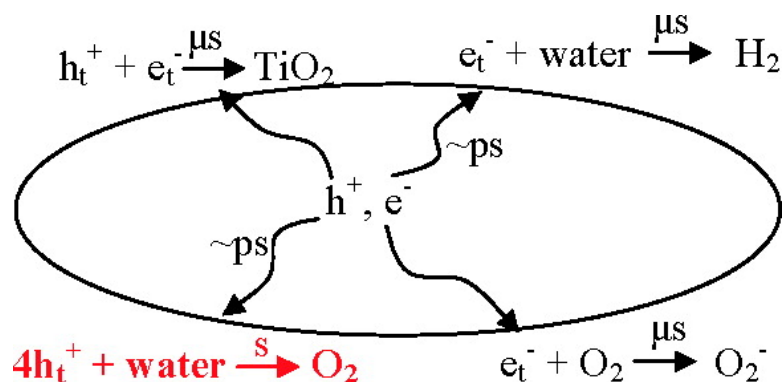


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Mechanism of Photocatalytic Water Splitting in TiO₂. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry

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Abstract: We show for the first time that the photogenerated hole lifetime in TiO₂ is a strong determinant of the ability of TiO₂ to split water. Hole lifetimes were measured using transient absorption spectroscopy over a range of excitation intensities. The lifetimes of the holes were modulated by the use of exogenous scavengers and were also found to vary systematically with the excitation intensity. In all cases the quantum yield of oxygen production is found to be linked to the light intensity used, ranging from below 1 sun equivalent to nearly 1 sun equivalent. We also provide evidence that oxygen production requires four photons for each molecule of oxygen, which is reminiscent of the natural photosynthetic water-splitting mechanism. This in turn suggests a mechanism for oxygen production which requires four-hole chemistry, presumably via three, as yet unidentified intermediates. It is also shown that at excitation densities on the order of 1 sun, nongeminate electron–hole recombination limits the quantum yield significantly.

Introduction

Solar radiation has the potential to be a sustainable energy source which is both environmentally clean and economically viable. It is however a serious challenge to efficiently convert and store solar energy.¹ Photocatalytic H₂ production by water splitting is one potential route,² but only low conversion efficiencies have so far been reported: for example, less than 1% quantum efficiency on In_{0.9}Ni_{0.1}TaO₄³ and about 2.5% on (Ga_{1-x}Zn_x)(N_{1-x}O_x) solid solution^{4,5} at 420 nm. These efficiencies are far from the threshold target of 10% conversion of the overall solar energy.^{6,7}

The efficiency of photocatalytic reactions, including water splitting for H₂ production and the decomposition of contaminants for environmental purification, strongly depends on three factors: efficient optical absorption by the photocatalyst, efficient creation of charge carriers, and efficient use of the charge carriers in the photocatalytic processes. UV light and visible light constitute approximately 47% of solar irradiation,³ which makes the target photocatalytic efficiency of greater than 10%

a challenging one. One extensively cited study⁸ has reported that 90% of photoelectrons and photoholes recombine within 10 ns, and several other studies also show 60–80% of electrons recombine with holes on a nanosecond time scale in TiO₂ colloid.^{9,10} This observation suggests that it would be very difficult to achieve high efficiency for water splitting in TiO₂ as the reactive steps would have to occur on a time scale faster than this. On the other hand, we have previously shown that electron recombination happens on a microsecond time scale when low intensity excitation is used in degassed acetonitrile¹¹ and Tamaki et al. also observed that the geminate recombination of electron and hole did not take place before 1 ns under weak laser intensity in air.¹² Measuring and understanding charge carriers including both electron and hole kinetics in candidate photocatalysts is therefore an important step in evaluating the materials and mechanisms that underlie water splitting by inorganic materials. Given its important role in photocatalysis, surprisingly few such studies exist. Most of the previous work has focused on the reaction pathway of catalysis or on the intermediates, such as studies of water oxidation on TiO₂ single crystal by photoluminescence,¹³ electron dynamics using time-

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resolved laser absorption^{14–17} and ESR spectroscopy,^{18,19} and organic oxidation by FTIR spectroscopy.²⁰ A systematic study of the situation in water splitting was not able to observe the reactive steps between the photogenerated charge carriers and water.¹⁶

It is often assumed that production of one molecule of oxygen from two water molecules requires four holes and therefore four photons. This assumption is based on the four-hole requirement of the water-splitting process in natural photosynthesis. Despite this reasonable assumption, there is no evidence for this basic mechanistic requirement in any of the water-splitting photocatalysts studied to date. In particular, there are many reports of H₂ production without the concurrent production of O₂ from pure water splitting on several semiconductors, such as TiO₂,^{21,22} InMO₄ (M = V, Nb, and Ta),^{23,24} and some W-based oxides.^{25,26} Oxygen production has only been reported with the aid of an electron sacrificial reagent.^{27,28}

There have been no studies, to our knowledge, of the kinetics associated with O₂ production by semiconductor photocatalysts, although it has been suggested in at least one system that H₂ production probably occurs on a hundreds of microsecond time scale.²⁹ Similarly, while there are numerous reports regarding the dynamics of photoelectrons,^{8,10} there are few such studies of photohole dynamics. Bahnemann et al. investigated the photoholes using methyl viologen or Pt as electron scavenger with intense laser (10–34 mJ/pulse) excitation in TiO₂ colloid.¹⁰ In this study the dynamics of charge carriers was found to be dominated by their rapid recombination. Tamaki et al. used a lower laser intensity to observe the nature of the dynamics of photoholes in the absence of electron scavengers^{16,17} and obtained the dynamics of photoholes by subtracting electron absorption from the whole absorption, indirectly monitoring hole absorption spectrum peaks at 500 nm in TiO₂. They also investigated the reactions between alcohol and the photoholes and found that oxidation rates of the absorbed alcohol are consistent with the absorption decay of photoholes.

In this publication, we first confirm the spectral fingerprint of photoholes and photoelectrons in nanocrystalline TiO₂ (nc-TiO₂) films, and then systematically research the observed

dynamics of photoholes under weak laser excitation down to levels below 1 photon/nanoparticle. Further, we compare O₂ evolution using different electron scavengers and investigate the quantum yield (QY) of O₂ production as a function of photon number to determine the number of holes required to produce one molecule of oxygen. In parallel, the kinetics of water oxidation for O₂ production are also studied to explore the time scale of O₂ evolution as a preliminary attempt to elucidate the rate-determining step in water splitting. Finally, we use this new information to suggest some factors that must be addressed to maximize the efficiency of photocatalytic water splitting in both TiO₂ and other materials.

Experimental Section

Nanocrystalline TiO₂ Film Preparation (nc-TiO₂ Film). Nanocrystalline titanium oxide colloid was prepared by aqueous hydrolysis of titanium isopropoxide as described in our previous publications.^{11,30} All reagents were of commercial grade and were used as received from Sigma-Aldrich or their subsidiaries, unless stated otherwise. In a typical procedure, 40 mL of Ti(OⁱPr)₄ (98%) was mixed with 9.1 g of glacial acetic acid under argon and stirred for 10 min. The mixture was then injected into 0.1 M nitric acid and heated at 80 °C for 8 h. After cooling, the solution was diluted to 5 wt % TiO₂ and then autoclaved at 220 °C for 12 h. The prepared mixture was finally concentrated to a colloid comprised of 12.5 wt % TiO₂ particles. The diameter of the TiO₂ particles was determined as ca. 15 nm by scanning electron microscopy. Microscope glass slides, used as the substrate for the nc-TiO₂ film, were cleaned by sonicating in acetone for 30 min and then in deionized water for another 30 min prior to use. Nanocrystalline films were prepared using the doctor-blade technique. Following drying in air for 20 min, films were sintered at 723 K for 30 min. The resulting films were an average 3 μm thick checked by a profilometer (Alpha-Step 200, Tencor Instruments) and consisted of over 90% anatase.³⁰ The surface area was determined by Brunauer–Emmett–Teller (BET) analysis to be about 100 m²/g. The films were cut into 1 × 1.5 cm² pieces and stored in a dry atmosphere for use.

Oxygen Production from Water. Oxygen production was measured with an oxygen membrane polarographic electrode (Rank Brothers Ltd., Cambridge, U.K.) in a closed standard chamber supplied by Rank Brothers Ltd. which transmits ~60% of the laser beam at 355 nm. Films were inserted into the chamber filled with 6.4 mL of an aqueous solution containing different electron scavengers. All experiments were performed at 293 K maintained by a water jacket connected to a thermostatic bath. The oxygen concentration was monitored as a function of illumination time and incident photon flux. For the former measurement, a Xe lamp (UV energy of 1.5 mW/cm²) was focused on the chamber to excite the charge carriers in nc-TiO₂ film. For the latter measurement, the third harmonic of a pulsed and frequency-controlled Nd:YAG laser (Continuum, Surelite I-10) operated at 355 nm was used to provide an accurate photon flux. The photon flux intensity was changed by neutral density filters and measured by a laser energy meter (meter, FieldMaxII-Top; sensor, J25, Coherent Inc.).

The electron scavenger/separator included Ag⁺ ion and platinum (Pt) metallic particle. When Ag⁺ ion was the electron scavenger, O₂ production was performed over nc-TiO₂ film placed in 2 mM AgNO₃ aqueous solution. When Pt particles were used, then O₂ production was performed over nc-TiO₂ film containing Pt particles in deionized water. We used two methods to prepare the nc-TiO₂ film containing Pt particles. One was to coat a paste prepared by mixing homogeneously the above prepared nc-TiO₂ colloid (12.5 wt % TiO₂) and hexachloroplatinic acid in 2-propanol (0.5 wt % Pt) in a volume ratio of 0.6, 1, 2, or 4 onto a glass substrate (named

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Pt–TiO₂; the weight percentage of Pt in Pt–TiO₂ is shown in the Supporting Information), and the other was to coat first the nc-TiO₂ film and then the Pt particles onto the nc-TiO₂ film (named Pt/TiO₂).

Transient Absorption Studies. The transient absorption spectra (TAS) of charge carriers in nc-TiO₂ film were measured by two laser systems corresponding to different time scales. On the microsecond–millisecond (μ s–ms) time scale, a PTI GL-3300 nitrogen laser was used as the excitation source (337 nm, 0.6 mJ/pulse, 0.7 Hz, and 1 ns pulse duration) and a 100 W tungsten lamp provided the probe light. On the nanosecond (ns) time scale, a third harmonic of a Nd:YAG laser (Ultra, Big Sky Laser Tech. Inc.) was employed as the excitation source (355 nm, 0.8 mJ/pulse, 0.7 Hz, and 10 ns pulse duration) and a 75 W Xe lamp provided the probe light. A liquid light guide was utilized to transmit the laser pulse to the sample. For measuring the intensity dependence, optical neutral filters were placed between the light guide and the sample. The wavelength of the probe light was controlled by monochromators before and after the sample. The photocurrent from the detectors was processed by an AC-coupled preamplifier to extract the transient signals, which was magnified by a home-built amplifier–filter system. The signals were recorded with a digital oscilloscope (Tektronix TDS220) and transferred to a computer for analysis. The DC offset of the photocurrent from the detector was subtracted using the preamplifier, and thus small absorbance changes ($<10^{-5}$) could be measured. The film samples were placed in a sealed quartz cuvette for measurements. For the Pt–TiO₂ film, the transient absorption studies were carried out in argon (Ar) atmosphere, and for the nc-TiO₂ film with Ag⁺ ions, the transient absorption studies were carried out in AgNO₃ aqueous solution purged with Ar to remove the dissolved O₂. All TAS were obtained following averaging of 100–300 pulses on each time scale. In this work, Δ OD is the transient absorption change.

Results

Oxygen Production from Water. An efficient electron scavenger is a great benefit when it comes to studying hole dynamics and the reaction between water and photoholes. After testing of the reported electron scavengers including methyl viologen (MV²⁺), tetranitromethane, Ce(SO₄)₂, Pt, and Ag⁺,³¹ Pt and Ag⁺ were selected to function as electron acceptors for this study. Figure 1 shows the kinetics of O₂ evolution.³² Without electron scavengers on naked nc-TiO₂ film, the O₂ reading (trace b) decreases linearly with light illumination, suggesting that O₂ is consumed with zero-order kinetics, consistent with previous publications,^{33,34} and ascribed to O₂ reduction by photoelectrons. With Pt–TiO₂ film, O₂ is consumed even faster, again in agreement with previous findings that no oxygen is detected

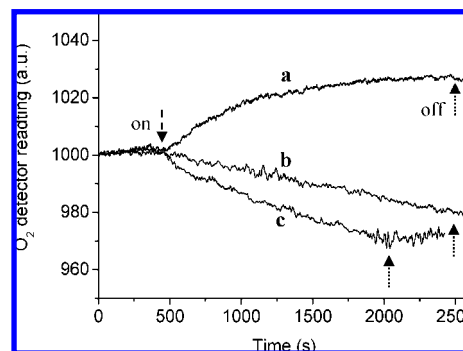


Figure 1. O₂ levels during Xe lamp illumination (UV intensity of 1.5 mW/cm²) in (a) 2 mM AgNO₃ aqueous solution over nc-TiO₂ film, (b) pure water over nc-TiO₂ film, and (c) pure water over Pt–TiO₂ film. On, turn on Xe lamp; off, turn off the lamp. Clearly, O₂ is produced in condition (a) but consumed in (b) and (c).

under similar conditions.^{34–36} However, with Ag⁺ as an electron scavenger a significant amount of O₂ can be produced. All traces in Figure 1 remain more or less flat after turning off the lamp, confirming that the reading change is due to O₂ photoproduction or photoconsumption.

For oxygen production, there is an assumption that one oxygen molecule requires four photons, but there has never been any evidence of such a stoichiometric relationship from any inorganic artificial water-splitting system, although it is of course well-known in natural photosynthetic water splitting.^{37–39} We attempted to find some evidence for the relationship between the number of holes created and the number of oxygen molecules produced. Figure 2 shows the quantum yield (QY) of O₂ production as a function of the photon number⁴⁰ absorbed per nanoparticle using Ag⁺ ions as electron scavengers (how to calculate the photon number per TiO₂ nanoparticle is shown in the Supporting Information). In order to avoid the reaction of holes from multiple laser pulses, the laser repetition rate was adjusted to 0.7 Hz, so that all holes created by a previous pulse are gone before the next one. The results are shown in Figure 2a. The optical absorbance of the 3 μ m nc-TiO₂ film was checked. It shows that 14% of incident light is transmitted through by the film at 355 nm, indicating that the excitation density is approximately homogeneous through the thickness of the film. The maximum quantum yield is nearly 18%, and this maximum occurs at an illumination intensity of 4 photons/particle. This is exactly what would be expected if the holes were not able to migrate between nanoparticles on the time scale of reaction and is the first evidence for four-hole photochemistry in an inorganic solid state photocatalyst. To further clarify the point, we change the laser frequency to 10 Hz, represented in Figure 2b. In this case the maximum quantum yield is now significantly lower at 12% and peaks at 1 photon/nanoparticle. This is because under these conditions holes from multiple laser pulses combine to produce oxygen and the maximum efficiency

- (31) MV²⁺ is only used in alkaline condition to ensure its adsorption on TiO₂ surface.⁴⁸ In addition, the produced MV⁺ has a wide absorption around 600 nm, overlapping with the reported hole absorption around 475 nm. Hereby MV²⁺ is not a suitable electron scavenger in gaseous environment and neutral solution. Tetranitromethane and Ce(SO₄)₂ have low solubility in water and the latter has optical absorption around 450 nm, so they are not very suitable as electron scavengers in aqueous solution yet. Furthermore, MV²⁺ and tetranitromethane are very toxic to the environment. Pt is used to select as a cocatalyst to accelerate H₂ production partially because of its ability of trapping/separating electrons.²¹ Ag⁺ also is a common electron scavenger.
- (32) Before turning on the Xe lamp, the O₂ detector was calibrated with O₂-saturated deionized water and the reading was adjusted to 1000. Following a 500 s baseline, the Xe lamp was turned on and the reading was recorded continuously. After a certain time, the lamp was turned off and the reading was still recorded to avoid a change in reading due to leaking.
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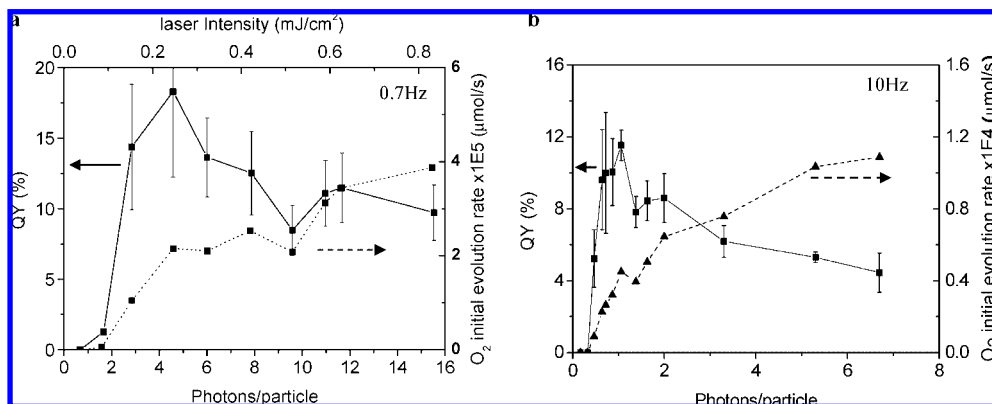


Figure 2. Quantum yield (QY, left axis) and O_2 production rate (right axis) as a function of excitation intensity expressed as photon number absorbed per pulse per TiO_2 particle. In the data Ag^+ is electron scavenger and the experiments are performed at two pulse frequencies: (a) 0.7 and (b) 10 Hz. At 0.7 Hz there are no photoholes left between pulses and all of the oxygen production has to be from holes produced by a single laser pulse. The peak at 4 photons/particle suggests a four-hole mechanism and that the holes do not migrate between particles efficiently. At 10 Hz holes from multiple pulses can combine to produce oxygen and the peak QY at 1 photon/particle suggests that the limiting factor here is electron–hole recombination at higher illumination intensities.

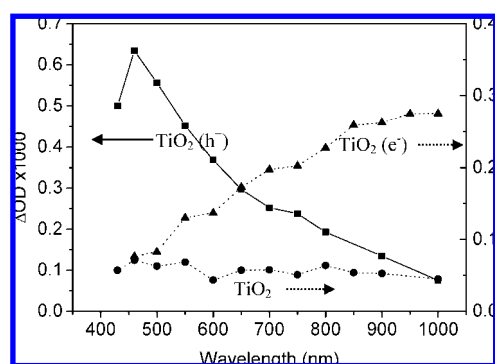


Figure 3. Wavelength dependence of transient absorption of photogenerated charge carriers in nc- TiO_2 film after band-gap excitation with excitation wavelength of 337 nm and intensity of $350 \mu J/cm^2$. Data were collected at a time delay of 20 μs for photogenerated electrons ($TiO_2(e^-)$) with methanol as hole scavenger and holes ($TiO_2(h^+)$) with Pt(1.4 wt %) as electron scavenger in argon. Hole absorption peaks at 460 nm and electron absorption increases with increasing wavelength up to 1000 nm.

therefore occurs when there is a suitable balance between charge carrier production and recombination, occurring at an excitation density of 1 photon/particle. It is worth noting that the QY is $<4\%$ when the photon flux is ~ 1 sun (~ 20 photons/ TiO_2/s with the repetition rate of 10 Hz; see Discussion), indicating that strong recombination of charge carriers is the limiting factor at solar illumination levels in TiO_2 .

Direct Observation of Photogenerated Charge Carriers. In this section, we report the measured dynamics of the charge carriers, in particular holes in nc- TiO_2 film. Figure 3 shows the transient absorption spectra (TAS) of photoelectrons ($TiO_2(e^-)$) and photoholes ($TiO_2(h^+)$) with the relevant scavengers. Two different samples, Pt/ TiO_2 and Pt- TiO_2 , were employed to investigate the TAS of the photoholes, which are found to be essentially identical on the two types of sample. Compared with Pt/ TiO_2 which has commonly been used as an electron trapper,⁴¹ the amount of Pt in Pt- TiO_2 film can be controlled more conveniently and accurately. The optimal Pt loading judged from the maximum signal for photoholes is nearly 1.4 wt % (see Figure S1 in the Supporting Information), in good agreement

with the reported experimental results of photocatalytic H_2 production.^{5,42,43} We therefore used Pt(1.4 wt %)- TiO_2 for all further investigation.

As expected, photohole absorption peaked at 460 nm is directly observed using Pt as an electron scavenger, in agreement with previous indirect observations under weak laser intensity.¹⁶ This suggests that Pt looks like a reasonably effective electron scavenger under these conditions. Photoelectron absorption is also monitored using methanol as a hole scavenger, and the broad spectrum recorded is consistent with our previous research.⁴⁴ It is worth noting that free photoholes and photoelectrons are reportedly trapped in 1–10 ps;^{8,16,45} in this regard we only observed the relaxed charge carriers in the work. Based on their fingerprints, we next selected 460 and 800 nm to investigate the dynamics of relaxed photoholes and photoelectrons, respectively.

Figure 4 shows the dynamics of photoholes and photoelectrons after weak laser excitation ($350 \mu J/cm^2$). As seen in the figure, the photoholes and photoelectrons have the identical dynamics attributed to the natural recombination of photoelectrons and photoholes without any other quenching. The dynamics of charge carriers in 15 nm nc- TiO_2 film are however highly sensitive to laser intensity as one would expect and as shown in Figure 5. Figure 5a is the TAS of photoholes on the nanosecond time scale. The decay shows that 57% of charge carriers recombines within 400 ns when using $530 \mu J/cm^2$, whereas only 29% of charge carriers recombines within 1000 ns after laser excitation of $350 \mu J/cm^2$ and almost no recombination occurs on the nanosecond time scale when the laser excitation density is dropped to $170 \mu J/cm^2$. Therefore, the recombination of charge carriers is strongly dependent on the excitation intensity. Figure 5b shows the hole or electron dynamics on the microsecond time scale. Of particular note is that, with very low excitation density ($60 \mu J/cm^2$), recombination becomes quite slow even on the microsecond time scale. In fact, it can be found that the lifetime of charge carriers in our film is so long that they probably are still present by the time the

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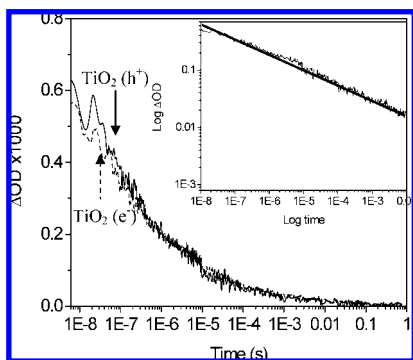


Figure 4. Temporal profile of transient absorption spectra of photoholes ($\text{TiO}_2(\text{h}^+)$) and photoelectrons ($\text{TiO}_2(\text{e}^-)$) in nc- TiO_2 film after band-gap excitation with laser intensity of $350 \mu\text{J}/\text{cm}^2$ in argon atmosphere. The inset is a log–log plot, and the gray line is a fitting to the plot. It is shown that natural recombination predominates in pure TiO_2 , which obeys a power law corresponding to trapping–detrapping effect.

next laser pulse arrives. A repetition rate of 0.7 Hz thus is used to monitor dynamics, avoiding the accumulation of charge carriers produced from different laser pulses.

Figure 6 compares dynamics of the photoelectrons and photoholes with different scavengers at low excitation density. The observed recombination exhibits the short lifetime of charge carriers on a microsecond time scale, in agreement with our previous reports.^{11,46} With methanol as a hole scavenger, the lifetime t_{50} (the time for concentration of charge carriers to decrease by half) of photoelectrons reaches 0.7 s. It is also clear that methanol can trap photoholes very rapidly (<10 ns as shown in the inset). Yamakata et al. reported that photoelectrons react with water on the time scale of hundreds of microseconds.²⁹ It is reasonable therefore that H_2 can be easily evolved with methanol as a hole acceptor. With Pt as an electron acceptor, the lifetime t_{50} of photoholes is ca. $500 \mu\text{s}$ and O_2 evolution cannot be detected, whereas with Ag^+ as electron scavenger oxygen evolution is readily detected. The reasons for these differences will be discussed below.

Kinetics of Reactions between Photoholes and Water. We have observed the dynamics of long-lived photoholes with Pt as electron scavenger, which does indeed show that Pt can act as a scavenger; however, we did not detect O_2 evolution from water in agreement with other publications under similar conditions.³⁶ On the other hand, when Ag^+ is used as an electron scavenger, O_2 is readily produced. In both cases the initial reactions between electrons and Pt or Ag^+ appear to occur within the laser pulse excitation (<10 ns, Figures S2 and S3 in the Supporting Information). The hole dynamics in these two cases is however very different, as shown in Figure 7. The lifetime t_{50} of the holes is 0.27 s with Ag and $500 \mu\text{s}$ with Pt (see Figure 6). This suggests that the free energy associated with electron sequestration by Pt may be much lower than that with Ag^+ , so leading to very different hole lifetimes.

Discussion

Charge Carriers. We have directly observed photoholes and photoelectrons in nc- TiO_2 film with respective scavengers and confirmed that hole absorption peaks at ~ 460 nm. Electron absorption appears to be very sensitive to the experimental

conditions.^{36,47,48} Bahnemann et al. reported that photoelectrons have a maximum absorption at 600 nm in pH 2.3 aqueous solution,¹⁰ and we found that the absorption peak is strongly dependent on pH value in aqueous solution.⁴⁹ In this research the absorption spectrum of the photogenerated electrons increases with increasing the wavelength up to 1000 nm (in inert gas), similar to the findings of Yoshihara et al.¹⁷ obtained in deaerated neutral solution.

A dominant conclusion from our work is that excitation intensity has a strong impact not only on the lifetime of the transient decay of holes but also on the dynamics in nc- TiO_2 film, as represented in Figure 5. The dynamics are found to obey the power law with $\Delta\text{OD} \propto t^{-\alpha}$. As an example, we replot the dynamics of holes from nanoseconds to seconds using log–log (rather than linear–log), shown in the inset of Figure 4, which clearly shows the power law decay. As the laser intensities decrease, the lifetime of holes increases. The rate constant is calculated as $\sim 10^5 \text{ s}^{-1}$ after band-gap excitation of $350 \mu\text{J}/\text{cm}^2$. At very high excitation intensity the hole dynamics were reported to be monoexponential and the lifetime t_{50} remained more or less constant with varying intensity, attributed to the trap-filling model.¹⁷ However, we found that at low excitation intensity the dynamics are well fitted by a power law and the lifetime t_{50} increases with decreasing excitation intensity. This can be explained by the well-established trapping–detrapping model.^{50,51} In short, the basis of this model is that electrons have to be thermally detrapped from the distribution of titania states in order to move from one state to another. The intensity of light used determines the number of electron–hole pairs created and therefore both the number of states that are filled by electrons and the probability of an electron encountering a hole. Excellent agreement has been found between the kinetics of charge recombination in TiO_2 nanocrystalline films and the kinetics calculated from this model.^{50,51}

Bahnemann et al.¹⁰ reported that 80% of charge carriers recombined within 200 ns in 2.4 nm TiO_2 particles after band-gap excitation of 10 mJ/pulse energy (corresponding to photon density of $7.54 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ or $\gg 1$ sun irradiation⁵²), and Serpone et al.⁸ found that 100% recombined within 10 ns in 2.1 nm TiO_2 particles and 90% in 13 nm TiO_2 particles after band-gap excitation of 2.5 mJ/pulse energy (corresponding to photon density of $0.23 \mu\text{mol}\cdot\text{cm}^{-2}$). This previous work was undertaken at a high photon flux, leading to rapid nongeminate recombination of charge carriers.

We have found that recombination of holes and electrons is much more rapid at high excitation intensity, which is consistent with a suppressed quantum yield for oxygen production at these

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(52) Solar irradiance in peak irradiance is $1020 \text{ W}/\text{m}^2$. Average atmospheric conditions (clouds, dust, pollutants) reduce insolation by 20% through reflection and 3% through absorption.⁷ Calculations shows that the average photon density reaching the earth's surface in visible light region such as in Arizona is $4.4 \times 10^{-2} \text{ mol}/\text{cm}^2/\text{s}$ over 13 years (http://ag.arizona.edu/CEAC/research/archive/solar-radiation_kania.pdf). Taking into account 4% UV energy and 43% visible light energy in the solar spectrum and higher energy per photon in the UV light region, it is reasonable to use the photon density of $\sim 4 \times 10^{-2} \text{ mol}/\text{cm}^2/\text{s}$ to represent the total photon flux density of solar irradiation including UV and visible light.

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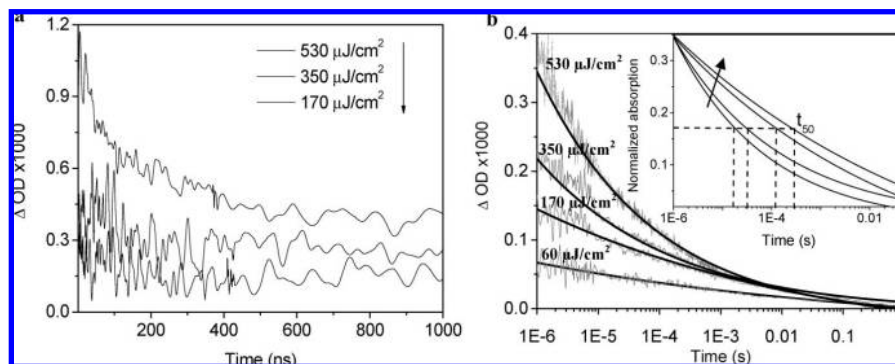


Figure 5. Transient absorption dynamics of $\text{TiO}_2(\text{h}^+)$ after different intensity excitations in nc- TiO_2 film under Ar atmosphere. (a) Excitation at 355 nm on nanosecond time scale and (b) at 337 nm on microsecond time scale and fitted curves, both probes at 460 nm. (Because dynamics of photoholes and photoelectrons are identical (see Figure 4), we show only photohole dynamics here.) The normalized fitted curves as the inset clearly show different lifetimes under different intensity excitations. The data demonstrate the significant increase in hole lifetime that is obtained at low excitation intensities.

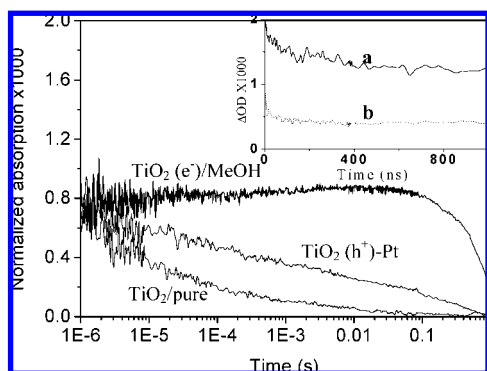


Figure 6. Transient absorption kinetics of $\text{TiO}_2(\text{e}^-)$ with methanol as hole scavenger, $\text{TiO}_2(\text{h}^+)$ with Pt(1.4 wt %) as electron scavenger, and natural recombination in nc- TiO_2 film after band-gap excitation with laser intensity of $350 \mu\text{J}/\text{cm}^2$ in argon atmosphere. The lifetime of charge carriers is prolonged after using relevant scavengers; the half-lifetime of holes is ca. $500 \mu\text{s}$ when Pt is the electron scavenger whereas the half-lifetime of electrons is 0.7 s when methanol is the hole scavenger. The inset is dynamics of hole observed at 460 nm in Pt- TiO_2 film on nanosecond time scale before (a) and after (b) adding methanol, indicating that absorption observed at 460 nm is attributed to holes and that the holes can transfer to the surface of nc- TiO_2 particle and subsequently react with methanol within the time resolution of the experiment (10 ns).

high excitation intensities. We also estimate that that 80–90% of charge carriers will also recombine in our film if the excitation intensity is as high as used in the previous studies, and therefore in agreement with previous publications. On the other hand, when laser intensity is much less, such as 530 or $350 \mu\text{J}/\text{cm}^2$, it is exhibited that nearly half the charge carriers or 70% of the charge carriers survive on the microsecond time scale. Therefore, it is found that the laser intensity (the photon flux) has a strong impact on the lifetime of charge carriers and high QY can be possibly obtained if the photon flux is low.

It has been reported that the trapped holes have a broad absorption extended to 1600 nm, including two peaks at 500 (strong) and 1200 nm (very weak).¹⁶ The former is attributed to deep trapped holes and the latter to shallow trapped holes, with the suggestion that the latter is more active.¹⁰ Our results exhibit that the relaxed holes monitored at 460 nm are very capable of producing oxygen. The wavelength dependence of hole absorption with Pt as electron scavenger (in Figure 3) shows a broad absorption up to 1000 nm, seeming similar to reports for photoholes by Yoshihara et al. However, our transient absorption spectroscopy data observed at 800 nm with Ag^+ as electron scavenger shows that the hole absorption is very weak

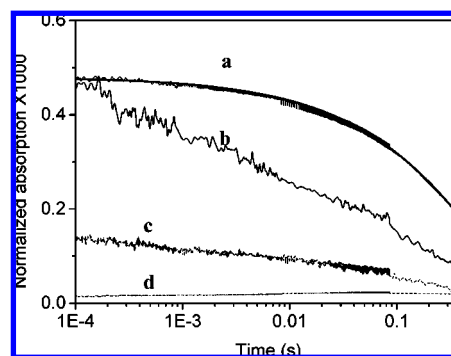


Figure 7. Transient absorption kinetics of $\text{TiO}_2(\text{h}^+)$ (solid line) and $\text{TiO}_2(\text{e}^-)$ (dotted line) with Ag^+ (traces a and d) and Pt (traces b and c) as the electron scavengers after band-gap excitation with laser wavelength of 337 nm and intensity of $350 \mu\text{J}/\text{cm}^2$. The black line (trace a) is the fit to the hole kinetics using Ag ions as electron scavenger. Using Ag^+ as electron scavenger, the transient decay of holes resulting from reaction between holes and water becomes very slow, in which the half-lifetime of holes is 0.27 s , much longer than that for Pt as electron scavenger, suggesting that O_2 production takes place on a time scale of seconds. In addition, spectra monitored at 800 nm ascribed to electron absorption implies less ability of trapping electron by Pt compared with Ag^+ .

at 800 nm (in Figure 7). Absorption above 800 nm is probably due to electron absorption under our experimental conditions.

Reactions Involving O_2 Production from Water. There have been reports that O_2 from water cannot be evolved by TiO_2 due to the photogenerated oxygen either remaining adsorbed on the TiO_2 surface and/or further reacting to form peroxotitanate complexes at the surface of TiO_2 particles⁵³ and H_2O_2 in solution.⁵⁴ It is also possible that the photogenerated holes may cause oxidation of the semiconductor surface, in which case TiO_2 itself acts as an electron donor.³⁶ From our results, it seems clear that O_2 can be consumed by TiO_2 and Pt- TiO_2 , whereby O_2 may be reduced to peroxide in tens of microseconds.^{10,29} If we use a hole scavenger to extend the electron lifetime to the seconds time scale, the reaction can occur on a millisecond time scale.^{11,55}

As the electrons are more or less consumed completely by Ag^+ (see Figure 7), the loss of holes should be due to their reaction with water. This is supported by the observation of O_2 production. The decay of the hole absorption is insignificant on a nanosecond time scale (Figure S3 in the Supporting Information), but rather does so on a much slower time scale. The half-life of the decay is 0.27 s . This leads to the conclusion that O_2 production occurs on the seconds time scale (0.27 s), much slower than H_2 production which happens on the hundreds

of microseconds time scale reported by Yamakata et al.²⁹ This suggests that, at least on TiO₂, the O₂ evolution rate is lower than that of H₂ production, and it is this that limits the overall rate of water splitting in this system under these conditions.

Although Ag⁺ and Pt both can initially trap electrons on a similar time scale (<10 ns), transient absorption spectra decays of holes are quite different, corresponding to different chemical processes. The former is attributed to reaction between water and holes, and the latter is recombination of electrons and holes. Tentatively fitting the dynamics of holes with Ag⁺ as electron scavenger (in Figure 7, trace a) to a stretched exponential decay, $\Delta OD \propto \exp[-(t/\tau)^\alpha]$, where $\alpha = 1$ corresponds to a standard monoexponential decay, gives $\alpha = 0.55$ and $\tau = 1.11$ s. The equivalent rate constant is thus ~ 0.9 s⁻¹, amazingly slow. Apparently the dynamics of holes changes from a power law described above in which recombination of holes and electrons dominates, to a stretched exponential law attributed to interfacial reaction when Ag⁺ is electron scavenger. Previous work has shown that the stretched monoexponential decay, namely pseudo-first-order decay, suggests one species is in excess between the bimolecular (here holes and water) reaction. From the slow water oxidation and the evidence for good mobility of holes demonstrated in the methanol oxidation experiments (inset in Figure 6), we conclude that holes have relatively easy access to the surface and that it is the interfacial reaction between holes and water that controls the water oxidation process.

In addition, the dynamics of holes with Pt as electron scavenger cannot be modeled by a simple exponential law or power law. It is reported that Pt possibly traps both electrons and holes, resulting in their recombination on Pt. On the other hand, we observed that O₂ can be reduced on the film, which takes place within tens of microseconds.²⁹ In addition, reaction between photoholes and surface hydroxide was reported on the nanosecond time scale. Therefore the transient absorption decay on Pt-TiO₂ is attributed to three possible processes: (1) Holes directly recombine with electrons on Pt. (2) Electrons are transferred to other molecules adsorbed on the TiO₂ surface through Pt and then recombine with holes on the surface adsorbed species. The most likely candidate for adsorbed molecules that might promote this mechanism is O₂. (3) Electrons recombine with surface hydroxide which has already trapped a hole.

A comparison of the results of using Pt and Ag⁺ as electron scavengers emphasizes the importance of efficient separation of holes from electrons and/or the effective sequestration of electrons to obtain long-lived holes, and that long-lived holes are a key factor in the efficiency of O₂ production which may be the rate-determining step in water splitting. To date, the most effective photocatalysts for water splitting incorporate cocatalysts including mainly NiO₂, Cr₂O₃, and RuO₂ semiconductors.^{3,5,33,57} Without these it is found that the mother photocatalyst is much less active for H₂ and O₂ production, where the cocatalysts might function to efficiently separate electrons from holes.

Conclusions

We confirm here that hole absorption in TiO₂ peaks at 460 nm and that electron absorption increases with increasing

wavelength up to 1000 nm. Recombination of holes and electrons in the absence of scavengers dominates the transient decay in the film, obeying a power law. Furthermore, the dynamics of charge carriers are strongly dependent on the excitation intensity.

For the first time, our data suggests that O₂ takes ~ 1 s to be produced under the conditions that we use. The effect of pulse repetition rate on the oxygen quantum yield is particularly illuminating. First, it confirms that the oxygen production itself takes ~ 1 s. Second, it shows that the quantum yield peaks at 4 photons/particle. This suggests both that there is very little migration of holes between nanoparticles on the time scale of water splitting and that we are indeed witnessing four-hole chemistry. The situation at a higher pulse repetition rate is dominated by the build-up of holes from successive pulses. In this case the quantum yield peaks at 1 photon/particle as this is the condition which maximizes electron-hole pair production while minimizing recombination, and is consistent with what we know from previous work on recombination dynamics in TiO₂.⁵⁸ If excitation is at the level of 1 sun, then the quantum yield drops by half due to the increased chance of electron-hole recombination in the presence of multiple electrons and multiple holes.

These results also have some implications for the photocatalytic degradation of organic compounds using TiO₂. Comparing methanol oxidation by holes (trace b in the inset of Figure 6) with water oxidation by holes (trace a in Figure 7) makes it clear that methanol oxidation occurs within the laser pulse duration (less than 10 ns) but water oxidation takes nearly 1 s. The former is a one-hole reaction and the latter involves four holes. Of course, it may well be that one hole reacting with surface hydroxide is also a fast process on the nanosecond second scale, which probably is the first step of O₂ production,⁴⁸ but what is seen in our experiment is determined by the, as-yet unidentified, rate-limiting step. It may well be that the limitations on photooxidation using TiO₂ so far are mostly due to the limitations on hole lifetime and that extending the hole lifetime will significantly increase the range of compounds that can be degraded in this way.

Overall, the results underline the importance of efficient electron sequestration by a scavenger or other means to reduce charge recombination, greatly increase hole lifetime, and thereby raise the quantum yield of oxygen production. In addition, it is found that O₂ production is controlled by the interfacial reaction, obeying a stretched exponential law, which may determine the efficiency of water splitting.

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Supporting Information Available: Calculation of photon number per TiO₂ nanoparticle; transient absorption study of photoholes as a function of Pt loading and kinetics of photoholes on the nanosecond time scale with Pt and Ag⁺ ions as electron scavengers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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