



Probing the interactions in composite of graphene oxide and polyazulene in ionic liquid by *in situ* spectroelectrochemistry

Milla Suominen ^{a, b, *}, Pia Damlin ^{b, **}, Carita Kvarnström ^b

^a Turku University Graduate School (UTUGS), Doctoral Programme in Physical and Chemical Sciences, Finland

^b Turku University Centre for Materials and Surfaces (MatSurf), Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, FIN-20014 Turku, Finland



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ABSTRACT

Polyazulene (PAz) and polyazulene/graphene oxide composite (PAz/GO) films were electrochemically deposited from a choline based ionic liquid (IL), and characterized with attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) using Kretschmann geometry, and UV–Vis spectroscopy during electropolymerization and electrochemical oxidation. The use of different ILs has been shown to affect the morphology and long term cycling stability of PAz while fabricating composites is known to sometimes dramatically affect the electronic properties of PAz. The aim of this work was to study how the use of a viscous IL and, furthermore, incorporating GO affected the structural, electronic and optical properties of PAz. Overall, the vibrational behavior of the composite was very similar to PAz. During positive doping, the doping-induced infrared active vibrations (IRAV) of the composite were found at higher wavenumbers indicating shorter conjugation of PAz in the composite. Comparison to previous works and to PAz electropolymerized from conventional organic electrolyte solution revealed that polymerization in the viscous IL leads to electroactive and stable PAz with shorter effective conjugation length. The correlation between IRAV bands of doped PAz and Raman bands of neutral materials are also discussed within the framework of effective conjugation coordinate model (ECC).

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1. Introduction

Azulene, isomer of naphthalene, is a non-alternant and non-benzenoid aromatic hydrocarbon utilized in various organic electronics, such as organic photovoltaics [1,2], nonlinear optical materials (NLO) [3], organic field effect transistors (OFETs) [4], and electrochromic applications [5]. Azulene monomer (Scheme 1) consists of a five-membered ring and a seven-membered ring fused together. Since the five-membered ring is electron rich while the seven-membered ring is electron poor, an unusually large dipole moment is produced (1.08 D) [6]. This polarizability of azulene and its derivatives leads to unique optical and electronic properties that can be applied in many aspects of organic electronics [7]. Azulene can be polymerized upon anodic oxidation by chemical and electrochemical route to polyazulene (PAz). The chemical

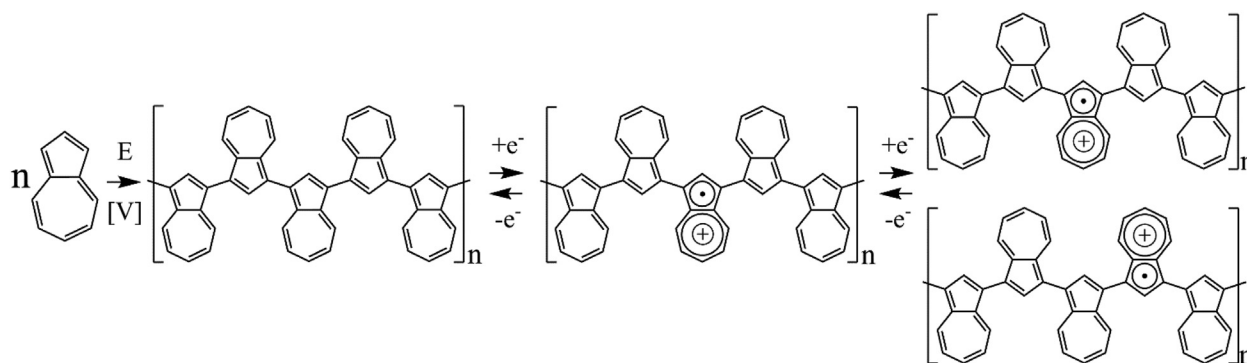
polymerization requires hazardous chemicals and results in rather low conductivity (1.22 S/cm) [8], while the electropolymerization of azulene occurs at low potentials and results in films with slightly higher conductivity (2.2 S/cm) [9]. PAz has been electropolymerized in organic solvents [10–14] and ionic liquids (ILs) [15–17], and it has also been copolymerized with different thiophenes [18,19]. The best quality PAz films are obtained in non-polar or only moderately polar solvents [11], and the use of ILs produces PAz films with higher capacity due to the formation of longer effective conjugation length [15,16], improved cycling stability [17], and uniform morphology [15,17].

The charge transport in PAz has been the subject of vigorous studies, both in conventional solvents and in ILs [16,20–24]. Charge is mainly transported in electronically conducting polymers (ECPs) with a nondegenerate ground state by the well-established radical cations and dications: polarons, polaron pairs and bipolarons [25]. These are additional energy states formed in the band gap region upon doping, and are accompanied by changes in the conformation of the polymer chain. A group of methods, that effectively probe the optical and electronic properties and the structural changes taking place during the doping process, is *in situ* spectroelectrochemistry

* Corresponding author. Turku University Graduate School (UTUGS), Doctoral Programme in Physical and Chemical Sciences, Finland.

** Corresponding author.

E-mail addresses: milsuo@utu.fi (M. Suominen), pia.damlin@utu.fi (P. Damlin).



Scheme 1. Structure of azulene and PAz as well as the proposed structures of the charged states induced by the oxidation of PAz.

[26]. In the earliest studies of PAz doping by electron spin resonance (ESR) spectroscopy and optical spectroscopy [20] as well as theoretical calculations [27] revealed that polarons and bipolarons are induced upon the oxidation of PAz. Later studies claim that polaron pairs (Scheme 1) rather than bipolarons are formed at higher doping levels [22]. It has also been a subject of debate whether the positive charges are accumulated in the seven-membered ring or in the five-membered ring [27]. The combination of PAz with fullerene [16], TiO₂ [28,29] and polymers [30] has resulted in changes of the electronic as well as optical properties observed using *in situ* spectroelectrochemical methods. This is mainly attributed to the electron donating or withdrawing properties of the added component. Additionally, shorter conjugation length of PAz has been realized in some of these composites [16,29]. Composites of carbon nanotubes (CNTs) and ECPs have also shown changes in the doping behavior [31–33]. Today, composites of modified graphene materials, mainly reduced graphene oxide (rGO), and ECPs are popular especially for energy storage applications [34]. To our knowledge, such composites with PAz have not been characterized by *in situ* spectroelectrochemistry. Successful application of novel materials in electronics applications requires thorough understanding of their structure and electronic properties.

We studied the electrochemical polymerization and p-doping of polyazulene (PAz) and polyazulene-graphene oxide (PAz/GO) composite in a choline-based ionic liquid using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) and UV-Vis spectroelectrochemistry. The electrolyte used during electropolymerization of azulene has a significant effect on polymer morphology and electrochemical activity: in lower viscosity ILs the morphology resembles films obtained in organic solvents while in very high viscosity electrolytes the networking between the polymer chains is poor resulting also in lower electroactivity [17]. An important parameter especially for energy storage materials is their long term cycling stability. Already by changing from organic solvent to IL, a significant improvement in the long term cycling of PAz film can be achieved [17], but the addition of graphene oxide (GO) can further improve this property [35]. The purpose of this work was to determine the similarities and differences in the structure and charge carrier formation between PAz and PAz/GO composite. Our results show that the polymer formed in a viscous IL comprises shorter conjugation length, and that addition of GO further shortens the effective conjugation. We focused on using the oxidized GO in this work, and did not reduce it to rGO with additional steps. However, some electro catalyzed reduction may occur during the electropolymerization since quite negative potentials were used. We have also discussed the similarities and differences of our films to previously published data, and conclude that charge transport and the structure of PAz is similar independent of polymerization medium.

2. Materials and methods

2.1. Materials

Azulene (Aldrich, 99%) and tetrabutylammonium tetrafluoroborate (TBA-BF₄) (Aldrich, 99%) were stored in ambient conditions. Anhydrous acetonitrile (ACN) (Sigma-Aldrich, 99.8%) and choline bis(trifluoromethylsulfonylimide) ([Choline][TFSI]) (Iolitech, 99%) were stored in an argon filled glove box. Azulene and ACN were used as received, while TBA-BF₄ was dried in vacuum oven at 80 °C for 1 h and [Choline][TFSI] at 45 °C for 2 h prior to use. GO was prepared from natural graphite (Alfa Aesar, 325 mesh) by modified Hummers method [36], and transferred to [Choline][TFSI] according to previously reported procedure [37]. All electrolytes were deaerated with dry N₂ prior to electrochemical measurements.

2.2. Electrode preparation

For all spectroelectrochemical analysis, a conventional three-electrode configuration was used where coiled Pt wire served as counter electrode and AgCl covered Ag wire served as pseudo reference electrode (calibrated vs. ferrocene). For *in situ* UV-Vis spectroelectrochemistry, 7 × 50 × 1.1 mm ITO coated quartz glass from Delta technologies (R_s = 8–12 Ω) was used as working electrode. The ITO glass substrates were cleaned by successive 10 min ultrasonication in acetone, ethanol and water. The substrates were rinsed thoroughly with water between each solvent. ZnSe hemisphere was applied as working electrode for *in situ* ATR-FTIR spectroelectrochemistry. The hemisphere was polished using 1 and ¼ μm diamond pastes (Struers) followed by Ar-plasma cleaning for 3 min. Pt was sputtered on the ZnSe crystal as conducting layer (3 nm for the analysis area of roughly 7 mm in diameter, and 28 nm for the surrounding area) using Leica EM ACE200 sputtering device.

2.3. *In situ* UV-Vis spectroelectrochemistry

The potential was controlled using Autolab PGSTAT101 potentiostat. Films were electrochemically synthesized by cycling the potential between –0.9 and 1.3 V (vs. Ag/AgCl) (3 cycles) at 50 mV/s. The films were then rinsed with dry ACN and submerged into 0.1 M TBA-BF₄ in ACN. The cell is depicted in Fig. S1a. Film was first charged and discharged with cyclic voltammetry between –0.4 and 1.0 V (vs. Ag/AgCl) using 20, 50, 100, 150 and 200 mV/s scan rates. During *in situ* measurement, a 2 mV/s scan rate was applied, and an absorbance spectrum was recorded every 100 mV using Cary 60 spectrophotometer (Agilent) with wavelength range from 190 to 1100 nm.

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