Electrochemistry Communications 46 (2014) 75–78

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Electrochemical nanopatterning of an electrogenerated photosensitive poly-[trisbipyridinyl-pyrrole ruthenium(II)] metallopolymer by nanosphere lithography

Luminita Fritea [a,b,c], Fatima Haddache [a,b], Bertrand Reuillard [a,b], Alan Le Goff [a,b], Karine Gorgy [a,b], Chantal Gondran [a,b], Michael Holzinger [a,b], Robert Săndulescu [c], Serge Cosnier [a,b,*]

[a] *Univ. Grenoble Alpes, DCM UMR 5250, F-38000 Grenoble, France*
[b] *CNRS, DCM UMR 5250, F-38000 Grenoble, France*
[c] *Analytical Chemistry Department, Faculty of Pharmacy, Iuliu Haţieganu University of Medicine and Pharmacy, Pasteur st. 4, 400349 Cluj-Napoca, Romania*

ARTICLE INFO

Article history:
Received 17 May 2014
Received in revised form 10 June 2014
Accepted 11 June 2014
Available online 19 June 2014

Keywords:
Nanosphere lithography
Ruthenium complexes
Electropolymerization
Metallopolymers
Photoelectrochemistry

ABSTRACT

900- and 100-nm-diameter polystyrene beads were combined with electrogenerated photosensitive poly-[tris(4,4-bis(3-pyrrol-1-ylpropyloxy)bipyridinyl)ruthenium(II)], (poly-[Ru^{II}-pyrrole]), metallopolymer on glassy carbon electrodes. Nanosphere lithography (NSL) with 900-nm-diameter microbead mask affords the realization of a nanostructured polymer (after dissolution of the polystyrene templates) with a typical highly-organized honeycomb nanostructure. NSL with 100-nm-diameter-nanobead mask allowed the achievement of a highly macroporous metallopolymer. The nanostructured Ru(II)-based metallopolymer was characterized by 3D laser scanning confocal microscopy and scanning electron microscopy (SEM). Electrochemical and photoelectrochemical studies demonstrate the enhancement of redox probe diffusion in the polymer layer for nanopatterned poly-[Ru^{II}-pyrrole]. This is accompanied with photocurrent enhancement for nanostructured polymer, especially in the case of poly-[Ru^{II}-pyrrole] obtained by the 100 nm-nanobead NSL.

1. Introduction

Metallopolymers, a particular class of redox polymers, are widely studied for many applications, ranging from molecular electronics to sensing or energy conversion [1,2]. In particular, electrogenerated metallopolymers have already demonstrated interesting properties in photovoltaics [3], photoelectrochemical immunosensors or aptasensors [4] and electrogenerated chemiluminescence [5].

Nanostructuration of photosensitive polymers is one important parameter for enhancement of photocurrent densities by increasing surface concentration of photosensitive units and diffusion of electron donors or acceptors. Different nanomaterials were used to form photosensitive highly porous nanostructures. The combination of polymers with carbon nanotubes, metal or metal oxide nanoparticles have represented efficient means for enhancement of photoelectrochemical properties [6,7]. For instance, we have demonstrated the easy functionalization of CNT electrodes with electrogenerated trisbipyridyl metal polypyrrole films [7–10].

Nanosphere lithography (NSL) employs polystyrene or silica beads to control the nano- and microstructuration of deposited materials such as metals [11–13] or conducting polymers [14–17]. When deposited on planar surfaces, these micro- or nanobeads can form highly ordered templates. After deposition of the materials by techniques as different as chemical vapor deposition or electropolymerization, polystyrene beads are easily removed by simple dissolution in organic solvents, leaving a highly porous and highly ordered surface with controlled nanostructure [18]. In particular, we have recently demonstrated the controlled porosity of functional electrogenerated polypyrroles for immobilization of enzymes [19]. In the present study, we have combined NSL with electropolymerization of a Ru(II)-pyrrole monomer, *tris[4,4-bis(3-pyrrol-1-ylpropyloxy)bipyridinyl]ruthenium(II) hexafluorophosphate, Ru^{II}-pyrrole*. This monomer was chosen because the photosensitive center bears 6 pyrrole monomers, increasing further crosslinking during electropolymerization and subsequent stability of the as-formed metallopolymer. By using different bead diameters (900 and 100 nm), we demonstrate the successful use of NSL to achieve highly ordered porosity in photosensitive metallopolymers. Nanostructured metallopolymers exhibit highly reproducible porosity. Enhanced photocurrents, inversely proportional to the polystyrene-bead-diameter size, measured in the presence of pentaaminechlorocobalt(III) chloride as an oxidative quencher, is observed.

---

* Corresponding author at: Univ. Grenoble Alpes, DCM UMR 5250, F-38000 Grenoble, France, CNRS, DCM UMR 5250, F-38000 Grenoble, France.
E-mail address: serge.cosnier@ujf-grenoble.fr (S. Cosnier).

http://dx.doi.org/10.1016/j.elecom.2014.06.012
1388-2481/© 2014 Elsevier B.V. All rights reserved.

2. Experimental

2.1. Methods and instrumentation

All reagents and chemicals were purchased from Aldrich, except acetonitrile (Rathburn, HPLC grade). All chemicals were of analytical grade and used as received. *Tris[4,4 bis(3-pyrrol-1-ylpropyloxy) bipyridinyl]ruthenium(II) hexafluorophosphate* (Ru^{II}-pyrrole) was synthesized according to a reported procedure [8].

2.2. Electrochemical instrumentation

All electrochemical studies were performed with a conventional three-electrode system using Ag/AgCl reference in acetonitrile (MeCN) or a saturated calomel electrode (SCE) in water. A Pt wire electrode was used as counter electrode. The working electrodes were 5-mm-diameter glassy carbon electrode (GCE), polished with 2 μm diamond paste, and followed by rinsing with distilled water and ethanol. Electrochemical experiments were conducted on an Autolab PGstat100 potentiostat.

2.3. Elaboration of electrodes and characterization

The templates were created as follows: 5 μl of 0.5 wt.% ethanol suspension of 900-nm-diameter polystyrene spheres were deposited by drop casting on GCEs and allowed to dry at room temperature for 10–30 min. The 100-nm-diameter nanosurface was produced in a similar manner by 3 × 5 μl deposition of 0.5 wt.% ethanol suspension of 100-nm-diameter polystyrene spheres. After the formation of poly-[Ru^{II}-pyrrole] film by scanning the potential repeatedly (5–10 scans) from 0 to 1.1 V vs Ag/AgCl, with 0.1 V s^{-1} scan rate in a 2 mM Ru(II)-pyrrole MeCN solution in 0.1 M LiClO$_4$, the resulting electrodes were immersed for 15–20 h in THF in order to remove the polystyrene template. The electrodes were rinsed with ethanol and distilled water. The morphology of the modified electrodes was investigated by SEM using an ULTRA 55 FESEM based on the GEMINI FESEM column with beam booster (Nanotechnology Systems Division, Carl Zeiss NTS GmbH, Germany) and tungsten gun. 3D and profile images were taken using a Keyence VK-X200 laser microscope.

2.4. Photocurrent generation experiments

An electrochemical cell with a quartz window was used for photocurrent generation experiments. The modified working electrode was placed in front of the quartz window and irradiated with a 200 W Hg lamp through UV and IR cutoff filters below 420 nm and beyond 630 nm with a surface light intensity of 11.2 μW cm^{-2}. In order to monitor the photogenerated currents, the modified electrodes were kept at 0 V vs SCE.

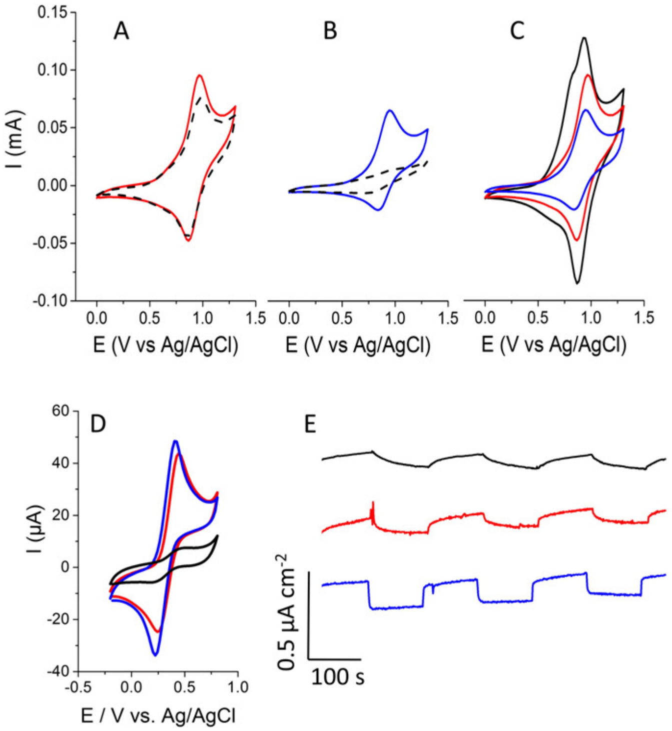

Fig. 2. Cyclic voltammograms of 2 mM poly-[Ru^{II}-pyrrole] in 0.1 M LiClO$_4$/MeCN of (A) 900-nm-diameter-microsphere-modified GCE before (dashed line) and after dissolution of the beads (red line); (B) 100-nm-diameter-nanosphere-modified GCE before (dashed line) and after dissolution of the beads (blue line); (C) cyclic voltammograms of modified GCE electrodes without nanosphere (black line), 900-nm-diameter-microsphere-modified GCE (red line) and 100-nm-diameter-nanosphere-modified GCE (blue line); (D) cyclic voltammograms of 1 mM ferrocene at modified GCE electrodes without nanosphere (black line), 900-nm-diameter-microsphere-modified GCE (red line) and 100-nm-diameter-nanosphere-modified GCE ($v = 0.05$ V s^{-1}) (blue line); (E) cathodic photocurrent measurements for modified GCE electrodes without nanosphere (black line), 900-nm-diameter-microsphere-modified GCE (red line) and 100-nm-diameter-nanosphere-modified GCE (blue line), for three successive 100-second exposure to visible light in the presence of 15 mM pentaaminechlorocobalt(III) chloride in 0.1 M acetate buffer, pH 5 ($E_{applied} = 0$ V vs SCE).

3. Results and discussion

Nanostructured poly-[Ru^{II}-pyrrole]-modified electrodes were prepared in two successive steps. A solution of polystyrene beads (900 and 100 nm; conc in solvent) is drop-casted on GCEs. A closely-packed and highly ordered nanosphere network homogenously covers the surface of the electrode. Then, Ru^{II}-pyrrole was electropolymerized around the deposited nanobeads with a precise control over electropolymerization conditions. We chose cyclic voltammetry (CV) techniques, as it allows a control over scan rate, potential window and number of CV scans. Fig. 1

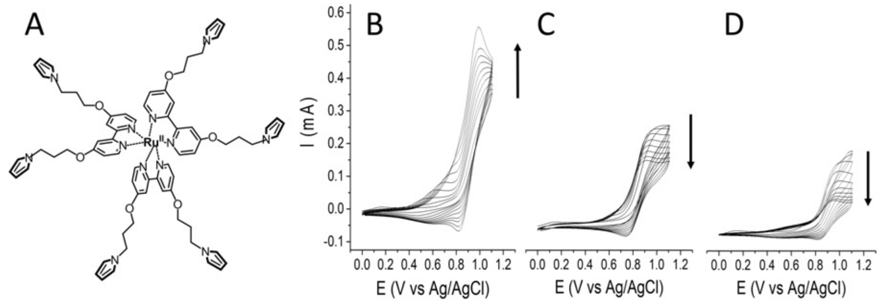

Fig. 1. (A) Structure of [tris(4,4-bis(3-pyrrol-1-ylpropyloxy)bipyridinyl)]ruthenium(II) Ru^{II}-pyrrole complex; (B) cyclic voltammograms (10 scans) of 2 mM of Ru^{II}-pyrrole in 0.1 M LiClO$_4$/MeCN at GCE, (C) 900-nm-diameter microsphere-modified, and (D) 100-nm-diameter-nanosphere-modified GCE ($v = 0.1$ V s^{-1}).