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Construction of multifunctional materials by intrachannel modification of NIPA hydrogel with PANI-metal composites

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ABSTRACT

Composites containing conductive polymers and Au and Ag nanoparticles were introduced into the environmentally sensitive poly(N-isopropylacrylamide) hydrogel channels. The composites were synthesized directly in the channels by two phase polymerization procedure. In the first step the unmodified hydrogel was placed in a solution containing the oxidizing agent ($HAuCl_4$ or $AgNO_3$), and in the second step it was placed in a solution of aniline in nitrobenzene. The presence of polyaniline and metal nanoparticles increased conductivity of both types (ionic and electron) while the hydrogel properties, such as: flexibility, plasticity and ability to phase transition, were preserved. The presence of nobel-metal nanostructures added catalytical activity to the new materials. Optical and SEM investigations revealed that polymer-metal composites were uniformly distributed in the entire gel samples. NIPA-PANI-Au composites exhibited a sharp volume phase transition in response to changes in temperature and ionic strength. That behavior was similar to unmodified poly (N-isopropylacrylamide) hydrogel. The new material was electroactive and had electrocatalytical properties towards electrooxidation of ethanol. Electroactivity of the modified gel was a strong function of the swelling ratio; the shrinking process enhanced the voltammetric response.

1. Introduction

Composite materials containing hydrogels, conducting polymers and metal nanoparticles are interesting materials due to preserving by them of the unique properties of separate ingredients. These properties are: a) removal of large amount of solvent; this is typical for hydrogels, b) good conductivity typical for conducting polymers and metals, and C) catalytical properties usually observed for metal nanoparticles. This unique composition of properties opens a wide range of possible applications for the hybrid materials in biosensors, drug delivery systems, batteries and other electrochemical applications.

Poly(N-isopropylacrylamide) gels belong to a large group of materials known as polymeric hydrogels. The polymer chains are cross-linked and the gels are filled with an aqueous solution. These gels exhibit a drastic transition from the swollen state, where they are filled with a liquid, to the shrunken state. The transition is reversible. During the shrinking process most of solvent is removed from the polymeric network. The transition process can be initiated by a change in one of several factors, e.g. temperature [1], pH [2], and ionic strength [3]. NIPA hydrogels and their derivatives are considered as good candidates for drug delivery systems [4,5], environmental sensitive switches [6] and materials for biosensors [7,8] and optoelectronics devices [9,10].

Introduction of a new phase, such as conductive polymer with metal particles, to the gel matrix may lead to potentially very promising electrode platforms with new possibilities of applications compared to pure hydrogels. Such modified gels should exhibit good conductivity, due to the presence of metal nanoparticles, and enhanced catalytic activity typical for those metal nanocrystals. Thus the composite materials can be used as catalysts [11,12], in sensors [13,14] biosensors [15,16] and supercapacitors [17,18], and even as an antibacterial material used against gram positive bacteria – *B. subtilis* [19]. A combination of composite materials with enzymes can lead to improved specificity of constructed biosensors [20,21].

Oxidative-radical polymerization is a useful pathway that enables formation of composite materials based on conducting polymers. It can be carried out in one- or two-phase system, where monomer particles and the oxidant ions are present in one solution or are separated in two immiscible liquids. Usually, the two-phase polymerization procedure was limited to synthesis of pure conducting polymers [22,23] and conducting polymers with incorporated metal nanoparticles [24,25]. Then the synthesis occurred at the boundary of two immiscible solutions - aqueous and organic - containing the oxidant ions and the

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monomer particles, respectively [26]. Previously, we have shown how to obtain a conducting polymer-metal nanoparticles composite on various solid substrates [27]. Also, we have shown how to fill a hydrogel polymeric network with a conducting polymer by applying the specific two-phase synthesis [28]. Firstly, the gel samples were filled with a solution of the oxidizer ions and then they were kept in contact with an organic solution of the monomer.

In this work we employed a newly developed- and easy way of obtaining hybrid materials built out of NIPA hydrogel, polyaniline and gold or silver nanoparticels. We wanted to obtain materials with homogeneously distributed metal nanoparticles in the conducting-polymer matrix, and further, evenly distributed polyaniline in the pores of a NIPA hydrogel network. The prepared composites exhibited a sharp volume phase transition, typical for NIPA hydrogels, in response to change in temperature and ionic strength. We expected that the obtained new materials were conductive, electroactive and had good electrocatalytical properties.

2. Experimental

2.1. Materials

NIPA-gel substrates: *N*-isopropylacrylamide, *N,N′*-methylenebisacrylamide, ammonium persulphate, and *N,N,N′,N′*-tetramethylethylenediamine were purchased from Aldrich. Reagents used for the conducting-polymer-metal composite synthesis, i.e.: aniline, nitrobenzene, tetrachloroauric acid, silver nitrate, HCl and $HClO_4$ (served as the supporting electrolyte) were purchased from POCh. All reagents were at least of p.a. purity. Purified water was obtained from a Mili-Q Plus/Milipore purification system; conductivity of water was $0.056\,\mu S\,cm^{-1}$.

2.2. Preparation of poly(N-isopropylacrylamide) gel/polyaniline-metal nanoparticles (NIPA-PANI-met) composites

Poly(N-isopropylacrylamide) (NIPA) gels were synthesized in glass tubes and capillaries of inner diameter 7.9 mm and ca. 500 µm, respectively, using free-radical solution copolymerization according to the procedure described previously [29]. The dried samples of the NIPA polymer were placed in water cooled to 5 °C and kept there for 48 h to achieve the complete swelling process. Then the gel samples were immersed in $HAuClO_4$ and $AgNO_3$ solutions of different concentrations: 0.0001 to 0.1 M $HAuCl_4$ and 0.5 to 2 M $AgNO_3$. The appropriate volume of added solutions was calculated taking into consideration the volumes of the gel sample and the required final concentration of oxidants (0.7 M for $AgNO_3$ and 0.1 M for $HAuCl_4$). After 2 h the gel samples were transferred to a 0.5 M aniline solution in nitrobenzene. The process of oxidation of aniline lasted 48 h at room temperature. Then the composite samples were immersed into ethanol for a few days to terminate the oxidation process and to wash away the residual chemicals. During the purification process ethanol was exchanged several times and the excess of conducting polymer that initially remained on the surface of the gel, was removed. Finally, the samples were washed thoroughly with deionized water to make sure the polyaniline was present in the base state.

2.3. SEM investigation

Examination of surface of dried gel samples were performed using a FE-SEM, Merlin, Zeiss (Germany). Before the examination each sample was covered with a 1–2 nm thin film of Au-Pd alloy to avoid electrical charging of the sample surface. The layers of the alloy were sputtered using a Polaron SC7620 Mini Sputter Coater.

2.4. Electrochemical measurements

Voltammetric measurements were performed in the three-electrode system using a VersaSTAT 4 (Ametek, USA) potentiostat. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire served as the auxiliary electrode. Glassy carbon cylinders (1.1 mm in diameter and 7 mm in length) served as the working electrodes. The cylinders were physically inserted into the gel materials.

2.5. Conductivity measurements

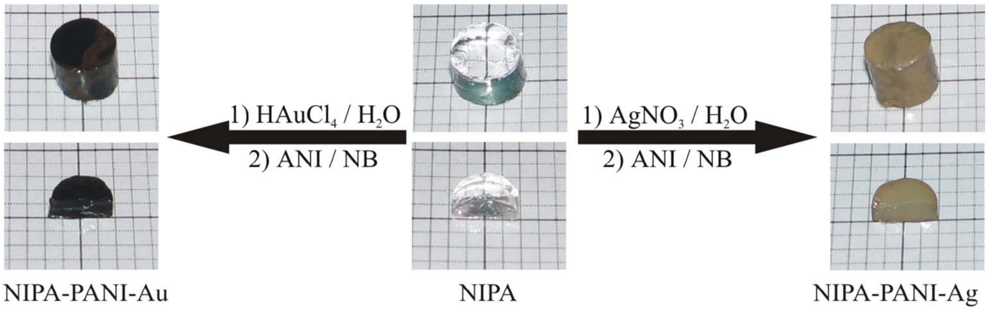
The conductance was measured using a conductance meter, Radiometer model CDM230, with a CDC241–9 conductivity cell. The cell constant (k) was determined using conductivity standard solutions purchased from Fluka. Its value was determined as $1.10\,cm^{-1} \pm 0.01\,cm^{-1}$ ($k \pm s(k)$).

2.6. Measurement of swelling ratio of modified gel rods

The purified composite samples were inserted into a water-jacked cell filled with water. The changes in gel volume, caused by changes in temperature or in concentration of acid ($HClO_4$) were determined from the changes in sample diameter by using an inverted optical microscope (Olympus, model PME 3) equipped with a calibrated scale. The swelling ratio for the rod-shaped gels was approximated as $V/V_o = (d/d_o)^3$, where V and Vo represent the equilibrium volume of the hydrogel and the initial gel volume, d is the diameter of the gel rod, and d_o denotes the diameter of the glass tube in which the gel was synthesized (see Scheme 1).

3. Results and discussion

Morphology and distribution of the conducting polymer and metal nanoparticles in NIPA hydrogel matrix were observed using the SEM technique with different detectors. The pure NIPA and NIPA-PANI-metal samples were prepared for the SEM investigation from their swollen state by freezing them in liquid nitrogen and then freeze-dried. Columns A, B and C in Fig. 1 show cross sections of the lyophilized NIPA hydrogel, NIPA-PANI-Au hydrogel obtained with lower $HAuCl_4$ concentration, and NIPA-PANI-Au hydrogel obtained with proper $HAuCl_4$ concentration (0.1 M), respectively. It can be seen that



Scheme 1. Scheme of NIPA hydrogel modification with PANI-metal composites and cylindrical NIPA, NIPA-PANI-Au and NIPA-PANI-Ag samples. Bottom row: horizontal and vertical cross sections of gel samples.