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A new strategy towards electroactive polymer–inorganic nanostructure composites. Silver nanoparticles inside polypyrrole matrix with pendant titanocene dichloride complexes

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ABSTRACT

Proposed synthesis route is oriented towards hybrid materials, in which inorganic nanoparticles are distributed mostly inside the film of a polymer with conjugated chain far away from its external surface in contact with solution. Its principal idea is to perform the electrodeposition of these particles from a solute precursor in conditions where the electronic transport across the film is so slow that it represents a rate-determining step of the process and the reduction of precursor molecules takes place deeply inside the pores of the film. Such situation is realized in conjugated polymers functionalized by pendant redox-active centers, if the deposition process occurs in the potential range of their redox activity. Important advantage of this procedure consists in the absence of any additional surface-active or stabilizing agent which has to be used if the nanoparticles are incorporated into the growing film from their solubilized colloidal solution. Sizes of these particles may be varied in a controllable manner by the duration of the process and other parameters of the system.

This approach has been successfully realized for deposition of silver nanoparticles inside the polymer with polypyrrole matrix and titanocene dichloride (**$TcCl_2$**) complex attached to each monomer unit, poly(titanocene-propyl-pyrrole), p(Tc3Py). Redox transformation of these $TcCl_2$ centers in contact with acetonitrile (AN) solution takes place in the negative potential range (starting at about −0.9 V vs. Ag/0.01 M Ag^+ in AN) separated from the interval of the matrix conductivity by broad non-electroactivity potential range. To prevent the reduction of silver cation in the range of the polymer conductivity, i.e. to shift the silver deposition potential strongly in the negative direction, 0.1 M TEACl solution in AN was used as electrolyte in addition to silver cation. Excess of chloride ions results in complete transformation of solute silver into soluble complex anion, $AgCl_2^-$, whose reduction wave at the polymer-coated electrode overlaps with the wave due to reduction of pendant $TcCl_2$ centers. Presence of chloride anions in solution results also in reversible type of the redox transformation of titanium, Ti(IV)/Ti(III), inside $TcCl_2$ complexes, that is a prerequisite for the electronic transport across the film via hopping mechanism.

Process of $AgCl_2^-$ complex ion electroreduction at the p(Tc3Py) modified electrode has been studied by means of electrochemical methods and EQCM. Synthesized composite material: electroactive polymer–nanoparticles has been characterized by SEM-EDX, AFM and TEM-SAED-EDS. Nanoparticles are composed of Ag(0), their crystallography demonstrating the bulk-metal fcc state and the one with fivefold symmetry (isohedral structure).

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1. Introduction

Numerous recent studies are oriented to synthesis of composite materials combining a polymer skeleton with incorporated inorganic structures, see e.g. references in [1–5]. Polymers with conju-

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gated chains are frequently used as the former component [6–9] in view of their advantageous properties which include a low oxidation potential of their monomer (it allows one to carry out their polymerization by chemical or electrochemical oxidation), electronic and ionic conductivity (at certain conditions), porous morphology. The second component may represent a transition metal or an alloy [10–13], an oxide [14–16], a salt [17,18] which are dispersed up to a submicrometer or nanometer size, see also numerous references in review [7], p. 112.

Such systems have demonstrated original properties making them prospective for applications e.g. in catalysis and electrocatalysis [16,19–23], sensors [24–28], micro and nanoelectronics [29], photovoltaics [30,31], batteries and capacitors [32,33], electrochromism [18].

Many synthetic routes towards such hybrid materials exploit electrochemical means. In particular, two approaches have been used in numerous publications devoted to materials which include a conjugated polymer and a dispersed transition metal.

In one of them metal nanoparticles are produced initially as a colloidal solution so that they are entrapped by growing polymer phase (in the form of polymer globules or a film at electrode surface) in the course of electrochemical or chemical oxidation of the monomer [34–38], see also Refs. in [7]. Important advantages of this procedure are: (1) sizes of metal particles are determined by their synthesis protocol, in particular, in certain cases one can ensure low polydispersity of the particle size; (2) these particles are frequently distributed in a uniform manner within the whole polymer phase (across the film or inside a polymer globule). However, to avoid the sedimentation of the initial colloidal solution one has to cover nanoparticles with a protective layer which is generally incorporated inside the composite material together with particles, thus affecting their properties, e.g. in catalysis. Besides, electrochemical procedures are realized usually with addition of a background electrolyte (to ensure a sufficient conductivity of the solution), as a result the counter-charge of the polymer matrix is presented mostly by its ions, thus leading to a low density of the particle distribution inside the material.

Another synthetic route applied mostly for film-coated electrodes is based on the opposite sequence of steps, starting from the polymer film deposition followed by electrodeposition of metal particles from its solute precursors, in particular metal cations [11,39] or metal complex [40], see also references therein and in [7]. A slightly different principle is used in “electroless deposition” where the reduction of the metal precursors is made by the reduced form of the polymer film [41–43] or polymer suspension [44]. An important merit of these approaches is the absence of any protecting layer around generated metal particles while they are stabilized against agglomeration/fusion owing to the surrounding polymer matrix. On the other hand, it is more difficult to achieve the homogeneity in sizes of these particles as well as in their spatial distribution across the film, with frequent tendency to form large-size deposit near the external boundary of the film oriented to the solution. These problems are closely related to a sufficiently high electronic conductivity of the polymer matrix (necessary to transport the electronic charge from the electrode to the deposition sites) which exceeds strongly (in terms of the flux density) the rate of the precursor diffusion across the film.

The basic principle of our approach to the synthesis of such materials is to diminish the rate of the electronic transfer across the film (but avoiding to make the film insulating), to make it the limiting stage of the whole metal deposition process. Another crucial factor is a specific morphological structure of conjugated polymer films electrodeposited at electrode surface [45]: a thin non-porous (“compact”) layer of the polymer is formed at the early stage of deposition while the further polymer growth results in granular or fibrillar morphology [46–50].

This combination of features should modify radically the character of the deposited metal, compared to that for the process based on the electronic conductivity of the polymer matrix. The compact polymer layer prevents the precursor species to react directly at the electrode surface while a low electronic conductivity is to minimize the distance from the electrode/film interface where the reduction of precursor molecules takes place since they may penetrate easily across the porous part of the film. As a result, the metal should be deposited principally near the interface between the compact and porous layers.

If the porous structure of the polymer consists mostly of pores of a nanometer scale one can expect that the deposited metal will be distributed inside these pores, thus ensuring a high density of nuclei inside this area. These nuclei will grow progressively in the course of the further current passage so that their size may be regulated by the consumed reduction charge, i.e. it may be adjusted to the need of an application.

In the actual study we have demonstrated how this strategy may be realized for the process of silver nanoparticle generation inside films of poly(titanocene-propyl-pyrrole), **p(Tc3Py)**, combining the polypyrrole matrix with an electroactive complex, titanocene dichloride, $(C_5H_5)_2TiCl_2$ [51,52].

2. Experimental

All electrochemical experiments were performed in a conventional, single compartment cell with a platinum wire counter electrode (CE) and Ag/0.01 M $AgNO_3$ + 0.1 M $TBAPF_6$ in AN (RE), the latter solution being separated by double frit with intermediate background solution (0.1 M $TBAPF_6$ + AN). All potentials below are referred to this reference electrode. Its potential *vs.* aq. SCE is 0.32 V [51]. Formal potential of the Fc/Fc^+ couple in AN vs. RE is 0.10 V. More detailed information on the cell and procedures is available in [51].

Measurements were carried out on a Pt disk electrode of surface area of 0.009 cm^2, HOPG electrode of surface area of 0.3 cm^2, ITO electrode of surface area of about 0.8 cm^2 or Au thin film electrodes deposited on 10 MHz AT-cut quartz crystals (International Crystal Manufacturing Co. Ltd., Oklahoma City, OK), with piezoelectrically and electrochemically active areas of 0.21 cm^2 and 0.23 cm^2, respectively. Electrochemical measurements were performed by means of potentiostat AUTOLAB PGSTAT 30 (Ecochemie, The Netherlands), while EQCM studies were carried out using a QCM unit (Type M3, UELKO, Poland) combined with AUTOLAB. All measurements were made at room temperature (23 ± 2 °C).

The measured change of resonant frequency (Δf) was recalculated into the change of mass of the surface layer (Δm) according to the Sauerbrey equation [53], which for 10 MHz quartz crystal may be written in the form:

$$\Delta m\ (g) = -1.1 \times 10^{-9} \Delta f (Hz) \qquad (1)$$

The proportionality factor in this relation (within ±2%) was found by calibration for silver deposition on a bare Au EQCM electrode both in aqueous and acetonitrile (AN) solutions. Repeatability of the EQCM measurements was very good: the dispersion of the slope of Δm–Q plots obtained from three independent experiments was within ±(3–5)%.

Salts, $TBAPF_6$ (Fluka) and tetraethylammonium chloride, TEACl (Aldrich), were dried under vacuum at 80 °C for several hours prior to use. $AgNO_3$ (Aldrich) was used without further purification. AN was HPLC grade (Aldrich) with initial water content <0.005%.

Deposition of silver was performed from 0.002 M solution of $AgCl_2^-$ complex in AN, formed in the mixed 0.002 M $AgNO_3$ + 0.1 M TEACl solution. All solutions were thoroughly deaerated by vacuum pumping and filling with dry argon prior to experiments.

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