Surface modification of poly-3, 4-ethylenedioxythiophene by unconventional UV CuBr laser

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Poly-3,4-ethylenedioxythiophene (PEDOT) (Fig. 1) stands out in the field of electronically conducting polymers for the possibility to obtain after bulk or surface modification exemplary properties suitable for applications in microelectronic, photovoltaic, sensing and catalytic devices. The key for fine tuning of the surface properties is the development of suitable pre-treatments.

The goal of the present work is to study the influence of deep ultraviolet (DUV) laser irradiation on the chemical, electrochemical and morphological characteristics of PEDOT, as well as on the resulting modification of polymer surface activity with respect to metal deposition. An unconventional Cu⁺ Ne-CuBr laser oscillating at 248.6 nm is utilized [1]. Electrochemical measurements, SEM, XPS and EPR spectroscopy are used to study irradiated and non-irradiated polymer samples.

PEDOT layers are electrodeposited at constant anodic potential on platinum substrates using an aqueous microemulsion [2]. After the electrodeposition the PEDOT layers are treated with DUV light at an exposition dose of 40 J cm⁻² by two approaches depending on the aim of the investigations. The first one is an irradiation of the whole polymer layer for electrochemical and EPR measurements. The second one is irradiation of the half of the layer using a mask for investigations by means of XPS or used for deposition of copper species.

It is found that the laser irradiation does not influence the electrochemical activity, the morphology (Fig. 2) and the paramagnetic system of the bulk PEDOT layer. At the same time, XPS analyses (Fig.3) of non-irradiated and irradiated PEDOT layers show that the laser treatment leads to a change of the relative amounts of the chemical elements (carbon, sulfur and oxygen) involved in PEDOT. The XPS core level spectra reveal a lowering of the O(1s) and S(2p) signals from the irradiated part of the PEDOT and simultaneously a shift of the binding energy of C(1s). The deconvoluted spectra of C(1s) (Figs. 4a and 4b) show a decrease of the oxygen to carbon and sulfur to carbon bonds and increase of the carbon to carbon bonds on the irradiated part. Thus the UV laser exposure modifies the polymer surface.

After UV irradiation through a mask, copper crystals are electrodeposited on the PEDOT layers. SEM images of the copper crystals deposited on non-irradiated and irradiated parts of PEDOT layer (Figs. 5a and 5b, respectively) show a two-fold increase in the number n of copper crystals in the case of the DUV irradiated layer. The revealed DUV effect on the metal deposition in PEDOT is important for potential application of metal-modified PEDOT layers for electrocatalytic purposes.
Fig. 1. Chemical structure of PEDOT

Fig. 2. SEM images of the surface of non-irradiated and irradiated PEDOT.

Fig. 3. XPS core level spectra of O(1s), S(2p) and C(1s) obtained on non-irradiated and irradiated parts of PEDOT.

Fig. 4. Deconvoluted C(1s) core level spectra obtained on non-irradiated (a) and irradiated (b) parts of PEDOT

(a) $n = 2.8 \times 10^7 \text{ cm}^{-2}$

(b) $n = 5.6 \times 10^7 \text{ cm}^{-2}$

Fig. 5. SEM images of non-irradiated (a) and irradiated (b) parts of Cu-modified PEDOT layer