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Measurement of laser activated electron tunneling from semiconductor zinc oxide to adsorbed organic molecules by a matrix assisted laser desorption ionization mass spectrometer

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ABSTRACT

Measurement of light induced heterogeneous electron transfer is important for understanding of fundamental processes involved in chemistry, physics and biology, which is still challenging by current techniques. Laser activated electron tunneling (LAET) from semiconductor metal oxides was observed and characterized by a MALDI (matrix assisted laser desorption ionization) mass spectrometer in this work. Nanoparticles of ZnO were placed on a MALDI sample plate. Free fatty acids and derivatives were used as models of organic compounds and directly deposited on the surface of ZnO nanoparticles. Irradiation of UV laser ($\lambda = 355$ nm) with energy more than the band gap of ZnO produces ions that can be detected in negative mode. When TiO_2 nanoparticles with similar band gap but much lower electron mobility were used, these ions were not observed unless the voltage on the sample plate was increased. The experimental results indicate that laser induced electron tunneling is dependent on the electron mobility and the strength of the electric field. Capture of low energy electrons by charge-deficient atoms of adsorbed organic molecules causes unpaired electron-directed cleavages of chemical bonds in a non-ergodic pathway. In positive detection mode, electron tunneling cannot be observed due to the reverse moving direction of electrons. It should be able to expect that laser desorption ionization mass spectrometry is a new technique capable of probing the dynamics of electron tunneling. LAET offers advantages as a new ionization dissociation method for mass spectrometry.

1. Introduction

Understanding of the mechanism of photoinduced heterogeneous electron transfer across the semiconductor–molecule interface is not only conceptually important but also practically necessary in the research fields such as the utilization of solar energy [1], design of new generations of photovoltaic devices [2] as well as elucidation of photosynthesis in chemical and biological systems [3]. The irradiation of photons with energy more than the semiconductor band gap usually generates electrons and holes that can quickly undergo annihilation processes before they can be captured [4]. Because these charge carriers can only remain in the time scale of picoseconds, research efforts have been focused on how to precisely probe the dynamics of the ultrafast electron transfer [5–7].

Time-resolved transient spectroscopic techniques have been developed to study the process of ultrafast electron transfer [8,9]. In either case, detailed structural and electronic information is obscured in the ensemble-averaged measurements without spatial resolution. Although scanning tunneling microscope (STM) in combination with the *in situ* irradiation of laser pulses is able to probe the tunneling of photoexcited electrons from a STM tip with spatial resolution even down to the atomic scale [10–12], limited success in this direction has been achieved due to every kind of experimental challenges such as the requirement of sharp tip, very clean surface, precise control of vibration and thermal effects from light illumination [13,14]. In particular, the lack of information on kinetic energies of tunneling electrons and the inability to resolve chemical structure motivate the seeking of other avenues.

Modern mass spectrometry (MS) has emerged as a powerful technique with high sensitivity, high throughput and high mass accuracy for detection of gaseous ions [15]. In a routine UV (ultraviolet)-MALDI (matrix assisted laser desorption ionization) analysis, acidic organic molecules with chromophores that can absorb laser energy *via* electronic excitation such as CHCA (cyano-4-hydroxycinnamic acid) were usually used as matrix materials to form co-crystals with analytes [16,17]. Analytes were rapidly heated, evaporated and protonated with the irradiation of laser beams. Formation of positive and negative ions occurs in gas phase [18,19]. In this work, we are demonstrating that MALDI can be a new approach for studying of the laser activated electron

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tunneling (LAET) from semiconductors to deposited molecules and consequent cleavages of chemical bonds. Herein, ion formation on semiconductors such as ZnO and TiO_2 is a solid-state process. There are several advantages of MALDI-MS based techniques over that of spectroscopic and STM techniques for studies of the dynamics of photoinduced electron transfer. (1) The implemented laser head provides a convenient means for *in site* irradiation of laser pulses on semiconductor nanoparticules deposited on the sample plate. (2) Resultant electrons and holes can be instantly separated and accelerated by the intrinsic electric field present in the ion source chamber of the MALDI mass spectrometer. Therefore, the recombination of electrons and holes confronted by spectroscopic techniques is effectively inhibited. (3) The high vacuum condition in the mass spectrometer simplifies the interpretation of interactions among photons, semiconductor nanoparticules and organic molecules deposited on the surface of semiconductor nanoparticules. Electronic noises resulting from air or other environmental species can be eliminated. (4) Tunneling of electrons from the conduction band of the semiconductor to the organic molecules can be directly monitored by a mass analyzer that is integrated with the ion source chamber. Capture of electrons or holes converts neutral organic molecules to charged ions and then tunneling electrons with energy above bond dissociation cause ion fragmentation. The observed ion intensities are dependent on kinetic energy of thermal electrons (or holes). Dual modes of positive ion detection and negative ion detection make it possible to identify versatile ions resulting from the capture of electrons and subsequent fragmentation. Both spectroscopic and STM techniques can only detect the transfer but not the kinetic properties of tunneling electrons. (5) Thermal fluctuation associated with laser irradiation causes serious instability problems in STM and spectroscopic techniques. By using MALDI-MS, velocity variation in the initial burst of ions and neutrals produced by the laser pulse can be minimized by the well-established time-lag-extraction technique. (6) Adjustable laser beam size of MALDI-MS enables the flexible analysis of selected surfaces. The smaller the beam size, the higher spatial resolution of MALDI-MS analysis can be achieved.

In addition to the mechanistic studies, laser activated electron tunneling (LAET) offers unique features as a new ionization dissociation method for MALDI-MS. In mass spectrometry, desorption/ionization [20–23] and ion activation/dissociation [24–27] are two important features through which samples are transformed into gaseous ions and dissociated into fragment ions for structural information. LAET combines the advantages of conventional electron- and photon-based ionization dissociation approaches. Previously developed low energy electron capture/transfer dissociation (ECD/ETD) is either technically challenging to accommodate a dense population of near thermal electrons in the instruments or complicated by the need of an extra CI (chemical ionization) source and reagent gases. And photon-based approaches require the incorporation of chromophores and wavelength tunable lasers. LAET generates electrons instantly with the *in situ* irradiation of ultraviolet laser on nanoparticles of semiconductions such as zinc oxide that has high UV absorption and electron mobility. It can be envisioned that LAET is not only able to provide insights into the mechanism of interfacial electron transfer but also open a new fascinating avenue in the research area of laser chemistry.

2. Experimental

2.1. Instrumentation

All MALDI experiments were performed on a Synapt G2 HDMS system made by Waters Corp. (Milford, USA) in sensitivity mode. It is equipped with an Nd: YAG high repetition laser head (355 nm). Laser pulse width is 3 ns and pulse energy is 100 μJ@200 Hz. Optimized voltages for routine analysis are 85.6 V and 105.3 V on the sample plate and the aperture, respectively. Changes on voltages can be conveniently carried out from the MS Tune page of the instrumental control software. In negative detection mode, the instrument was calibrated by using sodium formate and free fatty acid C16:0 was used as the lock-mass for additional calibration. In positive detection mode, the instrument was calibrated by using polyethylene glycol and Glu1-fibrinopeptide B was used as the lock-mass for additional calibration. The laser energy was set between 300 and 500 units. All MS and MS/MS experiments were automatically acquired along a spiral route. The acquisition time for the lock mass standard and each sample spot was 10 s and 90 s, respectively. The laser fire rate was set as 200 Hz. All MS spectra and MS/MS spectra were interpreted manually according to the accurate masses and fragment ion patterns.

2.2. Materials and reagents

High speed centrifuge (Anke TGL-16B) was purchased from Anting Scientific (Shanghai, China). High speed refrigerated centrifuge (Neofuge 15R) was purchased from Heal Force (Hongkong, China). MS grade water, acetonitrile and methanol were purchased from Fisher Scientific (Fair Lawn, USA). Nanoparticles of titanium dioxide, isopropanol, cyano-4-hydroxycinnamic acid (CHCA) and NH_4HCO_3 were purchased from Sigma–Aldrich (St. Louis, USA). Acetone, hexane, chloroform and $ZnSO_4{\cdot}7H_2O$ of analytical grade reagents were purchased from Guoyao (Beijing, China). All standard free fatty acids, fatty acid methyl esters and triglycerides were purchased from Nu-Chek Prep, Inc. (Elysian, USA). Cell lysis buffer was purchased from Shenergy Biocolor Bioscience and Biotechnology (Shanghai, China).

2.3. Experimental procedures

2.3.1. Preparation and characterization of nanoparticles of zinc oxide and titanium dioxide

Stock solutions of $ZnSO_4$ (1 mol L^{-1}) and NH_4HCO_3 (1 mol L^{-1}) were prepared in pure water. Add 30 ml of NH_4HCO_3 (1 mol L^{-1}) drop by drop to the solution of 15 ml of $ZnSO_4$ (1 mol L^{-1}) with stirring at 60 °C. Keep stirring at 60 °C for 2 h. Centrifuge at 2000 *g* for 2 min. Wash the precipitates by pure water three times until neutral and then dry at 100 °C for 200 min. The dried particles were calcinated at 500 °C for 2 h. Nanoparticles of zinx oxide were characterized by scan electron microscope (JEOL, Japan), X-ray diffraction and infrared spectroscopy (Bruker, USA). Store the nanoparticles at room temperature for the following experiments. As shown in Supplementary Fig. 1, the resultant nanoparticles are spherical and have uniform size around 20–30 nm, providing the sites with high surface reactivity. The peaks at different crystal planes of synthesized nano zinc oxide match with that of reported values [28]. Broadening and weak intensities of peaks were observed mainly due to nano-size effect [29]. Adsorbed hydroxyl groups on the surface of nano zinc oxide were confirmed by the strong and broad absorption at around 3400 cm^{-1} in the infrared spectrum, which resulting from the stretching vibration of O—H bond. Nanoparticles of anatase titanium dioxide (~25 nm) were purchased from Sigma. Supplementary Fig. 2 shows the characteristics of SEM, XRD and IR spectra of anatase titanium dioxide.

2.3.2. Sample preparation and deposition on the MALDI plate

Nanoparticles of zinc oxide or titanium dioxide were suspended in the solution of isopropanol (10 mg 150 μL^{-1}) and sonicated for 10 min. Pipette 1 μl of the suspension onto the MALDI plate. After nanoparticles were air dried, pipette 1 μl of samples such as standard free fatty acids, fatty acid methyl esters, triglycerides, or plant