-Electronic Supporting Information ESI -

Fibre optic ratiometric fluorescence pH sensor for monitoring corrosion in concrete

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Materials and Instrumentation

All materials were used as received and all experiments were carried out under ambient conditions, unless otherwise noted. Hydrophobic CdSe/ZnS core-shell quantum dots (λ_{em} = 610 +/- 5 nm) and hydrophobic ZnCdSe/ZnS core-shell quantum dots (λ_{em} = 440 +/- 5 nm) were purchased from PlasmaChem GmbH (Berlin, Germany). Fractions of 10 mg were dispersed in 1.0 mL of toluene (z.A., ACS, min. 99.5%, from TH. Geyer GmbH & Co. KG, Renningen, Germany), and stored in the fridge. Wet ethanol (puriss., Ph.Eur., min. 95.1%) and ethanol (absolute z.A., ACS, min. 99.9%) were also purchased from TH. Geyer. Polystyrene granulate (M ~ 320.000 g/mol) was purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany). A solution of 4.0 g of polystyrene in 10.0 mL of toluene was used in all experiments. The indicated amounts of QDs were added, followed by sufficient stirring to ensure homogeneity. Thymol blue was purchased from Merck KGaA (Darmstadt, Germany); a stock solution of a mass concentration of 1.0 mg/mL in absolute ethanol was prepared by brief ultrasonication, which was then stored in the fridge. The hydrogel used was the polyurethane based HydroMed D4 from AdvanSource Biomaterials Corp. (Wilmington, MA, USA). Ethanolic solutions of the D4 hydrogel were prepared in an optimized hydrogel to ethanol (wet, 95.1%) ratio for the desired application. Different amounts of the thymol blue stock solution were added to the hydrogel solutions as indicated.

First characterization of the sensor layers was carried out in 96 well black polystyrene microplates with transparent non-binding flat bottom from Greiner Bio-One (Kremsmünster, Austria). The microwell based sensor arrays were analysed by means of a TECAN Inifity M200Pro microplate-reader (Tecan Group Ltd., Männedorf, Switzerland) with 405 nm excitation. Ceramic tubes for the sensor chips were purchased from Rauschert Heinersdorf-Pressig GmbH (Judenbach-Heinersdorf, Germany). The Y-fibre used for the characterization of the sensor heads was an Ocean Optics (Largo, FL, USA) QR400-7-UV-VIS Premium 400 µm Reflection Probe of 2 m length. In additional experiments, the Y-fibre was replaced by two single glass fibres from Thorlabs (FT600UMT – Ø 600 µm core multimode optical fibre) cut to a length of 1 m which were sticked to the PS cover layer. Both fibre optic systems were analysed with an Ocean Optics HR2000+ spectrofluorometer using a LDM405 diode laser from Thorlabs (Newton, NJ, USA) as excitation source (λ = 405 ± 10 nm).

Preparation procedure for microplate based sensor arrays

For all measurements in microplates, the preparation of the sensing material was carried out in the following way: To 4.0 g of a solution of PS in toluene (4.0 g of PS in 10.0 mL of toluene), 80 μL of a dispersion of CdSe/ZnS QDs (emitting at 610 nm; c = 10 mg/mL) and 400 μL of a dispersion of ZnCdSe/ZnS QDs (emitting at 440 nm; c = 10 mg/mL) were added and mixed by stirring. Then, 3 drops (approx. 60 mg) of the PS mixture were added into each of the wells. After drying overnight, 3 drops (approx. 35 mg) of a solution of D4 hydrogel in ethanol (0.9 g D4 in 6.0 g of ethanol, wet) and 8 mL of a solution of TB in absolute ethanol (1.0 mg TB per mL ethanol) were added on top of the PS layer. After drying and before adding the buffer solutions, the microplates were analysed by absorption and fluorescence spectroscopy. After addition of 0.2 mL of the respective buffer solution, the wells were incubated for 10 min at room temperature before performing spectroscopic analysis. For a first set of experiments, buffer solutions in a range from pH 10.5 to pH 12.5 (in intervals of 0.5 pH units) were used. To determine the transition point of the pH sensitive system more precisely, glycine buffers[1] in a pH range from 11.0, to 12.0 (in intervals of 0.2 pH units) were prepared. The results of both sets of experiment were combined in order to obtain the precise titration curve presented here. All experiments were carried out in triplicates (3 wells per set) and the average of the respective values was determined. In the all graphs shown here, the averaged datasets are shown.

Reversibility tests

Four sensors chips were used for reversibility tests. The sensors were placed in demineralized water with an average pH value of 7.77 and in a sodium hydroxide solution with an average pH value of 12.18. Within 30 days, five alternations were conducted and the resting time in each solution was between two to five days. The pH value of the solution was checked for every measurement by means of a pH meter. The sensors and the solutions were stored at a constant ambient temperature of 20 °C in a temperature chamber.

In an initial step, the inner volume of the new and dry sensors was filled with demineralized water with a pipette. This should avoid the arise of an air bubble in front of the sensor membrane, which hinders the electrolytical transport of ions. Then, the sensors were placed in the sodium hydroxide solution at a pH value of 12.45 for three days. To measure the

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[1] R. Kaltofen, R. Opitz, K. Schuman and J. Ziemann, *Tabellenbuch Chemie*, Verlag Harri Deutsch, Frankfurt am Main, 8th edn., 1998, 182-186.

spectra, the sensors are extracted from the solution and positioned in front of the fibre optic. Remaining liquids are dapped off to avoid undesired reflections. After the measurement, the inner volume is refilled with demineralised water again to avoid the occurrence of air bubbles. Then, the sensors are placed in demineralised water for four days. Finally, the spectra were measured again to complete the alternation. Five alternations were conducted which lead to ten measurement values for one sensor in total.

pH sensors embedded in screed

The four sensors used for the reversibility tests were embedded into screed samples. Before the preparation of the test specimens, the sensors were stored in deionised water for several days until their embedment. Remaining liquid was dapped off before installation. Then, the sensors are pressed into a transparent plexiglass cylinder. This covers the sensors and the fibres against the fresh screed paste. In addition, the plexiglass cylinder aligns the blue holder of the fibres in front of the sensor membrane as shown in figure S4. The four fabricated screed samples have a size of 12 cm x 8 cm x 4 cm. The sensors are positioned in the middle of the sample in approximately 2 cm depth.

For the embedment, a cementitious screed with a compressive strength of ≥ 25 Nmm^{-2}, a flexural strength of ≥ 5 Nmm^{-2}, and with aggregate sizes of 0 – 5 mm is used (CT-C25-F5 according to EN 131813). The screed was purchased from a local construction market in form of bagged good of 30 kg. The screed is maxit plan 425 of the company maxit (Franken Maxit Mauermörtel GmbH & Co, Kasendorf, Germany). The required mixing water during concreting is recommended to be between 0.116 lkg^{-1} to 0.15 lkg^{-1}. For preparation of the specimens, 10 kg screed were mixed with 1.33 l of ordinary tab water. The mass of screed and tab water were checked by a balance. All four screed samples are made of the same charge of the screed mixture. After concreting, the samples remained in the wooden casting for approximately 20 hours. Then, the samples were released from the casing and stored in a climate chamber at an ambient temperature of 23 °C and 50 % relative humidity. In the first five days, one sensor was measured every minute. Then, the waiting time of the monitoring was increased to 1 hour. Besides the monitoring of one sensor, the three other sensors were measured manually two to three times per week (see Figure 5).

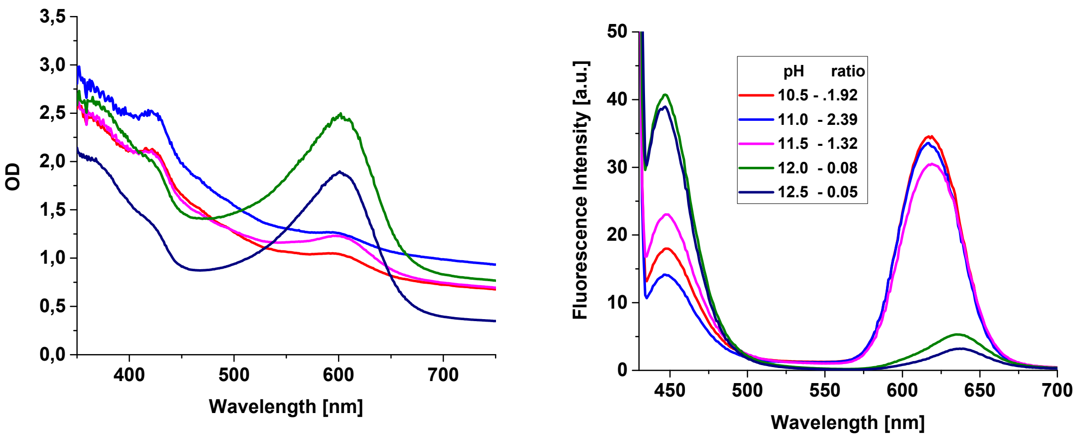

Figure S1 Absorption (left) and emission (right) spectra of QD/PS – D4/TB bilayers in 96 well microplates upon treatment with buffer solutions of the indicated pH. The ratios were calculated by dividing the fluorescence intensities at 617 nm and 448 nm, respectively. λ_{exc} = 405 nm.

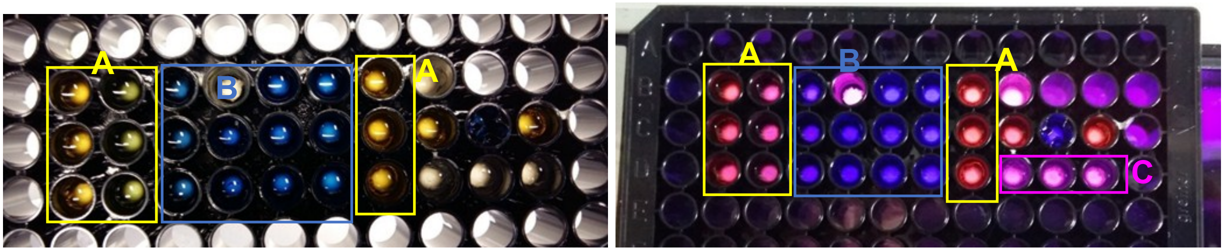

Figure S2 96 well microplate loaded with bilayers of QD/PS and D4/TB without (left) and with (right) UV-illumination to visualize the changes in colour of the pH sensitive TB (left) and the effects on the fluorescence emission of the QDs (right). All pictures taken from the top of the microplate, the D4/TB layer is thereby located on top of the QD/PS layer.

In the left picture the yellow wells contain neutral water and the thymol blue dye is of yellow color (zones A). The blue wells containing basic aqueous solution, thus the thymol blue dye is of blue color (zone B). White wells are empty. In the right picture the same wells show either red or blue fluorescence emission, respectively. Pink emission is observed in three wells were no thymol blue dye is present resulting from dual wavelength QDs emission (Field C).

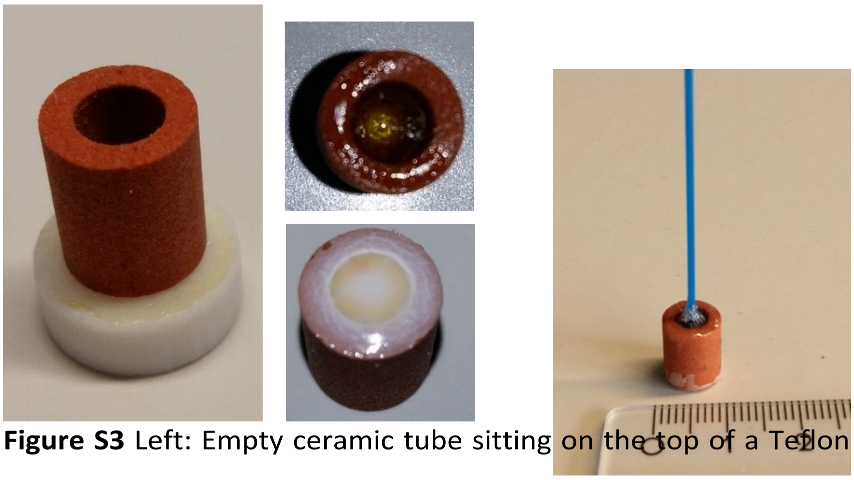

Figure S3 Left: Empty ceramic tube sitting on the top of a Teflon stopper. Middle top: View of the cavity filled with D4 /TB cavity. Middle bottom: View of the cavity filled with PS/QD and sealed with PS. Right: Prototype of the complete sensor chip with glued fibre to use in concrete.

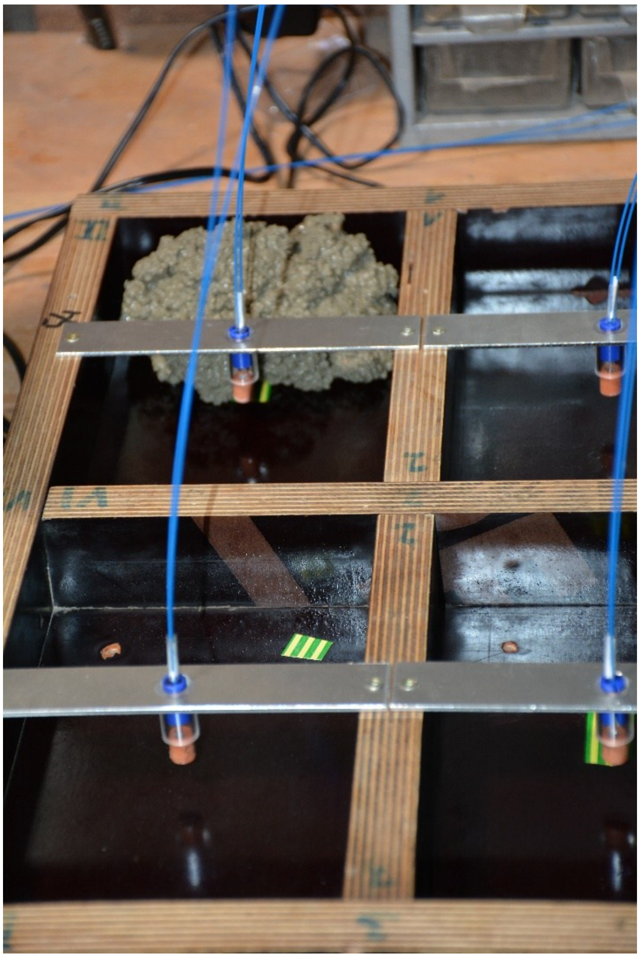

Figure S4 Positioning of the four sensors during concreting.