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Macroporous indium tin oxide electrode layers as conducting substrates for immobilization of bulky electroactive guests

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ABSTRACT

Macroporous indium tin oxide (ITO) electrodes with a defined uniform pore size were prepared via direct co-assembly of ultra-small indium tin hydroxide (nano-ITOH) nanoparticles and poly(methyl methacrylate) (PMMA) beads. The use of nano-ITOH nanoparticles enables a facile large-scale fabrication of homogeneous crack-free coatings with good adhesion to the substrate, good optical quality and tunable thickness, which easily transform at 400 °C into crystalline ITO with similar morphology. Macroporous ITO films exhibit reasonably high electric conductivity of $4.0 \pm 0.3\,\mathrm{S\,cm^{-1}}$ and open interconnected pores with a uniform size of ca. 300 nm, which makes them suitable conducting platforms for immobilization of bulky redox species or for deposition of functional electroactive layers. Deposition of functional semiconducting layers on the walls of the porous ITO scaffold was shown for titanium dioxide, which penetrates the ITO framework as shown by transmission electron microscopy (TEM) analysis of a cross-section. The obtained layers were used as conducting substrates for the immobilization of the heme proteins cytochrome c and hemoglobin, which demonstrate a direct electron transfer to the macroporous ITO electrode. Surface coverage of cytochrome c adsorbed on the macroporous ITO electrode is more than 12 times higher than on a planar one, reaching $400\,\mathrm{pmol\,cm^{-2}}$ for a film of ca. 360 nm in thickness. Hemoglobin adsorbed on the macroporous ITO electrodes also demonstrates a noticeably high surface coverage of ca. $160 \pm 20\,\mathrm{pmol\,cm^{-2}}$, which is roughly 7–10 times higher than the theoretical value for monolayer coverage.

1. Introduction

The deposition of nanostructured electrode layers with a defined morphology is an important challenge in modern electrochemistry, as it enables the controlled design of complex electrochemical systems [1,2]. Transparent conducting oxides (TCOs) play a special role in electrochemistry, being used as transparent electrode layers for optoelectrochemical and electrochromic applications as well as spectroelectrochemistry. Dense flat layers of TCOs such as doped indium, tin or zinc oxides have been known and used for a long time, but only recently has the fabrication of conducting 3D-TCO networks been reported [3–12]. Such architectures are especially attractive as conducting hosts for immobilized species owing to their large interface area enabling high loading of functional redox guests, electrical conductivity of the framework providing direct communication with the incorporated species, and optical transparency allowing interactions with light.

Since the first publication in 2006 [3], several porous TCO architectures have been developed, including indium tin oxide [3,7,8,10,11] and doped tin oxide [4,6,9,12]. The major efforts have been aimed at the fabrication of mesoporous TCO materials with pore sizes of about 10 nm. Such morphologies feature a very high surface area enabling high loading of functional guests. However, the relatively small pore diameter precludes the incorporation of bulkier moieties, especially larger biological entities such as enzymes or protein complexes. This stimulated the quest for materials with larger pores, particularly those in the macropore range (i.e., over 50 nm).

Macroporous films offer distinctive morphological features, such as an open porous architecture enabling efficient mass transfer, an interconnected framework beneficial for charge

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transport processes, and large pore sizes advantageous for the incorporation of bulky guest species or functional layers. They are usually made using latex beads as templates for the porosity. Typical protocols involve either infiltration of the voids of ordered bead arrays with different TCO precursors (the so-called infiltration method involving the bead assembly and their subsequent infiltration with suitable precursors), or direct co-assembly of the TCO precursors and the latex beads (the so-called co-deposition method) [13–18]. The latter method may offer a better control over the precursor-to-template ratios, simplicity and shorter fabrication times, provided the accompanying challenges, such as colloid stability, can be overcome.

Fabrication of the macroporous TCO layers with pores several tenths to several hundreds of nanometers in size has been reported by Ozin et al. [19,20] and Xu et al. [21,22], who fabricated periodic macroporous antimony doped tin oxide (ATO) films and fluorine doped tin oxide (FTO) films with inverse opal structures. In ref. [23] the disordered template of polystyrene spheres was infiltrated by atomic layer deposition by alternating pulses of organometallic precursors and a hydrolytic polycondensation agent. Alternatively, macroporous nanobead FTO electrodes were obtained by the assembly of hollow FTO nanobeads [24]. Finally, disordered macroporous foams of undoped In_2O_3 and SnO_2 were prepared by the impregnation of cellulose membranes with preformed nanoparticles [14].

For the preparation of TCO films, where the suitable crystallinity is a major prerequisite for a successful performance, the use of pre-formed crystalline nanoparticles as building blocks was shown to be advantageous [4,7,14,20]. Classical sol-gel techniques, which provide basically amorphous material requiring a heat treatment to achieve sufficient crystallinity, often do not give sufficient control over the crystallinity. The particle-based procedures can overcome this limitation, but the success of this preparation route depends on the availability of suitable building blocks for the assembly of 3D-porous structures. The nanoparticles used for the assembly have to be completely dispersible in polar solvents compatible with the PMMA beads.

We describe the fabrication of transparent conducting indium tin oxide (ITO) electrodes with a uniform macroporous structure. The developed procedure is based on controlled co-assembly of ultra-small indium tin hydroxide (nano-ITOH) nanoparticles developed earlier in our group [7] and poly(methyl methacrylate) (PMMA) latex beads, leading to macroporous layers with pores several hundreds of nanometers in size. The perfect dispersibility of nano-ITOH without any stabilizing agents, their preferential interaction with the hydrophilic part of templates leading to their self-assembly, and a facile transformation of the assembled hydroxides into crystalline ITO with similar morphology make them very attractive building blocks for the preparation of nanostructured ITO materials with controlled morphologies. In this paper we demonstrate the use of nano-ITOH nanoparticles for the facile large-scale deposition of 3D-macroporous ITO electrodes featuring optical transparency and a large conducting interface.

2. Experimental part

2.1. Synthesis of macroporous ITO thin film electrodes

Macroporous indium tin oxide (ITO) electrodes used in this work were prepared by direct co-assembly of poly(methyl methacrylate) beads (PMMA) and indium tin hydroxide nanoparticles (nano-ITOH). PMMA beads with diameters of 370 nm and 100 nm were synthesized according to the emulsion polymerization route described elsewhere [25,26]. In a typical procedure, bidistilled water (98.0 mL, Millipore Q grade) was degassed with nitrogen in a three-necked flask for 1 h, before sodium dodecylsulfate (5.6 mg) and methylmethacrylate (35.5 g) were added. The monomer mixture was stirred for 1 h at 90 °C in nitrogen atmosphere to obtain a homogenous emulsion. A solution of potassium peroxodisulfate (56 mg) in water (2 mL) was injected to initiate the polymerization. The solution turned white within 5 minutes, indicating the formation of polymer particles. The reaction was continued for 2 h at 90 °C, before the flask was exposed to air and cooled with an ice bath. The colloidal solution was stirred overnight, filtered through glass wool and washed three times by centrifugation (50000 rcf; 30 minutes) and redispersion in water. Indium tin nanohydroxides were prepared by a procedure described elsewhere [7]. Briefly, 0.091 g of tin (IV) chloride (Aldrich) was added to a clear solution of 0.698 g of indium (III) chloride (ABCR) in 7 mL of ethylene glycol (Sigma-Aldrich, ≥99%, used without further drying). Dissolution of all the salts is very exothermal and has to be performed at 0 °C in the ice bath under stirring. The molar ratio of tin and indium was 1: 9 mol: mol. Separately, 0.420 g of sodium hydroxide (Aldrich, 97%) was dissolved in 7 mL of ethylene glycol at 0 °C. Both solutions were combined at 0 °C and stirred for another 15 minutes. The mixture was transferred into a Teflon or glas-lined autoclave, which was kept in a pre-heated laboratory oven at 205 °C for 24 hours. After reaction the autoclave was taken out the oven and cooled down in air. The formed product was separated by centrifugation (47800 rcf for 20 min). The precipitate was washed once in ca. 14 ml of bidistilled water (manual stirring) and centrifuged again at 47800 rcf for 20 min. The water should be decanted immediately after centrifugation to prevent redispersion of ITOH nanoparticles. The still wet pellet resulting from centrifugation was collected and stored in a closed vessel to prevent drying. The solid content of the collected material was determined for each new batch gravimetrically by weighing of a certain amount before and after evaporation of water. The average solid content in the washed nanoparticles after centrifugation was 40 ± 10%.

For the fabrication of macroporous films, still wet nano-ITOH nanoparticles (300 mg) containing 100 mg dry inorganic content were dispersed in 0.75 mL water (Millipore Q grade), stirred at room temperature until the colloidal solution turned transparent or slightly opaque (this process taking up to 2 days), and ultrasonicated for 30 min. Separately, an aqueous colloidal PMMA suspension (15 wt %) was stirred for 1 hour and ultrasonicated for 30 min. The amount of PMMA beads is calculated from the weight of the ITOH nanoparticles (dry content) as 3 weight parts of PMMA to 1 weight part of ITOH; in this example corresponding to 2 ml of 15 wt % PMMA dispersion. Finally, hydroxypropyl cellulose (HPC) (M_W ca. 100000, from Sigma-Aldrich) was added to a combined solution of PMMA and nano-ITOH, stirred together for 3-4 hours and ultrasonicated for 30 min. The amount of cellulose corresponds to 10 wt % of the PMMA beads; in this example it is 30 mg of HPC in a total volume of 3 ml, which corresponds to 1 wt % HPC. The homogeneous dispersion was dip coated onto glass or planar ITO substrates, dried at room temperature and calcined in air at 400 °C (achieved with a ramp of 13 °C min^{-1}) for 30 min. The film thickness of one layer was around 400 nm after calcination. Thicker films of up to several micrometers in thickness can be obtained by repeated coating. For multiple coating, the films were heated after each dip coating step at 80 °C for 45 min and finally calcined according to the procedure described above. The best film quality was obtained for the solution containing 1 wt % HPC at dip coating rate of 0.63 mm s^{-1}. The relative humidity and the temperature in the coating chamber were 35 % and 20 °C, respectively. To improve the electrical conductivity of the ITO layers, they were additionally heated in forming gas (composed of 5 % hydrogen and 95 % nitrogen) at 400 °C (achieved with a ramp of 2 °C min^{-1}) for 30 min.