Electronic Supplementary Material (ESI) for Materials Horizons. This journal is © The Royal Society of Chemistry 2015

Supporting Information

Bringing One-Dimensional Photonic Crystals to a New Light: An Electrophotonic Platform for Chemical Mass Transport Visualisation and Cell Monitoring

Ida Pavlichenko^{a,b}, Ellen Broda^b, Yoshiyuki Fukuda^c, Katalin Szendrei^b, Anna Katharina Hatz^b, Giuseppe Scarpa^d, Paolo Lugli^{d,e}, Christoph Bräuchle^{b,e} and Bettina V. Lotsch^{a,b,e,*}

- ^a Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany
- ^b Department of Chemistry, Ludwig Maximilian University (LMU), Butenandtstrasse 5-13 (D), 81377 Munich, Germany.
- ^c Max Planck Institute of Biochemistry, Am Klopferspitz 18, 82152 Martinsried, Germany
- ^d Institute of Nanoelectronics, Technical University of Munich, Arcisstrasse 21, D-80333 Munich, Germany
- ^eNanosystems Initiative Munich (NIM) and Center for Nanoscience, Schellingstraße 4, 80799 Munich, Germany

Experimental

PC fabrication: The photonic crystals were assembled by sequential deposition of TiO₂ and SiO₂ nanoparticle suspensions on a clean glass slide (VWR microscope slides, 2.5×2.5 cm²) or a round cover glass (Thermo scientific, $\emptyset = 5$ cm) previously activated by air plasma treatment (Femto, Diener Electronic). TiO₂ nanoparticles (hydrodynamic diameter 7-20 nm) were synthesized by the method described elsewhere.²⁸ Briefly, tetraethyl orthotitanate (12.50 mL, Sigma-Aldrich) was added dropwise to HNO₃ (75 mL, 0.1 M) under vigorous stirring, and heated for 8 h at 80 °C; subsequently, the obtained product was sonicated (Elmasonic S10) at 25°C for 10 hr. To wash the synthesized nanoparticles, first, acetone (40 mL) was added to the suspension to initiate particle flocculation. After centrifugation of the suspension at 23000 rpm (Sigma 3-30K) at 15 °C for 20 min, the precipitate was redispersed in methanol (75 mL), providing a concentration of around 20 mg mL⁻¹. SiO₂ colloids for the PCs presented in the Figures 2, 3 (LUDOX SM-30, 30 wt % in H₂O, Sigma-Aldrich) with a hydrodynamic diameter of 6-10 nm were diluted with distilled water using a ratio of 2:5, and the colloids for the PCs shown in Figures 4, 5, 6, 7 (LUDOX TMA, 34 wt % in H₂O, Sigma-Aldrich) with a hydrodynamic diameter of 20-30 nm were diluted with methanol (Merck) using a ratio of 1:20. Both suspensions were filtered using hydrophilic syringe filters (SPARTAN 13, 0.2 and 0.45 μm, regenerated cellulose membrane). Thin layers of TiO₂ and SiO₂ were produced by using the spin-coating technique (Laurell WS-650SZ-6NPP/LITE) at 25 °C and relative humidity of the spin-coating chamber between 36% and 45%. The glass slides were alternatingly covered by 200-250 µl of TiO2 and SiO2 suspensions and accelerated at 1500 rpm s⁻¹ to final rotation speeds ranging from 3500 to 4000 rpm. The total spin-coating process for each layer was completed in 60 s. Afterwards, the sample was put into a muffle furnace (Nabertherm, L3/11/B810) for calcination at 400°C for 15 min. The same procedure was applied to

deposit the desired number of 6-9 bilayers. The refractive indices of single thin films at various ethanol saturation pressures were characterized by spectroscopic ellipsometry (performed on a Sopra Semilab PS-100 ellipsometric porosimeter in the spectral range of 300-900 nm at angle of incidence of 75°) by using the Cauchy model. Scanning electron microscopy (SEM) micrograph was recorded with JEOL JSM-6500F at 5 kV.

Chemical analyte sensing: The PDMS chamber was prepared with the Sylgard 184 Elastomer Kit (Dow Corning) as described elsewhere.¹¹ First, PDMS was combined with the curing agent in 10:1 ratio and the dish was filled to a height of approximately 4-5 mm. Then the mixture was covered with a Parafilm for around 30 min to allow the air bubbles to disappear, and then cured in the oven at 120 °C for 1 h. Afterwards, in a 2.5 x 2.5 cm² square piece of the PDMS mold a window of $\approx 2x2$ cm² was cut out, providing the chamber for the vapor. An inlet for the gas tube was constructed by piercing a syringe needle through one side of the chamber and then inserting a pipette tip, which was connected with the external flow controllers. The outlet for the gas chamber was provided by cutting out a $\approx 1x1$ mm hole in the neighboring side of the chamber. To deliver the vaporized analyte of interest into the chamber under the desired relative pressure (p/p^0) , digital mass flow controllers (EL-FLOW F201CV-500RAD-33-V and μ-FLOW L01-RAD11-0-80S, Bronkhorst High-Tech) were used. The carrier gas nitrogen (flow rate 200 ml min⁻¹) and the liquid ethanol (flow rate was varied between 0 and 1.5 g h⁻¹) were dosed into the heated CEM (Controlled Evaporation and Mixing) system (W101A-130-K, Bronkhorst High-Tech), where ethanol was vaporized at 100 °C and mixed with the carrier gas, and further delivered into the test chamber (note that during the delivery of the vaporized analyte into the chamber the digital mass flow controllers provide an oscillating flow pattern, which results in a measurement error during recording of the spectra, which tends to increase at higher relative pressures). The ethanol relative pressure p/p^0 (i.e. the ratio of partial ethanol pressure (p) and saturation pressure (p^0)) was calculated using the software *FLUIDAT* in the subsection "CEM calculation". Contact angle of the ethanol droplet on the surface of the 1D PC was measured with an optical tensiometer (Theta Lite, TL100). The samples were investigated with a light microscope (Leica DM 2500M with 12 V halogen lamp) combined with a 3-megapixel CMOS camera (DFC295, Leica) and interfaced with a miniature UV-Vis spectrometer (Ocean Optics USB2000+) and an optical fiber (Ocean Optics, QP400-2-UV-BX). A narrow-band light source - a green LED (M530D1, Thorlabs) - was fixed to an 8x5 cm² aluminium heat sink and powered by a sourcemeter at 8 mA (Keithley 2636A System). The slim Si photodiode power sensor (S130C, Thorlabs) operating in the wavelength range of 400-1000 nm was connected to the power meter interface (PM 100USB, Thorlabs) and aligned above the measurement chamber. For the analysis of the solvent diffusion described in Figure 3, a closed PDMS chamber was pierced with a syringe needle through one side, while the chamber was ventilated with a N₂ gas at a low flow speed of 50 mL min⁻¹. Afterwards an approximately 3 µL droplet of ethanol was injected to the area of observation avoiding stage vibrations. The evaporation process accompanied by the color change of the 1D PC was recorded using the Leica LAS 3.8 software, and subsequently the film frames in RGB format with an area of ≈ 0.1 mm² (as illustrated in Figure 3b) were extracted by

using the software VirtualDub 1.9.11 and analyzed with ImageJ plugins. A set of true-color (RGB) frames was then converted into the time-dependent grayscale relative luminance matrices (Y(x,y,t)) by using Equation 1, which were further used to construct a kymograph with the Image J plugin.

Cell monitoring: For the cell experiments 1D PCs were sterilized in 70% ethanol for 1 h. Subsequently, the samples were allowed to dry in a sterile laminar flow hood under ultra-violet illumination. For the experiments shown in Figure 5 the BHK-21 (syrian hamster kidney fibroblasts, ATCC (CCL 10)) cell culture medium composed of 500 mL minimum essential medium (MEM) and L-Glutamine (Gibco® 31095-029), 50 mL FBS (fetal bovine serum, Gibco®, 16000-044), 5.5 mL non-essential amino acids (Gibco® 11140-035, 100x) and 5.5 mL Penicillin and Streptomycin (Gibco® 15140-122, Pen 10000 U mL⁻ 1 , Str 10000 µg mL $^{-1}$) was used. The BHK-21 cell density on the seeding day was 6 x 10 4 cells per ø35 mm Petri dish (Falcon 35/3001, polystyrene). The culture was incubated at 37 °C with 7% CO₂ gas. For analysis purposes the BHK-21 cells were fixed onto the 1D PC with 4 % paraformaldehyde in 0.1 M PB (phosphate buffer) for 30 min, and afterwards washed three times with PBS at room temperature (r.t.). Atomic force microscopy (AFM) measurement of the cell topography shown in Figure 5e was performed on a MFP-3D AFM (Asylum Research, Santa Barbara) in air, in tapping mode. For the fluorescent staining the 1D PC was soaked with Buffer G (0.1 % Triton X-100, 5% normal goat serum in PBS) for 10 min at r. t., then it was washed three times with PBS for 10 min at r. t. and incubated with Buffer G containing 1/1000 dilution of phalloidin-tetramethylrhodamine B isothiocyanate (phalloidin-TRITC, 0.5 mg mL⁻¹, Sigma-Aldrich) for actin staining, and again washed three times in PBS. Hoechst 33342 (1 µl, 1 mg mL⁻¹, Sigma-Aldrich) in PBS was added for nuclear staining. Figure 5f was captured on an Axiovert 200M (Zeiss) epifluorescence microscope with ZEISS LD Achroplan objective 40x/NA 0.6, equipped with a motorized stage (DC 120100, Märzhäuser, Wetzlar, Germany), CCD camera (AxioCam MRm, Zeiss), a short-wavelength mercury lamp, and fluorescent filter sets (Zeiss filter set 01 and AHF F46-005). The BHK-21-covered 1D PCs shown were investigated with a light microscope (Leica DM 2500M) integrated with a miniature UV-Vis spectrometer (Ocean Optics USB2000+) and an optical fiber (Ocean Optics, QP400-2-UV-BX). For the experiments shown in the Figures 6, 7 HuH7 cells (Human hepatocellular liver carcinoma, wildtype) were cultured in Dulbecco's Modified Eagle Medium: Nutrient Mixture F-12 (DMEM/F-12, Gibco®, life technologies, Carlsbad, SA) supplemented with 10% FBS (Gibco®) in a 5% CO₂-containing atmosphere at 37 °C. The cells were seeded into a sterile Petri dish (Falcon 35/3001, polystyrene) onto a small piece of a 1D PC with a cell density of 1.3 x 10⁵ and incubated for 24 and 48 h. For the measurements, the 1D PC with adhered HuH7 cells was transferred into a Petri dish with a glass bottom (Mat Tek P356-0-14-C, glass #0, ø = 35 mm) and covered with 2 mL of CO₂-independent medium (Gibco®) supplemented with 10% FBS. A custom-built wide-field microscope, based on a Nikon Ti Eclipse microscope with an oil immersion objective CFI Plan Apochromat TIRF 60x/ NA 1.45 integrated with a motorized XY scanning stage (MAC 6000, Ludl Electronic Products), 532 nm laser (DLTS 200 Soliton) and EM-CCD camera chip (iXon+ DV884, Andor Technology) was used for the optical experiments with the HuH7 cells. The cell lysis observed in Figure 6 a-d was achieved by adding 100-400 µL of sodium dodecyl sulfate (SDS, 1.5% aq., SigmaAldrich) to a glass bottom Petri dish containing the 1D PC in 2 mL of CO₂-independent medium. The power signal was monitored with a Si Photodiode Power Sensor (S130C, Thorlabs) mounted 5 mm above the Petri dish. Cell coverage estimation (see Figure 7) was done by scanning the 1D PC surface in a phase-contrast transillumination mode with a motorized stage in a "COMB" (snake-like) fashion in 8 adjacent positions with the area of $64 \mu m^2$ (60x magnification).

Response time measurements

To measure the time response of the 1D PC after exposure to ethanol vapor (see Figure S1) we used a setup based on a controlled evaporation mixer (CEM) and liquid and gas mass flow controllers already described in the section "Chemical analyte sensing" above, and delivered the vaporized ethanol into the chamber with a 1D PC under elative pressures of 20%, 50% and 100%. We have registered the change of reflection corresponding to a wavelength of 810 nm of the photonic spectra shown in Figure 2b with a "strip chart" tool in the Ocean Optics Spectra Suite.

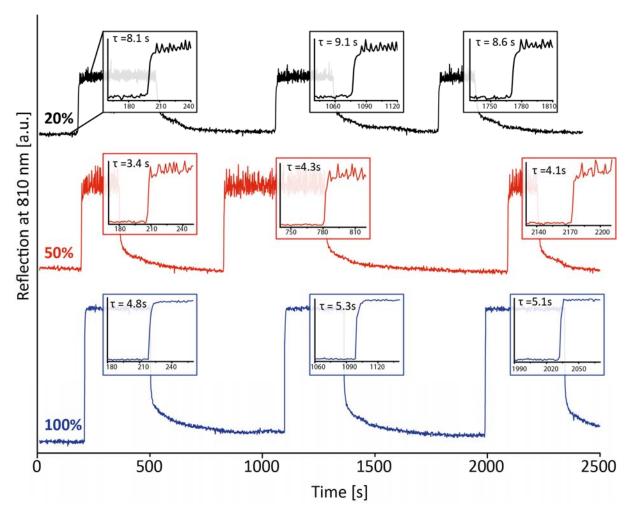


Figure S1. Response curves for ethanol relative pressure changes from 0% to 20% (top black curve), from 0% to 50% (middle red curve) and from 0% to 100% (bottom blue curve).

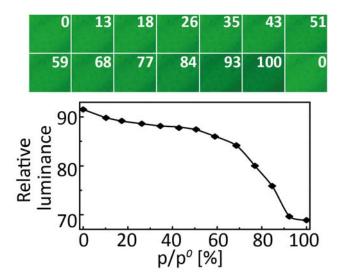


Figure S2. Top: photographs of the PC surface captured with a CMOS imaging array, taken at $0 < p/p^0$ < 100% (p/p^0 values are indicated in the corner of each image), bottom: relative luminance analysis of the top photographs used for the calibration of the image in Figure 4f.