



## Effects of high frequency ultrasound irradiation on doping level and electroactivity of conducting polymers: Influence of OH• radicals



Abdeslam Et Taouil<sup>a,\*</sup>, Fabrice Lallemand<sup>a</sup>, Jean-Yves Hihn<sup>a</sup>, Loïc Hallez<sup>a</sup>,  
Virginie Blondeau-Patissier<sup>b</sup>

<sup>a</sup> Équipe Sonochimie et Réactivité des Surfaces, Institut UTINAM, UMR 6213 CNRS, Université de Franche-Comté, 30 Avenue de l'observatoire, 25009 Besançon Cedex, France

<sup>b</sup> FEMTO-ST, UMR 6174 CNRS, Université de Franche-Comté, Département Temps Fréquence, 26, Chemin de l'Épitaphe, 25030 Besançon Cedex, France

### ARTICLE INFO

#### Article history:

Received 15 March 2013

Received in revised form

6 May 2013

Accepted 7 May 2013

Available online 15 May 2013

#### Keywords:

High frequency ultrasound

Electropolymerization

OH• radicals

Doping level

Electroactivity

### ABSTRACT

Chemical effects of ultrasound on conducting polymers were studied, especially the effects of OH• radicals. In spite of OH• radicals formation by ultrasound, electroactivity of sonicated films is not degraded. That was explained by the too low concentration of these active species generated in irradiated media. These same radical species are, for the first time, claimed to be at the origin of the increase in doping level which has always been observed for conducting polymer films grown under ultrasound irradiation.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

The effect of high power ultrasound on electrochemical systems is an active research area [1] and many applications can be found from surface cleaning and preparation to deposition of metals [2–4]. The main effect of wave propagation is the formation of cavitation bubbles, as their violent collapse generates mechanical, thermal and chemical modifications. Then, it was obvious to apply such process to an original class of materials: conducting polymers which exhibit good electronic conductivity in their partially oxidized state, as shown in a recent review [5].

Previous studies have been initiated by Osawa et al. in the late 80s [6] and since then, many studies have been dedicated to use of ultrasound during electrosynthesis of conducting polymers [7–14]. However, they were mainly conducted at low frequencies, typically 20 or 45 kHz. At these frequencies, cavitation bubbles collapse violently generating shock waves and micro-jets directed toward the surface responsible for mass transfer enhancement [15] and continuous surface activation [16]. Thus, ultrasound can lead to partial destruction of the films [17]. More recently, studies carried out by our group [18–21] showed that at high frequency ultrasound, destructive effects on polymer deposits were

quenched while retaining beneficial aspects of ultrasound irradiation. It led to thinner, more homogenous and more compact structure for polymer coatings. That was assumed to be the result of changes during film growth process thanks to mechanical effects of ultrasound. The possibility to control surface morphology is very attracting, as this property is very important for many applications *i.e.* sensors elaboration or corrosion protection [22]. A complementary explanation would come from a better solubilization of monomers, leading to the observed topography [23,24].

Another interesting phenomenon, observed for low and high frequency irradiation, is an increase in doping level for irradiated polymers. An increase from 25% to 33% was observed for high frequency exposure [5,18–21]. However, mechanisms leading to such modification in doping level remain unclear. Two possibilities are to be considered:

- The energy released during cavitation bubbles implosion enables the breaking of bonds within the film and the formation of charged species in the polymer structure. Osawa et al. emitted the hypothesis of an increase of interactions with doping ions [6].
- OH• radicals formed during wave propagation oxidize the film and lead to the formation of additional polarons and bipolarons structures.

\* Corresponding author. Tel.: +33 (0)381666863; fax: +33 (0)381666858.  
E-mail address: [abdeslam.et.taouil@univ-fcomte.fr](mailto:abdeslam.et.taouil@univ-fcomte.fr) (A. Et Taouil).

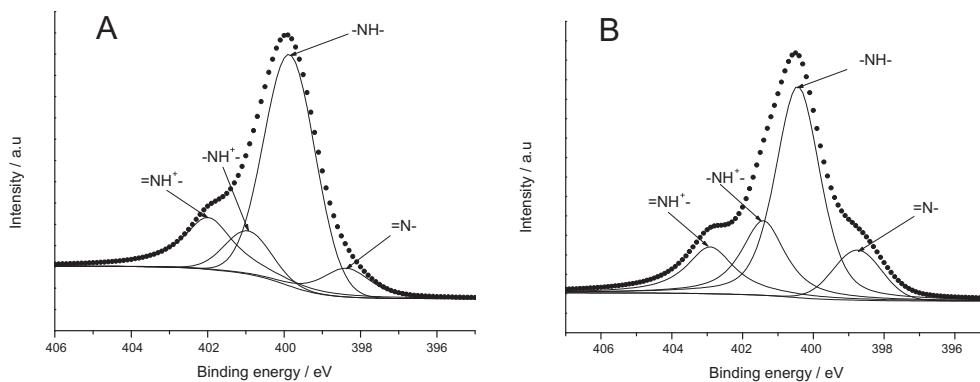


Fig. 1. N1s region from XPS analysis of PPy electro synthesized in (0.1 M Py + 0.1 M LiClO<sub>4</sub>) and then A) irradiated 5 min with US and B) immersed 5 min in (1 mM H<sub>2</sub>O<sub>2</sub> + 1 mM Fe<sup>2+</sup>).

Indeed, major consequence of ultrasound chemical effects is the formation of active radical species, especially OH• radicals, by solvent sonolysis [25,26]. In spite of that, no negative effect is seen on irradiated polymers' electroactivity while these radicals have been proved to be highly destructive towards redox properties of such organic films through overoxidation which is characterized by film dedoping and incorporation of carbonyl groups on β position of the aromatic ring breaking chain electronic conjugation [27].

The present work will investigate the action of these chemical effects *i.e.* production of radical species on polymer films exposed to high frequency ultrasound irradiation and clarify the origin of the increase in doping level.

## 2. Materials and methods

Pyrrole monomer (ACROS ≥ 99%, 109-97-7) was distilled at 10 mm Hg before use. De-ionized water (solvent) is distilled twice before use (Milli-Q, resistivity 18 MΩ/cm). All other chemicals were purchased from ACROS (analytical grade) and used as received without further purification.

All experiments were performed at an ultrasonic frequency of 500 kHz with an electrical power of 25 W, in a 750 ml cell. Ultrasound is produced parallel to the liquid surface, face to face with the

working electrode surface. The circular transducers consist of PZT piezoelectric ceramics fixed on circular plates (56 mm) made of glass.

The sonoreactor was characterized in previous works [18,20] by calorimetry and mass transfer measurements. Sonochemiluminescence imaging of luminol revealed high concentration of ultrasound activity at the interface solution/air, where the substrate

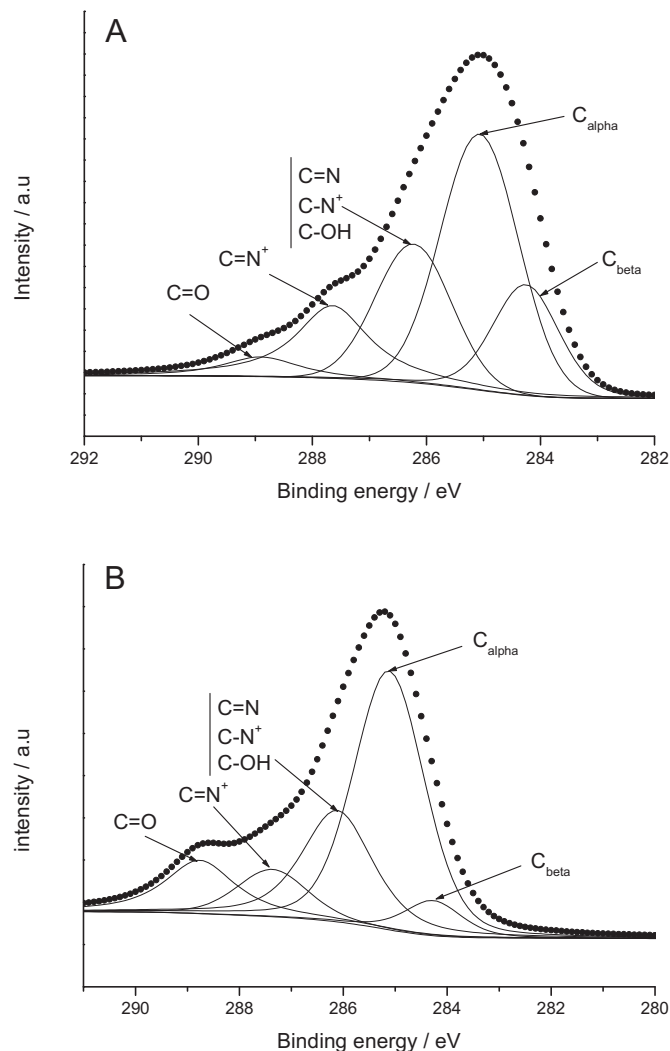


Fig. 3. C1s region from XPS analysis of PPy electro synthesized in (0.1 M Py + 0.1 M LiClO<sub>4</sub>) A) irradiated 5 min with US and B) immersed 5 min in (2 mM H<sub>2</sub>O<sub>2</sub> + 1 mM Fe<sup>2+</sup>).

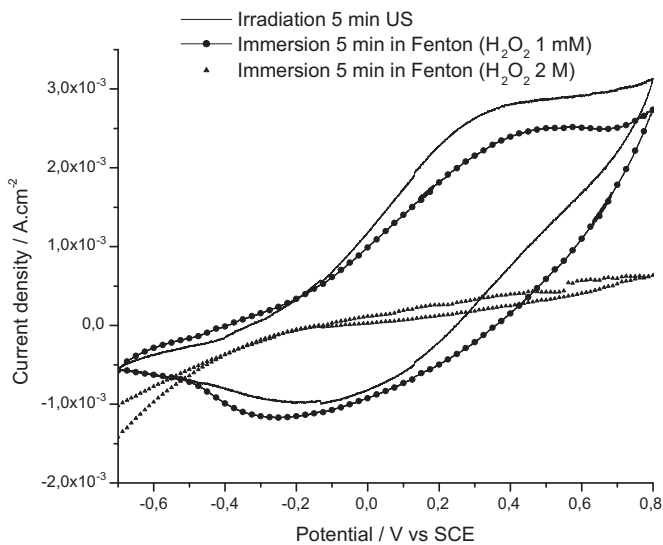


Fig. 2. Electrochemical response in aqueous 0.1 M LiClO<sub>4</sub> of PPy electro synthesized in (0.1 M Py + 0.1 M LiClO<sub>4</sub>) and then irradiated 5 min with US or immersed 5 min in (1 mM H<sub>2</sub>O<sub>2</sub> + 1 mM Fe<sup>2+</sup>) or immersed 5 min in (2 mM H<sub>2</sub>O<sub>2</sub> + 1 mM Fe<sup>2+</sup>).

Download English Version:

<https://daneshyari.com/en/article/5202218>

Download Persian Version:

<https://daneshyari.com/article/5202218>

[Daneshyari.com](https://daneshyari.com)