

COMPOSITE NANOMEMBRANES FOR ELECTROCHEMICAL SENSING

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Received 18 April 2012; accepted 20 April 2012.

1. Introduction

Artificial freestanding ultrathin nanoparticle membranes, as materials of nanoscale thickness with little or no substrate support, belong to the frequently studied nanostructures [1 and citations therein]. Being the objects quite near to ideal 2D structures, they exhibit unusual properties required for various applications in electronic, photonic and sensing devices. It is expected that the changed morphology and electronic structure between the macro- and nanoscales can lead to usefully altered electrode reactions and mechanisms. Thus, the use of nano-objects in electroanalysis became an area of research which is continually expanding. An overview of the investigations carried out in the field nanoparticles in electroanalytical chemistry, including deviations from Cottrellian behaviour, was given in two successive papers [2, 3]. Similarly, thin films and membrane systems show theoretical current-time responses that deviate from Cottrell behaviour [4]. Recently, we have shown that the electroactive hydrophobic end of the molecule used for the Langmuir-Blodgett film modification of an electrode can induce a change in the kinetic of observed redox reactions [5]. Later, we have reported a sensing protocol based on the anomalous non-Cottrellian diffusion towards nanostructured surfaces [6]. The potassium ferrocyanide oxidation on a gold disc electrode covered with a system of nanoparticle membranes was investigated using a kinetic-sensitive volt coulometric method. Kinetic changes were induced by the altered electrode surface morphology, i.e., micro-sized superparamagnetic nanoparticle membranes were curved and partially damaged under the influence of the applied magnetic field. The targeted changes in the non-Cottrellian diffusion towards the working electrode surface resulted in a marked amplification of the measured volt coulometric signal. Moreover, the observed effect depends on the membrane elasticity and fragility, which may give rise to the construction of sensors based on the influence of various physical, chemical or biological external agents on the superparamagnetic nanoparticle membrane Young's moduli. In this paper we analyze the charge transfer processes at the electrode covered with various types of nanomembranes, including a composite nanomembrane FeO nanoparticles / organic semiconductor polythiophene (P3HT).

2. Experimental results

Electrochemical experiments were carried out in a typical three-electrode electrochemical cell equipped with an Ag/AgCl reference electrode and a Pt auxiliary electrode. UV-cleaned gold discs were covered with nanoparticle membranes, with P3HT thin films, and with bilayers formed of nanoparticle membranes covered with P3HT thin films. The drop-casting technique was used for the preparation of nanoparticle membranes composed of FeO nanoparticles (approx. 4 nm in the nanoparticle core diameter) encapsulated in an organic envelope. The volume of the nanoparticle dispersion used to cast was $\sim 2 \mu\text{l}$, the concentration of nanoparticles dispersed in chloroform was of the order of

10^{12} particles per μl . The samples were dried at room temperature in ambient atmosphere, the average thickness of the prepared film was $\sim 10 \mu\text{m}$. Langmuir-Blodgett technique was used for the preparation of P3HT thin films. Monomolecular layer of P3HT was 10-times transferred onto the bare Au electrode and on nanoparticle membrane covered Au electrode by the Langmuir-Blodgett technique. The commercially available computer-controlled Langmuir trough (Type KSV-NIMA LB KM 2003 large) was used. The surface pressure was measured by the Willhelmy plate method. P3HT dissolved in chloroform was spread on the subphase and allowed 15 min before compression for solvent evaporation. The water subphase (deionized, $20 \text{ M}\Omega \text{ cm}$) was thermostated to the temperature $17 \text{ }^\circ\text{C}$. The prepared layered structures, attached to a glass tube with the silicon glue, were used as working electrodes (diameter $\sim 1.5 \text{ mm}$). A neodymium magnet ($\sim 1 \text{ T}$) was used to induce changes in the surface morphology of prepared membranes with incorporated FeO nanoparticles. The magnet was positioned at a distance of $\sim 5 \text{ mm}$ above the sample for 10 seconds.

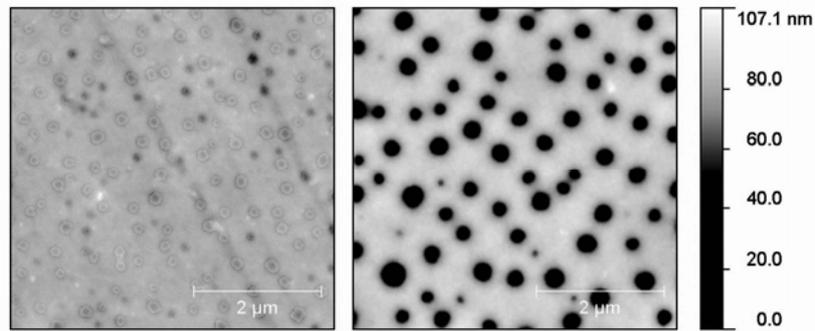


Fig.1: *AFM image (tapping mode) of nanomembranes (FeO nanoparticles) – before (left) and after (right) magnetic field application.*

The transient current flowing through the working electrode in response to an applied potential pulse during the potential scan, was integrated and the diffusion limited non-Cottrellian transient charge was sampled at three different events t_1 , $5t_1$, and $9t_1$ in the interval between subsequent excitation pulses. The sampled values were combined on the basis of the multipoint analysis principles to obtain volt-coulometric signal described as

$$\Delta q_D \propto \sqrt{t_C} \left[\left(\frac{t_1}{t_C} \right)^\beta - 2 \left(\frac{5t_1}{t_C} \right)^\beta + \left(\frac{9t_1}{t_C} \right)^\beta \right]. \quad (1)$$

The irregular (rough, porous or partially active) electrode geometry can and does cause current density inhomogeneities which in turn yield deviations from ideal behaviour. Fractals offer an efficient way to handle such irregularity in general terms. Therefore, rough and partially active electrodes are frequently modelled using fractal concepts, their surface roughness is often characterized as self-affine fractal. Diffusion-limited processes on such interfaces show anomalous behavior of the reaction flux. As a consequence of fractal electrode surface, the diffusion current is dependent on time as $i \propto t^{-(D_f-1)/2}$, where D_f is the fractal dimension [7]. For a smooth, two-dimensional interface ($D_f = 2$) the Cottrell behaviour $i \propto t^{-1/2}$ is obtained. Rough interface is characterised by $D_f > 2$, $D_f < 2$ was reported for partially blocked surface or active islands on inactive support [8]. Performed volt-coulometric experiment provides a simple way for the determination of parameters β and D_f . These parameters can be evaluated using Eq. (1) for two various sampling times t_1 , or from an individual charge vs. time response to the applied pulse. A shift towards higher surface roughness (higher D_f) was observed studying the potassium ferrocyanide oxidation (activation potential $\sim 0.3 \text{ V}$) at the nanomembrane microstructured by the applied magnetic

field (see Fig.1). Corresponding data sets are shown on Fig. 2. Here, also the potential of multipoint analysis in the selectivity enhancement is demonstrated.

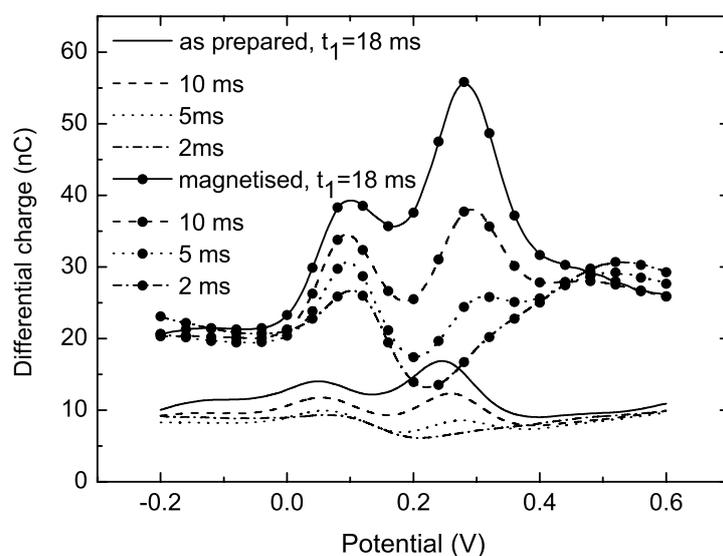


Fig.2: Voltcoulometric response of 2mM potassium ferrocyanide in 0.1 M NaCl on as prepared and magnetised nanomembrane (FeO nanoparticles) – influence of the chosen sampling scheme.

Finally, an experiment with layered composite nanomembranes, FeO nanoparticles / P3HT, was performed to study the role of electrically active sites on the nanomembrane surface in the redox electrochemistry. The results are depicted on Fig. 3.

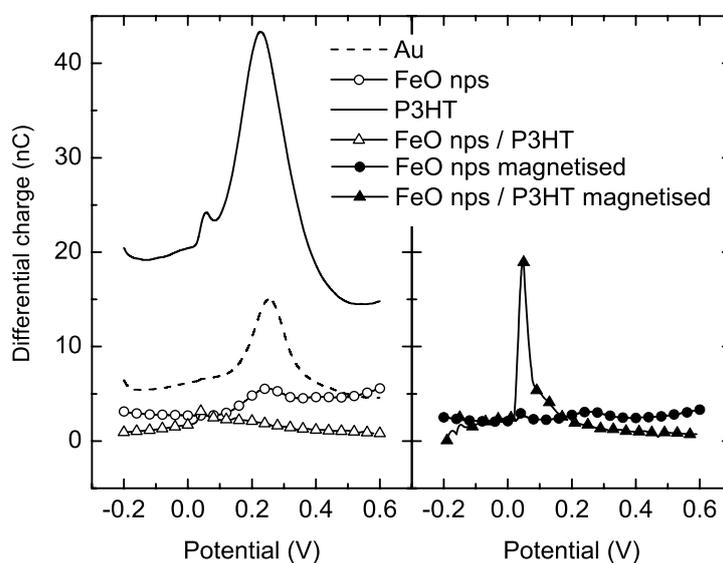


Fig.3: Voltcoulometric response of 50 ng/ml Cu^{2+} solution in 0.1 M NaCl on various types of nanomembranes (FeO nanoparticles, P3HT, FeO nanoparticles / P3HT composite; left part – as prepared nanomembranes, right part – magnetised nanomembranes).

Changes in the surface microstructure of nanoparticle membrane caused by the magnetic field application did not result in the sensitivity enhancement of the copper ions detection. A marked sensitivity enhancement as compared to bare Au electrode was reached in the case of

the electrode modification with the P3HT thin film, the electrochemical oxidation of Cu^{2+} to copper was detected. Similarly, strong electrochemical signal was observed at the region corresponding to an ECE (Electrochemical-Chemical-Electrochemical) reaction on the magnetised composite nanomembrane (FeO nanoparticles / P3HT).

3. Discussion and conclusion

The comparison of potassium ferrocyanide and copper redox reactions taking place at the nanoparticle membrane surface indicates an important role of charged complexes formed on such nanomembrane, namely on the metallic nanoparticle core immersed in the aqueous environment. While the volt coulometric signal of ferrocyanide was markedly amplified, the reaction of copper remained almost unchanged. On the other hand, an amplification of copper redox signal was observed for the Au electrode modified with 10 LB layers of the electroactive semiconducting thin film, P3HT. Based on the performed measurements an assumption should be made that the charge state of the species to be analysed, as well as the surface charge of the working electrode, play an important role in the observed kinetic behaviour of the studied redox system. Finally, a composite nanomembrane was prepared by the LB modification of the superparamagnetic nanomembrane with P3HT. On such a nanomembrane, the copper redox reaction was markedly altered as compared to all the previously studied electrodes (bare Au electrode, P3HT modified electrode, FeO nanoparticles modified electrode). Here, an ECE reaction manifested by two closed peaks, first of them being probably interrupted by a chemical reaction, has been observed instead of the typical $\text{Cu}^{2+} + 2 e^{-} \rightarrow \text{Cu}$ two-electron transfer.

While mechanical robustness is critically important for the majority of freestanding nanomembranes applications, our sensor profits from their fragility and elasticity. We have presented a sensing protocol based on the changes in kinetics of redox reactions. Changes in the morphology of nanomembranes with incorporated superparamagnetic nanoparticles caused by the magnetic field resulted in marked sensitivity enhancement and, moreover, such changes can contribute to a higher selectivity in measured signals.

Acknowledgement

This work was supported by the ASFEU project Competence center for new materials, advanced technologies and energy, Activity 4.2, ITMS code 26240220073, supported by the Research & Development Operational Programme funded by the ERDF, by Centre of Excellence SAS for Functionalized Multiphase Materials (FUN-MAT) and by Slovak grant agency VEGA contract No.: 2/0093/10.

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