

Supporting information

Inverse opals with reactive surface chemistry as sensors for aqueous pollutants

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Materials and methods

Inverse opal fabrication IOs were prepared according to the procedure reported by Hatton et al.¹ First, templating polystyrene colloidal particles with a diameter of 340 nm were prepared using the surfactant-free polymerization technique.^{2,3} In brief, 10 g of styrene (stabilizer free, removed by passing over a column of neutral alumina), 0.1 g of acrylic acid, and 0.1 g of ammonium persulfate were added to 240 mL of DI water. The reaction was heated to 80 °C under nitrogen atmosphere and stirred for 24 hours. After cooling, the particles were cleaned by centrifugation at 11000 rpm for 20 minutes. The cleaning procedure was repeated 3 times.

Then, a pre-hydrolyzed solution of tetraethylorthosilicate (TEOS) was prepared by stirring 1 mL of TEOS, 1 mL of 0.1 M HCl, and 1.5 mL of EtOH at room temperature for 1 hour. 12 mL of previously synthesized 0.1 wt.% colloidal dispersion and 75 µL of pre-hydrolyzed TEOS solution were added to a vial. A 6x1 cm piece of silicon wafer rinsed with EtOH several times, dried and treated with O₂ plasma (Diener Electronics-100W-10 min) was then suspended vertically into the vial, and the solution was slowly evaporated in an oven at 65 °C over 5 days. Finally, the samples were calcined at 500 °C (5 h: 20-500 °C- 2 h: 500 °C- natural cooling) to remove the templating PS particles and sinter the silica matrix. All reagents were from purchased from Merck and used as received unless stated otherwise.

Schiff base synthesis The Schiff base synthesis procedure was based on the work of Shervedani et al.⁴ 250 µmol of Salicylaldehyde and 250 µmol 5-Amino-1,3,4-thiadiazol-2-thiol were dissolved in 1 mL of dry methanol, and a drop of 30% acetic acid was added. The mixture was stirred at 45 °C for 1 hour. The product was then filtered, recrystallized in ethanol and dried under vacuum overnight. The final product has the following NMR signals: **¹H-NMR (CDCl₃, 300 MHz): δ (ppm)** 10.95 (s, 1H), 9.83 (s, 1H), 8.67 (s, 1H), 7.34–7.07 (m, 2H), 6.99–6.77 (m, 2H), 3.46 (m, 2H), 3.04–2.94 (m, 2H), 1.17 (s, 1H).

Surface functionalization The functionalization procedure consists of 3 steps. First, the surface was activated by O₂ plasma (Diener Electronics-100W-10 min). Second, the surface was functionalized with trimethoxyvinylsilane (TMVS) by immersing the substrates in a 0.2 wt.% TMVS toluene solution under light stirring at 80°C. After 24 hours, the samples were rinsed with fresh toluene and EtOH. Third, a thiol-ene reaction between the vinyl bond of the silane and the thiol group of the Schiff base was carried out.⁵ In a typical reaction, 15 mg of Schiff base were dissolved in 20 mL of DMF. Then, 10 mg of azobisisobutyronitrile (AIBN) and one substrate were added to the reaction mixture. The reaction was heated to 80 °C for 2 hours. The samples were rinsed with DMF, immersed in EtOH for 30 minutes, and dried with N₂. Both reactions are expected to give nearly 100% yield when done on flat substrates, and be slightly less efficient when performed in confinement due to diffusion limitations.

Both microscope slides and IOs prepared as stated above were functionalized using this procedure. All reagents were purchased from Merck and used as received unless stated otherwise.

Exposure to metal ions and revealing solution In a first step, samples functionalized with Schiff base (1) were exposed for 1 hour to a 5 mM solution of freshly dissolved metal chloride in 60 v/v% of EtOH in H₂O. Specifically, FeCl₂ was used as a precursor for Fe²⁺, FeCl₃ for Fe³⁺, CuCl₂ for Cu²⁺ and AlCl₃ for Al³⁺. After this step, the samples were first immersed for 5 minutes in EtOH, and then thoroughly rinsed with EtOH and dried with N₂. Finally, a drop of 20 v/v% EtOH in H₂O was used to investigate the wetting behavior of the system.

Scanning electrochemical microscopy IOs were characterized by scanning electron microscopy (SEM) imaging. The images were acquired with a Zeiss Gemini 500 by Zeiss working at 1 kV, equipped with an inlens detector.

Contact angle measurements Static contact angles were measured using a drop shape analyser (DSA 100, Krüss) using 3 µL of water or 20% EtOH water solution droplets.

X-ray photoelectron spectroscopy XPS analysis was performed with a Quantera II instrument (Physical Electronic) with monochromatic Al K-alpha X-ray radiation and ≤ 7.5 µm spatial resolution. The measurements were operated with 15 kV. Survey spectra from 0 to 1100 eV binding energy were obtained at 112 eV pass energy.

Reflectance spectra measurements For reflectance measures, a Zeiss Axio Z2 (Zeiss, Germany) coupled with a MCS CCD UV-NIR spectrometer (Zeiss, Germany) was used. The spectra were acquired using a 10x magnification lens with a numerical aperture of 0.5 (ED Epiplan NEOFLUAR 20x/0.25 HD DIC, Zeiss), with a squared spot size of 40 μm x 40 μm .

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- 3 N. Vogel, L. de Viguier, U. Jonas, C. K. Weiss and K. Landfester, *Adv. Funct. Mater.*, 2011, **21**, 3064–3073.
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Notes and references

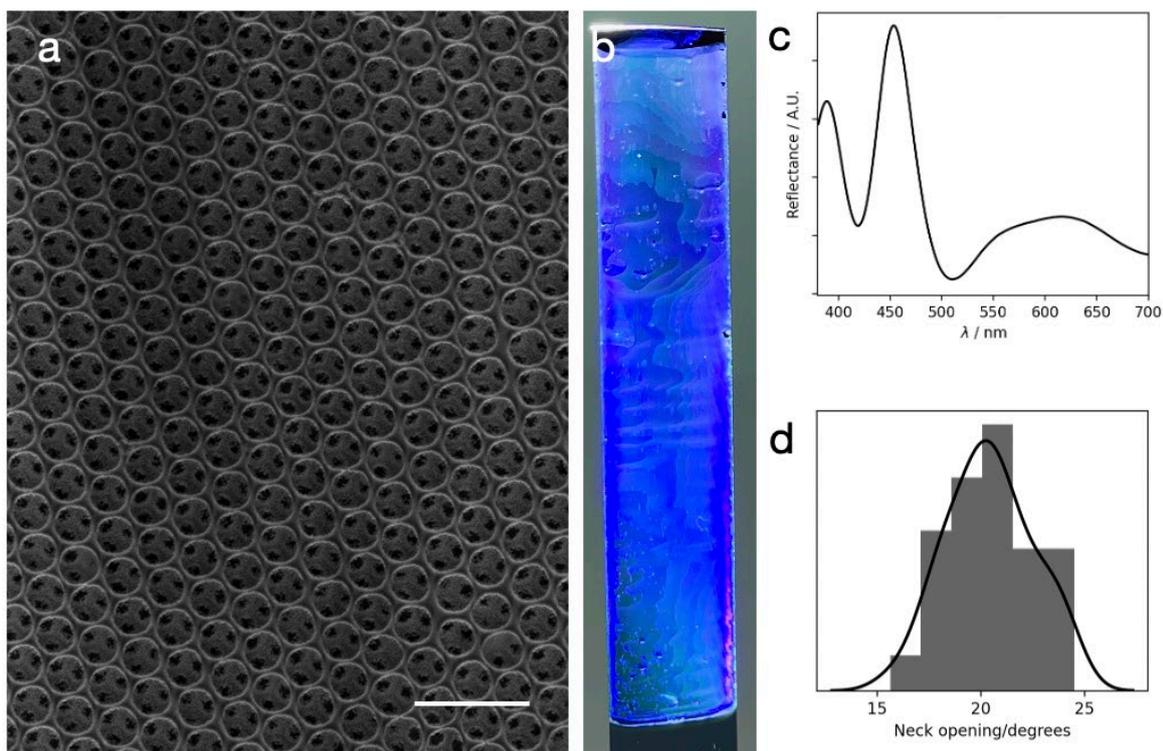


Figure S1. Inverse opals characterization. (a) SEM image of an IO. Scalebar is 1 μm . (b) Photograph of an inverse opal and (c) reflectance spectra. (d) Size distribution of neck openings. $N=70$.

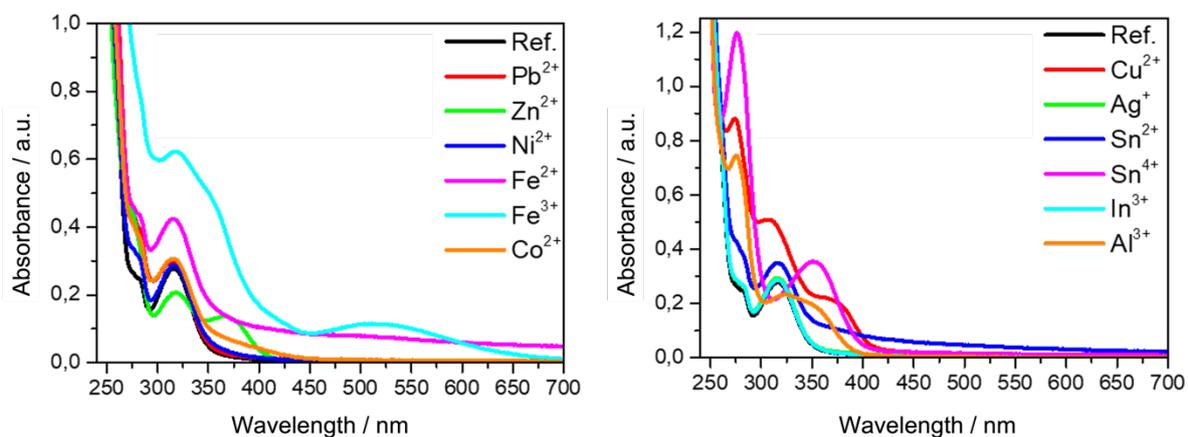


Figure S2. UV-Vis-Spectra of 100 μM Schiff base (1) in Acetonitrile with equivalent concentration of metal ions. Schiff base (1) has its absorption maximum at 315 nm with a shoulder at 280 nm. The Schiff Base interacts with the cations of zinc, cobalt, copper, tin(IV), aluminum and particularly strongly with iron(III). The iron(III) cations cause a distinct color change from yellow to red, visible in the UV-Vis spectrum as a broad band between 450-670 nm with a maximum at about 520 nm.