

1 **Supporting Information**

2 3 **Grafting submicron titania particles with gold nanoparticles using droplet** 4 **microfluidics**

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6

7 **SI-1 Detailed experimental procedures**

8 If not stated differently, the chemicals were purchased from Sigma Aldrich, Switzerland.
9

10 **Fabrication of the polydimethylsiloxane (PDMS) chips**

11 Microfluidic PDMS chips were made using the soft lithography technique. To this end, a mold was fabricated using
12 the negative photoresist SU8. A 40 μm thick layer of SU8 (GM1070 from Gersteltec, Switzerland) was spread on a
13 silicon wafer by spinning it at 1933 rpm for 40 sec. Soft baking of the resist was done by heating it to 130°C during
14 50 min, keeping the temperature at 130°C for 5 min and cooling it down to room temperature during 50 min. To
15 structure the resist, parts of it were exposed to UV light with a total dose of 360 mJ/cm^2 . This was followed by a
16 post-exposure bake during which the furnace temperature was raised to 100°C during 40 min, kept at 100°C for 40
17 min and then cooled down to room temperature during 1 h 30 min. The resist was then developed in propylene
18 glycol monomethyl ether acetate during 20 min. Finally, the SU8 mold was cleaned with isopropanol.

19 PDMS chips containing microchannels were then obtained by pouring a degassed mixture of PDMS and
20 polymerization catalyst (Sylgard 184 from Dow Corning) into the mold and curing it at 60°C overnight. After
21 punching holes for the inlets and the outlet into the chip, the microchannels were formed by bonding a piece of
22 PDMS-coated glass to the PDMS molded part using oxygen-plasma. To recover the native hydrophobicity of
23 PDMS, the chips were heated to 120°C for 2 h.

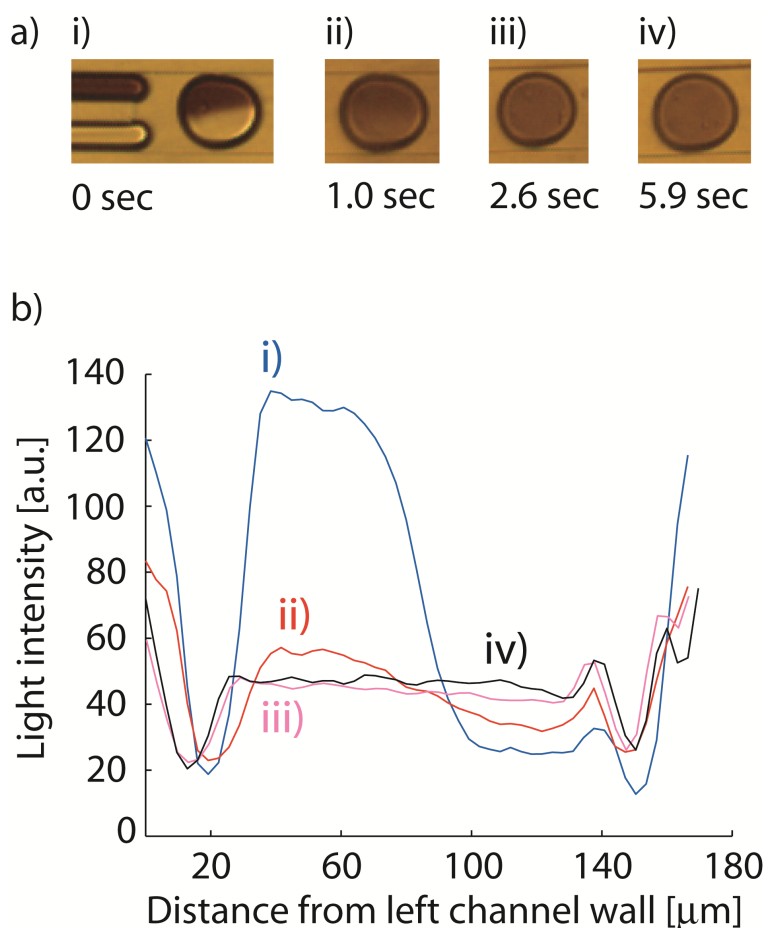
24 **Design and mixing in the microfluidic device**

25 All channels are 40 μm deep. The width of the central channel is 160 μm . The two side-channels are 36 μm wide
26 and form an angle of 45° with the main channel. The separating wall in the middle of the main channel is 50 μm
27 wide and ends 225 μm downstream of the junction of the side channels with the main channel. In their narrowest
28 point, the constrictions (length: 175 μm) are 50 μm wide, at the widest point, they are 110 μm wide. The spacing
29 between the constrictions is 385 μm , and the total length of the straight, central channel from the junctions to the
30 outlet is 21.1 mm.

31 Figure i a) shows micrographs of droplets after increasing residence time inside the microchannel. Figure i b) shows
32 color intensity plots along the short axes (perpendicular to the flow direction) of the droplets depicted in Figure i a).
33 After 2.6 sec (curve iii), the color difference between the right and the left side of the droplet is reduced to 90%.

34 As the continuous phase, we chose oleic acid (OA) due to its good wetting of native PDMS and high viscosity ($\mu =$
35 27.64 $\text{mPa}\cdot\text{s}$). Experiments to characterize the chip were done with pure and ink-labeled de-ionized water (DI) as
36 dispersed phase. Ink (4001) was purchased from Pelikan, Germany. The high-speed camera (model GMCLTR1)
37 used to analyze the generation of droplets and the mixing inside the droplets is from Mikrotron, Germany.

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3 **Figure i: a) Time-lapse image sequence of mixing in laterally merging droplets. b) Color intensity plot along**
4 **the short axis of the droplets shown in a). Mixing completes after ~5.9 sec (curve iv).**

5 **Synthesis of porous TiO₂ particles**

6 Following a protocol from ref. [1], porous TiO₂ particles were synthesized in a 200 mL-bottle under continuous
7 stirring at 400 rpm. 1.24 g dodecylamine were dissolved in 50 mL methanol with 25 mL acetonitrile and 360 μL DI
8 water. After addition of 2 mL titania isopropoxide, the solution was mixed for 18 h. The TiO₂ nanoparticles were
9 washed 4 times with methanol and dried at 60°C overnight.

10 **Infiltration of TiO₂ particles with 4-aminophenyl acetic acid (APA)**

11 To infiltrate porous TiO₂ particles with APA, 300 mg (0.1 M) or 30 mg (0.01 M) APA were dissolved in 20 mL
12 ethanol in a warm oil bath (35°C) under stirring (600 rpm). After 40 minutes, 300 mg porous TiO₂ particles were
13 added and mixed with the APA solution overnight. This colloid was then treated in a high-pressure reaction vessel
14 (type 4744, Parr Instrument Co., Moline, IL) at 80°C under indigenously built pressure for 2 h. To remove free APA
15 from the solution, the particles were washed 5 times with DI water.

16 **Operation of the microfluidic chip**

17 To inject the liquids into the microfluidic chip, we used microliter syringes (from ILS, Stützerbach, Germany) and
18 syringe pumps (from Cetoni GmbH, Korbussen, Germany). The concentration of APA-infiltrated TiO₂ particles was
19 adjusted to 30 mg/mL, and to stabilize the particles in water, we added 0.5 μL of silicone surfactant (Superwetting
20 agent Q2-5211 from Dow Corning, Switzerland) to 20 mL of colloid. This amount was found to be sufficient to
21 suspend the particles in water, while still allowing for subsequent on-chip merging of droplets. Droplet formation

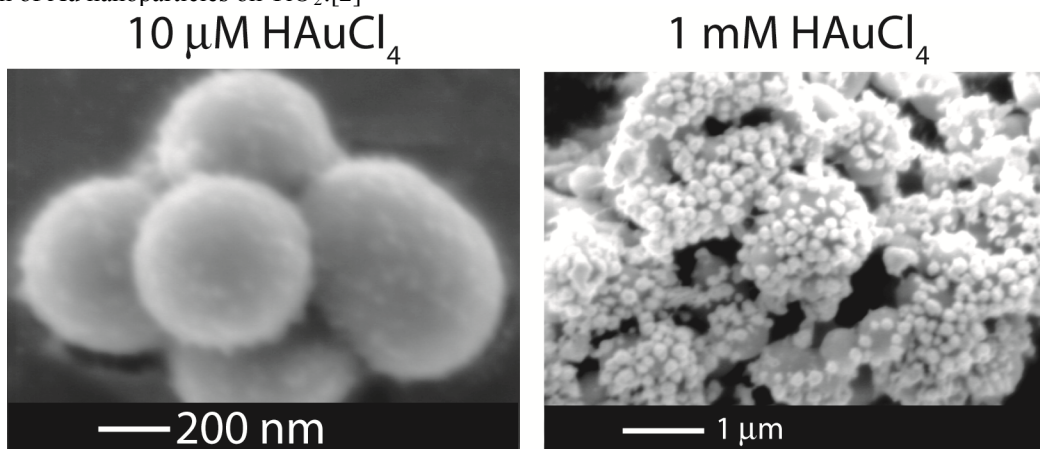
1 and merging was observed via a high-speed camera (Motion Blitz LTR from Mikrotron GmbH, Unterschleissheim,
2 Germany).

3 SI-2 Optical and physico-chemical analysis

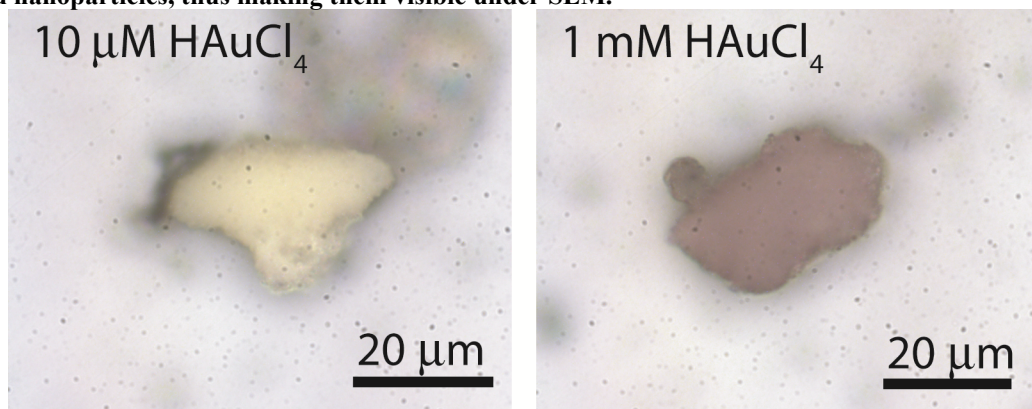
4 Microscopic inspection of the Au/TiO₂ nanocomposites

5 TEM images were taken with a FEI CM12 transmission electron microscope from Philips and a Gatan CCD
6 multiscan camera.

7 To show the homogeneity of the samples, we collected the reaction products from on-chip syntheses with 0.01 M
8 APA and 10 μM or 1 mM HAuCl₄ on silicon dies and inspected them under a scanning electron microscope (SEM;
9 XLF-30 FEG from Philips) and under an optical microscope (see Figures i and ii). The photographs from the
10 inspection with an optical microscope show that the color of the Au-grafted TiO₂ particles is homogeneous
11 throughout the whole sample and shifts to the red at higher concentration of HAuCl₄, which is indicative of the
12 formation of Au nanoparticles on TiO₂. [2]



13
14 **Figure ii: SEM images of TiO₂ particles with 0.01 M APA and grafted with Au nanoparticles, showing the**
15 **homogeneity of the synthesized product. The samples were heated to 476°C for 12 hours to induce the fusion**
16 **of the Au nanoparticles, thus making them visible under SEM.**



17
18 **Figure iii: Optical microscope images of the reaction products from the syntheses with 10 μM and 1 mM**
19 **HAuCl₄ and 0.01 M APA.**

20 BET analysis

21 A 5-point BET analysis was performed using a Gemini 2375 surface analyzer from Micrometrics. Previous to the
22 adsorption measurements, the sample was dried in a flowing-gas degassing unit (Micrometric FlowPrep 060) at
23 200°C under a constant nitrogen gas flow. The relative adsorption pressures (actual pressure/saturation pressure)
24 were 0.05, 0.1125, 0.175, 0.2375 and 0.3.

FTIR analysis of the TiO₂ particles with APA

To confirm the presence of APA on TiO₂ particles, we analyzed them with a Fourier Transform Infrared (FTIR) spectrometer (Spectrum One FT-IR from Perkin Elmer) that is equipped with a single reflection attenuated total reflectance system from Specac. Spectra were taken using standard parameters (range 4000 cm⁻¹ to 450 cm⁻¹; resolution 4 cm⁻¹, 100 scans) and the supplied Perkin elmer software Spectrum v3.02.

Figure iii shows the spectra from TiO₂ particles (blue curve), TiO₂ particles infiltrated with APA (red curve) and APA (black curve). In the spectrum of APA, we find a peak at 3000 cm⁻¹ which we ascribe to the asymmetric vibration mode of OH. Presence of NH is confirmed via the peak at 1596 cm⁻¹ (scissoring vibration mode), and the signals at 1579 cm⁻¹, 1514 cm⁻¹ and 1283 cm⁻¹ show the presence of a carboxylic acid group. The curve from APA-TiO₂ completely resembles the spectrum from APA, from which we conclude the presence of APA on TiO₂ particles.

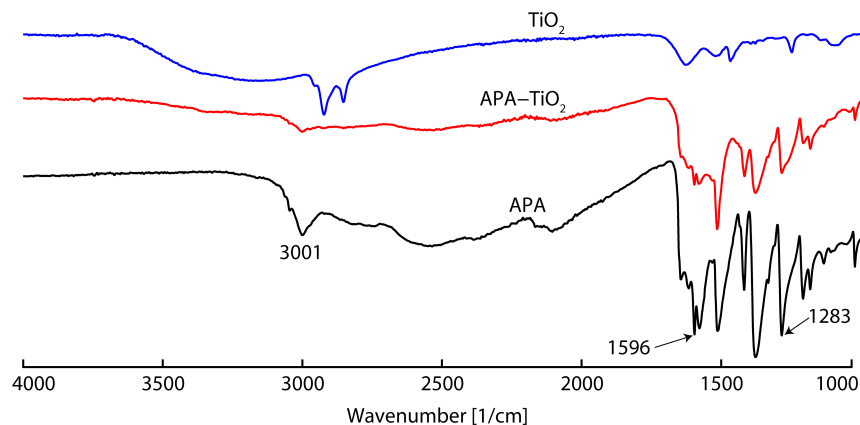


Figure iv: FTIR spectra of TiO₂ particles, TiO₂ particles with APA and pure APA. The curve of APA-TiO₂ resembles the spectrum of APA, indicating the presence of APA on TiO₂.

EDX analysis of the Au/TiO₂ nanocomposites

The EDX spectrum of TiO₂/Au nanocomposites indicates the presence of Ti, Au and O atoms in the samples. The prominent Si K α peak is due to the silicon die acting as a support of the sample.

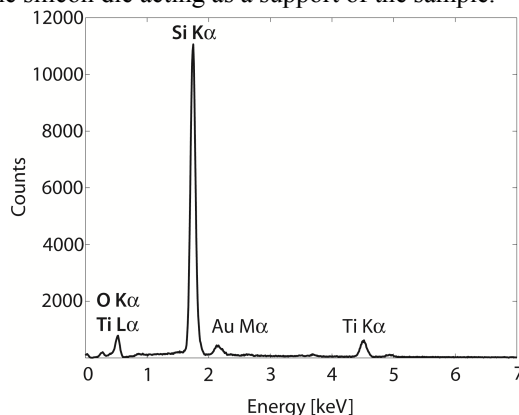


Figure v: EDX spectrum of TiO₂ particles grafted with Au nanoparticles. APA concentration:0.01 M; HAuCl₄ concentration:1 mM.

Video 1

Alternating generation and apical merging of TiO₂ colloidal and HAuCl₄ droplets. The video can be accessed as https://documents.epfl.ch/users/w/wa/wacker/www/DropletMerger_v2.avi

References

- 1
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