Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

A Fiber-Optic Nanoplasmonic Hydrogen Sensor via Pattern-Transfer of Nanofabricated PdAu Alloy Nanostructures

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METHODS

Optical fiber preparation. Optical multimode fibers with 300 μm core diameter were used (FT300EMT Thorlabs, Inc.). Prior to the pattern transfer, the fiber buffer coating was removed over a 1 cm section at one fiber end using a fiber stripper, to reveal the hard fluoropolymer (TECS) cladding. This cladding was then removed by soaking in acetone for 1 h, exposing the SiO_2 fiber core onto which the nanopattern then was transferred (Figure S3). The exposed fiber was then rinsed in DI water and gently dried in a N_2 gas stream. As the last preparation step, we then deposited a 300 nm Al film at the tip of the fiber using an e-beam evaporator (Lesker PVD 225 Evaporator, base pressure < $5x10^{-7}$ Torr, 1 Å deposition rate) to create an optical mirror.

Alloy nanoparticle array nanofabrication and transfer onto the optical fiber. Borofloat glass (Schott Scandinavia AB) was used as the parent substrate (10 x 10 mm^2) for the nanofabrication of the nanoparticle arrays. Prior to fabrication the substrates were cleaned with subsequent sonication in acetone, isopropyl alcohol (IPA) and DI water. Once dried, the 100 nm Cr and 10 nm C films were deposited in sequence onto the substrates by e-beam evaporation (AVAC HVC600, base pressure < $5x10^{-6}$ Torr, 1 Å deposition rate). The nanofabrication of the pure Au and Pd nanodisk array with 170x25 nm dimensions was performed using the Hole-Mask Colloidal Lithography (HCL) method described in detail elsewhere[1] without any modifications, directly on the C-layer The fabrication of the PdAu alloy nanoparticle arrays followed precisely the steps of our HCL-based alloy nanofabrication method.[2] For the transfer process the substrates were first immersed in Cr-etchant solution (Sunchem AB, NiCr etchant 650095, composition: ceric ammonium nitrate 10–15%, nitric acid 15–20%, DI water 60–70%) for at least 20 min. The complete removal of the Cr-layer was signaled by a substrate color change (Figure S3). Once the Cr-layer was removed, the C-film with the nanoparticle array on top, which still is loosely

residing on the glass, was moved into pure DI water. Due to the hydrophobicity of the C-film, there it readily detaches from the glass and floats up to the water-air interface, from which it is picked up by the stripped tip of the optical fiber (Figure S3). As the last step, 10 min reactive oxygen plasma etching was employed (150 W, 250 mTorr, Plasma Therm Batchtop RIE 95m) to remove the C-film, leaving only the nanostructures on the fiber.

Dark field scattering spectroscopy. The scattering spectrum of the PdAu alloy nanoparticles was obtained by an upright optical microscope (Nikon eclipse LV1009 and Nikon 10x LU Plan Fluor objective). An Andor Shamrock SR-303i spectrometer (grating 150 lines/mm and blazing wavelength 800 nm) was used together with an Andor Newton 920 CCD camera for collecting the spectrum. Light was coupled to the optical fiber via a lamp (AvaLight-Hal-S, Avantes). The light scattered from the nanoparticles via excitation by the evanescent field of the fiber was normalized by the spectrum of the light source, which was collected by coupling light into an equivalent fiber without alloy particles and directing the unclad end of the fiber towards the objective.

Hydrogen sensing experiments. A schematic of the experimental setup used is shown in Figure S4. In detail, the fiber sensors were inserted into a quartz tube gas flow reactor system (Insplorion X1, Insplorion AB) through a gas-tight teflon channel. The reactor was connected to a series of flow controllers (Bronkhorst ΔP) regulating the H_2 partial pressure in the Ar carrier gas, with a total flow rate of 100 mL min^{-1}. The working temperature in the reactor was controlled by a heating coil around the quartz tube and by a thermocouple-based feedback loop via a Eurotherm temperature controller. The optical sensing experiments were conducted by connecting the fiber sensor to a bifurcated fiber (BFY105HS02 coupled with B10125A multimode SMA905 connectors, Thorlabs, Inc.) *via* an SMA fiber connector (BFT1 bare fiber

terminator, Thorlabs, Inc.). It is important to note here that the connection to the fiber sensor was achieved by a physical clamping, and thus is extremely sensitive to movement. The ends of the bifurcated fiber were connected to a halogen lamp (AvaLight-Hal-S, Avantes) and a fixed grating spectrophotometer (AvaSpec HS-TEC, Avantes), respectively. Prior to measurements the sensors were exposed to at least 10 cycles of alternating Ar and 25% H_2 in Ar. Data collection was carried out using the Insplorer® software (Insplorion AB). All measurements were performed at 30 ^{o}C.

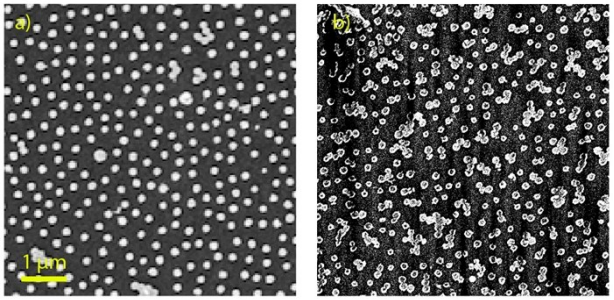

Figure S1. SEM images of a quasi-random array of the layered Au-Pd nanodisks on (a) the parent substrate before annealing and transfer and (b) after the transfer process to a fiber.

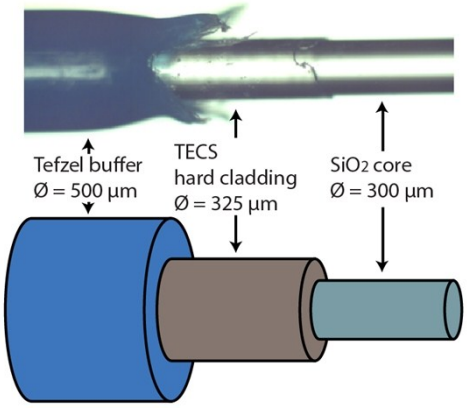

Figure S2. Optical micrograph of the optical fiber used (top) and a corresponding schematic illustration (bottom) showing the core, the cladding and the buffer coating with their respective diameters. The removal of the fiber coating and cladding is described in the Methods section in the main text. The schematic is not drawn to scale.

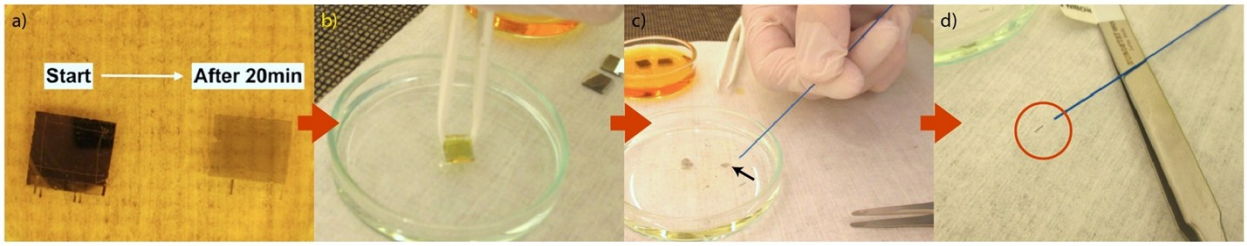

Figure S3. Photographs of the pattern transfer process. (a) The Cr-etching process depicting a newly (left) and 20-min dipped (right) glass substrate containing the alloy nanostructures on the C-transfer layer. As can be seen, complete removal of Cr after 20 min induces a distinct color change of the sample as it becomes more transparent. The detached C-film stays on the glass substrate and therefore the substrate can be used to transfer the C-film into DI water, as shown in (b). (c) In water the C-film will spontaneously float up to the water-air interface (pointed by the arrow). A fiber can thus conveniently pick up this film. (d) Once gently dried, the C-film conformally resides on the fiber (red circle). From here the oxygen plasma step can then be applied.

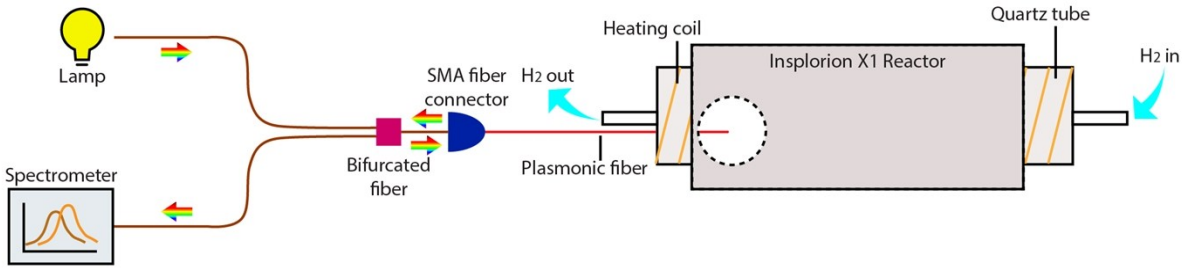

Figure S4. Schematic depiction of the experimental setup for nanoplasmonic fiber hydrogen sensing measurements. The nanoplasmonic fiber sensor is coupled to a bifurcated fiber via an SMA connector. However, the connection towards the sensor fiber is only made *via* simple clamping, which renders the arrangement extremely sensitive to fiber movement. The ends of the bifurcated fiber are connected to a light source and a spectrometer. The nanoplasmonic fiber sensor end decorated with the alloy nanostructures is put inside a flow reactor through a gas-tight teflon channel. The reactor allows controlled temperature and gas environment.

References

1 H. Fredriksson, Y. Alaverdyan, A. Dmitriev, C. Langhammer, D. S. Sutherland, M. Zäch and B. Kasemo, *Adv. Mater.*, 2007, **19**, 4297–4302.

2 F. A. A. Nugroho, B. Iandolo, J. B. Wagner and C. Langhammer, *ACS Nano*, 2016, **10**, 2871–2879.