

## Supporting Information

### Designing the Au-TiO<sub>2</sub> interface in inverse opal photocatalysts

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# 1. Experimental details

## 1.1 Chemicals

All chemicals were used as received without further purification. Acetone, Acrylic acid (99%), ammonium persulfate (98%), L-ascorbic acid ( $\geq 98\%$ ), Gold (III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\geq 99.9\%$ ), methylene blue (MB,  $\geq 82\%$ ), polyvinylpyrrolidone (PVP,  $M_w = 55000 \text{ g mol}^{-1}$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ,  $\geq 99.0\%$ ), sodium citrate tribasic dihydrate ( $\geq 99.0\%$ ), styrene ( $\geq 99\%$ ), and tannic acid (99%) were purchased from Sigma-Aldrich. Absolute ethanol (EtOH) was purchased from KOPTEC. Titanium dioxide nanocrystals ( $\text{TiO}_2\text{-NH}_4$ , 10 wt %) was received from Nyacol Nano Technologies. Ultrapure deionised water (Millipore Milli-Q grade,  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was used and all glassware was cleaned with fresh aqua regia ( $\text{HCl}/\text{HNO}_3$ , 3 : 1 volume ratio) before use.

## 1.2 Synthesis

### Gold nanoparticle synthesis

Citrate-capped gold nanoparticles (Au NPs) were obtained using an adapted version of the procedure described by Piella et al.<sup>1</sup> First, 600 mL of 2.2 mM trisodium citrate in Milli-Q (MQ) water was added to a 1 L three-neck round-bottom flask, attached with an ice water-cooled reflux condenser. The flask was carefully placed in an oil bath heated at 70 °C, while magnetically stirring at 400 rpm. Next, 400  $\mu\text{L}$  of 2.5 mM tannic acid solution and 4 mL of 150 mM  $\text{K}_2\text{CO}_3$  solution were added. After 30 min of continuous stirring, 4 mL 25 mM  $\text{HAuCl}_4$  solution was rapidly injected to the reaction mixture, resulting in a color change from yellow to black, ultimately turning to deep red in 10 min. Next, 220 mL of the reaction mixture was removed, and 220 mL of 2.2 mM sodium citrate solution was added. After 30 min stirring, 2 ml 25 mM  $\text{HAuCl}_4$  was added twice at 10-min time intervals. Next, the reaction mixture was allowed to cool down to room temperature. A ligand exchange was carried out by adding 6 mL of a  $0.1 \text{ g mL}^{-1}$  PVP solution to 600 mL of citrate-capped Au NP solution. The solution was stirred at 400 rpm overnight. The PVP-capped Au NP solution was stored in the dark.

### Synthesis of carboxylic acid-capped polystyrene colloids

Carboxylate-functionalized polystyrene (PS) colloidal colloids were synthesized by a surfactant free emulsion polymerization method using styrene with acrylic acid as co-monomers and ammonium persulfate as the initiator, using a previously published method.<sup>2</sup>

### Synthesis of $\text{TiO}_2$ inverse opal films

The inverse opal (IO) films were synthesized using a modified protocol.<sup>3</sup> First, 5 cm  $\times$  1 cm rectangular strips were cut from an Si wafer with a diamond scribe. The Si wafers were rinsed with EtOH and MQ water, then dried with compressed air. Thereafter, the Si wafers were cleaned by plasma for 2 min under 50%  $\text{O}_2/\text{N}_2$  prior to use (Diener Femto PCCE). The co-assembly solution was prepared by adding 0.89 mL of 2.24 wt % carboxylic acid-capped PS colloids and 19.11 mL MQ water to a 20 mL glass vial. Next, 32.5  $\mu\text{L}$   $\text{TiO}_2$  nanocrystals (NCs) was pipetted on top of the solution without mixing to each glass vial, which is equivalent to approximately 4 mg  $\text{TiO}_2$ . The plasma cleaned Si wafers were vertically submerged into the assembly solution, and clamped at the top of the vials by binder clips such that the wafers do not touch the walls of the vial. The vials were carefully placed in a vibration-isolated oven at 75 °C and left undisturbed for two days to dry completely. Thereafter, the samples were calcined at 500 °C for 2 h with a heating ramp of 1.6 °C/min to remove the PS colloids, yielding the  $\text{TiO}_2$  inverse opal structure.

## Synthesis of Au/TiO<sub>2</sub> inverse opal films

*Three-component co-assembly (Au/TiO<sub>2</sub>-in).* For the synthesis of Au/TiO<sub>2</sub> IO films with embedded NPs, a three-component co-assembly was performed with carboxylate-functionalized PS colloids, TiO<sub>2</sub> NCs and citrate-capped Au NPs.<sup>4</sup> The synthesis steps were followed as described earlier for the synthesis of TiO<sub>2</sub> IO films, but the co-assembly solution was modified by adding 6.56 mL of citrate-capped Au NPs to 0.89 mL of 2.24 wt % PS colloids, diluted to a final volume of 20 mL with MQ water, which would eventually yield Au/TiO<sub>2</sub>-in with 3 wt % Au loading, determined with ICP-MS (Table 1).

*Two-component co-assembly (Au/TiO<sub>2</sub>-on).* For the synthesis of Au/TiO<sub>2</sub> IO films with non-embedded NPs (*i.e.*, NPs on the TiO<sub>2</sub> support surface), a two-component co-assembly with carboxylate-functionalized PS colloids and TiO<sub>2</sub> NCs was first performed as described in the synthesis of TiO<sub>2</sub> IO films. Evaporation-induced Au NP deposition was then conducted on the as-prepared TiO<sub>2</sub> IO films. To achieve 5 wt % Au loading, 6.56 mL of PVP-capped Au NPs was diluted to a final volume of 20 mL with MQ water in a 20 ml glass vial. Subsequently, the as-prepared TiO<sub>2</sub> IO film was vertically immersed in the diluted Au NP dispersion and clamped with binder clips in such a manner to avoid contact with the vial walls. The vials were placed in a vibrationally-isolated oven at 75 °C undisturbed for two days. Samples were then heated in the same oven at 140 °C for 1 h to remove any residual water before further characterization and catalytic testing .

### 1.3 Physical characterization

The samples were characterized with reflective light microscopy, scanning electron microscopy (SEM), bright field-transmission electron microscopy (BF-TEM), scanning transmission electron microscopic (STEM) tomography, ultraviolet-visible (UV-Vis) spectroscopy, and inductively coupled plasma-mass spectrometry (ICP-MS). Details are presented below.

**Microscopy.** Optical images were captured in bright-field reflective mode with a ZEISS Axio Imager 2. SEM images were obtained with a secondary electron (in-lens) detector and backscattered electron detector using a Zeiss Gemini 360 operating at an acceleration voltage of 2.5 kV and working distance of 7 nm. Prior to SEM imaging, the sample film was immobilized on the sample holder with carbon tape. BF-TEM images were acquired with a JEOL F200 microscope operating with an acceleration voltage of 200 kV. Prior to TEM imaging, samples were dispersed in absolute ethanol and drop-casted onto a Formvar/Carbon copper grid (200 mesh, Ted Pella). STEM tomography measurements were performed on a Talos F200X, operated at 200 kV. Prior to tomography measurements, fiducial markers (Au NPs, 15 nm) were deposited onto a Formvar/Carbon copper grid before sample deposition. The tomography data were reconstructed with IMOD software using a weighted back-projection algorithm.<sup>5</sup>

**UV-vis spectroscopy.** UV-vis spectra were recorded with a DU 720 (Beckman Coulter) spectrophotometer in a range of 300 nm to 800 nm. The samples were measured in a plastic cuvette with a path length of 1 cm.

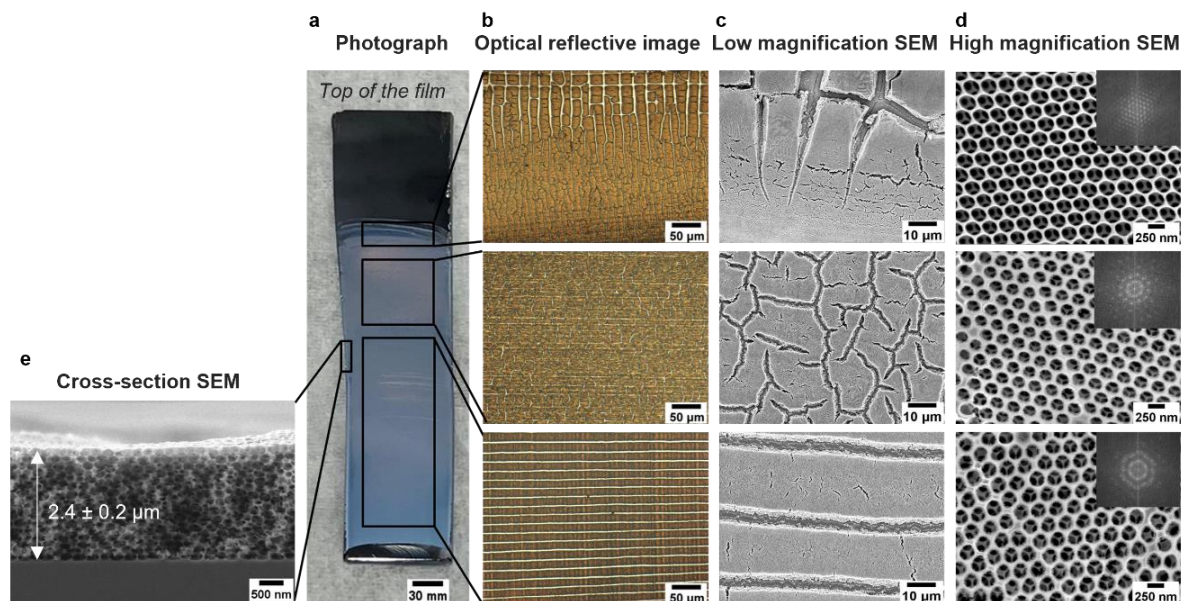
**Elemental analysis.** The Au metal weight loading was quantified with ICP-MS using Thermo Fisher Scientific iCAP RQ. Prior to the measurement, the samples were digested with aqua regia for 72 h. Calibration solutions for Au were prepared just before the measurements by diluting standard solutions of HAuCl<sub>4</sub> (1000 ppm in 2% HNO<sub>3</sub>) in a 1.4% w/w HNO<sub>3</sub> solution.

## 1.4 Photocatalytic evaluation

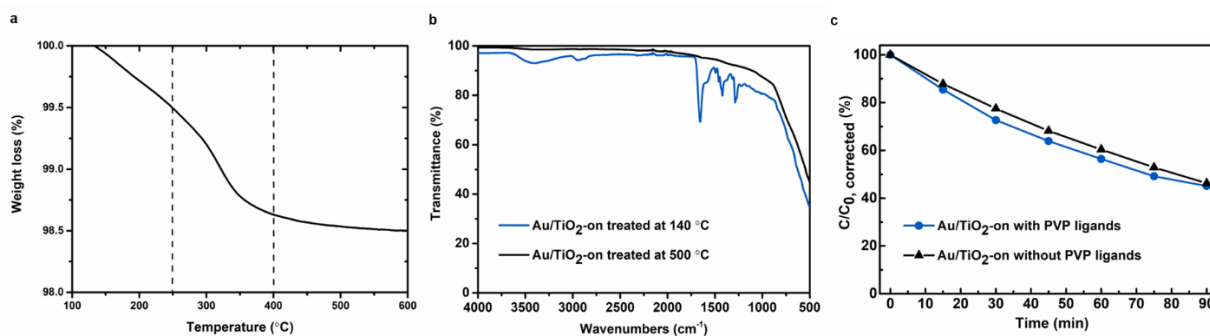
### Methylene blue photodegradation

The photocatalytic activity of the IO films was studied through the degradation of methylene blue (MB) under light irradiation. Tests were carried out in a 30 ml square glass vial containing 25 ml of 15  $\mu$ M MB solution. A metal plate was placed under the vial to remove heat from the solution during light irradiation. The IO film was plasma-cleaned for 2 min under 50% O<sub>2</sub>/N<sub>2</sub> to remove surface contaminants, immersed in the vial containing MB, and kept steady with binder clips on top of the vial. The solution was irradiated with a 450 W Xe lamp with a transmittance range 200–2500 nm, while the solution was stirred at 350 rpm using a magnetic stir bar. For all samples, the initial temperature of the MB solution was measured  $25\pm 1.4^\circ\text{C}$  and increases to  $31\pm 0.2^\circ\text{C}$  after 90 min. The pH of the MB solution remained constant at 6. The degradation of MB was determined by calculating the relative concentration with respect to the extinction of the characteristic peak at 664 nm, acquired using UV-vis spectroscopy of the MB solution every 15 min. For the cycling stability tests, the used films were calcined at 300 °C for 2 h after each catalytic cycle to remove any adsorbed MB that would block active sites (Fig. S9).

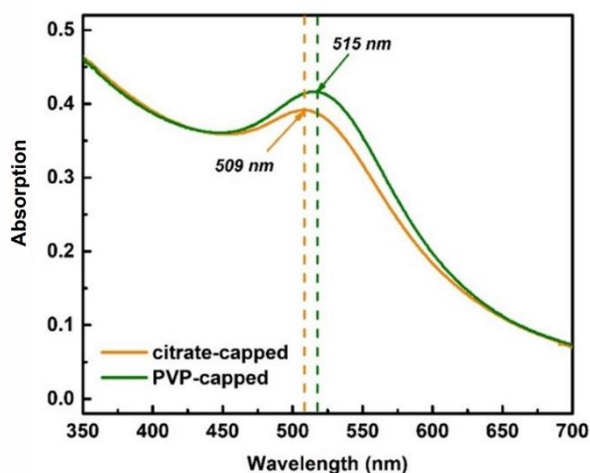
## 2. Supporting data



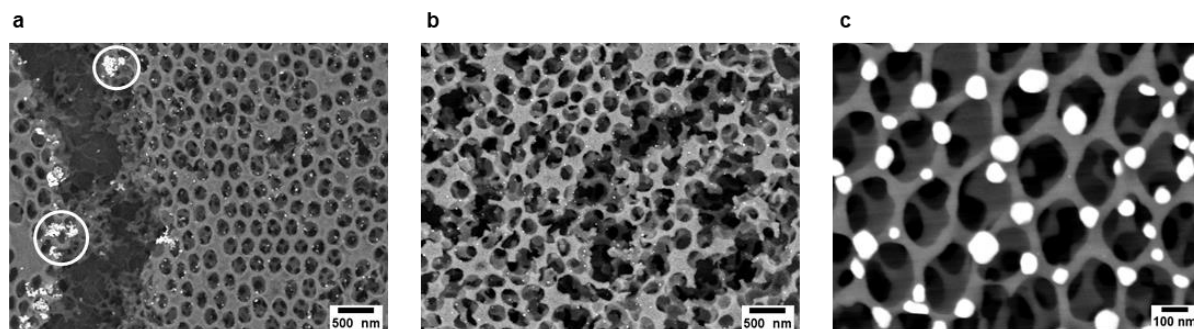
**Fig. S1** (a) Optical photograph of a representative  $\text{TiO}_2$  inverse opal film, further characterized with (b) optical reflective microscopy, (c) low-magnification SEM, (d) high-magnification SEM with the corresponding fast Fourier-transform (FFT) pattern, and (e) cross-section SEM.



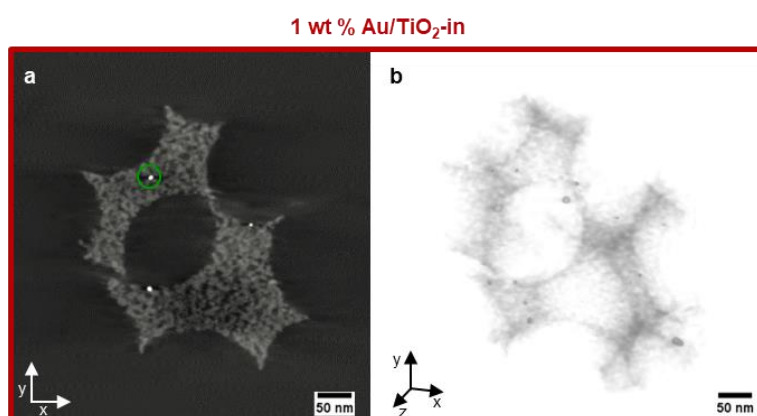
**Fig. S2** (a) TGA curve of PVP(55K)-capped Au NPs on  $\text{TiO}_2$  (P25, Degussa) under 20%  $\text{O}_2/\text{Ar}$  after a pre-treatment at 110 °C for 10 min to remove residual water. (b) FTIR spectra of 1.4 wt %  $\text{Au}/\text{TiO}_2\text{-on}$  after a heat treatment at 140 °C (blue) and 500 °C (black). (c) Comparison of photocatalytic degradation of methylene blue by 1.4 wt %  $\text{Au}/\text{TiO}_2\text{-on}$  with and without PVP ligands, respectively pretreated at 140 °C (blue) and at 500 °C (black).



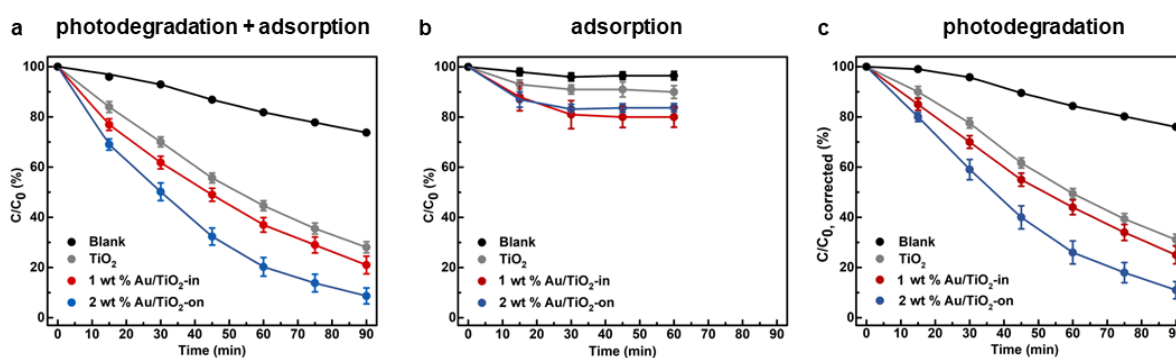
**Fig. S3** UV-vis spectra of Au NPs stabilized with citrate and PVP ligands, normalized at 400 nm. The dotted lines representing the LSPR positions align with 5 nm Au NPs.<sup>1</sup> The peak shift upon ligand exchange can be attributed to a change in local dielectric environment.<sup>6</sup>



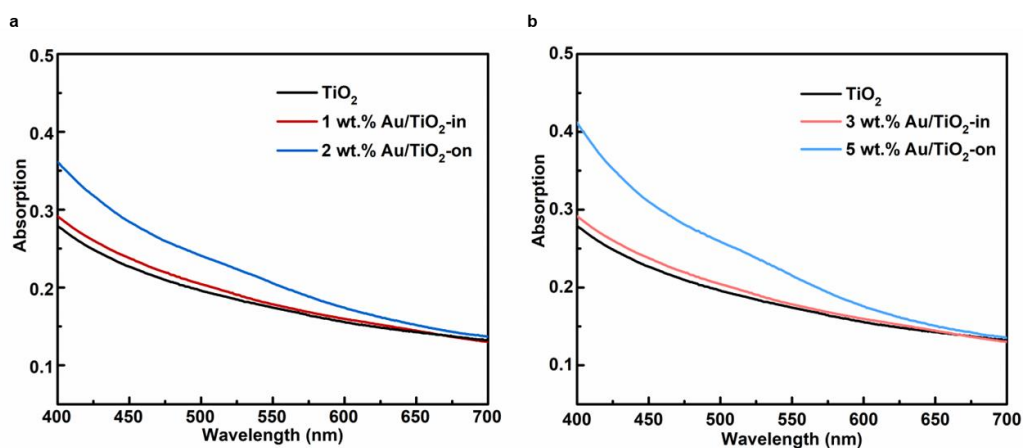
**Fig. S4** SEM images of Au/TiO<sub>2</sub> IO films prepared using unoptimized procedures. (a) Au/TiO<sub>2</sub>-on synthesized with citrate-capped Au NPs exhibit NP sintering (circled). (b) Au/TiO<sub>2</sub>-in synthesized with PVP-capped Au NPs show macroscopic disorder and a loss of the inverse opal structure. (c) Au/TiO<sub>2</sub>-on synthesized with PVP-stabilized Au NPs after calcination (500°C for 2 h) show severe NP sintering.



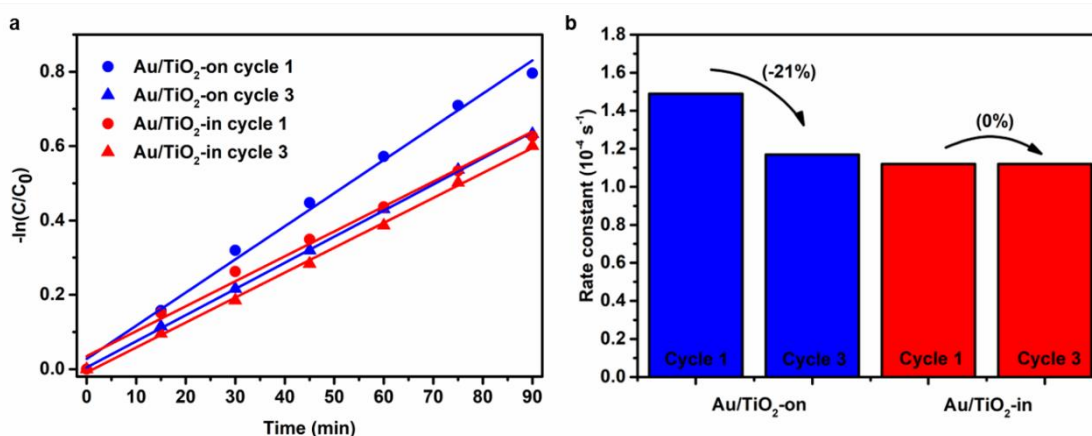
**Fig. S5** Two-dimensional scanning transmission electron microscopy (STEM) projections of 1 wt % (a) Au/TiO<sub>2</sub>-in with the corresponding three-dimensional tomographic reconstruction (b). Au NPs are shown as bright white spots in (a) and dark spots in (b). The green circle in (a) indicate an embedded Au NP.



**Fig. S6** Illustrative example showing correction for MB adsorption effect. The relative MB concentration (%) over time (a) before and (c) after correcting for (b) adsorption. (b) was determined by measuring the MB concentration in the absence of light – any decrease in MB concentration was due to adsorption onto the film and not due to photodegradation due to the dark conditions. Blank represents a solution of MB without any catalyst.



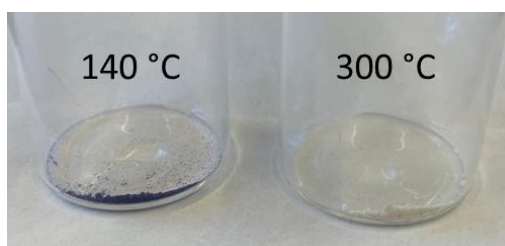
**Fig. S7** UV-vis absorption spectra of aqueous dispersed  $TiO_2$ , Au/ $TiO_2$ -in and Au/ $TiO_2$ -on IO at (a) lower and (b) higher Au metal loading obtained by fragmentizing the IO films into a powder form.



**Fig. S8** The cycling stability tests of a 1.4 wt % Au/TiO<sub>2</sub>-on and a 0.7 wt % Au/TiO<sub>2</sub>-in IO film in the photocatalytic degradation of MB. (a) MB decomposition kinetics expressed as  $-\ln(C/C_0)$  over reaction time for the first and third cycle, and (b) the derived corresponding first-order rate constants.

**Table S1** ICP-MS analysis of the Au/TiO<sub>2</sub> IO films used for the stability test to assess Au leaching after three cycles.

Sample	Experimentally measured Au loading (wt %)	Leached Au NPs (%)
Au/TiO <sub>2</sub> -on (fresh)	1.4	
Au/TiO <sub>2</sub> -on (after 3 cycles of catalytic testing)	0.3	80%
Au/TiO <sub>2</sub> -in (fresh)	0.7	
Au/TiO <sub>2</sub> -in (after 3 cycles of catalytic testing)	0.4	43%



**Fig. S9** MB adsorbed on TiO<sub>2</sub> (P25, Degussa) after a thermal treatment at 140 °C and 300 °C under static air for 2h. The removal of MB at 300 °C was observed by the disappearance of its characteristic blue color on the TiO<sub>2</sub> powders.

### 3. References

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