

# UV copper ion laser treatment of poly(3,4-ethylenedioxythiophene)

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The influence of ultraviolet (UV) 248.6 nm Cu<sup>+</sup> Ne-CuBr laser treatment on the chemical, electrochemical and morphological characteristics of electrodeposited conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) layers, as well as on the PEDOT surface activity with respect to metal deposition, is studied. Irradiated and non-irradiated polymer samples are characterized by means of electrochemical measurements, SEM, XPS and EPR spectroscopy. It is found that the laser treatment does not influence the electrochemical activity, the morphology and the paramagnetic response of the PEDOT layers. XPS analysis shows that the laser treatment leads to a change in the relative amounts of the chemical elements (carbon, sulphur and oxygen) involved in PEDOT. Thus, the UV irradiation modifies the polymer surface and allows a significant activation of the process of copper deposition on PEDOT.

(Received November 1, 2006; accepted December 21, 2006)

**Keywords:** PEDOT, Laser treatment, Conducting polymers

## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT), with a chemical structure depicted in Fig. 1, is one of the well known electrically conducting polymers with unique properties enabling its use as an active component in electronic, sensing and catalytic devices [1].

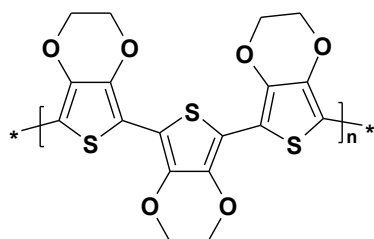


Fig. 1. Chemical structure of PEDOT.

This polymer, with high conductivity, is very stable in the doped state and remains almost unaltered in conventional environmental conditions. PEDOT properties are strongly dependent on the surface morphology, the chemical and physical structure, which in turn can be modified via a variety of solvents [2], macroanions [3], metal particles [4-7] or post-deposition treatments [8, 9].

There are many ways to modify the polymer so that it exhibits more preferable surface properties. The use of UV lasers in polymer science is of interest because they may be used as analytical tools and for many applications in material processing.

The aim of the present study is to show the influence of UV laser irradiation on the chemical, electrochemical and morphological characteristics of PEDOT, as well as

on the modification of polymer surface activity with respect to metal deposition. An UV Cu<sup>+</sup> Ne-CuBr laser oscillating at 248.6 nm line is used.

## 2. Experimental

### 2.1 UV laser set-up

For sample irradiation, an UV Cu<sup>+</sup> laser excited by a Ne-CuBr nanosecond pulse longitudinal discharge is used [10]. In this laser, Cu atoms as active particles are provided by an electron impact dissociation of the CuBr molecules.

The detailed description of the UV Cu<sup>+</sup> Ne-CuBr laser, including the laser tube, excitation scheme, discharge conditions and output parameters are shown in [11]. The laser operates at five Cu<sup>+</sup> lines – 248.6 nm, 252.9 nm, 259.7 nm, 260.0 nm and 270.3 nm. The maximal average output power at a multiline output is 1.3 W. The average laser power and the peak pulse power at the 248.6 nm laser line are 0.85 W and 3.25 W, respectively, at a laser pulse duration (FWHM) of 10 μs and pulse repetition frequency of 20 kHz. A schematic diagram of the experimental setup is shown in Fig. 2.

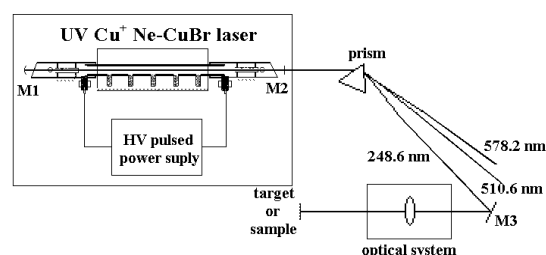


Fig. 2. Schematic diagram of the laser experimental setup.

The optical system provides irradiation of large-size samples with uniform transverse distribution of the laser radiation (Fig. 3). This is achieved by using a convex lens and a mask applied for cutting out the low-power wings of the transverse beam distribution. In this way the polymer layers are irradiated uniformly at an exposition dose of  $40 \text{ J cm}^{-2}$ .

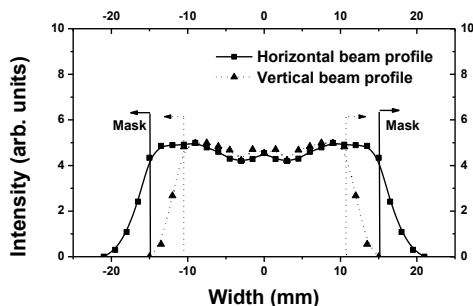


Fig. 3. Transverse beam distribution of the laser radiation.

## 2.2. PEDOT film preparation, UV treatment, metal deposition and experimental techniques

Electropolymerisation of PEDOT layers is performed at a constant anodic potential using an aqueous microemulsion [12]. A platinum plate is used as a working electrode. The polymerization charge passed during PEDOT synthesis is used for estimating the thickness of the PEDOT layers on a  $240 \text{ mC cm}^{-2}$  per  $1 \mu\text{m}$  basis.

After electrodeposition on the platinum plate electrode, the PEDOT layers are treated with laser light at the 248.6 nm line by two approaches, depending of the aim of the investigations. The first one is irradiation of the whole surface of the polymer layer and the second one is irradiation of half of the layer surface using a mask for a correct comparison of the irradiated and non-irradiated parts of the sample. The time of irradiation is less than 5 minutes.

For investigations by means of Electron Paramagnetic Resonance (EPR), the whole polymer surface is treated with UV light. EPR measurements are performed with an X-band BRUKER ER 200D-SRC spectrometer using 100 kHz modulation of the magnetic field.

The second approach of the laser treatment is used for comparing the irradiated and non-irradiated parts of the PEDOT layers by means of X-ray Photoelectron Spectroscopy (XPS) or used for electrodeposition of copper species. XPS is performed using an ESCALAB Mk II spectrometer with a base pressure of  $5 \cdot 10^{-9}$  mbar with non-monochromatized  $\text{MgK}\alpha$  X-Rays at  $h\nu = 1253.6 \text{ eV}$  and energy 20 eV.

Copper electrodeposition on PEDOT is performed in an aqueous solution of 0.033 M  $\text{CuSO}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$  at constant potential.

Scanning Electron Microscopy (SEM) imaging is accomplished with a Superprobe 733 (JEOL).

## 3. Results and discussion

### 3.1. Electrochemical, SEM and EPR measurements of PEDOT films

The electrochemical investigations show that no electrochemical changes occur after irradiation of the synthesized PEDOT layers. SEM images of the non-irradiated and irradiated parts of the PEDOT layer show no visible changes of the surface morphology.

EPR spectra of irradiated and non-irradiated samples of PEDOT layers have identical paramagnetic signals: line width ( $\Delta H = 0.8 \text{ mT}$ ) and g-factor ( $g = 2.002 \pm 0.0002$ ) (Fig. 4) showing that the concentration of the paramagnetic centres and  $\pi$ -electron structure of the polymer do not change after UV light treatment.

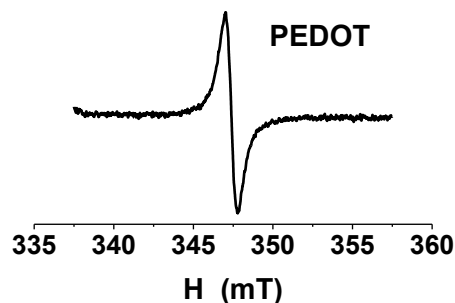


Fig. 4. EPR spectrum of PEDOT.

Bearing in mind the unaltered electrochemical stability, paramagnetic response and surface morphology after UV treatment, it can be assumed that the polymer layer preserves its volume characteristics.

### 3.2. Chemical analysis of PEDOT layers

XPS measurements were used to study whether chemical modifications on the surface of PEDOT (at nanometer depths) take place upon UV treatment.

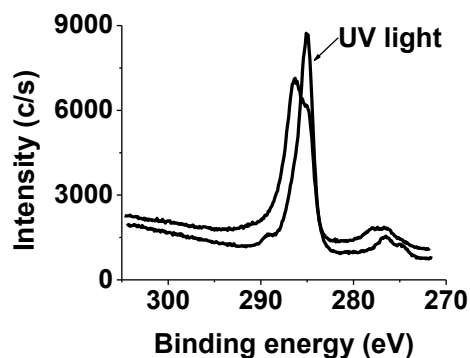


Fig. 5. C (1s) core level spectra of non-irradiated and irradiated PEDOT.

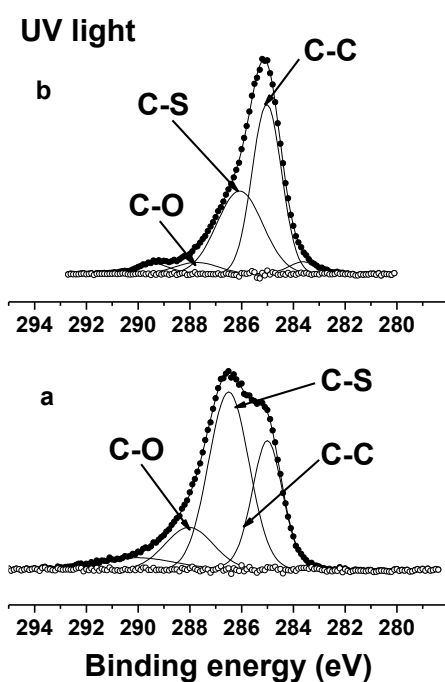


Fig. 6. Deconvolution of C (1s) core level spectra of PEDOT layer on non-irradiated (a) and irradiated (b) parts of the PEDOT.

The O (1s) and S (2p) peaks (not shown here) do not change noticeably, with the exception of the intensity of the peaks. Both signals from the irradiated part of the PEDOT show lower intensities. The major changes occur in the C (1s) core level spectra, depicted in Fig. 5.

The deconvolution spectra of C (1s) are shown in Figs 6a and 6b. The spectrum of the non-irradiated part of the polymer layer (Fig. 6a) consists of two main peaks at 285 eV and 286.5 eV. The peak at 285 eV corresponds to saturated and conjugated carbon atoms in PEDOT chains (C-C) and to carbon atoms bound to hydrogen atoms (C-H). The main peak at 286.5 eV is derived from carbon atoms bound to sulfur (C-S) in PEDOT. In addition, there is a low intensity feature at 288 eV corresponding to C-O bonds accompanied by a weak feature at 290.06 eV, most probably attributed to a  $\pi-\pi^*$  “shake up” signal due to the thiophene ring [13]. The irradiated part of the PEDOT layer (Fig. 6b) consists of the same peaks, but the intensity has changed completely.

The relative changes of the C/O, C/S and O/S atomic ratios on the irradiated part of the polymer are used to analyze the surface composition modification. The C/O, C/S and O/S signal ratios are found to increase by factors of 1.2, 1.4 and 1.2, respectively, pointing to an increased relative carbon content at the UV – treated surface.

Thus, the laser induced changes in the oxidation states of the C (1s) spectra, detected by XPS, should be related to changes of the PEDOT surface most probably resulting from destruction of C-S bonds.

### 3.3. Copper electrodeposition

The electroreduction of copper ions on PEDOT layers has been investigated in a series of papers [5-7]. Copper crystals and/or stabilized copper species are formed, depending on the experimental conditions. The next aim of this investigation is to reveal the role of the established UV – induced surface modification of PEDOT on the copper electrocrystallization.

After UV irradiation through a mask, the samples are transferred in the copper containing solution and subjected to a potentiostatic reduction potential  $E = 0.21$  V vs. a standard hydrogen electrode. Figs. 7a and 7b show SEM images of copper crystals electrodeposited on the non-irradiated and the irradiated parts of the PEDOT layer, respectively. The average number density of the copper crystals on both parts of the polymer layer is  $2.8 \times 10^7$  cm<sup>-2</sup> and  $5.6 \times 10^7$  cm<sup>-2</sup>. Thus the UV irradiation of the PEDOT layer results in a two-fold increase in the number density of copper crystals, most probably due to the creation of new surface active sites.

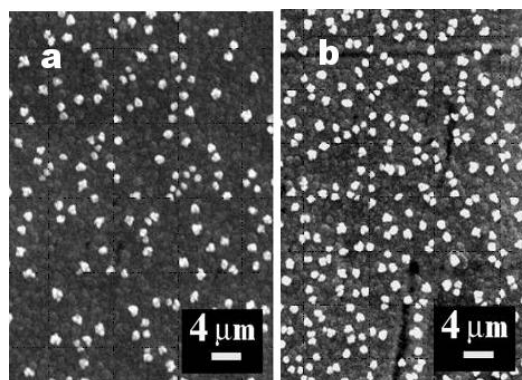


Fig. 7. SEM images of the non-irradiated (a) and the irradiated (b) parts of the Cu-PEDOT layer.

### 4. Conclusions

This investigation shows that irradiation of the PEDOT layers with a 248.6 nm laser line does not influence the electrochemical behaviour, the surface morphology and the  $\pi$ -electron structure of the conducting polymer. At the same time, XPS analysis reveals a considerable decrease in the relative amounts of oxygen and sulfur and an increase in the carbon content at the UV – treated surface. It can be concluded that the UV light – PEDOT interaction leads to the destruction of C-S bonding the polymer surface.

This laser modification of the polymer surface most probably creates additional energetically favoured locations at the polymer surface, or so called active sites. As a result, the number density and amount of the electrodeposited copper particles on the PEDOT layer increases twofold. It is important to note that the catalytic activity of metal particle/polymer composite materials depends on the number and location of the metal species

[14]. Thus, the revealed UV-induced effect on the metal deposition in PEDOT is important for eventual applications of metal-modified PEDOT layers for electrocatalytic purposes.

### Acknowledgements

This study is supported by Grants No.X-1405 and No.F-1204 of the Ministry of Education and Science of Bulgaria and by FP6 European project NANOPHEN (INCO-CT-2005-016696).

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