

Supporting Information

Gold Nanoparticle-Decorated Diatom Biosilica: A Favorable Catalyst for the Oxidation of D-Glucose

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Cultivation

The diatom species *Stephanopyxis turris* (*S. turris*), *Eucampia zodiacus* (*E. zodiacus*) and *Thalassiosira pseudonana* (*T. pseudonana*) have been isolated from the North Sea in June 2004 by Prof. Manfred Sumper (Regensburg). Cultivation was performed in a 20 L polycarbonate vessel (Nalgene) with artificial seawater (ASW) medium prepared according to the protocol of the North East Pacific Culture Collection⁴⁵. Diatoms grew in 20 L of sterile filtrated (0.2 μm , Kleenpak) ASW medium for 2 to 4 weeks. A RUMED 1301 light thermostat (18°C, 12 h/12 h day/night cycle, ca. 1000 lux) provided constant growing conditions. Adjustment of the rising pH to 8.0 – 8.2 was carried out with 2.5 mol L⁻¹ HCl. The cells were harvested by consecutive filtration of the culture medium with a 1 μm nylon mesh (Stockhausen Sieb- und Filtererzeugnisse) and subsequent centrifugation (Heraeus biofuge primo, swinging bucket rotor, 1000 RCF). The resulting pellets were frozen with liquid nitrogen and stored at -20°C.

Synthesis of Gold Nanoparticles (Au-NP)

29 mL of 2 wt% H₂AuCl₄ · 3 H₂O were added to 500 mL of mili Q pure water and stirred continuously. 11.6 mL of 1 wt% sodium citrate solution were added, followed by

quick addition of 5.8 mL sodium borohydride (NaBH_4) in ice cooled sodium citrate solution (0.085 g NaBH_4 and 0.5 g sodium citrate in 50 mL deionized water). The solution turned immediately red. The Au-NP were concentrated using Viavaspin 20 (Sartorius) with a molecular weight cutoff of 30,000 kDa.

Decomposition of the samples for ICP-OES measurements

150 μL HF, 150 μL HCl and 150 μL HNO_3 (Merck, suprapur) were added to dry biosilica in a microvial. The microvial was placed into a pressure vessel containing 3 mL ultrapure water. The vessels were placed into a microwave (Mars, CEM) and heated to 130°C with a power of 1600 W (ramp: 5 min, hold time: 15 min, cooling time: 20 min). Afterwards, complex formation to boron fluoride was carried out: 1.5 mL saturated boric acid were added to the microvial which was placed in a microwave (1600 W, 110°C, ramp: 5 min, hold time: 10 min, cooling time: 20 min). The clear and colorless liquids from both the microvial and the pressure vessel were mixed and filled up with water to 15 mL.

HPAEC (High-performance anion-exchange chromatography) procedure

The carbohydrate composition of reaction mixtures and standard substances was analyzed via the 817 Bioscan system at room temperature (Metrohm, Ionenanalytik) equipped with a pump and degas module (WellChrom K-1001, Knauer). Separation of monosaccharides was achieved on a Metrosep Carb 2 column (4 x 250 mm) under isocratic elution conditions at a flow rate of 0.6 mL/min. The samples were diluted in the elution solution (200 mM NaOH + 200 mM NaOAc) and thereof 100 μL was injected on the column. The amperometric detection (PAD, Metrohm, Ionenanalytik)

was conducted at a measure potential of $E_1 = +0.05$ V (400 ms) with regeneration potentials $E_2 = +0.2$ V (200 ms) and $E_3 = -0.8$ V (400 ms). The obtained data was analyzed and formatted by IC Net (v 2.3).

S1

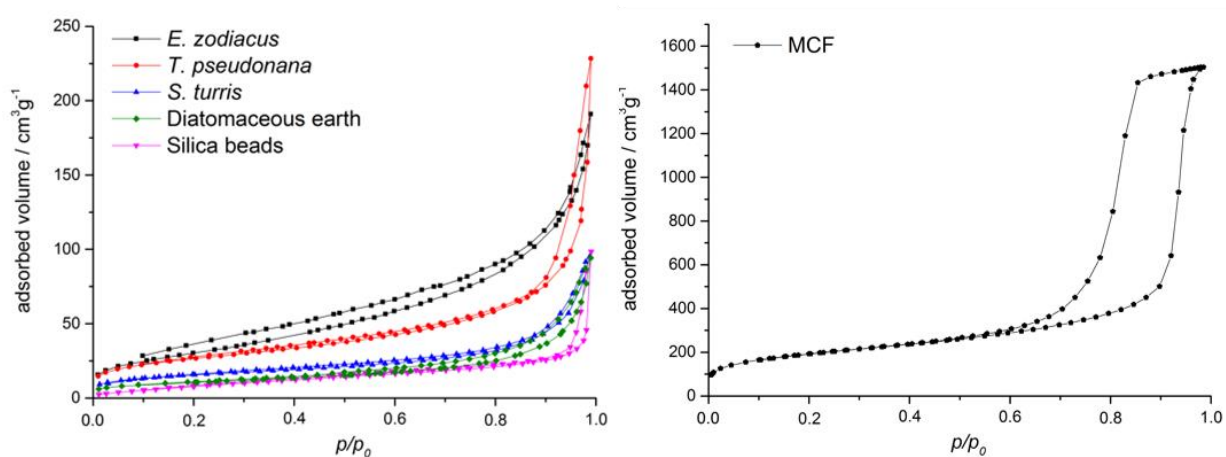


Fig. S1: Nitrogen physisorption isotherms (-196°C) of all silica materials.

S2

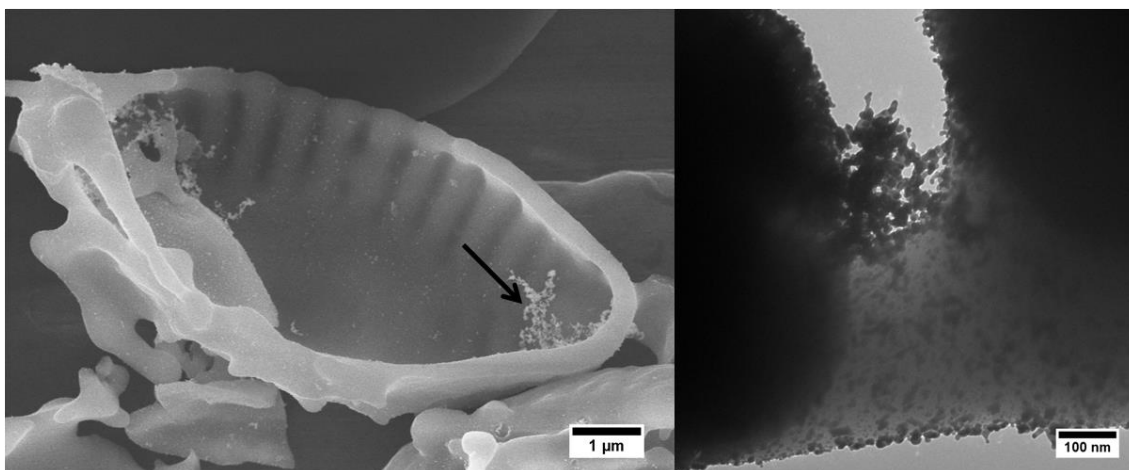


Fig. S2: SEM (left) and TEM image (right) of gold agglomerates (arrow) on diatomaceous earth.

S3

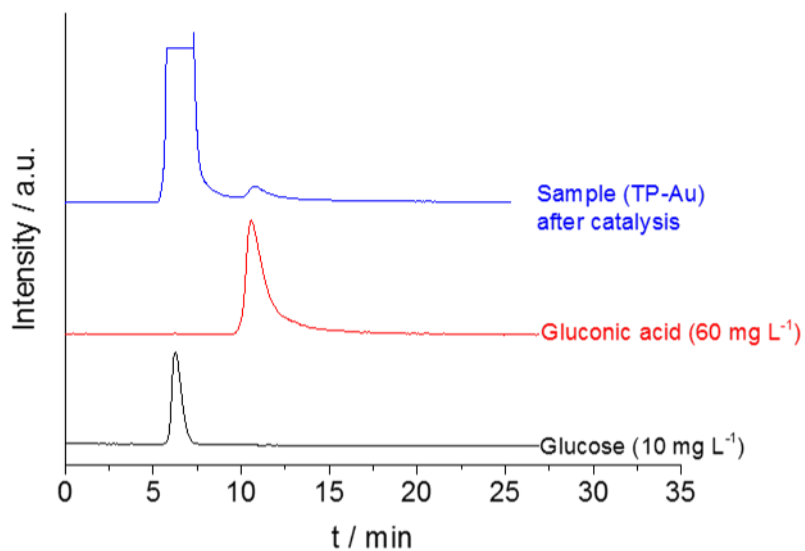


Fig. S3: Selectivity of the catalytic reaction measured with HPAEC.

S4

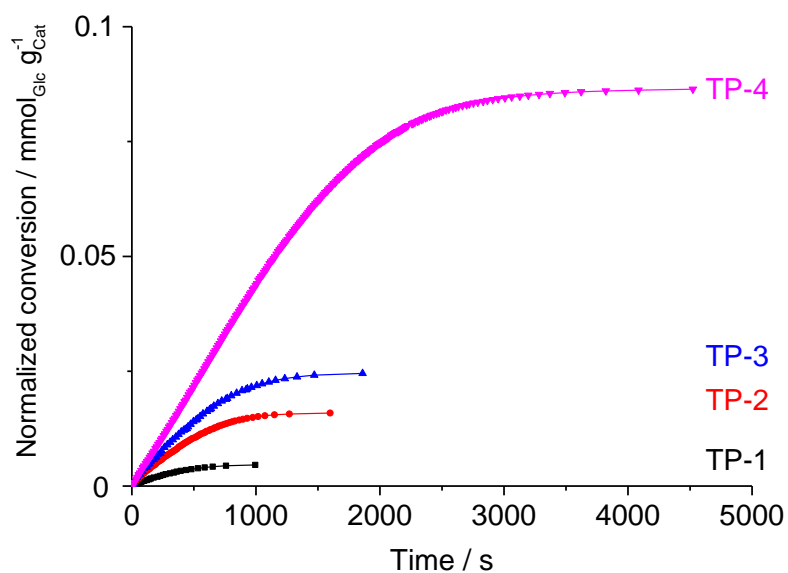


Fig. S4: Conversion of *T. pseudonana* biosilica with different Au-NP loadings regarding amount of catalyst.

S5

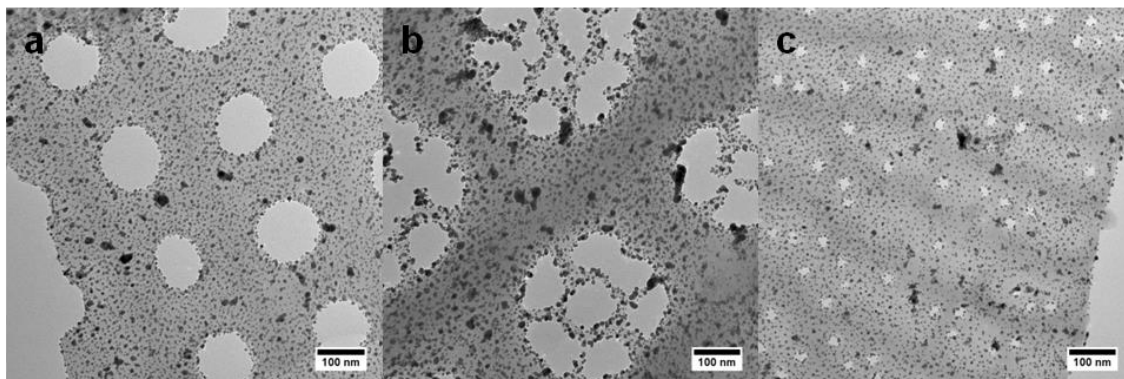


Fig. S5: TEM images of Au-NP saturated *S. turris* (a), *E. zodiacus* (b), and *T. pseudonana* (c).

(45) Harrison, P. J.; Waters, R. E.; Taylor, F. J. R. *J. Phycol.* **1980**, 16, 28-35.