Electrochemical Fabrication and Characterization of Porous Silicon/Polypyrrole Composites and Chemical Sensing of Organic Vapors

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Electrochemical functionalization of porous silicon surface with polypyrrole via cyclic voltammetry method is presented. Surface morphology and spatial distribution of elements in the porous silicon/polypyrrole layer were inspected using Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy, respectively. Changes of surface chemical composition during electrodeposition were determined by Fourier-transform infrared spectrometry. Porous silicon samples were subsequently tested for selectivity improvement of photoluminescence sensor response in chemical sensors of organic vapors. Combined effect of polarity and size of detected analytes played a decisive role in interaction of analyte with polypyrrole layer and determined modified sensor response of porous silicon/polypyrrole composite.

1. INTRODUCTION

Porous silicon (PS) based materials have many applications in the field of chemical sensors [1]. Porous structure of the material and large internal surface imply a high sensitivity of physical and

chemical properties on the presence of chemical compounds which makes these materials very promising for commercial sensors [2]. Various transducer principles have been proposed for silicon nanocrystals, based on changes of resistance [3,4], capacitance [5,6], ellipsometric parameters [7], photoluminescence [8] and reflectivity [9]. Porous silicon composites provide modified functionality comparing to as-prepared porous silicon and expand its applicability [10]. Functionalized surface of porous silicon responds in a different way to the presence of chemical compounds and makes possible to improve selectivity of sensor response. Combination of various functionalized sensor elements in a sensor array – electronic nose or (in gas phase measurements) – enables construction of sensors capable to measure single analyte in a mixture.

Electrodeposition of a conductive polymer on porous silicon is an attractive surface functionalization method [11,12,13]. Conductive polymer composites have attracted attention in many fields of applications like biomedical tools, batteries, functional electrodes, electrochromic devices, sensors etc. [14]. Combination with conducting polymer improves mechanical and electrical properties of porous silicon [15] and enhances its stability against oxidation [16]. Fabrication of porous silicon/polypyrrole composites offers a synergetic approach for enhancement of both chemical stability of porous silicon surface and mechanical properties of conductive polymer what expand application potential of both materials. Manipulation with native polypyrrole (PPy) films represents a problem from the mechanical point of view [17]. Several electrochemical way of combining these materials – galvanostatic [12,18,19], potentiostatic [20] or cyclic voltammetry approach [21] were used.

In this work we have used cyclic voltammetry procedure for fabrication of porous silicon/polypyrrole (PS/PPy) composites. The motivation for this work is construction of a simple sensor array – PS hydrogen terminated sample and PS/PPy composite – for photoluminescence detection of analyte in a mixture. For operation of the sensor array the understanding of sensor response mechanism – i.e. how the presence of various analytes affects photoluminescence intensity – is of crucial importance. The principal mechanism of photoluminescence quenching of as-prepared porous silicon in gas phase detection of organic compounds is already known [22], explanation of mechanism for porous silicon functionalized with conductive polymer is the aim of this paper. We have extended our previous study [23] using improved fabrication technology, optimization of PPy electrodeposition by variation of fabrication parameters, characterization by SEM/EDX and measurement of photoluminescence sensor responses that enabled quantitative evaluation of observed data for real applications.

Macroporous silicon was fabricated from lightly doped p-type substrates by electrochemical anodic dissolution. Our goal in polypyrrole electrodeposition of porous silicon was to prepare samples with PPy layer of thickness that would neither prevent excitation light absorption nor photoluminescence emission from silicon nanocrystals present inside porous silicon matrix. Parameters influencing the polypyrrole formation on macroporous silicon pore walls like chemical state of surface, oxidation potential and number of scans are discussed. Prepared PS/PPy composites were characterized by scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis and Fourier-transform infrared (FTIR) spectroscopy. Photoluminescence from as-prepared porous silicon and porous silicon/PPy composite was subsequently studied in the presence of controlled amounts of linear aliphatic alcohols. Changes of photoluminescence response due to polypyrrole

electrodeposition onto PS surface were evaluated and sensor response sensitivity and characteristic concentration were determined. The role of analyte polarity and size during its interaction with polypyrrole layer and possible mechanism of processes behind the observed behavior is discussed.

2. EXPERIMENTAL PART

2.1. Fabrication of porous silicon/polypyrrole composite

Electrochemical etching of crystalline silicon in a HF + EtOH mixture was performed in a Teflon cell with two electrodes. Silicon wafer was connected as an anode and a Pt disc as a counter electrode (cathode). Silicon was etched at current densities in range of 5-20 mA/cm^2 for 30 to 60 minutes. Polypyrrole electrodeposition onto porous silicon surface was carried out in a three electrode cell. Prior the electrodeposition, Pt auxiliary electrode was separately purified by the cycling in 0.5 M H$_2$SO$_4$ (connected as working electrode). Afterwards ferrocene solution (1 mM) was used to determine the potential of a reference electrode in acetonitrile. The used reference electrode was a saturated calomel electrode (SCE) with salt bridge containing base electrolyte solution (0.05 M Bu$_4$NClO$_4$ in acetonitrile). Polypyrrole was electrodeposited on porous silicon surface by cyclic voltammetry using a PGSTAT101 potentiostat (Methrohm Autolab, Netherlands) in acetonitrile with 0.05 M Bu$_4$NClO$_4$. Detailed conditions are described later. All electrolytes were bubbled with argon before cyclic voltammetry experiments for about 10 minutes and purged during the potential scans.

2.2 Chemicals and materials

Crystalline silicon (Czochralski type, p-type boron doped, <100> crystallographic orientation, specific resistivity ~10 Ωcm) was purchased from ON Semiconductors (Rožnov, Czech Republic). Silicon wafers were cleaned in 48% hydrofluoric acid (Pliva Lachema, semiconductor grade) for 15 minutes before etching procedure. Ethanol (96%, spectroscopic grade, Lach-Ner, Czech Republic), ferrocene (p.a., Sigma-Aldrich, USA) and tetrabutylammonium perchlorate (Fluka, purissimum for electrochemistry, USA) were used as purchased. Acetonitrile and pyrrole (Sigma-Aldrich, USA) were dried over freshly activated 3 Å molecular sieves (Sigma-Aldrich, USA) for two days and distilled immediately before use under argon or vacuum, respectively. Solvents were prepared on a vacuum line and handled under an atmosphere of dry argon. Analytes used for measurements of photoluminescence sensor response (linear alcohols, aromatics) were dried over 3 Å molecular sieves.

2.3. Characterization of porous silicon/polypyrrole composite

Porous silicon and porous silicon/polypyrrole samples were characterized by means of scanning electron microscopy equipped with EDX analysis, Fourier-transform infrared spectroscopy and photoluminescence (PL) spectroscopy. SEM measurements were performed using Mira I microscope (TESCAN, Czech Republic) working at 15 or 30 keV electron beam energy and equipped with a Bruker detector for EDX analysis. FTIR measurements were performed using iN10 infrared

microscope-spectrometer (Thermo Fisher Scientific, USA) with cooled MCT/A detector in a transmission mode with resolution of 4 cm^{-1}. Standard aperture was 150×150 μm. Photoluminescence of PS and PS/PPy samples was excited at 375 nm using an UV LED RLT 370-10 diode (Roithner Lasertechnik, Austria) at 10 mA modulated by FG720F function generator (Motech, Taiwan), analyzed using an HT20 monochromator (Jobin-Yvon, France) and detected with R3896 photomultiplier (Hamamatsu, Japan). Signal was processed with a lock-in amplifier SR 830 (Stanford Research Systems, USA). For measurements of gas phase photoluminescence sensor response at various analyte concentrations the photoluminescence setup was combined with a system for preparation of controlled amount of detected analytes in a measurement cell (optode). Photoluminescence was collected near spectral maximum, spectral width of monochromator slit was 16 nm. The system have operated in two modes: 1. a purging mode, when a porous silicon sample in the optode is purged with pure nitrogen and, 2. a closed-cycle mode, when an injection of precise amounts of analytes by means of a Hamilton syringe into system results in an environment with defined analyte concentration in proximity of porous silicon surface. Repeating of purging and injection modes allowed to measure concentration dependence of photoluminescence sensor response toward detected analytes [24]. Measurements of photoluminescence quenching response with sensor elements were performed for about two weeks.

3. RESULTS AND DISCUSSION

3.1. Preparation of porous silicon/polypyrrole composites

Macroporous silicon was prepared by electrochemical etching of crystalline silicon in a HF:EtOH=1:2.5 mixture (HF concentration ~14 wt.%). After fabrication porous silicon samples were washed several times in dried acetonitrile and immediately transferred into a three electrode electrochemical cell.

Cyclic voltammetry of porous silicon was performed in the potential range from -0.2 V to +1.2 V vs. SCE at scan rate 100 mV/s. At first, the porous silicon sample was cycled in base electrolyte (0.05 M Bu$_4$NClO$_4$ in acetonitrile) for about 10 or 20 minutes (i.e. 20 or 40 cycles) – Fig. 1A. Afterwards pyrrole was added into base electrolyte (total pyrrole concentration in the base electrolyte solution was 0.1 M) and for presented sample next 100 cycles followed – Fig. 1B. The total number of cycles varied between 100-300, PS samples with various thicknesses of polypyrrole layer were prepared. Samples prepared at 300 cycles had black surface and did not show any visible photoluminescence.

After pyrrole addition and deaeration by argon the initial cycles (number varied from 2 to ~40 for various PS samples) remained very similar to those before polypyrrole addition and without a noticeable change indicating polymerization. The number of initial cycles depended on sample preparation conditions and post-treatment of porous silicon surface – for PS samples prepared at current density of 5 mA/cm^2 the number depended on sample thickness and time delay between the porous silicon preparation and electrodeposition of polypyrrole. This behavior can be explained by partial oxidation of pore walls [25] and for PPy nucleation a sufficiently high upper oxidation potential has to be applied. Several electrodeposition procedures with upper potential of 1.1 V and 1.3 V were

performed as well. For upper potential of 1.1 V the rate of PPy nucleation inside pores was very low and no PPy film was deposited. For upper potential of 1.3 V overoxidation of polypyrrole and uneven PPy film coverage on porous silicon surface was observed.
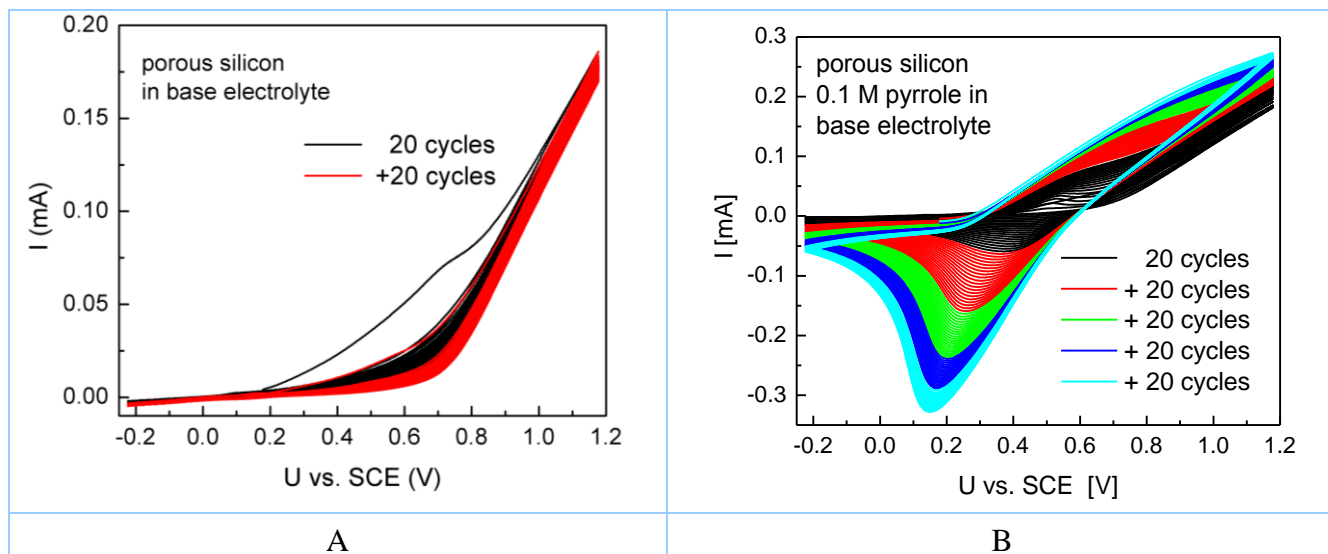

Figure 1. Cyclic voltammograms for porous silicon working electrode in (**A**) base electrolyte (0.05 M Bu$_4$NClO$_4$ in acetonitrile) and (**B**) pyrrole (0.1 M) in base electrolyte.

The polypyrrole deposition onto porous silicon pore walls followed after initial cycles. This effect was accompanied by the slow increase of anodic current to higher values together with a small shift of oxidation peak toward higher potentials. Simultaneously an obvious evolution of cathodic current with the growth of polypyrrole layer accompanied by a small shift of reduction peak toward lower potentials was observed. After polypyrrole electrodeposition the cell was disassembled and porous silicon/polypyrrole samples were washed in acetonitrile and dried in vacuum.

3.2. Characterization of porous silicon/polypyrrole composites by SEM and EDX.

Filling of the porous silicon walls with polypyrrole was inspected for several samples using SEM and EDX analysis. Figure 2 shows a top view of as-prepared PS (A) and of PS/PPy composite (B). Large open pores are observed with diameters between 1-2 μm for as-prepared porous silicon sample. On contrary, pores in PS/PPy composite were covered with a PPy layer with the mean diameter of pore openings below 0.5 μm. This reduced size of macropores does not limit gas phase sensing of volatile organic compounds.
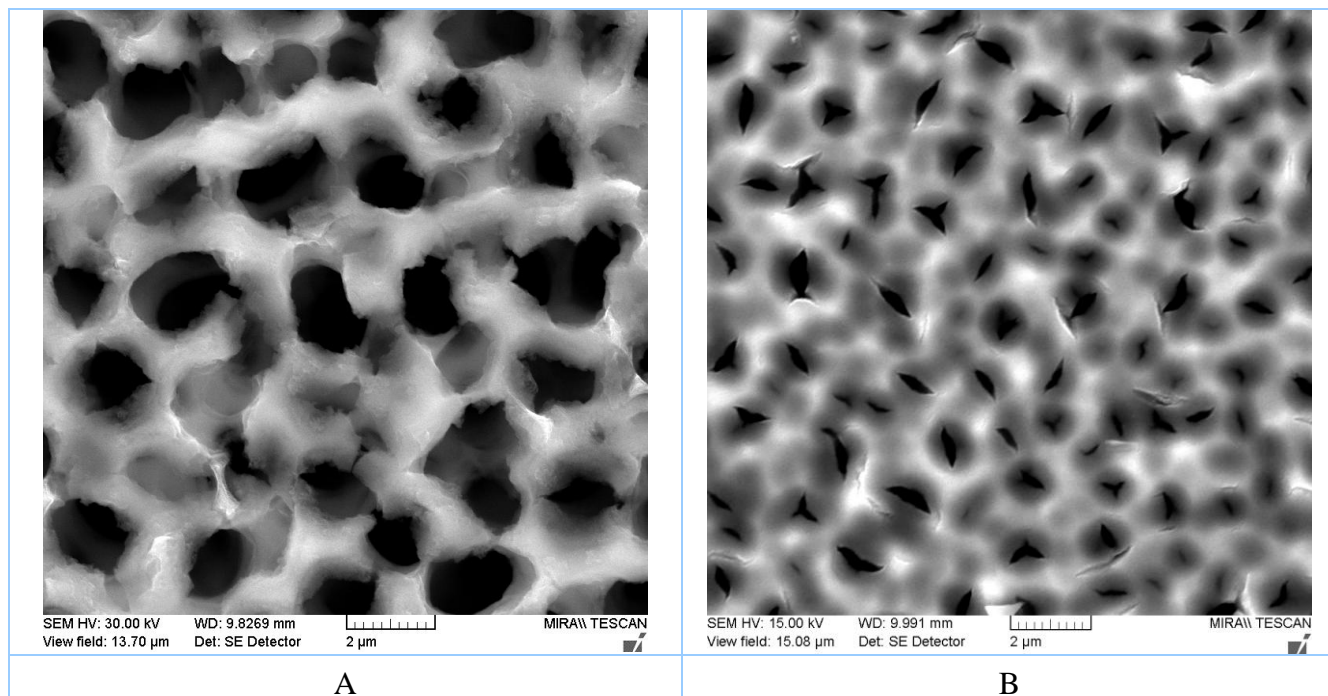
Figure 2. Scanning electron micrographs of top surface for (**A**) as-prepared porous silicon and (**B**) porous silicon/polypyrrole composite.

To resolve an internal morphology of PS/PPy layer, a SEM cross-sectional view of samples is presented in Fig. 3A. Inside the layer we can see a thin film covering internal surface of pores. A film with smaller pore diameter is present on the top of a sample explaining the local pore contraction in the top view SEM images. An EDX analysis of the whole spatial region in Fig. 3A was performed to find out the elemental composition of the layer. Spatially resolved X-ray spectra for a given sample position allowed to evaluate a relative atomic abundance and distribution profiles of elements. Results for relative atomic abundance are presented in Fig. 3B; taking into account an experimental error of about 1% the atomic ratio of carbon and nitrogen corresponds to their atomic ratio in pyrrole. For inspection of the course of electrodeposition process spatial distribution profiles for oxygen and carbon are presented in Fig. 3C and Fig. 3D, respectively. These maps are combined with SEM picture in order to visualize the distribution of elements in the layer.

The SEM/EDX pictures are consistent with the electrodeposition mechanism of polypyrrole onto porous silicon that starts with pore oxidation and subsequent growing of PPy layer on the pore walls and finally on the top of the sample [25]. Our SEM and EDX analyses clearly show both the oxidation of internal surface and coverage of the pores with polypyrrole. On the other hand, an enhanced concentration of polypyrrole and oxygen on the outer sample surface indicates a preferential oxidation and polypyrrole growth on the sample surface. Top surface preferential oxidation was observed in EDX of aged as-prepared porous silicon as well (not shown). For our purpose – chemical sensing in gas phase – we need only partially covered internal surface of pores in order to be able to excite and to observe visible photoluminescence as too thick layers of conducting polymers efficiently absorb excitation light.
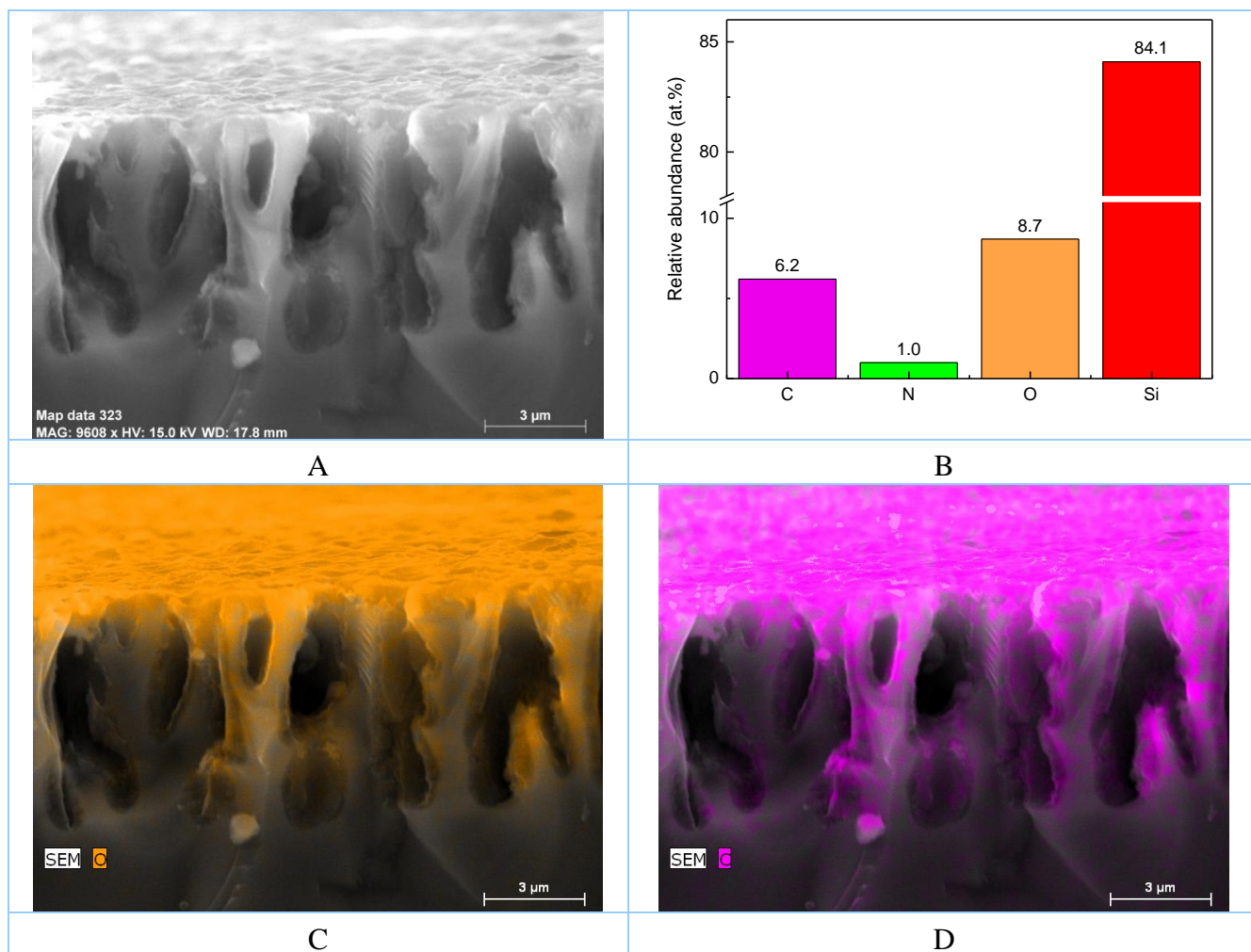
Figure 3. SEM cross-sectional view of porous silicon/polypyrrole composite (**A**), relative atomic abundance of the spatial region depicted in (A) for carbon, nitrogen, oxygen and silicon based on EDX analysis (**B**). EXD maps of elemental distribution for oxygen (**C**) and carbon (**D**).

3.3. FTIR analysis

FTIR spectra of as-prepared PS sample and PS/PPy composite before and after polypyrrole deposition are in the Fig. 4. The spectrum of as-prepared PS shows characteristic bands related to SiH_x absorption, the stretching modes at 2087 and 2115 cm^{-1}, the bending mode at 910 cm^{-1} and a broad shoulder with maximum near 1070 cm^{-1} corresponding to Si-O-Si antisymmetric vibration. The presence of the peak in freshly prepared porous silicon is due to the presence of oxygen in Czochralski type silicon substrate − this peak is present in IR spectrum of crystalline silicon as well (not shown). On the other hand, partial oxidation of PS surface during FTIR measurement in air cannot be excluded.
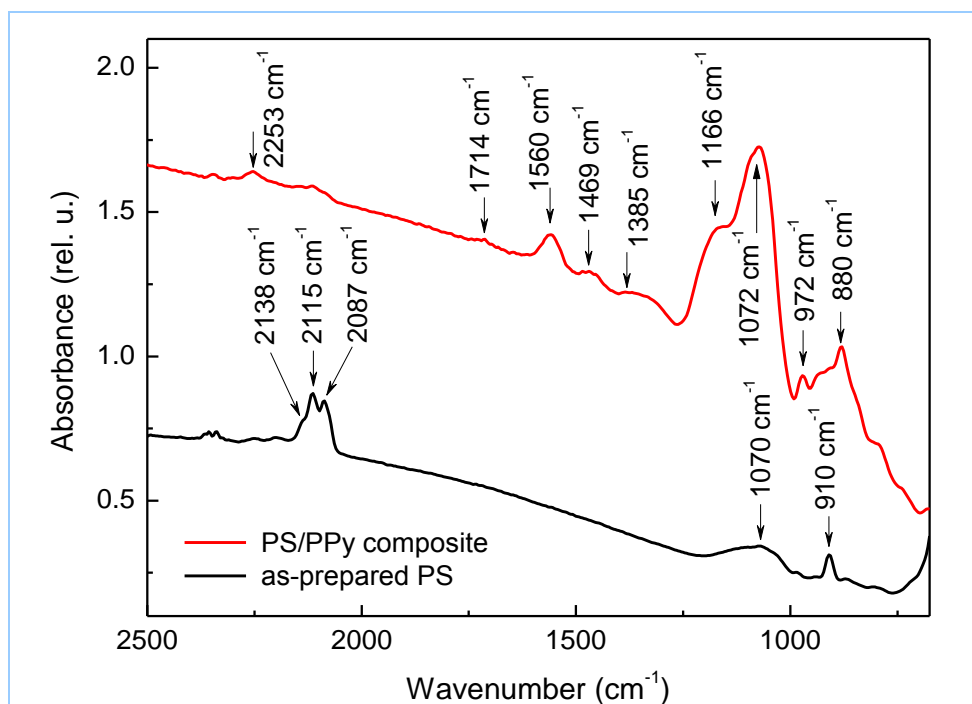
Figure 4. FTIR spectra of as-prepared porous silicon and porous silicon/polypyrrole composite.

The assignment of vibration modes of PS/PPy composite follows earlier works [16, 24]. It follows from the FTIR spectrum that Si-H bonds are nearly completely replaced by Si-O and Si-C bonds. Residual shoulders of SiH_x stretching modes are present as well as a small peak at 2253 cm^{-1} from stretching mode of $OSi-H_x$. The spectrum dominates sharp absorption peak at 1074 cm^{-1} corresponding to Si-O-Si antisymmetric vibration accompanied with a peak at 1166 cm^{-1}, which is assigned to breathing vibration of the pyrrole ring [26]. A smaller peak at 1560 cm^{-1} corresponds to C=C stretching vibration, peaks at 1469 cm^{-1} and 1385 cm^{-1} to C-N stretching vibration and C-N in-plane deformation, respectively. Small shoulder at 1714 cm^{-1} indicates partial overoxidation during polypyrrole electrodeposition. Peaks around 2350 cm^{-1} are related to the presence of CO_2. We did not observe broad bands around 3500 cm^{-1} (the region is not shown in the Fig. 4) corresponding to O-H stretching vibration as compared to our earlier work [23] what indicates the importance of sample fabrication using water-free solvents and Schlenk techniques.
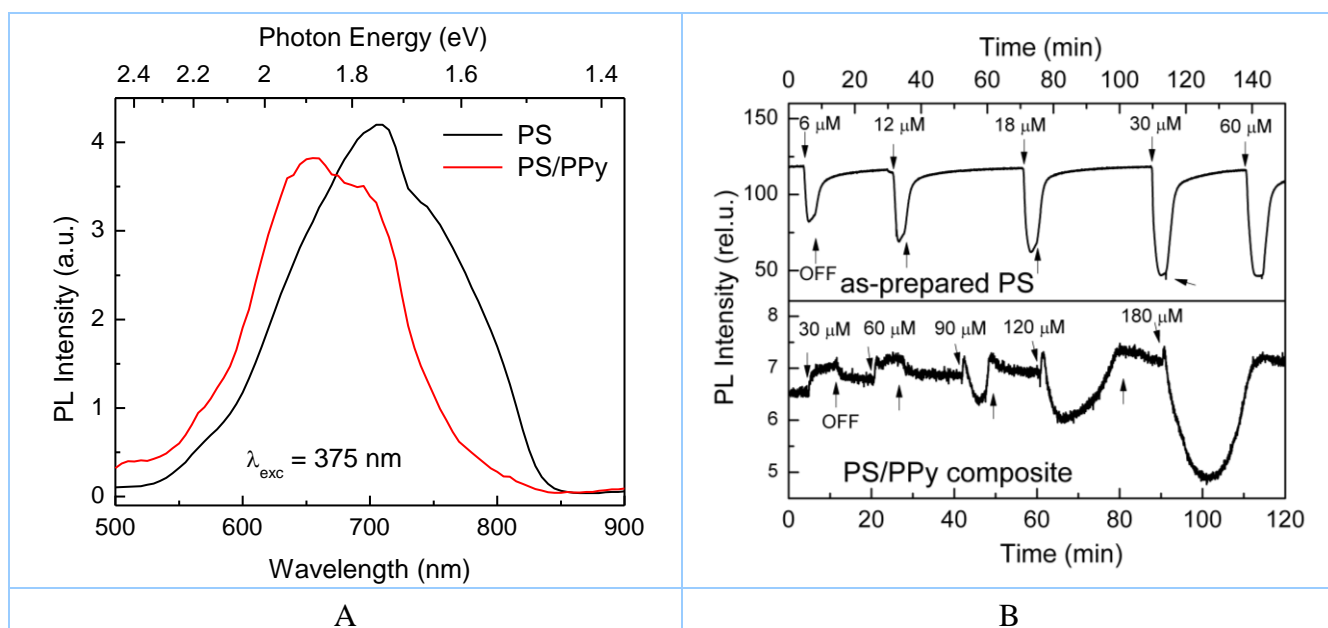
3.4. Gas phase photoluminescence sensor response to linear alcohols

Photoluminescence of silicon nanocrystals is their unique property as compared to crystalline silicon and is used in many applications. Room temperature photoluminescence spectra (uncorrected to spectral response) of as-prepared porous silicon sample and porous silicon/polypyrrole composite are in Fig. 5A. Broad photoluminescence band of as-prepared porous silicon has spectral maximum near 700 nm and corresponds to the S-band with origin in radiative recombination in silicon nanocrystals [27]. Photoluminescence band from PS/PPy composite is blue shifted as compared to as-prepared PS due to partial surface oxidation [27] and coverage with polypyrrole film.

　　　　Physical properties of porous silicon, including photoluminescence, are strongly influenced by the presence of chemical compounds. In case of as-prepared porous silicon a photoluminescence quenching is observed [8]. This transducer scheme is used for detection of single chemical compounds. In this study we would like to focus on photoluminescence quenching response of linear alcohols to demonstrate particular features of as-prepared and functionalized porous silicon surface in the process of chemical sensing.

　　　　An example of photoluminescence quenching responses of porous silicon in the presence of 1-hexanol is in upper part of Fig. 5B. At times denoted by downwards arrows controlled amounts of hexanol were injected into system; total concentrations of hexanol are depicted above the arrows. After photoluminescence intensity reached new level, system was purged with nitrogen at times denoted by upwards arrows and label OFF (denoted only for the first time). The sensor responses for PS/PPy composite are in the lower part of Fig. 5B.
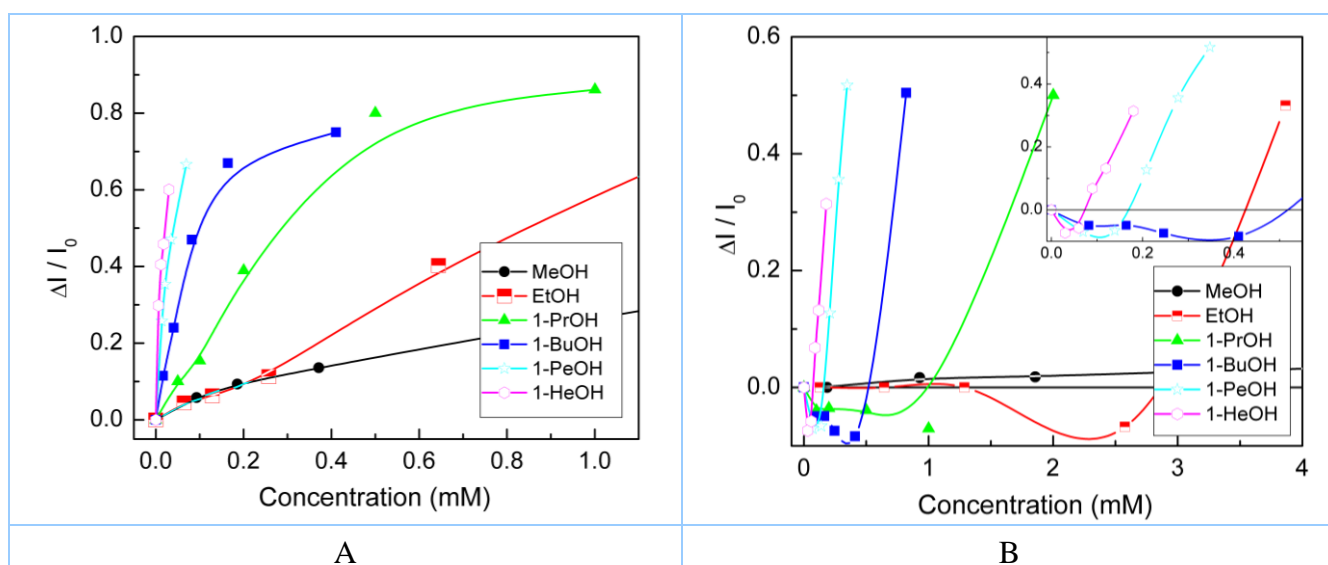

Figure 5. Room-temperature photoluminescence spectra of as-prepared porous silicon and porous silicon/polypyrrole composite (**A**). Photoluminescence sensor response at 700 nm of as-prepared PS and PS/PPy composite to various concentrations of hexanol vapors (**B**).

　　　　The photoluminescence quenching behavior for as-prepared porous silicon is typical for gas phase measurement with a porous medium. When analyte is introduced to porous silicon surface, an adsorption of analyte is followed by capillary condensation inside pores of porous silicon resulting in photoluminescence quenching. This process is relatively fast (time constant is from seconds to tens of seconds, depending on concentration), whereas desorption is significantly slower (time constant ranges from minutes to tens of minutes). The magnitude of the photoluminescence quenching is determined by real concentration of analyte inside porous matrix and quenching strength [28].

　　　　For real sensor applications one always needs to detect an analyte of interest in a mixture what implies a need for a molecular selector. Polypyrrole is a material used for various types of chemosensors and its using as a part of PS/PPy composite could introduce a molecular selection

process into photoluminescence quenching of porous silicon. A combination of PS/PPy composite with as-prepared PS in a sensor array can bring another enhancement of sensor response selectivity. In lower part of Fig. 5B we can see the time evolution of photoluminescence sensor responses for PS/PPy composite. For low analyte concentration the behavior of sensor response is just opposite as expected for hydrogen-terminated porous silicon. Instead of photoluminescence quenching a photoluminescence enhancement was observed. For higher concentrations the sensor response was composed of photoluminescence enhancement followed by quenching. The photoluminescence intensity of PS/PPy composite was about two orders of magnitude lower as compared to as-prepared PS.

For quantitative comparison of photoluminescence sensor responses we need to quantify photoluminescence quenching. We used relative photoluminescence quenching $\Delta I/I_0$ as a principal parameter, where I_0 is actual level of PL intensity and ΔI is change of PL intensity in the presence of analyte. In order to compare sensor response for various analytes and various sensors we depicted dependence of sensor response as a function of analyte concentration in Fig. 6.

Figure 6. Photoluminescence quenching responses toward linear alcohols as a function of concentration for as-prepared porous silicon (**A**) and porous silicon/polypyrrole composite (**B**).

As-prepared PS (Fig. 6A) provides a typical sensor response – a linear behavior for low concentrations is followed by saturation at higher concentrations. A monotonic increase of sensitivity of sensor response (the slope of the dependence of PL sensor response vs. concentration) in the selected set of linear alcohols was observed as well (for numerical values see Table 1). PS/PPy composite sensor response behavior (Fig. 6B) was similar to PS response of hydrogen-terminated PS only in case of methanol. After very slow increase of PL quenching response for low concentrations followed by a much steeper increase for intermediate concentrations (out of range in the Fig. 6B) and saturation at higher concentrations. Higher alcohols, starting with ethanol, provided a photoluminescence enhancement followed by photoluminescence quenching at a concentration characteristic for a particular analyte and finally a saturation of sensor response at higher concentrations (not shown). Two features are apparent from the Fig. 6B: *i*) the characteristic

concentration, at which transition from PL enhancement to PL quenching is observed, decreases with increasing size of alcohol molecule; *ii*) sensor response sensitivity is monotonically falling with increasing size of alcohol molecule (Table 1).
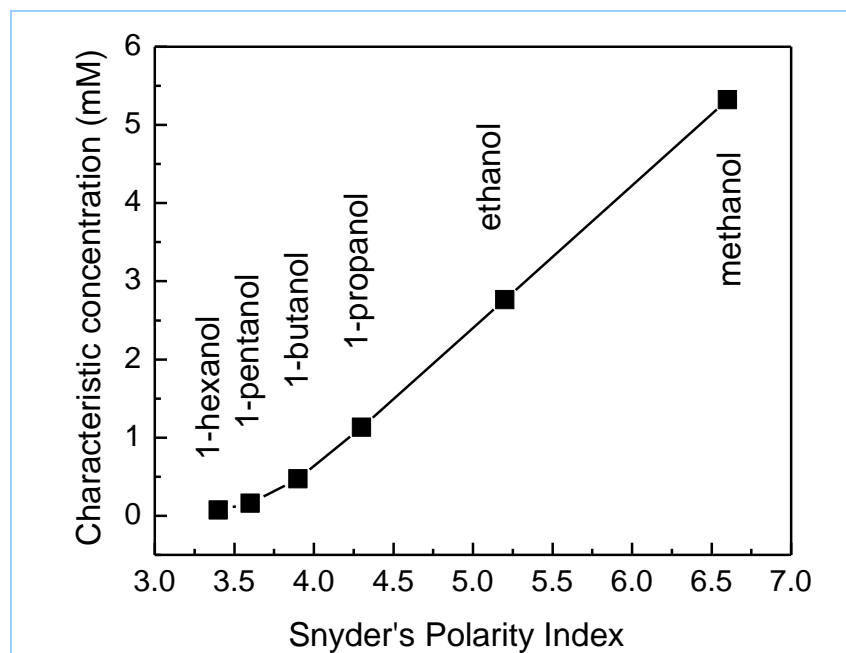
Figure 7. Dependence of characteristic concentration on Snyder's polarity index for linear aliphatic alcohols. Data were extracted from Fig. 6B and connecting line is a guide for eye.

This observed behavior can be explained by interaction of detected analytes with a thin PPy/oxide layer on the sample top and inside porous matrix as revealed by SEM. Characteristic concentration corresponds to adsorption capacity of the PPy/oxide layer. For detected molecules – linear alcohols – it monotonically increases with their polarity. This behavior is analogous to one recently observed for oxidized and carboxyl functionalized porous silicon [24]. The values of characteristic concentrations were estimated from Fig. 6B to check the validity of this assumption. For methanol characteristic concentrations was obtained from the intercept of the steeper part of the concentration dependence of the PL sensor response with the x-axis (not shown in Fig. 6B), for other alcohols characteristic concentration was attributed to concentration corresponding to zero value of PL response in the rising part of the dependency (Fig. 6B). Presentation of the dependence of characteristic concentration requires a suitable parameter for polarity. Some authors proposed for description of polarity the dipole moment of the molecule as a parameter of the choice [8]. For linear alcohols a problem arises due to non-monotonical behavior of dipole moment although from organic chemistry it is well known that polarity of linear alcohols is decreasing with the length of (nonpolar) carbon chain. We propose as a Snyder's polarity index well known from liquid chromatography [29] as a suitable polarity measure. In Fig. 7, there is a dependence of characteristic concentration as a function of polarity index. We can see a very good linear behavior confirming the role of the polarity in the PL sensor response behavior of PS/PPy composite (taking into account error of characteristic

concentration). This observation is important for applications in chemical sensing of mixtures consisting of components of different polarity – PS/PPy composite element in a sensor array represents a polarity dependent transducer.

The second obvious difference between as-prepared PS and PS/PPy composite is a monotonical growth of PL enhancement sensitivity (decrease of PL quenching sensitivity) with the size of alcohol molecule. Table 1 summarizes numerical values of these slopes for detected analytes (for methanol no PL enhancement was observed, slope has positive sign). These values were estimated from linear part of PL sensor response dependence as a function of analyte concentration (for low analyte concentrations).

Table 1. Variations in sensor response sensitivity of photoluminescence quenching in a homological set of linear alcohols for as-prepared PS and PS/PPy composite (low concentration range).

Analyte	Number of carbon atoms	Sensitivity of PL quenching (mM^{-1})	
		as-prepared PS	PS/PPy composite
methanol	1	0.174	0.007
ethanol	2	0.579	-0.027
1-propanol	3	1.60	-0.053
1-butanol	4	5.63	-0.185
1-pentanol	5	17.2	-1.00
1-hexanol	6	49.9	-2.46

The explanation of this second feature of PL sensor response concentration dependence of PS/PPy composite consists in the interaction of detected analyte with polypyrrole coverage of porous silicon surface that is only partially transparent to excitation light. This layer reduces intensity of excitation light that reaches silicon nanocrystals inside porous matrix and decreases the PL intensity as well. Observed PL enhancement for low analyte concentrations (except for methanol) is most probably related to the analyte adsorption/absorption induced opening of the protective layer. This opening is followed by increase of polypyrrole layer transparency to incident excitation light and is related to the size of molecule. The mechanism of this process in not fully understood yet, two possible explanations include polymer expansion [30] or angular movement of small polymer parts at the porous silicon surface [31] due to change of electrochemical potential change induced by incorporation of alcohol molecules in the polypyrrole film. Now we are neither able to provide a proper parameter of molecular size for explanation of enhancement of transmissivity of polypyrrole films during interaction with alcohol molecules nor to discriminate between these two possible mechanisms.

4. CONCLUSIONS

Macroporous silicon was electrochemically functionalized with polypyrrole. Fabrication was performed with purified chemicals using Schlenk techniques and experimental conditions were optimized for gas phase chemosensors applications. SEM and EDX analysis revealed changes in

porous silicon morphology during electrochemical deposition of polypyrrole and demonstrated preferential deposition in the top of the porous silicon layer. FTIR spectroscopy confirmed replacement of Si-H bonds with Si-O bonds and the successful polypyrrole electrodeposition. Photoluminescence sensor response of as-prepared PS and PS/PPy composite were measured for a set of linear alcohols in gas phase. Interaction of detected analyte with polypyrrole layer was demonstrated by photoluminescence enhancement at low analyte concentrations. Observed behavior was explained by polarity dependent adsorption/absorption of detected molecules at/into polypyrrole layer and size effect of detected molecules in enhancement of light transmission through polypyrrole film. Polarity dependent photoluminescence sensor response of PS/PPy composite at low analyte concentrations as compared to as-prepared PS could be utilized in sensor arrays for selectivity improvement in detection of mixtures of chemical compounds.

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