4-Aminothiophenol Photodimerization Without Plasmons

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SUPPORTING INFORMATION

Table of Contents

S0. Experimental Details
S1-S5. Control experiments on different types of TiO₂ supports
S6. Additional Raman spectra of Fig 1d
S7-S10. Control experiments on PATP droplets
S11. Control experiments on P25 TiO₂ nanoparticles in the absence of PATP
S12. Confocal Raman experiments of PATP powders with and without oxygen
S13. NaN₃ Raman reference spectrum
S14. Control experiment without NaN₃
S0. Experimental Details

Chemicals

4-aminothiophenol powder (purity >97%), ethanol (99.8%) and sodium azide (>99.5%) were purchased by Merck-Sigma-Aldrich and utilized without any further purification. The technical specifications of commercial P25-TiO$_2$ Aerioxide® nanopowders (Evonik) can be found in the online version of material datasheet. Commercial ZnO nanopowders (average size<100 nm) were purchased by Merck-Sigma-Aldrich. The monodisperse nano- (average size 235±1 nm) and micro-(average size: 6.47±32 µm) spheres were purchased by Microparticles GmbH. The SiO$_2$/TiO$_2$ core/shell microspheres (T-rex) were fabricated by following the experimental protocol reported in ref. 2. The planar thin films were achieved with the same procedure, without using silica spheres.

Confocal microRaman experiments

The confocal microRaman experiments were carried out by a high-resolution Raman microscope (Labram HR-800, Horiba/Jobin-Yvon), equipped a Syncerity CCD detector and an Olympus B-41 microscope stage, with 4 optical objectives (10X, 50X, 50X Long Working Distance, LWD and 100X). The optical images were acquired directly from the Raman microscope stage. The Raman spectra were acquired with a 50X LWD objective (Numerical Aperture, N. A. 0.50). The in-situ, temperature Raman measurements were carried out with a Linkam HFS-91 thermal stage, using the same optical objective. This stage was also utilized for the measurements in the absence of oxygen. The anoxic conditions were obtained by saturating the chamber with pure nitrogen. Confocal analyses to differentiate surface and interior of the PATP crystals were carried out by progressively changing the focal plane through the crystals under analysis.

At least 10 different regions were analyzed for each sample tested in Raman experiments. NaN$_3$ was utilized as a singlet oxygen quencher. 7 milligrams of NaN$_3$ in methanol were dissolved in 100 µL of a 10$^{-2}$ M solution of PATP and the final mixture was dropped on a silicon substrate for
Raman characterization. The same experiments were repeated by reducing the amount of NaN₃ by a factor of 2 and 10, respectively.

References:

1) P25-TiO₂ Aeroside® datasheet available at products-re.evonik.com

2) Alessandri, I. Enhancing Raman Scattering without Plasmons: Unprecedented Sensitivity Achieved by TiO₂ Shell-Based Resonators *J. Am. Chem. Soc.* **2013**, 135, 5541-5544
S1. Control Experiment 1: PATP on P25-TiO$_2$ irradiated at 1.6 mW/µm$^2$

Laser irradiation: 633 nm, 1.6 mW/µm$^2$

![Optical microscope image showing the effects of He-Ne (λ=633 nm) laser irradiation at 1.6 mW/µm$^2$ on P25 nanopowders previously soaked in a 10$^{-4}$ M PATP ethanol solution. The dark dot indicated by the red arrow shows the laser footprint. Scale bar: 5 µm.]

**Figure S1.**

S2. Control Experiment 2: PATP on P25-TiO$_2$ irradiated at 16 µW/µm$^2$

![Raman spectra of P25 TiO$_2$ nanopowders previously soaked in a 10$^{-4}$ M PATP ethanol solution, irradiated at 633 nm, 16 µW/µm$^2$). The Raman spectra have been stacked for clarity.]

**Figure S2.**
S3. Control Experiment 3: PATP on planar TiO$_2$ irradiated at 0.16 mW/$\mu$m$^2$

![Raman spectra of anatase TiO$_2$ planar thin films previously soaked in a PATP 10$^{-4}$ M ethanol solution irradiated at 633 nm, 0.16 mW/$\mu$m$^2$). The Raman spectra have been stacked for clarity.](image)

**Figure S3.** Raman spectra of anatase TiO$_2$ planar thin films previously soaked in a PATP 10$^{-4}$ M ethanol solution irradiated at 633 nm, 0.16 mW/$\mu$m$^2$). The Raman spectra have been stacked for clarity.

S4. Control Experiment 4: Photo-oxidation of PATP on planar T-rex beads.

![Optical microscope images showing the effects of 633 nm laser irradiation (1.6 mW/$\mu$m$^2$) on SiO$_2$/TiO$_2$ core/shell microspheres (T-rex beads). Scale bars: 5 $\mu$m.](image)

**Figure S4.** Optical microscope images showing the effects of 633 nm laser irradiation (1.6 mW/$\mu$m$^2$) on SiO$_2$/TiO$_2$ core/shell microspheres (T-rex beads). Scale bars: 5 $\mu$m.
S5. Control Experiment 5: Complete sequence of spectra of Figure 1d.

**Figure S5.** Sequence of Raman spectra of PATP supported on 6.5 micron-sized SiO$_2$ microspheres irradiated at 633 nm for 1 s. Spectra from 0 to 16 s of total irradiation are shown at increasing steps of 2 s. In figure 1d of the main text only spectra at t=0 and 16 s were shown for clarity.
S6. Control Experiment 6: Effect of laser irradiation on small PATP droplets

Figure S6. Optical microscope images showing examples of the effects of 633 nm laser irradiation (1.6 mW/µm²) on PATP small droplets. Scale bars: 5 µm.
S7. Control Experiment 7: Raman spectra of big and small PATP droplets irradiated at 0.16 mW/µm²

Figure S7. Temporal evolution of the PATP (and DMAB) Raman spectra for a) big (i.e. >30 µm) and small (i.e. <5 µm) droplets, irradiated at 0.16 mW/µm².
S8. Control Experiment 8: Effect of prolonged irradiation at $\lambda=785$ nm on small PATP droplets

Figure S8. Raman spectra of PATP small (< 5 µm) droplets irradiated at 785 nm (260 mW/µm²) at different exposure time. The spectra were stacked for clarity.
S9. Control Experiment 9: In situ thermal heating experiments

**Figure S9.** *In-situ* thermal heating of PATP powders irradiated at 785 nm in a Linkam cell. The acquisition time for each scan was 10 s.
Figure S10. Raman spectrum of P25 soaked in ethanol in the absence of PATP and irradiated under the same conditions (633 nm, 0.16 mW/µm²) of experiment shown in Figure 1 (main text). The Raman spectra have been stacked for clarity. The inset shows a zoomed view of the 1000-1800 cm⁻¹ region.
S11. Control Experiment 11: Raman spectra of big PATP droplets aged in air overnight under laser irradiation at 1.6 $\mu$W/mm$^2$.

![Big droplet aged in air overnight (1.6 mW/µm$^2$)](image)

**Figure S11.** Temporal evolution of the PATP (and DMAB) Raman spectra for big (i.e. >30 µm) droplets aged overnight, irradiated at 1.6 mW/µm$^2$. 
S12. Control experiment 12: Confocal Raman experiments with and without oxygen

**Figure S12.** Temporal evolution of the Raman spectra of PAPT powders irradiated at 633 nm, 1.6 mW/µm² on a) surface and b) inner (bulk) regions of the crystals, obtained by confocal microscopy acquisition at different penetration depth (see the scheme on the right). The spectra acquired from the inner regions of the samples are analogous to those acquired in nitrogen-saturated atmosphere. The corresponding optical microscope images are shown (scale bar: 5 µm). In the case of surface focusing (Panel a), the formation of the laser footprint is indicated by the red circle. No morphological modification was observed either for interior regions or oxygen-free surfaces (Panel b).
S13. Control Experiment 13: Raman spectrum of NaN$_3$ powder.

Figure S13. Raman spectrum of NaN$_3$ powder (reference).
S14. Control Experiment 14: Effects of irradiation at 1.6 mW/µm² on small bubbles without NaN₃

Figure S14. Effect of irradiation at 1.6 mW/µm² on a PATP small bubble (Concentration of the original solution: 10⁻³ M) in the absence of NaN₃. Scale bars: 5 µm.