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Papatya C. Sevinc

Xiao Wang

Yuanmin Wang

Dai Zhang

Alfred J. Meixner

See next page for additional authors

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Author(s)

Papatya C. Sevinc, Xiao Wang, Yuanmin Wang, Dai Zhang, Alfred J. Meixner, and H. Peter Lu

Simultaneous Spectroscopic and Topographic Near-Field Imaging of TiO₂ Single Surface States and Interfacial Electronic CouplingPapatya C. Sevinc,^{S,†} Xiao Wang,^{S,‡} Yuanmin Wang,[†] Dai Zhang,[‡] Alfred J. Meixner,^{*,‡} and H. Peter Lu^{*,†}[†]Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, United States[‡]Institut für Physikalische und Theoretische Chemie, Eberhard-Karls-Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany**S** Supporting Information

ABSTRACT: We have probed single surface states and the involved interfacial charge transfer coupling on the TiO₂ surface using confocal as well as tip-enhanced near-field topographic–spectroscopic imaging analysis on a niobium-doped rutile TiO₂(110) surface. The confocal images excited with a radially polarized donut mode render ring-shaped excitation patterns typical for quantum systems with two perpendicular transition dipole moments. The tip-enhanced near-field optical images of single surface states are visualized by the strong exciton plasmon–polariton coupling localized at the subdomain boundaries with a spatial resolution of ~15 nm (far beyond the optical diffraction limit). We suggest that the abundant surface states in the doped TiO₂ generate excitons under laser excitation which are strongly coupled to the surface plasmon–polaritons of the Au tip. Moreover, the interfacial electronic molecule–substrate coupling has been characterized by probing the molecule-perturbed surface states distribution and the associated specific Raman vibrational modes. The imaging and characterization of the surface states and their distributions on TiO₂ surfaces at nanoscale are critically relevant to a deep understanding of interfacial electron transfer dynamics and energetics involving in solar energy conversion, photocatalysis, and mechanistic understanding of surface-enhanced Raman scattering spectroscopy.

KEYWORDS: Single electronic surface states, nanoscale imaging, near-field topographic–spectroscopic imaging, electronic coupling, interfacial electron transfer

Interfacial electron transfer at molecule/semiconductor interfaces has been widely investigated due to its extensive applications in solar energy conversion, photocatalysis, and molecular electronics.^{1–3} Because of the unique properties of adequate photostability, nontoxicity, low-cost, and high catalytic reactivity, molecule/TiO₂ systems have attracted significant attention. It has been demonstrated that the interfacial electron transfer rate at the molecule/TiO₂ interface is strongly regulated by the molecule–semiconductor interactions, such as driving force of the free energy gap, the vibrational relaxation energy of the adsorbed molecules, the surface vibrational modes of TiO₂, and the electronic coupling between the molecules and TiO₂, etc.^{1–4} In a dye-sensitized system, the hot excited electron injects, for example, from the lowest unoccupied molecular orbital (LUMO) into the conduction band or energetically accessible surface states of the semiconductors. In particular, surface states inside the band gap usually provide a dominant pathway for the injected electrons through Lévy type non-Browning motion such as trapping, detrapping, and scattering.^{5–7} It has been demonstrated that, due to the important role of the surface traps, the electron transport rate in single crystal TiO₂ nanowires, polycrystalline TiO₂ nanowires, and nanotubes can be as slow as in TiO₂ nanoparticle electrodes.^{8–10} Hence, a fundamental under-

standing of surface states, such as their nanoscale distribution, optical properties, and involved charge transfer coupling, is crucial to the promotion of the photoelectrical performance of the semiconductor devices.

Surface states and their distribution, which describe the two-dimensional carrier profiles and determine the electronic properties of semiconductor surfaces, have been studied by photoemission spectroscopy,¹¹ surface photovoltage spectroscopy,¹² scanning capacitance microscopy,¹³ scanning spreading resistance microscopy,¹⁴ scanning tunneling microscopy,¹⁵ and Kelvin probe force microscopy.¹⁶ In this report, single surface states on the pristine TiO₂ surface and molecule–substrate electronic coupling have been probed using a parabolic-mirror-assisted confocal and tip-enhanced near-field microscopy excited by a highly focused radially polarized laser beam. The unique technique can provide in the confocal mode distinct diffraction limited excitation patterns which reflect the dimensionality of the quantum system,¹⁷ and when an additional sharp tip is brought in the focus for further confining the optical field and tip enhanced

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Figure 1. (A) Schematic illustration of a parabolic-mirror-assisted ultramicroscope. A sharp Au tip is adjusted into the center of a vertically polarized, diffraction limited focus as created by an incident radially polarized laser beam. The tip serves as an optical antenna providing intense local electromagnetic (EM) field enhancement at the tip apex for local excitation and emission to the optical far-field. (B) Laser illumination is applied in a radially polarized mode to obtain the strongest EM enhancement at the tip apex as visualized by the diffraction limited, circular luminescence emission pattern of sharp Au nanocones.

near-field excitation, we can simultaneously get nanoscale topography, optical imaging, and the chemical identification of a specific single surface state with a spatial resolution of ~ 15 nm. Strong exciton plasmon–polariton coupling at the TiO_2/Au tip nanogap reveals the high spatially and optically resolved two-dimensional distributions of the TiO_2 surface states. The nanoscale imaging and the involved charge transfer coupling of the surface states at the molecule/ TiO_2 interface have been further investigated by monitoring the density of molecule-perturbed surface states, energy distribution, and the specific Raman vibrational modes.

Niobium doped (0.17%) rutile TiO_2 single crystals (Commercial Crystal Laboratories, Inc.) and Alizarin (Sigma-Aldrich) were used as purchased. For a control experiment, TiO_2 nanoparticles (size, ~ 13 nm) were prepared using titanium isopropoxide as precursor according to a literature protocol.¹⁸ The parabolic-mirror-assisted optical near-field microscope as described in previous publications was used for recording simultaneously correlated topographic and near-field optical images with ultrahigh spatial resolution.^{19,20} Briefly, a high-NA parabolic mirror was used to focus a radially polarized He–Ne laser beam ($\lambda = 632.8$ nm) as the excitation source to a diffraction limited focus on the sample surface. The field distribution in the focal center surrounded by a ring with a fraction of electric field in the sample plane that is radially polarized. The scattered or luminescence light from the illuminated sample region was collected by the same mirror (Figure 1A) and directed onto an avalanche photodiode (APD) operated in the single photon counting mode for confocal imaging or onto the entrance slit of a spectrograph combined with a liquid-nitrogen-cooled CCD camera for spectra recording. For super-resolution imaging, a sharp electrochemically etched Au tip with an apex radius of about 10 nm was brought into

Figure 2. Nanoscale topographic (A) and superimposed near-field optical (red) and topographic (blue) images (B) of the Nb-doped rutile TiO_2 (110) surface. As shown in image (B), strong exciton plasmon–polariton coupling is localized at the spot- or ribbon-like subdomain boundaries, which is evidenced by the anticorrelated topographic (blue) near-field optical (red) line profiles (C).

the focus to within a few nanometers (1–3 nm) to the sample surface (Figure 1A). The Au tip serves as a local probe for recording the sample topography and as an optical antenna for recording correlated near-field optical images of the sample surface. A schematic illustration of a parabolic-mirror-assisted ultramicroscope is shown in Figure 1A together with the diffraction limited luminescence image of a sharp Au nanocone on a silicon surface (Figure 1B, excited by the longitudinal central field component in the focus).

Transparent conducting oxide accessible for both photons and charge carriers has wide applications in photovoltaic, photocatalysis, and molecular electronics. Compared with tin-doped indium oxide (ITO), recently, Nb-doped titanium oxide (NTO) has attracted more attention due to its high transparency in visible light and low cost.^{21–23} Herein, we choose NTO as a model substrate, and the results obtained from this system provide a characteristic identification and analysis of surface states and their involved electronic coupling at a semiconductor surface. The same approaches can be directly applied to other similar systems in research and technology developments.

Panels A and B of Figure 2 show a simultaneously recorded topographic and near-field optical imaging result of a clean Nb-doped rutile TiO_2 (110) single crystal surface. The correlated images show that the surface is rough with a number of spots or ribbon-like nanoscale features. A strong optical enhancement is observed at the nanostructure subdomain boundaries (red spots) (Figure 2B). We suggest that the optical enhancement is originated from the surface-state exciton plasmon–polariton coupling of the semiconductor surface with the Au tip. It has been reported that, besides the band gap transition band at about 3.2 eV, there are additional broad low-energy bands (1.5–2.5 eV) in the absorption spectrum of the Nb-doped TiO_2 . These low-energy bands have been assigned to be the deep trap states within the band gap,^{24,25} and these trap states are most likely the origin of the surface states that we observed. Under 632.8 nm laser excitation in our imaging experiments, the electron transitions from the valence band (nearly oxygen 2p orbital character) of TiO_2 to the energetically accessible deep trap states form the excitons, and the energy-comparable excitons and tip plasmon–polaritons strongly couple at the TiO_2/Au tip nanogap. Considering the doped Nb^{5+} donor locates 0.09 eV below the

Figure 3. Optical response of the abundant surface states of the Nb-doped rutile TiO_2 (110) surface. (A₁) Confocal imaging and (A₂) Raman/luminescence spectra of TiO_2 (110) surface. (B₁) Confocal imaging and (B₂) Raman/luminescence spectra of TiO_2 (110) surface with alizarin (1 μM). All the Raman spectra shown here are typical ones that were collected from single sites. (C₁) Near-field optical imaging and (C₂) a zoom-in line profile of TiO_2 (110) surface covered with alizarin (1 μM).

conduction band of rutile TiO_2 ,²⁴ the physical nature of most trap states inside the band gap may originate from the bridging oxygen vacancies²⁶ or interstitial Ti atoms.²⁷ Strong exciton plasmon–polariton coupling occurring between the tip apex and the sample surface enhances both the population of surface states and the creation and radiative decay of excitons at the subdomain boundaries, which is reasonable because there are more defects or irregular microscopic structures at these sites as compared to the bulk. This phenomenon is also quantitatively evidenced by the anticorrelated line profiles of the topography height and optical intensity as shown in Figure 2C. On the basis of the line profile, a spatial and optical resolution of ~ 22 nm is typically deduced for the imaging of the surface states of TiO_2 , which is far beyond the optical diffraction limit. We suggest that the majority of the imaged surface states are single states, although we cannot rule out the existence of the possible clusters of surfaces states due to our spatial resolution and signal-to-noise ratio in the imaging measurements. Our attribution is primarily based on panels A₁ and B₁ in Figure 3 which show confocal images of the Nb-doped TiO_2 (110) surface under the conditions of without (A) and with alizarin (B), respectively. Most of the hot spots in the confocal image (without the tip) in Figure 3A₁ show as donut-shape features, and only a small number of them show as circular or ellipsoidal-shaped spots. Such different diffraction limited fluorescence excitation patterns can only be observed when single quantum systems are raster scanned through the field distribution of a tightly focused radially polarized laser beam. Since the excitation rate is proportional to the square of the projection of the transition dipole moment onto the electric field as

$$R_{\text{exc}} \propto |\vec{E} \cdot \vec{D}|^2$$

distinct excitation patterns are observed if single quantum systems, such as a single molecules, defects, or surface states, are imaged, revealing their orientation and the dimensionality of

their optical transition. We have calculated the optical patterns of quantum systems with one dipole moment, two perpendicular dipole moments (lying in one plane), or three perpendicular dipole moments excited by radially polarized laser beams (see Supporting Information). Only for quantum systems with a two-dimensional transition dipole moment as recently found for excitons in quantum dots¹⁷ we can observe circular patterns. Here, the ring patterns suggest that the transition dipole moment of the surface states can assume two perpendicular orientations with the same probability and both lying in the surface plane. This is consistent with recent quantum-chemical calculations which suggest that O-vacancy formation in rutile $\text{Ti}(110)$ surface results in two excess electrons occupying 3d orbitals on Ti atoms neighboring the vacancy.²⁸

The observed surface states at the subdomain boundaries are expected to play a crucial role in the charge transport process on the semiconductor surfaces. For a molecule adsorbed on the semiconductor surface, the surface state charge-transfer pathways will be primarily affected by the density and energy distributions of the surface states. To characterize these important parameters, alizarin/ TiO_2 , which is a typical system with strong electronic coupling at the molecule/semiconductor interface,^{29,30} is selected to investigate the density of molecule perturbed surface states, energy landscape, and the interfacial charge transfer coupling. We note that most of the hot spots in the images (Figure 3B₁) are bright coffee-bean-shape spots, and some of them still show as donut-shape features (see Supporting Information, Figure S₂). We suggest that this is due to different electronic coupling strength between alizarin and TiO_2 : Specifically, (i) for the strong coupled alizarin– TiO_2 cases, the surface states are dark and do not show up in the image and hence we observe significantly fewer bright spots; (ii) for the weak coupled alizarin– TiO_2 cases, the emission patterns of the single surface states are likely perturbed by the alizarin molecule and shown as coffee-bean-like shape with only one transition dipole moment;

Figure 4. (A) Schematic illustration of the surface states distribution in Nb-doped TiO₂ and the electronic delocalization at the TiO₂/alizarin interface. (B) Strong electronic coupling and delocalization at the TiO₂/alizarin interface can be proved by the appearance of the 646 cm⁻¹ line in confocal resonance Raman spectrum from the sample surface recorded by 532 nm excitation.

(iii) for the remaining sites without alizarin, the surface states show as donut- or coffee-bean-like patterns depending on the tilt angles of transition dipole moments of the surface states.

Figure 3C₁ shows the near-field optical imaging of TiO₂ with alizarin at a resolution of ~15 nm (Figure 3C₂). Apparently, the density of the surface states has significantly decreased (~60%) with alizarin adsorbed on the TiO₂ surface. We have also measured the spectra of the doped TiO₂ (110) surface under the conditions without (Figure 3A₂) and with alizarin (Figure 3B₂). For both cases, we observed the typical vibrational modes A_{1g} (612 cm⁻¹) and E_g (450 cm⁻¹) of rutile TiO₂ single crystal.³¹ Moreover, we found that the photoluminescence background of the spectra, i.e., emission from the surface states, shows a prominent blue shift from 1.78 to 1.82 eV (Figure 3B₂), after that alizarin was adsorbed on the TiO₂ single crystal surface. Considering there is strong electronic coupling between TiO₂ and alizarin,^{29,30} we suggest that there is an electronic delocalization coupling occurring at the alizarin/TiO₂ interface; i.e., the electron at the highest occupied molecular orbital (HOMO, here it refers to π orbital of alizarin) has significantly delocalized to the energetically accessible deep trap states of TiO₂. The interfacial electronic delocalization results in the blue-shifted surface states emission, which primarily originated from electron trap states with higher energy level. Furthermore, there is an identified charge transfer absorption band that peaked around 500 nm in alizarin/TiO₂ interfacial electron transfer systems reported by our previous work and in the literature.^{27,28} On the other hand, we note that the possibility is negligible for alizarin alone or an alizarin–TiO₂ charge transfer complex to contribute to the

observed emission in Figure 3B₁ because the absorption cross sections of both of them are very low under 632.8 nm laser excitation.^{29,30} This is also consistent with the measured spectrum (Figure 3B₂) in which only the Raman signal from TiO₂ was observed. All of these observations and results provide spectroscopic evidence of the surface states involving exciton plasmon–polariton coupling at the TiO₂/Au tip nanogap.

In addition, the strong electronic coupling and delocalization at the alizarin/TiO₂ interface have been further demonstrated by an experiment using surface-enhanced resonance Raman spectroscopy excited at 532 nm that can effectively excite the alizarin–TiO₂ charge transfer complex. As shown in Figure 4B, we observed direct evidence of the formation of the alizarin–TiO₂ charge transfer complex: besides the normal vibrational modes from alizarin, we also observed a new Raman peak at 646 cm⁻¹, which is a typical Ti–O stretching mode from a bridging Ti–O–C bond.^{29,30} The strong C–O stretching at 1330 cm⁻¹ reveals that the alizarin–TiO₂ charge transfer complex forms primarily through the hydroxyl groups of alizarin and a Ti atom of TiO₂ surface.

In summary, the surface states and the involved charge transfer coupling at the Nb-doped rutile TiO₂ (110) surface have been studied using confocal imaging with radially polarized donut-mode and correlated topographic and spectroscopic ultramicroscopy with a best resolution of ~15 nm. Electron transitions from the valence band to the abundant surface states form excitons and then generate the strong exciton plasmon–polariton coupling at TiO₂/Au tip nanogap. For the alizarin perturbed TiO₂ surface, electronic delocalization may occur at the molecule/TiO₂ interface and can be demonstrated by a blue shift of the luminescence background and the appearance of the additional 646 cm⁻¹ line in the resonance Raman spectrum. The results presented here provide direct evidence of the crucial roles of surface states in solar energy conversion, photocatalysis, molecular electronics, and surface-enhanced Raman scattering spectroscopy enhancement.

■ ASSOCIATED CONTENT

S Supporting Information. A numerical simulation and more confocal images for characterizing single surface states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: H. Peter Lu, hplu@bgsu.edu; Alfred J. Meixner, alfred.meixner@uni-tuebingen.de.

Author Contributions

^SThese authors contributed to the work equally.

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