Supplementary Information

In Situ Raman Study of the Photoinduced Behavior of Dye Molecules on TiO₂(*hkl*) Single Crystal Surfaces

Sheng-Pei Zhang, Jia-Sheng Lin, Rong-Kun Lin, Petar M. Radjenovic, Wei-Min Yang, Juan Xu, Jin-Chao Dong,* Zhi-Lin Yang, Wei Hang,* Zhong-Qun Tian,* and Jian-Feng Li*

Corresponding Author: Li@xmu.edu.cn (Jian-Feng Li); jinchaodong1209@126.com (Jin-Chao Dong); weihang@xmu.edu.cn (Wei Hang); zqtian@xmu.edu.cn (Zhong-Qun Tian);

Experiment Sections

Materials and Methods

Reagents

Sodium citrate (99.0%), chloroauric acid (99.99%), and (3-aminopropyl) trimethoxysilane (APTMS) (97%) were purchased from Alfa Aesar; sodium silicate solution (27% SiO₂) was purchased from Sigma-Aldrich; acetonitrile (99.8% spectral grade) was purchased from Alfa Aesar; ethanol (99.7%) was purchased from Sinopharm Chemical Reagent Co. Ltd.; and the dye, ditetrabutylammonium cis-bis(isothiocyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)ruthenium[II] (N719), was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were used without further purification. Milli-Q water (~ 18.2 M Ω ·cm) was used throughout the study.

Preparation of Rutile single crystal

The rutile TiO₂(001), TiO₂ (110), TiO₂ (111) $5 \times 5 \times 0.5 \text{ mm}^3$ were purchased from Hefei Kejing Materials Technology Co., Ltd. First, TiO₂ was immersed in a solution of ethanol solution containing $5 \times 10^{-4} \text{ M}$ of N719. TiO₂ was extracted from the solution after 12 hours, and the single crystal surface was rinsed with ethanol three times and has no obvious color change in order to remove physically adsorbed N719 molecules.

Preparation of 55 nm Au @ ~2 nm SiO₂ nanoparticles (SHINs)

A detailed preparation method is described using our previously reported 55 nm Au@2 nm SiO₂ SHIN. 55 nm Au NPs were prepared according to the sodium citrate reduction method. First, a solution of 200 mL (0.01 wt%) of HAuCl₄ was placed in a 500 mL round bottom flask and then stirred with heating until the solution boiled. Next, 1.4 mL (1 wt%) of sodium citrate solution was quickly added to the above solution, and it was observed that the color of solution changed from light black to dark red and finally to brownish red after 20 min; the solution was then allowed cool to room temperature. SHINs were then synthesized as follows: 30 mL of the 55 nm Au NPs solution was added to a round bottom flask at room temperature under continuous stirring, and then 400 μ L of (3-aminopropyl) trimethoxysilane (APTMS) (1 mM) was added. After stirring the reaction for 15 minutes at room temperature, a solution of 3.2 mL (0.54 wt%) of Na₂SiO₃ (pH ~10) was added to the solution and shaken for 15 min. After a further 3 minutes, the mixed sample was transferred to a 98 °C water bath and stirred for 30 minutes. The solution was then rapidly cooled in an ice bath and centrifuged three times. Finally, the concentrated SHINs are diluted with ultrapure milli-Q water.

Raman measurements

The Raman spectra were carried out on a confocal XploRA Raman microscope system (Jobin-Yvon France). The excitation wavelength was 638 nm (1.5 mW) and a 50× microscope objective with a numerical aperture of 0.55 was used in all Raman measurements. Raman spectrum shown here was acquired over a collection time of 10 s and are the average of two acquisitions.

Mass spectrometry measurements

 $TiO_2(hkl)$ single crystals were put in a cuvette with a 5 \times 10⁻⁴ M concentration of N719 in ethanol solution, and the single crystal surface was irradiated by 405 nm laser. After 36 hours, the solution was extracted for mass spectroscopic measurements. Experiments were performed on a micrOTOF-Q impact II mass spectrometer (Bruker Daltonics) with the following instrumental

parameters: high voltage -4.5 kV, 4 mL/min flowrate of dry gas (nitrogen) with a temperature set to 180 °C, scan range: m/z 50 - 1500, and the solvent spray was injected into the system at a flowrate of 180 μ L/h.

UV-visible absorption spectroscopy

Absorption spectra were collected on an UV-Vis spectrophotometer (UNICO, UV2012C / PC / PCS).

DFT calculation method

Model building

The rutile $TiO_2(hkl)$ surfaces were modelled with full 3D periodic boundary conditions, and the slabs and their images were separated by a vacuum space of 20 Å. $TiO_2(111)$ was modelled by a five O-Ti-O tri-layer slab, and the box size was 16.393 × 31.177 Å³ shown in Supplementary Fig.4a. $TiO_2(110)$ was modelled by a five O-Ti-O tri-layer slab similarly, and the box size was 11.836 × 12.994 × 35.530 Å³, as shown in Supplementary Fig.4b. $TiO_2(001)$ was modeled by a four O-Ti-O tri-layer slab, and the box size was size was 13.782 × 13.782 × 31.836 Å³, as shown by Figure S7.

Computational setup

Density functional theory (DFT) calculations were carried out using the freely available program package CP2K/Quickstep.² We used Perdew-Burke-Ernzerhof (PBE) functional with Grimme's dispersion correction. And the core electrons were represented by analytic Goedecker-Teter-Hutter (GTH) pseudopotentials.³ The basis sets for the valence electrons were (4s2 3d10 for Ti, 2s2 2p4 for O, 3s2 3p4 for S, 2s2 2p5 for N, 2s2 2p2 for C, 1s1 for H) were short-ranged (less diffuse) double- ζ basis functions with one set of polarization functions (DZVP).⁴ The adsorption energies of the molecules on the TiO₂ surface were calculated by the formula: Ead = E(TiO₂-molecular) – E(TiO₂-surface) – E(molecular) and the energy reaction (ER) was calculated by the formula: ER = E(TiO₂-S-C-N-Ph) – E(TiO₂-S) – E(C-N-Ph).

Results and Discussion



Fig. S1 Raman spectra of N719 adsorbed on rutile TiO₂(001) / (110) / (111) single crystal surfaces in acetonitrile.



Fig. S2 Molecular structure of N719.



Fig. S3 The UV-vis absorption spectrum of N719 molecules.



Fig. S4 The Raman spectra of $\rm TiO_2(001)$ with (red line) and without SHINs (black line).



Fig. S5 Raman signal of rutile TiO₂(111) single crystal surface in acetonitrile under 638nm and 638nm + 405 nm laser illumination.

$$v = \left(\frac{1}{\lambda_{ex(nm)}} - \frac{1}{\lambda_{rs(nm)}}\right) \times 10^7 \ (cm^{-1})$$

v: Raman shift $\lambda_{ex(nm)}$: excitation wavelength $\lambda_{rs(nm)}$: Raman scattering wavelength

Fig. S6 Formula used to calculate the Raman shift.



Fig. S7 Continuously scanned in situ SERS spectra of rutile TiO₂(110) under the 405 nm laser illumination in acetonitrile taken every 4 minutes.



Fig. S8 Top view configuration of the Ph-N=C=S binding group adsorbed on (a) TiO₂(111), (b) TiO₂(110), and (c) TiO₂(001).
Top view configuration of the S atom adsorbed on (d) TiO₂(111), (e) TiO₂(110), and (f) TiO₂(001). Dissociation energies for the C=S functional group on TiO₂(111), TiO₂(110) and TiO₂(001) are 3.5 eV, 2.52 eV and 2.08 eV, respectively.



Fig. S9 Mass spectra of N719 on rutile $TiO_2(001)$, $TiO_2(110)$, and $TiO_2(111)$ in the N719 containing ethanol solution under the 405 nm laser illumination for 12 hours.

- 1. J. F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y. Zhou, D. Y. Wu, B. Ren, Z. L. Wang, Z. Q. Tian, *Nature* 2010, **464**, 392.
- 2. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, Compu. Phys. Commun. 2005, 167, 103-128.
- 3. (a) S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* 1996, **54**, 1703. (b) C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B* 1998, **58**, 3641.
- 4. J. VandeVondele, J. Hutter, J. Chem. Phys. 2007, 127, 114105.