

INVESTIGATION OF ION DIFFUSION TOWARDS PLASMONIC SURFACES

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1. Introduction

Plasmonic sensors have recently attracted much attention. A review of synthesis and fabrication of plasmonic nanostructures, and applications of plasmonics nanostructures in sensing and chemical imaging has been published by Stewart et al. [1] The simplest and most successful sensors are based on the optical and electrical transduction and readout. The implementation of electrochemistry with plasmonic nanostructures for combined electrical and optical signal transduction has been reviewed by Dahlin et al. [2] The fundamental understanding of how electrochemical potentials influence the plasmon resonances in different nanostructures (in nanoparticles, nanowires, nanoholes or simply in films of nanoscale thickness) is necessary for successful preparation of plasmonic sensors based on the combined optical, electrical, and electrochemical readout. Moreover, as in electrochemistry with plasmonic nanostructures electrochemical potentials influence the plasmon resonances, the influence of plasmon resonance on the kinetic of redox reaction can be anticipated, too.

The past few decades have seen a massive and continued interest in studying electrochemical processes at artificially structured electrodes. Such electrochemical sensors provide sensitive, selective, and easy to use approaches to the detection of many chemical species, e.g. environmental pollutants, biomolecules, drugs etc. The issue raised in this paper is to study the kinetic of the diffusion towards plasmonic surfaces in dark and under illumination with white LED diode. The possibility to use anomalous charge transfer towards plasmonic surfaces in electrochemical sensorics will be discussed, too.

2. Experimental results

Electrochemical experiments were carried out in the electrochemical microcell (see Fig. 1) built on ITO substrate coated with a plasmonic nanoparticle thin film and equipped with an Ag/AgCl reference electrode and a Pt auxiliary electrode. Langmuir-Blodgett technique was used for the preparation of plasmonic monolayer of Ag nanoparticles. The commercially available computer-controlled Langmuir trough (Type KSV-NIMA LB KM 2003 large) was used for this purpose. The surface pressure was measured by the Willhelmy plate method. The Ag nanoparticles of diameter ~10 nm encapsulated in an organic envelope (oleic acid and oleyl amine) and dissolved in chloroform were spread on the subphase and allowed 15 min before compression for solvent evaporation. The water subphase (deionized, 20 MΩ cm) was thermostated to the temperature 17 °C. Kinetic sensitive volt coulometry [3] was used for the study of a sensor based on the detection of the varied diffusion kinetic towards plasmonic electrodes in dark and under illumination. The chronocoulometric data were used for the description of the charge transport kinetics of species under interest at the

plasmonic electrodes in dark and under illumination. In the course of all performed experiments 1 mM solution of potassium ferrocyanide in 0.1 M NaCl supporting electrolyte was used.

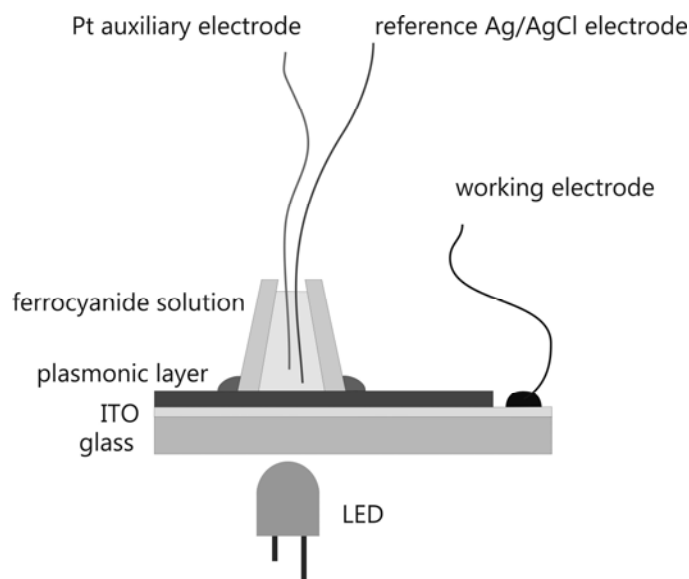


Fig. 1: *Experimental setup – sketch of the electrochemical microcell built on ITO substrate coated with a plasmonic thin film.*

The irregular rough or partially active electrode geometry can cause current density inhomogeneities which in turn yield deviations from ideal Cottrellian behaviour. Diffusion-limited processes on the rough or partially active electrodes 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 [4]. 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 [5]. Recently, the anomalous response in the Cottrell measurements was studied through roughness power spectrum based theory [6]. Here, it was shown that the simplified approach [5] of using one response exponent based scaling ansatz with an effective fractal dimension from the chronoamperometric data does not correspond to the measured fractal dimension from SEM and AFM. We suppose that a similar inexactness of a single power function description of the diffusion current dependence on time should be anticipated in the case of partially active electrodes, too.

Our recent progress in the apparatus development enable us a complex analysis of charge transfer kinetics from both the voltcoloumetric and chronocoloumetric data. The developed method is able to contribute to the elucidation of anomalous charge transfer origin at plasmonic surfaces and to finding the chances of its applications in sensorics. The obtained voltcoloumetric responses are shown in Fig. 2. Following parameters were used in the performed experiments: scan rate 3 mV/s, period 280 ms, sampling pulse duration 10 ms, sampling pulse amplitude - 0.05 V. Experimental data were processed for three chosen sets of sampling schemes. According to the rules published in [3], the chronocoloumetric data were sampled at 10 ms, 50 ms and 90 ms, at 2 ms, 10 ms and 18 ms, and at 1 ms, 5 ms and 9 ms after the trailing edge of the sampling pulse. The parameters D_f were determined by the power function fitting of the chronocoloumetric responses (see Fig 3.) obtained at the voltcoloumetric peaks maxima.

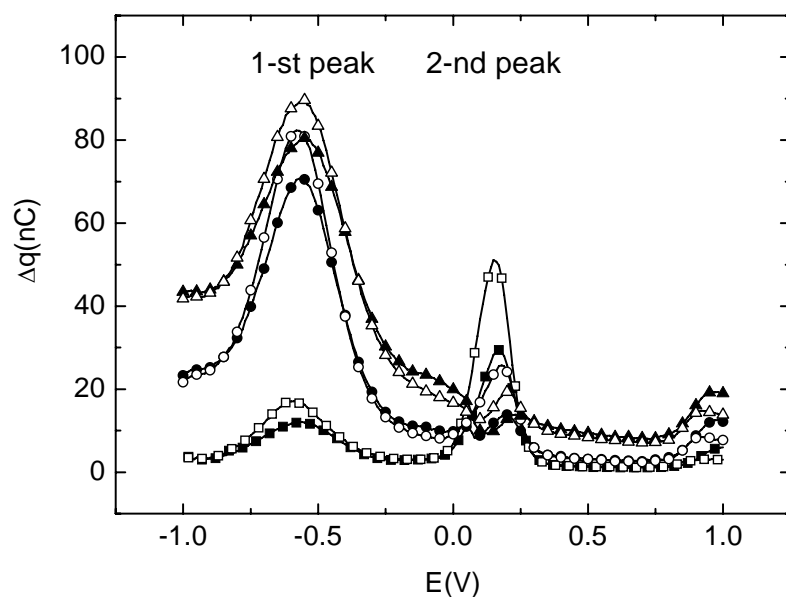


Fig. 2: Voltcoulometric responses of 1 mM potassium ferrocyanide obtained for various sampling schemes (10 ms, 50 ms, 90 ms – squares; 2 ms, 10 ms, 18 ms – circles; 1 ms, 5 ms, 9 ms – triangles) on a plasmonic electrode surface in dark (full squares, dots and triangles, respectively) and under illumination (open squares, dots and triangles, respectively).

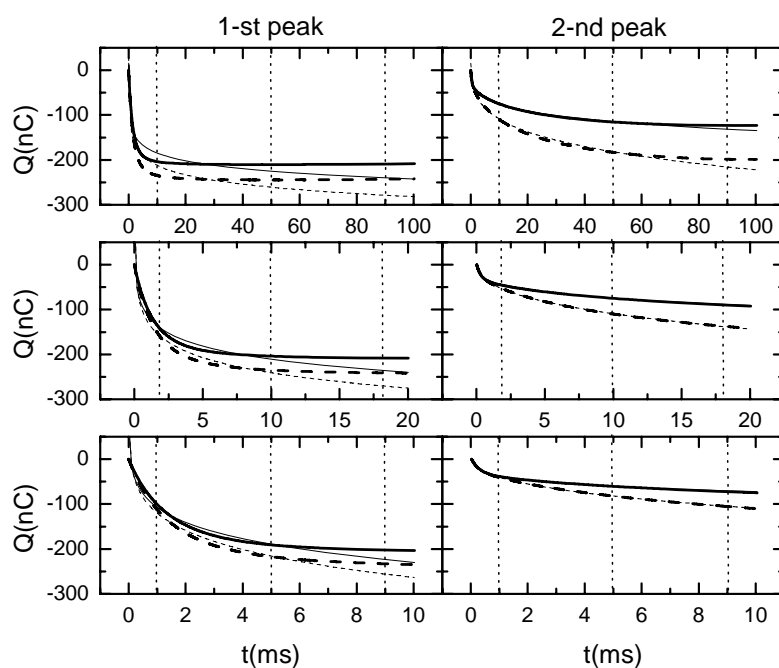


Fig. 3: Chronocoulometric responses of 1 mM potassium ferrocyanide obtained on a plasmonic electrode surface in dark (full lines) and under illumination (dash lines) in maxima of two voltcoulometric peaks depicted in Fig. 2; the power function fits are shown as hair lines. Dot vertical lines are set in the sampling events corresponding to the voltcoulometric signals depicted in Fig. 2

3. Discussion and conclusion

Two marked volt coulometric peaks were observed. The peak at + 0.16 V vs. Ag/AgCl can be assigned to ferrocyanide oxidation, the peak at - 0.6 V vs. Ag/AgCl to the hydrogen oxidation. Different volt coulometric behaviour was observed for these two reactions. The ferrocyanide peak dominates for longer sampling scheme and can be well-fitted by power function giving $D_f = 1.2$ in dark and $D_f = 1.7$ under illumination. On the other hand, the hydrogen peak dominates for short sampling scheme and no satisfactory single power function fit can be done. Such a markedly non-Cottrellian process can lead to an extreme amplification of volt coulometric signal [7].

We have shown, that depending on the nature of the detected ions the plasmonic electrode surface is able either amplify or suppress volt coulometric signal. This phenomenon should be of great importance in the sensitive and selective electrochemical sensing.

The values of D_f obtained by studying the potassium ferrocyanide oxidation at the plasmonic layer point to the presence of partially blocked surface or active islands on inactive support. Under the illumination, a shift towards higher D_f was observed accompanied with the ferrocyanide ions diffusion kinetic closer to the ideal Cottrellian one. This can be explained by the propagation of surface plasmon polaritons resulting in an apparently smoother electrode surface than is typical for nanostructured electrode coatings.

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