using different laser lines for excitation of Raman spectra. As a result, drastically different Raman spectra from the same polymer sample can be obtained using different excitation wavelength. Just in first pioneering works on Raman spectroscopy of polyaniline is has been observed that the blue laser line (457 nm) yields Raman spectra mostly of the reduced form of this polymer, and the resulting spectra are nearly insensitive to the degree of oxidation and protonation [2]. At the same time, the colored oxidised form appears strongly resonantly enhanced with the near infrared (NIR) excitation (1064 nm) [2]. Similarly, the insensitivity of polyaniline Raman spectra to the degree of its oxidation and protonation with the blue line excitation at 458 nm, along with a strong resonance for oxidised form at the red (676 nm), and NIR (1064 nm) excitation was noted [19,20]. At the same time, the use of two lines within the middle range, 488 nm and 514 nm, enabled to observe gradual spectral changes along with the gradual shift of electrode potential [19].

The present work has been aimed to a systematic comparative Raman spectroscopic study of electrodeposited polyaniline layer depending on its redox state and solution acidity with the use of three excitation lines – UV (325 nm), a blue line (442 nm), and a green line (532 nm). As far as we know, no Raman study of polyaniline with the potential-dependent UV excitation has been done yet.

2. Experimental

A BASi-Epsilon model (Bioanalytical systems Inc., USA) potentiostat was used in electrochemical experiments. A cylinder-shaped Teflon-based electrochemical cell have been used in Raman