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Fiber-optic detection of chlorine in water

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ABSTRACT

Monitoring of the chlorine content represents important issue of the control of water quality. Crucial points of this control are detection of low chlorine concentrations around 1 ppm and reversibility of chemical reactions between strong oxidation agent, chlorine and opto-chemical transducers used for the detection. This paper deals with fiber-optic detection of chlorine in water by using a commercially available absorption transducer *o*-phenylenediamine (*o*-PDA) electrochemically immobilized onto fiber-optic substrates coated with Indium–Tin-Oxide (ITO).

Sensitive layers of the absorption transducer *o*-PDA were prepared electrochemically by cyclic voltammetry. The layers were applied onto declad segments of polymer-clad silica fibers coated with a thin conductive ITO layer making the electrochemical deposition possible. Prepared detection elements were exposed to aqueous solutions of chlorine of various concentrations and spectral response and time response curves were measured. Oxidized sensitive layers were regenerated chemically by using a solution of sodium thiosulfate. A limit of detection of chlorine in water of about 0.14 ppm has been achieved, making the detection of chlorine in water within the hygienic limits feasible.

1. Introduction

Control and improvement of the quality of drinking water have attracted the attention of specialists as well as consumers all around the world for years. Since chlorination is the most frequently used way of disinfection of drinking water, the continual monitoring of chlorine content represents an important issue. Depending on the legislature and purpose, a minimum or maximum content of free chlorine (i.e. dissolved chlorine, and HClO, and ClO^-) in tap water between 0.08 and 0.8 ppm [1–3] is required or allowed. These relatively low values and strong oxidation effects of chlorine, making its reaction with opto-chemical transducers usually irreversible, represent important issues of analytical determination or detection of chlorine.

Apart from the development of a number of conventional, reliable but discontinuous analytical methods [4–9], some extrinsic sensors employing optical fibers or capillaries were tested [10–12]. An intrinsic optical sensor of chlorine relying on planar waveguides was proposed [13]. In this sensor, an opto-chemical transducer forming a sensitive layer of the sensor was regenerated electrochemically after its interaction with chlorinated water. A thin layer of Indium–Tin-Oxide (ITO) deposited in between a dielectric optical substrate and the sensitive transducer layer worked as a conductive and transparent electrode employed for the regeneration. An unconventional transducer, lutetium bipthalocyanine ($Lu(PC)_2$), applied onto a ITO-coated planar waveguide by vacuum evaporation was employed. A limit of detection (LOD) of around 1 ppm of chlorine was reported [14]. Recently, set of commercially available opto-chemical transducers immobilized onto planar waveguides electrochemically or by the sol–gel method has been tested [15,16] and the best LOD of 0.25 ppm has been obtained.

This paper focuses on fiber-optic detection of chlorine in water by using a commercially available absorption transducer *o*-phenylenediamine (*o*-PDA) electrochemically immobilized onto ITO-coated fiber-optic substrates.

2. Experimental

Polymer-clad silica (PCS) optical fibers with a core diameter of 360 μm and polydimethysiloxane cladding were used for the experiments. Segments of the fiber with an overall length of 30 cm were declad in a length of 12 cm and a thin ITO layer was deposited on this bare silica core from an ITO target (AK510, Umicore) by using DC magnetron sputtering (BAS 450 PM, Balzers). The deposition was performed at room temperature and at a partial pressure of argon of 0.8 Pa, by applying a stabilized power of 1 kW. Deposited

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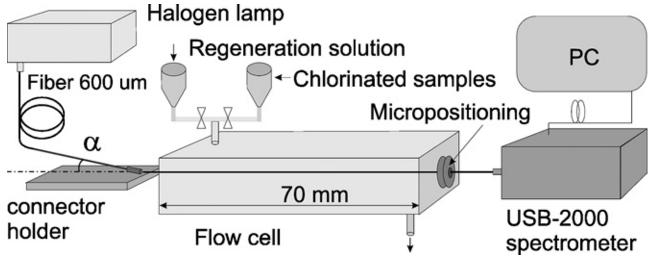

Fig. 1. Set-up for optical characterization.

layers were additionally annealed at 250 °C for 2 h in vacuum. The conductivity of ITO layers was determined by the conventional measurement of the resistance between two conductive contacts (silver paste Leitsilver G302) applied on both ends of the ITO-coated part of the fiber segment.

The ITO-coated fiber segments were electrochemically coated with a sensitive layer of *o*-PDA by using cyclic voltammetry (CV). For this purpose a potentiostat (PalmSens, Palm Instruments BV) with the common three-electrode system was used. In these experiments, the ITO-coated fiber segments were used as working electrodes, while a Pt-electrode and saturated calomel electrode served as counter and reference electrodes, respectively. The sensitive layers were deposited from 0.004 M solution of *o*-PDA (Aldrich, US) in 0.1 M sulfuric acid (Lachema, CR). Because of the strong influence of pH on CV [15,16], the solution was stabilized at pH 1.0. Forty CV cycles were performed within a potential range from −0.4 to +1.2 V using a 50 mV/s scan rate. In order to prevent damage of the ITO-coated fiber segments, eight CV runs of a pretreatment in a dilute sulfuric acid were applied.

Several optical characteristics of the prepared detection elements were determined. First of all, angular distributions of the output power of the declad and ITO-coated fiber segments were determined under their excitation with an inclined collimated beam [17]. An angle of incidence suitable for the selective excitation in the sensitivity experiments was determined from these measurements. Then, optical responses of the detection elements coated with ITO and sensitive layers to chlorine were characterized by using a set-up schematically shown in Fig. 1. The set-up consists of a special cell, halogen lamp (HL-2000-HP, Ocean Optics) and fiber-optics spectrometer (USB-2000, Ocean Optics). The position of the detection elements in the set-up was controlled by micropositioning ensuring reproducible measurement conditions.

Water samples were chlorinated by sodium hypochlorite (Roth, De) stabilized at pH 6.5. These samples at ambient temperature were injected into the cell and spectra of the output power were measured. Any stirring inside the cell was not applied. Spectral responses of the detection elements to chlorine were obtained by relating the optical power measured with a particular chlorine solution to that determined with water.

A solution containing 100 ppm of $Na_2S_2O_3$ (Lachema, CR) of pH 5 was tested for chemical regeneration of the sensitive layers after their interaction with chlorinated water samples. Time response curves were measured at the fixed wavelength of 650 nm when chlorinated and regenerating solutions were repeatedly applied. The concentration of chlorine in water was checked by using a Spectroquant Picco (Merck) device.

3. Results and discussion

CV curves measured during the deposition of *o*-PDA layers onto the bare silica core of the fiber segments can be seen from Fig. 2. These curves are similar to those measured during CV deposition of *o*-PDA layers onto planar substrates [16]. From Fig. 2 one can see that the current intensity increased with increasing the number of CV cycles. This result indicates that the deposited transducer layer is conductive itself and that the layer thickness increased during the CV process. The redox potentials of the transducer corresponding to local maxima (oxidation process $E_{ox} = -0.3$; +0.1 V) and minima (reduction process $E_{red} = -0.2$ V) can be determined from the CV curves.

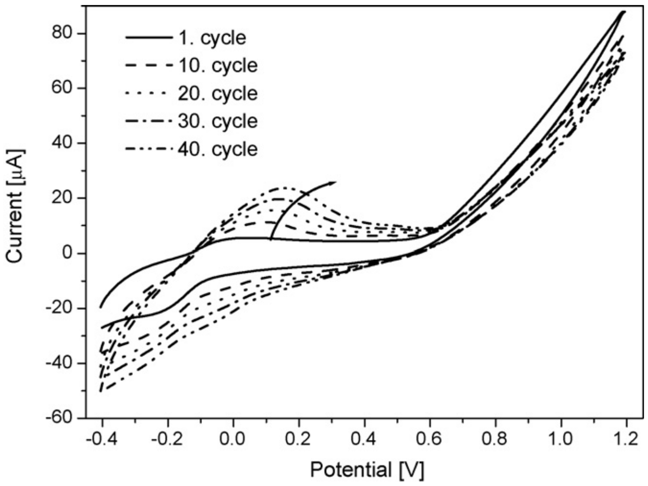

Fig. 2. CV curves of the *o*-PDA deposition.

As it is difficult to determine thickness of thin layers applied onto circular fiber substrates [18], the thickness of the applied ITO and *o*-PDA layers was only estimated. The estimation was based on values obtained from ellipsometric measurements of the layers of the same composition applied onto glass slides under conditions comparable with those used for coating of the fiber segments [16]. On this basis a thickness of ITO layer of around 30 nm and that of *o*-PDA layer of around 20 nm could be estimated. A typical appearance of the applied layers can be seen from Fig. 3. A proper quality of the applied ITO layer was characterized by a conductivity value of 1300 Ω/cm. This characteristic of the ITO layer made the CV deposition of sensitive *o*-PDA layers possible.

The comparison of the angular distributions of the output optical power of the PCS fiber and ITO-coated PCS fiber segments can be seen from Fig. 4. A very narrow distribution was measured with the

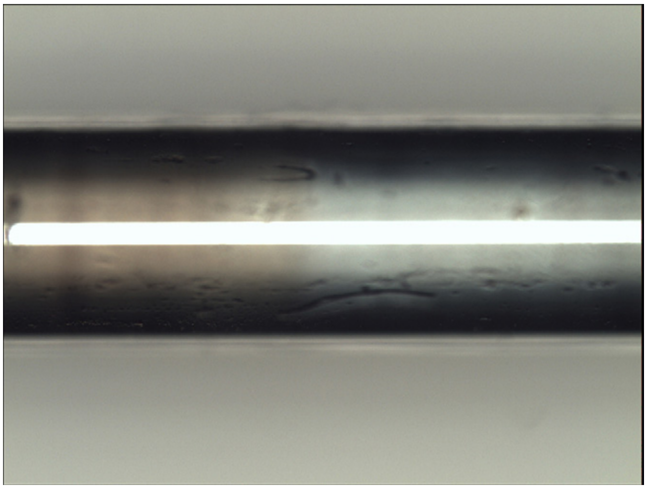

Fig. 3. Micro photo of the surface of PCS fiber coated with transparent ITO layer (right) and brown (dark) *o*-PDA layer (left).