

“Probing Redox Photocatalysis of Trapped Electrons and Holes on Single Sb-doped Titania Nanorod Surfaces”

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Materials and methods

(1) Synthesis of TiO₂ nanorods and its doping with antimony

Anatase TiO₂ nanorods were synthesized according to the literature with oleic acid (OA, from Sigma-Aldrich) and titanium (IV) isopropoxide (TTIP, from Sigma-Aldrich) at 270 °C for 2 h.¹ Pure TiO₂ nanorods were obtained by conducting size-selective precipitation from hexane/ethanol solution containing the product mixture. The final pure TiO₂ in hexane was obtained for the next step: doping. For the doping step, certain amount of tris (dimethylamido) antimony ([(CH₃)₂N]₃Sb) (from Sigma-Aldrich) dissolved in hexane was injected into the purified pristine TiO₂ nanorods solution in hexane with atomic ratio Sb/Ti = 1/100. The obtained mixture was stirred for 24 h under Argon atmosphere to get even distribution of Sb precursor on TiO₂ nanorods surface. The obtained mixture solution was named **Solution A**. The final Sb-doped TiO₂ nanorods were obtained by drying the above **Solution A** in air on a surface and sintered in air at 500°C for 2 h to remove the surface ligand oleic acid. It has been found the annealing of anatase TiO₂ at 500°C can maintain the anatase phase of TiO₂.²

Particle morphologies of doped or undoped TiO₂ nanorods were examined by transmission electron microscopy (TEM, JEOL LEM-4000FX) at 200 kV. Diffuse reflectance spectra were also obtained for the dry-pressed disk samples using a UV-Vis-NIR spectrophotometer (JASCO) equipped with ISN-470 integrating sphere assembly. Reflectance spectra were referenced to MgO.

(2) Single molecule experiment

For typical single molecule experiments, the diluted **Solution A** with Sb-doped TiO₂ nanorods was spin-coated on quartz slide surface. After dried in air, the quartz slide was annealed in air at 500°C for 2 h to remove ligand oleic acid. After cooled to room temperature, the quartz slide was washed with DI water to remove unbound nanorods. With similar method reported previously,³ a flow cell was made for single molecule experiments. In the experiments, the first step photobleaching the fluorescent dust or impurities in the channel by flowing in a blank air-saturated phosphate (50mM, pH7.3) buffer with flow rate 20 uL/min and shining high power density green laser (514 nm) for 30 min. In this way most of the fluorescent impurities could be photobleached. After that buffers containing different concentration substrate and quenchers(Amplex red from *Invitrogen*, DMSO and SOD are from *Sigma-Aldrich*) was flowed through the flow cell illuminated with laser at appropriate intensity. In this system the oxidant was formed in-situ on Sb-doped TiO₂ nanorods surface according to the Scheme 1. It leads to very low background signal compared with previous system,³ in which the reductant and oxidant were mixed before flowing through the channel.

Single-molecule fluorescence measurements were performed on a homebuilt prism-type total internal reflection (TIR) fluorescence microscope based on a Zeiss Axiovert 135 TV inverted microscope. A continuous wave 514 nm laser beam (Lexel Laser) of 10-15 mW was focused onto an area of ~138 × 138 μm² on the sample to

directly excite both the Sb-doped TiO₂ nanorods and the fluorescence of resorufin. The fluorescence of resorufin was collected by a 60X NA1.2 water-immersion objective (UPLSAPO60XW, Olympus), filtered by a filter (HQ545LP), and projected onto a camera (Andor iXon EMCCD, DV887DCS-BV), which is controlled by an Andor iXon software. All optical filters are from Chroma Technology Corp. The movies are analyzed using a home-written IDL program and Matlab program, which extracts the fluorescence intensity trajectories from localized fluorescence spots individually across the entire movie. The intensity of each bright spot in an image is obtained by integrating the signal counts over an area of $\sim 1 \times 1 \mu\text{m}^2$.

Nanomaterial Characterization and Control Experiments:

1. Control experiment with different quencher concentrations, laser intensities and the reproducibility of data.

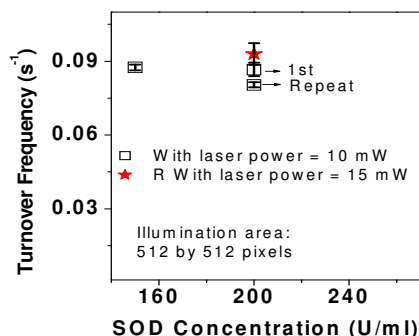


Figure S1. Control experiments with different SOD concentrations, laser intensities and repeating.

No obvious turnover frequency (TOF) difference between the experiments with SOD concentration 150U/ml and 200U/ml indicates 200U/ml of SOD is enough to quench all the superoxide radicals. Similarly for the quencher DMSO, it was found 20 mM of DMSO is sufficient to quench all the hydroxyl radicals on nanorod surface.

No obviously TOF difference between laser power 10 mW and 15 mW indicates the fluorescent bursts are not photo-induced.

By repeating the same experiment with exactly same conditions, it was found there is no obvious difference of TOF, indicating the system is stable.

2. Bleaching, blinking and further oxidation of product

We measured the photobleaching lifetime of resorufin. For this control experiment, a single layer of Sb-doped TiO₂ nanorod on quartz slide was made first by spin-coating. After been annealed at 500^oC for 2 h, the slide was washed thoroughly with nano-pure water. Then we immobilized resorufin molecules in a polymethyl-methacrylate (PMMA) (Aldrich) film by spin-coating 20 uL of 50 pM solution of resorufin in PMMA in toluene onto the Sb-doped TiO₂ surface. A $\sim 10 \mu\text{m}$ phosphate buffer layer (air-saturated) was then added on top of the PMMA film to provide an approximate aqueous environment. An uncoated coverslip was then used to sandwich sample for measurements on our TIR fluorescence microscope. After this step we started taking movie and 10 s later the laser with the same intensity used above in the normal single molecule experiments was turned on to illuminate the flow cell.

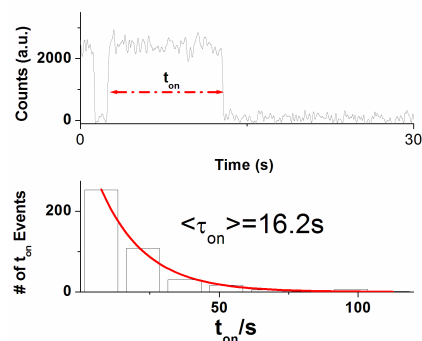


Figure S2. (Above) A typical blinking trajectory of a single product molecule on Sb-doped TiO₂ surface; (Bottom) t_{on} distribution obtained from about 100 single-product-molecule blinking trajectories.

From the single exponential fitting, it was found the averaged t_{on} for single molecule blinking is about 16 s. Then the averaged life-time of single product molecule before photobleaching should be longer than 16 s. The long averaged t_{on} also rules out the possible further oxidation of product by radicals. If the sudden decrease of fluorescence intensity is mainly due to the further oxidation of product, we cannot get such long t_{on} . This fact means in this system, the further oxidation of product by radicals is negligible.

3. **To rule out** that binding or unbinding of free resorufin in the solution to a Sb-doped TiO₂ nanorod is the cause of the burst behavior of fluorescence trajectories, we performed control experiments with only resorufin in solution at 10^{-8} M (~1% of the substrate solution) at the same flow rate. No digital signals were observed. This indicates that at this resorufin concentration, binding of free resorufin in solution to Sb-doped TiO₂ nanorod surface is insignificant in our single-nanoparticle catalysis experiments. Note that in the single-nanoparticle photocatalysis experiment, the resorufin is generated *in situ* from *pre-adsorbed* amplex-red, which does not involve a resorufin-binding process.

4. Ensemble experiment to show photocatalytic activity of Sb-Doped TiO₂ for Amplex red oxidation

In this experiment, the Sb-doped TiO₂ was deposited on a piece of glass surface (3 mg Sb-TiO₂ powder distributed evenly on 1X1 cm² glass surface). We first dipped the piece of glass with Sb-TiO₂ catalyst into water for 5 seconds to create water environment around catalyst, then illuminate the catalyst surface with 514 nm laser (~10 mW) for different times (0 min, 5 min and 8 min). After that the glass with catalyst was dipped into stirred amplex red phosphate buffer solution (pH 7.3), so that if there are any radicals formed on Sb-TiO₂ surface, these radicals will oxidize amplex red to form fluorescent product resorufin, which could be detected as shown on following figure. The black curve is the blank result with no light (0 min) illumination. It can be seen there is no product molecules formed in the solution, means without light illumination, no radicals formed on catalyst surface. When illuminated with 514 nm light for 5 min, as shown by the red curve, we can see the formation of resorufin which is formed from the oxidation of amplex red by radicals formed on Sb-TiO₂ surface. When we increase the illumination time, more product molecules formed due to the more radicals formed on catalyst surface (blue curve). This control experiment clearly shows the visible light (514 nm here) photocatalytic activity of the Sb-doped TiO₂.

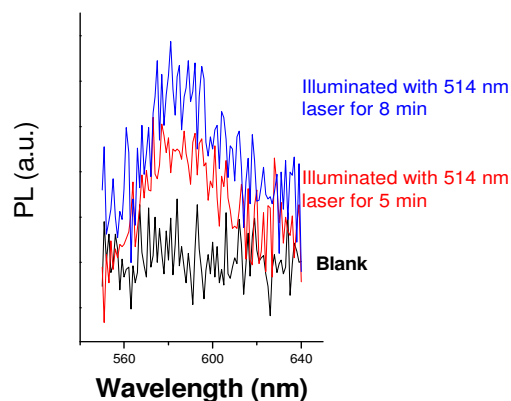


Figure S3. Ensemble control experiment to validate the photocatalytic activity of Sb-Doped TiO₂ for the oxidation of Amplex-red.

5. Key points about how to get clean or real single molecule catalytic signals

We have done the following additional controls and found, i) no digital fluorescence bursts were observed from the Sb-doped TiO₂ surface when both radical quenchers were added in the substrate solution on Sb-doped TiO₂ surface, ii) no digital signals were observed on pure TiO₂ surface or iii) in the absence of substrate. If laser excitation or binding of the probe molecules were to lead to significant turn ON, this would not be the case.

Quantitatively speaking, in our case, typically we detected no digital signal in these control experiments, implying that noncatalytic signal contributes zero. Thus, in our system all the signals are real and of catalytic origin.

Careful experiments helped us eliminate any artifacts: 1) We made clean flow cells; prepared all solutions with DI water; 2) Before taking movies, the field of view was photobleached with an intense laser for 30 min to remove all the fluorescent impurities on the surface; 3) Kept dye probes away from light when not in use; 4) Used fresh dye solution.

- (1) Joo, J.; Kwon, S. G.; Yu, T.; Cho, M.; Lee, J.; Yoon, J.; Hyeon, T. *J. Phys. Chem. B* **2005**, *109*, 15297.
- (2) Moon, J.; Takagi, H.; Fujishiro, Y.; Awano, M. *Journal of Materials Science* **2001**, *36*, 949.
- (3) Xu, W.; Kong, J. S.; Yeh, Y.-T. E.; Chen, P. *Nature Materials* **2008**, *7*, 992.