Electronic supporting information

At-line monitoring of hydrogen peroxide released from its photocatalytic and continuous synthesis

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1. EXPERIMENTAL SECTION

1.1 Materials and Instrumentation

Palladium(II)-6,13,20,27-tetrakis(4-fluorophenyl)tetrabenzoporphyrin (PdTPTBPF) was synthesized in house.¹ Poly(styrene-co-divinylbenzene) 8 μ m microspheres (PS/DVB) were purchased from Sigma Aldrich and stained following a previously published procedure.² A phase fluorimeter (Firesting O₂, Pyroscience GmbH, Germany) equipped with polished plastic optical fibers (Ø = 1 mm) was used for sensor read-out in flow cells. The phase fluorimeter was additionally equipped with two temperature sensors, PT100 (Pyroscience GmbH, Germany) for temperature compensation of O₂ measurements, and TPB430 (Pyroscience GmbH, Germany) for optical temperature measurements. LED array photon counts were performed with a LI-COR[®] Bioscience LI-250A light meter.

Microfluidic flow cells were kindly provided by Joanneum Research (Graz, Austria).³ The inlet and outlet were connected to the microfluidic set-up with commercially available nuts and ferrules (Upchurch ScientificTM). Poly(ethylene glycol terephthalate) (PET, Mylar[®]) was obtained from Goodfellow, USA. HydromedTM D7 from AdvanSource Biomaterials, USA. Silicone tubing (ID = 0.5 mm, OD = 2.5 mm) from microfluidic chipshop, Germany. PEEK tubing (ID = 0.03 in, OD = 1/16 in) from Sigma Aldrich. Flow is controlled with a peristaltic pump (MINIPULS 3, Gilson, USA).

1-Pentanol (CAS: 71-41-0) was purchased from Aldrich (Lot# 11215 118) in highest purity available. Potassium tetrachloroplatinate(II) (CAS: 10025-99-7) was purchased from ABGR (Lot# 1054460) in highest purity available. Sodium borohydride (CAS: 16940-66-2) was purchased from TCI (Lot# C2THH-FQ) in highest purity available. Polyethylenimine (CAS: 25987-06-8), PEI, branched, average Mw \approx 800, Mn \approx 600, was purchased from Sigma Aldrich (Lot# MKCG3800). Urea (CAS: 57-13-6) was purchased from Roth in highest purity available. Cetylpyridinium bromide hydrate (CAS: 202869-92-9), CPB, was purchased from Aldrich (Lot# MKCJ7015) in highest purity availabley. Tetraethylorthosilicate (CAS: 78-10-4), TEOS, was purchased from Fluka (Lot# 452425/1) in highest purity available. (3-Glycidyloxypropyl)trimethoxysilane (CAS: 2530-83-8) was purchased from Fluka (Lot# 1161184) in highest purity available.

1.2 Preparation of N-CND

The synthesis of the nitrogen-doped carbon nanodots (N-CNDs) was prepared according to a modified literature description by Kim et al.⁴

Briefly, citric acid (105 mg \cdot ml⁻¹) and ethylene diamine (33.5 μ L \cdot mL⁻¹) were dissolved in deionized water. The solution was transferred to a stainless steel autoclave reactor and heated at 200 °C for five hours. The autoclave was then allowed to cool to room temperature and a dark brown solution of N-CNDs was obtained. For purification, the solution was centrifuged at 15,000 rpm for 30 min to eliminate insoluble large particles. Then, the supernatant was dialyzed (molecular weight cut-off: 1,000 Da) against deionized water for three days. Afterwards, the purified solution was lyophilized to obtain a powder of N-CNDs.

1.3 Synthesis of Silica Supported Platinum Nanoparticles

Fibrous nanosilica supported platinum nanoparticles were synthesized following a previously reported procedure.⁵ The final product KCC-1-PEI/PtNPs is abbreviated PtNPs. Fibrous Nanosilica (KCC-1)

KCC-1 was synthesised using a microwave synthesizer (Monowave 50, Anton Paar GmbH, Austria). (1), a suspension of 200.1 mg CPB and 119.9 mg urea in 6 mL DI H₂O was formed by stirring at 1600 RPM for 1 h. (2), a solution of 6 mL cyclohexane, 300 μ L 1-pentanol, and 540 μ L TEOS was prepared. (1) was added dropwise to (2) while stirring at 1600 RPM. The mixture was stirred at 1600 RPM for 45 min, transferred to vials for microwave synthesis, and heated at 120 °C for 4 h while stirring. Afterwards,

the formed particles were centrifuged at 4000 RPM for 10 min and washed with ethanol and DI H_2O . At last, the obtained particles were calcinated at 550 °C for 6 h. Yield 66.8 mg.

Fibrous nanosilica supported platinum nanoparticles (KCC-1-PEI/PtNPs)

First, KCC-1 particles were modified with positively charged PEI to facilitate attachment of *in situ* grown platinum nanoparticles. 66.8 mg KCC-1 was degassed at 65 °C overnight, 77.6 mg GTMS dissolved in 390 μ L MeOH was added, and stirred at 60 °C for 1.5 h in a sealed vial. Meanwhile, 109.1 mg PEI was dissolved in 727 μ L MeOH while stirring at 60 °C in a sealed vial. The solution was added to the KCC-1 mixture and the vial was resealed and stirred. After 5 h at 60 °C, the mixture was centrifuged and washed three times with hot MeOH. The KCC-1-PEI particles were dried in vacuum at 65 °C overnight. Product 70.9 mg

7 mL DI H₂O was added to 70.9 mg KCC-1-PEI, ultrasonicated for 5 min and stirred for 20 min. Then, 1.42 mL 25 mM K₂PtCl₄ in DI H₂O was added, ultrasonicated for 30 min, and stirred for 2 h. Afterwards, 0.7 mL of freshly prepared 1 M NaBH4 in DI H₂O was added, and after a few minutes, the slightly red dispersion turned grey/dark and was completely black after 2 h with stirring. The mixture was centrifuged at 4000 RPM for 5 min and washed with ethanol and water. The final product, KCC-1-PEI/PtNPs, was obtained after drying in vacuum overnight. Product 53.9 mg.

1.4 Preparation of sensor formulations and foils

Sensor foils were prepared by knife coating liquid sensor formulations onto PET foils with a 3 MIL knife bar (approx. 75 μ m wet film). The sensor formulations are 2% (wt./wt.) PdTPTBPF indicator immobilized on PS/DVB beads dispersed in 7% (wt./wt.) D7 in 9:1 EtOH/H₂O (vol./vol.). Either no or 60 mg/mL PtNP is added to the sensor formulation to prepare O₂ or H₂O₂ sensor spots, respectively.

1.5 Measurements of H₂O₂

Sensor foils were cut out and glued into the flow cell with double sided adhesive tape. The cell was closed with pressure sensitive adhesive tape (ThermalSeal RTSTM, Excel Scientific, Inc., USA) and PET foil/double-sided tape on top. A 2-point O₂ calibration (in PBS or 2% Na₂SO₃) was performed with one flow cell, and the values transferred to other cells.

The sample solution was deoxygenated by passing it through a silicone tubing (30 cm) submerged in an O_2 scavenging solution (2% Na_2SO_3). PEEK tubing was used to connect the silicone tubing to the flow cell. Before use, the sensor was conditioned in flow overnight to remove residual oxygen. Calibrations were performed with 100 mM PBS and freshly prepared stock solutions (diluting 30% H_2O_2 , Roth). The values for the calibration curves are obtained from the corresponding response curves as an average over one minute.

1.6 LED Set-up

A power supply (MeanWell LPF-25D-36, and LED array (9x Luminus SST-10 UV 365nm-370nm) on SYSTEM sliders was obtained from LED-TECH.DE, Germany. The LED array was mounted on an aluminium block for cooling.

The AC/L wire (brown) of the LED power supply was connected to live (brown), the AC/N wire (blue) to neutral (blue) of a standard European plug (CEE 7/17). +V (red) and -V (blue) were soldered to the UV module.

To adjust the constant output current to different current levels, a screw terminal block was used to connect DIM+ (blue) and DIM- (white) to changeable resistors (10, 22, 47, and 82 k Ω). By altering resistances, the module was running the LED at different intensities

Due to heat development while running the set-up, the LED was screwed on a cooling block for safety reasons.

1.7 Flow reactor H₂O₂ production

 H_2O_2 production from N-CND was measured in a dark room to avoid "background production" of H_2O_2 from ambient light. The LED was further covered so that it only illuminated the capillary tube. The H_2O_2 sensor was connected to a 50 µL capillary tube (Blaubrand[®] intraMARK). The capillary tube was fixed to the LED array with custom-made 3D printed holders at a distance of 1 cm. Black tape was used to cover parts of the capillary tube to adjust residence time to 35 seconds.

All measurements were made with the same batch of N-CND. After calibrating the sensor, the set-up was conditioned in N-CND solution (2.5% w/v or 5% w/v in 100 mM PBS) with the LED turned off. Measurements were started once a stable signal was reached by switching the LED on and off with different resistors. The produced H_2O_2 is detected by the H_2O_2 sensor after approx. 5 minutes. The values of produced H_2O_2 are obtained as an average of the sensor response over 5 minutes, unless otherwise stated.

2. RESULTS

2.1 Calibrations of H₂O₂ sensor



Figure S1. Calibrations of the H_2O_2 sensor. O_2 Ref. (red line) is the amount of dissolved oxygen in the sample. H_2O_2 (blue line) is the amount of O_2 measured at the H_2O_2 sensor spot. ΔpO_2 (black line) is the difference between the two sensor spots and the amount of produced O_2 .

Figure S1 shows calibrations of the H_2O_2 sensor at 30 μ L/min (Figure S1A,B) and 50 μ L/min (Figure S1C,D) in PBS. Averages over 5 min of the ΔpO_2 in the response curves are used in the calibration curves.

The sensor equilibrates within a few minutes at both flow rates and is fully reversible. The small spikes in pO_2 (e.g., at min 66 in Figure S1C) are a result of stopping the flow to change H_2O_2 solution.



2.2 Photocatalytic H₂O₂ synthesis with N-CNDs

Figure S2. Sensor response to N-CND solutions (2.5% and 5%) at flow rates 30 μ L/min and 50 μ L/min. The legend in B) applies to all measurements. O_2 Ref. (red line) is the amount of dissolved oxygen in the sample. H2O2 (blue line) is the amount of O_2 measured at the H_2O_2 sensor spot. ΔpO_2 (black line) is the difference between the two sensor spots and the amount of produced O_2 . Big spikes are from air bubbles, for instance B) at min 70. Green boxes indicate when the LED array is turned on. Numbers in A) are the photon count, and applies to all measurements.



Figure S3. H_2O_2 production in N-CND solutions (2.5% and 5%) at flow rates 30 µL/min and 50 µL/min. The H_2O_2 production is calculated from ΔpO_2 in Figure S2 with the calibrations in Figure S1. Green boxes indicate when the LED array is turned on. Numbers in A) are the photon count, and applies to all measurements. The values of produced H_2O_2 in Figure 4 are obtained from the red boxes as an average.



Figure S4. A) Control experiment of H2O2 generation from increased temperature in dark in a 5% N-CND solution. $O_2 \operatorname{Ref.}$ (red line) is the amount of dissolved oxygen in the sample. H_2O_2 (blue line) is the amount of O_2 measured at the H_2O_2 sensor spot. ΔpO_2 (black line) is the difference between the two sensor spots and the amount of produced O_2 . Temp. (teal line) is the temperature of the N-CND solution measured with an optical sensor. B) Normalised absorbance of the N-CND solution (diluted 1:1) before and after heating.



Figure S5. Normalized absorbance of N-CND solutions before and after H_2O_2 productions. The solutions were collected 10 min after illumination stated at the outlet during the measurements seen in Figure S2A,B.

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