The positive effects of increased overpotentials counterparts.' The surface defect density appears to control photoreactivity. The efficiencies are supported by several studies.' The photodegradation of chloroform, pentachlorophenol, and many common organic pollutants in the presence of TiO$_2$ has been found to be less photoactive than their bulk-phase counterparts. However, in other work, size-quantized semiconductors have been made here to provide experimental details of the TiO$_2$ that generally has a higher photoreactivity than other available forms of TiO$_2$.

The variable photoefficiencies of the different forms of TiO$_2$ are related to their fundamental charge-carrier dynamics. In order to verify this relationship, we investigate the charge-carrier dynamics of Q-TiO$_2$ and P25 by TRMC measurements. The quantum efficiencies of Fe$^{3+}$-doped Q-TiO$_2$ and the observed TRMC decays are consistent with a mechanism involving fast trapping of valence-band holes as Fe$^{2+}$ and inhibition of charge-recombination.

The use of size-quantized semiconductors to increase photoefficiencies is supported by several studies. However, in other work, size-quantized semiconductors have been found to be less photoactive than their bulk-phase counterparts. In the latter cases, surface speciation and surface defects due to the necessity for electrode contacts. Efforts have been made here to provide experimental details of the TRMC technique, including the development of a novel sample holder that is usable in conjunction with conventional lasers.

When the crystallite dimension of a semiconductor particle falls below a critical radius of ca. 10 nm, the charge carriers appear to behave quantum-mechanically as a simple particle in a box. As a result of this confinement, the band edge shifts to yield larger redox potentials. The solvent reorganization Gibbs energy for charge transfer to a substrate, however, remains unchanged.

The increased driving force and the unchanged solvent reorganization Gibbs energy for charge transfer to a substrate, however, remains unchanged. The solvent reorganization Gibbs energy is expected to increase the rate constant of charge transfer in the normal Marcus region. Thus, the use of size-quantized semiconductor TiO$_2$ particles may result in increased photoefficiencies for systems in which the rate-limiting step is charge transfer.

One such system is the oxidation of trans-decalin within ns while the measured conductivity signal is due to conduction-band electrons remaining in the semiconductor lattice. The charge-carrier recombination lifetime and the charge-carrier recombination react with sorbed trans-decalin within ns while the measured conductivity signal is due to conduction-band electrons remaining in the semiconductor lattice.

The increased quantum efficiencies of Fe$^{3+}$-doped Q-TiO$_2$ and the observed TRMC decays are consistent with a mechanism involving fast trapping of valence-band holes as Fe$^{2+}$ and inhibition of charge-recombination.

The transparent colloid can be stored for over one year in a dark room (4 °C) without coagulation. To obtain a powdered sample, 150 ml of the colloidal solution was evaporated (35 °C) using a Rotavapor (model R110). The resulting film was dried with an N$_2$ stream to yield a white powder. Fe$^{3+}$-doped Q-TiO$_2$ was prepared by a similar procedure in the presence of Fe(NO$_3$)$_3$ to give an atomic doping level of 1%. Full incorporation of Fe$^{3+}$ into the lattice has been shown by other workers.

The bulk-phase semiconductors used were ZnO (Baker), x-Fe$_2$O$_3$ (hematite, Fisher), CdS (Alfa), and TiO$_2$ (Degussa P25 and Sachtleben Chemie S7, S13, S17, S18, S21 and S24). We used two separate batches of Degussa P25, which were obtained in 1988 (P25-A) and 1993 (P25-B).

**Experimental**

Q-TiO$_2$ was prepared by the controlled hydrolysis of titanium(iv) tetraisopropoxide. 5 ml Ti[OCH(CH$_3$)$_2$]$_4$ (Aldrich, 97%) dissolved in 100 ml isopropyl alcohol was added dropwise (90–120 min) with vigorous stirring to 900 ml doubly distilled water (2 °C) adjusted to pH 1.5 with HNO$_3$. The transparent colloidal solution was evaporated (35 °C) using a Rotavapor (model R110). The resulting film was dried with an N$_2$ stream to yield a white powder. Fe$^{3+}$-doped Q-TiO$_2$ was prepared by a similar procedure in the presence of Fe(NO$_3$)$_3$ to give an atomic doping level of 1%. Full incorporation of Fe$^{3+}$ into the lattice has been shown by other workers.

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Characterization

Particle sizes were determined by a Philips EM 430 transmission electron microscope (TEM) at 300 kV. Samples for TEM were prepared by placing a drop onto a copper mesh substrate covered with a carbon film, followed by removal of the excess liquid with a piece of thin filter paper and drying for 30 s under a tungsten lamp. A representative TEM micrograph is shown in Fig. 1. The sizes of the Q-particles ranged from 2 to 4 nm with a lattice spacing of 3.6 ± 0.1 Å. This spacing was in good agreement with the anatase (101) phase lattice spacing of 3.51 Å. X-Ray diffraction (XRD) analysis was carried out with powdered samples on a Scintag PAD5 model DMC-008 using 35 kV, 20 mA Cu-Kα (1.54 Å) radiation. The diffraction pattern of the Q-sized TiO₂ was also characteristic of anatase. The observed line broadening due to the presence of small crystallites was analysed by the Scherrer equation and showed that the particles were 3-4 nm in diameter.

Degussa P25 has been characterized previously. 30 nm crystallites composed of 80% anatase and 20% rutile aggregate to form particles with an average diameter of 1 μm. For the TRMC experiments, P25 (1.44 g l⁻¹) was suspended in HNO₃ (pH 1.5) and rotary evaporated to a dry powder. The characterization of the TiO₂ samples obtained from Sachtleben Chemie is shown in Table 1.

Irradiation

Steady-state photolyses were carried out in a slurry reactor to determine the initial rate constants for the degradation of chloroform (Baker), dichloroacetic acid (Spectrum Chemical Manufacturing, Inc.), carbon tetrachloride (Baker), pentachlorophenol (Aldrich), and 4-chlorophenol (Aldrich). Irradiations were performed with a 1000 W Xe arc lamp (Spindler and Hoyer). Light intensity was adjusted with neutral density filters. The chemical actinometer Aberchrome 540 was used to determine the incident light intensity, which was found to vary between 100 and 200 pmol 1⁻¹ min⁻¹ with the interference filter in place and to be 1000 pmol 1⁻¹ min⁻¹ with the longpass filter. Aqueous suspensions (35 ml) of the chlorinated compounds and TiO₂ (1.0 g l⁻¹) were prepared and the pH was adjusted by the addition of HNO₃. Initial degradation rates were determined by the total C₁⁻ release after 1 h illumination in the case of HCCI₃ (63 mmol l⁻¹), DCA (4.8 mmol l⁻¹) and CCl₄ (5.1 mmol l⁻¹) and by HPLC (Hewlett Packard Series 11090 Liquid Chromatograph) analysis for PCP (60 pmol 1⁻¹) and 4-CP (100 pmol 1⁻¹). Chloride concentrations were determined with an Orion chloride-selective electrode (model no. 9617B).

TRMC Measurements

A schematic diagram of the microwave conductivity apparatus is shown in Fig. 2. A Gunn diode microwave source (100 mW, 38.3 GHz, MACOM Inc.), a PIN diode microwave detector, a Comlinear model CLC206AI amplifier, a TEK 2440 digitizing oscilloscope, and an HP 432A power meter were coupled into the TRMC unit. The source, detector, and amplifier were enclosed in aluminium Faraday cages. The waveguide system was R-band WR-28 (0.711 cm x 0.356 cm). A Lambda Physik excimer laser (LPX 120) was used for a 308 nm, 50 ns pulse excitation source. Layered metal mesh removed by a 10 cm water filter. Depending upon the experiment, wavelengths were selected with an interference filter (Oriel, λ = 320 ± 5 nm), a longpass filter (Oriel, λ > 320 nm), or a bandpass filter (Corning 7-60-1, 320 < λ < 380 nm). The chemical actinometer Aberchrome 540 was used to determine the incident light intensity, which was found to vary between 100 and 200 pmol 1⁻¹ min⁻¹ with the interference filter in place and to be 1000 pmol 1⁻¹ min⁻¹ with the longpass filter. Aqueous suspensions (35 ml) of the chlorinated compounds and TiO₂ (1.0 g l⁻¹) were prepared and the pH was adjusted by the addition of HNO₃. Initial degradation rates were determined by the total Cl⁻ release after 1 h illumination in the case of HCCI₃ (63 mmol l⁻¹), DCA (4.8 mmol l⁻¹) and CCl₄ (5.1 mmol l⁻¹) and by HPLC (Hewlett Packard Series II 1090 Liquid Chromatograph) analysis for PCP (60 pmol 1⁻¹) and 4-CP (100 pmol 1⁻¹). Chloride concentrations were determined with an Orion chloride-selective electrode (model no. 9617B).

Table 1 TRMC results and photoreactivity data of commercial samples of TiO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m² g⁻¹)</th>
<th>Quantum* efficiency</th>
<th>Charge-carrier concentration constant/min⁻¹</th>
<th>Interfacial electron transfer rate constant/min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7</td>
<td>85</td>
<td>0.25%</td>
<td>0.60</td>
<td>0.12</td>
</tr>
<tr>
<td>S13</td>
<td>90</td>
<td>0.24%</td>
<td>1.28</td>
<td>0.06</td>
</tr>
<tr>
<td>S17</td>
<td>380</td>
<td>0.07%</td>
<td>0.12</td>
<td>n/a</td>
</tr>
<tr>
<td>S18</td>
<td>230</td>
<td>0.26%</td>
<td>0.52</td>
<td>0.16</td>
</tr>
<tr>
<td>S21</td>
<td>280</td>
<td>0.44%</td>
<td>0.52</td>
<td>0.34</td>
</tr>
<tr>
<td>S34</td>
<td>30</td>
<td>0.04%</td>
<td>0.16</td>
<td>n/a</td>
</tr>
<tr>
<td>S11B</td>
<td>50</td>
<td>0.39%</td>
<td>0.92</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* [HCCI₃] = 3.2 mmol 1⁻¹, [TiO₂] = 0.5 g l⁻¹, I = 214 μein 1⁻¹ min⁻¹, λ = 320 ± 5 nm, air equilibrated, pH 4-6.
interposed between the laser and the sample was used to control incident light intensity, which was 4.5 mJ per pulse otherwise stated. In a typical experiment, between 32 and 256 conductivity decays were averaged to improve the signal-to-noise ratio. The digitized data were transferred to a computer for storage and data analysis. The data were collected on four timescales (200 ns div.⁻¹, 2 μs div.⁻¹, 200 μs div.⁻¹ and 10 ms div.⁻¹). The transients were reproducible within 5% error.

The sample holder, which was designed especially for this series of experiments, is shown in Fig. 3. The top plate (i.e. short) has seven slits cut orthogonal to the propagating microwave mode so that the laser light can enter the waveguide while the microwaves are reflected back into the waveguide upon which the holder was pressed. The holder was positioned by the use of an aluminium block inserted from the rear of the waveguide upon which the holder was presssed.

The principles of the TRMC experiment have been discussed previously. Microwaves from the source pass through the sample and impact on the PIN diode detector, which then transforms the incident microwave power into a voltage for input to the oscilloscope. The absorbed microwave power is directly proportional to the conductivity of the sample, and it is determined by calibration. The change in absorbed microwave power, \( \Delta P \), due to a change in conductivity, \( \Delta \sigma \), caused by carrier excitation is given by eqn. (1) where \( P \) is the initial microwave power level.

\[
\frac{\Delta P(t)}{P} = A \Delta \sigma(t) \quad (1)
\]

The microwave power is transformed into a voltage, \( V \), by the PIN diode detector as \( P = V^2 \). For perturbations below 3%, the response is linear, as shown in eqn. (2).

\[
\frac{\Delta P}{P} = n \left( \frac{\Delta V}{V} \right) \quad (2)
\]

The proportionality constant, \( n \), is specific to the geometry of the apparatus and the sample, and it is determined by calibration. The change in absorbed microwave power, \( \Delta P \), due to a change in conductivity, \( \Delta \sigma \), caused by carrier excitation is given by eqn. (1) where \( P \) is the initial microwave power level.

\[
\Delta V(t) = \left( \frac{V A}{n} \right) \Delta \sigma(t) \quad (3)
\]

The temporal behaviour of the voltage observed at the digitizer and the conductivity of the sample are thus proportional.

**Principles of TRMC**

When free charge carriers couple to the electric field of the microwaves, absorption occurs. The strength of the interaction is expressed in terms of mobilities. The mobilities of a free electron in He gas (1 m² V⁻¹ s⁻¹), of free carriers in Si (0.2), of a hopping electron in an organic compound (10⁻³—10⁻⁴), of ions in solution (10⁻¹—10⁻⁶), and of dipole moments (10⁻⁴ to 10⁻¹²) reflect the relative coupling efficiencies at microwave frequencies. The interpretation of TRMC measurements of polar molecules in non-polar solvents and of free carriers in silicon are generally understood however, the interpretation of the conductivity decay of semiconductor particles with low carrier mobilities (<10⁻⁴ m² V⁻¹ s⁻¹) has not been addressed previously.

In high-mobility semiconductors such as GaAs (8900 m² V⁻¹ s⁻¹), Si (1950), ZnO (380) or CdS (400), the microwave absorption can be attributed to free carriers. For perturbations below 3% however, the interpretation of the conductivity decay is attributable entirely to free electrons. For low-mobility semiconductors, such as TiO₂ (10⁻⁶—10⁻⁵ m² V⁻¹ s⁻¹), and \( \alpha \)-Fe₂O₃ (10⁻⁵), the microwave absorbance may not be due exclusively to free carriers. The mobility of a shallow trap may be similar to that of a hopping electron in an organic compound (10⁻²—10⁻³ m² V⁻¹ s⁻¹); therefore, in these cases free and shallowly trapped carriers may simultaneously contribute to the conductivity decay of TiO₂.

**Results**

Initial degradation rates of chloroform as a function of the concentration of chloroform and the type of TiO₂ are illustrated in Fig. 4. At the solubility limit for aqueous chloroform (63 mmol L⁻¹), the quantum yield for chloride release is 0.4% for Q-TiO₂ and 1.6% for P25-A. Doping of the Q-TiO₂ with Fe³⁺ at 1.0 atom% shows an increase in the quantum yield to 2.0%. Initial degradation quantum efficiencies of chloroform, dichloroacetic acid (DCA), carbon tetrachloride, pentachlorophenol (PCP) and 4-chlorophenol (4-CP) are shown in Table 2 for Q-TiO₂ and P25-A. The quantum efficiencies obtained with Q-TiO₂ are less than those obtained with P25-A.

The observed microwave conductivity decays of ZnO, CdS, P25 and \( \alpha \)-Fe₂O₃ are shown in Fig. 5. Since the signal strengths and timescales of decay vary over several orders of magnitude, the signal strengths and timescales of decay vary over several orders of magnitude.
light intensity are shown in Fig. 6. Two linear regions are identified with half-lives of 100 ps and 1.7 ms. Several investigators have reported that the half-lives for conductivity decay in CdS and TiO$_2$ increase as the decay time increases; however, in the case of S17 and S24, the signal-to-noise ratio is too low to facilitate an exponential fit of the data. Discrepancies between similar samples in Tables 1 and 3 are due to differences in the pre-amplifier, the incident pulse energy (2.5 mJ in Table 1), CW illumination intensity, and batches of P25-B.

Table 2 Quantum efficiencies of Q-TiO$_2$ and Degussa P25-A towards photomineralization of chlorinated compounds

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Concentration/mmol l$^{-1}$</th>
<th>Measurement</th>
<th>$\Phi_{Q-TiO_2}$ (%)</th>
<th>$\Phi_{P25-A}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform$^a$</td>
<td>63</td>
<td>[Cl$^{-}$]</td>
<td>0.4</td>
<td>1.6</td>
</tr>
<tr>
<td>dichloroacetic acid$^a$</td>
<td>4.8</td>
<td>[Cl$^{-}$]</td>
<td>1.1</td>
<td>23.9</td>
</tr>
<tr>
<td>carbon tetrachloride$^a$</td>
<td>5.1</td>
<td>[Cl$^{-}$]</td>
<td>0.4</td>
<td>3.1</td>
</tr>
<tr>
<td>pentachlorophenol$^a$</td>
<td>60</td>
<td>[4-CP]</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>4-chlorophenol$^b$</td>
<td>100</td>
<td></td>
<td>0.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>

* 100 pmol l$^{-1}$ min$^{-1}$, 310 < $\lambda$/nm < 330, pH 2.5-3 (HNO$_3$), [TiO$_2$] = 1 g l$^{-1}$. * 0.1 mol l$^{-1}$ MeOH. * 1000 pmol l$^{-1}$ min$^{-1}$, $\lambda$ > 320 nm, pH 3 (HNO$_3$), [TiO$_2$] = 1 g l$^{-1}$.

For ZnO, the first half-life is 6.6 ps, and the second is 164 ps. Several investigators have reported that the half-lives for conductivity decay in CdS and TiO$_2$ increase as the decay time increases; however, in the case of S17 and S24, the signal-to-noise ratio is too low to facilitate an exponential fit of the data. Discrepancies between similar samples in Tables 1 and 3 are due to differences in the pre-amplifier, the incident pulse energy (2.5 mJ in Table 1), CW illumination intensity, and batches of P25-B.

A contour plot of the quantum efficiencies reported in Table 1 as a function of the recombination lifetime and the interfacial electron-transfer rate constant is shown in Fig. 9(a). The arrows on the data points for S17 and S24 indicate that the interfacial electron-transfer rate constant is unknown. The charge-carrier recombination lifetimes (vide infra) are the charge-carrier concentrations (at 100 ns) reported.

Table 3 TRMC results for Q-TiO$_2$, Fe$^{3+}$-doped Q-TiO$_2$, P25-A (NO$_3^-$) and P25-A (NO$_3^-$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative charge-carrier concentration (at 100 ns)/mV</th>
<th>Interfacial electron-transfer rate constant/ms$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q-TiO$_2$</td>
<td>3.1</td>
<td>0.052</td>
</tr>
<tr>
<td>Fe$^{3+}$-doped Q-TiO$_2$</td>
<td>1.0</td>
<td>0.078</td>
</tr>
<tr>
<td>P25-A (NO$_3^-$)</td>
<td>4.0</td>
<td>0.056</td>
</tr>
<tr>
<td>P25-A (NO$_3^-$)</td>
<td>2.9</td>
<td>0.085</td>
</tr>
</tbody>
</table>

The initial degradation rates of chloroform as a function of light intensity are shown in Fig. 6. Two linear regions are observed, and the cross-over occurs at 150 pmol l$^{-1}$ min$^{-1}$. The quantum efficiencies vary from 2.5% for $I = 50$ pmol l$^{-1}$ min$^{-1}$ to 0.3% for $I = 1490$ pmol l$^{-1}$ min$^{-1}$. In Fig. 7, the time-resolved conductivities at 100 ns of P25-A prepared in HNO$_3$ and trans-decalin are plotted as a function of the incident laser pulse energy. Two linear regions are identified with an apparent cross-over at a pulse energy of 6 mJ.

Representative conductivity decays for TRMC measurements of S7, S13, S17, S18, S21, S24 and P25-B are shown in Fig. 8. For most samples, the interfacial electron-transfer rate constants reported in Tables 1 and 3 are calculated by single-exponential fits of the conductivity data. However, in the case of S7 and S24, the signal-to-noise ratio is too low to facilitate an exponential fit of the data.

![Fig. 5](image5.png) Double log plot of time-resolved microwave conductivity decay of several powdered semiconductors supported in trans-decalin. ▲ ZnO; ○, CdS; ■, P25-A; ●, Al$_2$O$_3$.

![Fig. 6](image6.png) Degradation rate of chloroform as a function of light intensity. Conditions: pH 11 (NaOH), [P25-A] = 0.5 g l$^{-1}$, 320 < $\lambda$/nm < 380, air equilibrated.

![Fig. 7](image7.png) Effect of the incident laser pulse energy on the initial (100 ns) conductivity of P25-A prepared in HNO$_3$ and trans-decalin.
Fig. 8 Representative conductivity decays of Sachtleben and Degussa TiO₂ powders. A, (a) S13, (b) P25-B, (c) S18 and (d) S17, 2μs div.-¹. (b) Exponential fit of conductivity decay for P13, \( k = 0.056 \text{ ms}^{-1} \), 10 ms div.-¹.

Fig. 9 (a) Contour plot of quantum efficiency as a function of recombination lifetime (see explanation in main text) and interfacial electron-transfer rate constant. (b) Linear transformation of contour plot.

Fig. 10 Conductivity decays of P25-A (c), •: Q-TiO₂ (b), ▲ and Fe⁵⁺-doped Q-TiO₂ (d). Samples prepared by rotary evaporation from HNO₃ (pH 1.5) and supported in trans-decalin except for P25-A-no NO₃⁻ (a), ●, which was prepared without HNO₃. A, 200 ns div.-¹ timebase. B, 10 ms div.-¹ timebase.

Discussion

In previous papers, we proposed that the larger over-potentials in Q-TiO₂ vs. bulk-phase TiO₂ should lead to higher quantum yields.¹,²,³ However, the data in Fig. 4 clearly show that Q-TiO₂ is less photoreactive than P25-A. In similar experiments carried out with substrates representing a variety of postulated mechanistic pathways, including direct hole attack on HCCl₃ and DCA,²⁴ hydroxyl radical attack of 4-CP and PCP,²⁷⁻³¹,³⁵ and electron transfer to CCl₄,¹⁰,¹¹,⁴²,⁶⁰ the quantum efficiencies (cf. Table 1) ed in Tables 1 and 3. The contours drawn fit the function \( C = xy \). A plot of \( C \) vs. the product of \( x \) and \( y \) results in a straight line, as shown in Fig. 9(b) where \( C \) is the quantum efficiency and \( xy \) is the contour value, i.e. the product of the recombination lifetime and the interfacial electron-transfer rate constant, \( k \). The data points for S17 and S24 are calculated using \( k = 0.15 \text{ ms}^{-1} \) and the extrema of the arrows are calculated for \( k = 0.03 \text{ ms}^{-1} \) and \( k = 0.30 \text{ ms}^{-1} \). Fig. 9(b) demonstrates more clearly than Fig. 9(a) the correlations between photoreactivity and charge-carrier dynamics.

To investigate the effect of HNO₃, P25-A was prepared by rotary evaporation from an acidic slurry (HNO₃, pH 1.5) and was then supported in a trans-decalin paste for the conductivity measurements. In a separate preparation, P25-A was directly prepared as a paste in trans-decalin. The conductivity decays are shown in Fig. 10. It is apparent that the temporal behaviour of the coated and uncoated samples is similar. In addition, the conductivity decays of Q-TiO₂ and Fe⁵⁺-doped Q-TiO₂ are overlaid in Fig. 10. The TRMC measurements for these samples are summarized in Table 3.
obtained for Q-TiO₂ appear to be consistently lower than those obtained for bulk-phase P25. These data suggest several possibilities. On the one hand, the lower photoactivity of Q-TiO₂ may be due to an increased rate of charge-carrier recombination. On the other hand, there may be substantial differences in the interfacial charge-transfer rates between Q-TiO₂ and P25-A.

The differences between Q-TiO₂ and P25-A are at least partially understood by considering the preparation methods. Morphologies techniques at much lower temperatures. Different surface morphologies (e.g. hydroxylation density) may also be expected and the interfacial charge-transfer rates may be controlled by the relative formation of surface complexes on Q-TiO₂ as compared to P25-A.

The relationship between the charge-carrier recombination rate and quantum efficiency can be expressed as follows:

\[
\phi_{\text{transfer}} = \frac{\text{rate}_{\text{transfer}}}{\text{rate}_{\text{transfer}} + \text{rate}_{\text{recombination}}} \tag{4}
\]

If the charge-carrier recombination rate in Q-TiO₂ increases due to defects, then the quantum efficiency of interfacial charge transfer decreases and Q-TiO₂ should be less photoreactive than P25.

The observed conductivity decays in our TRMC experiments should yield the recombination rates of photogenerated free charge carriers. However, the TRMC response is influenced by other deactivation pathways such as interfacial charge transfer to adsorbed species. In these cases, the conductivity decays may be due to both recombination and charge transfer, and the data must be deconvoluted. We believe that the observed conductivity as shown in the absence of recombination or the conductivity localized during the laser pulse, the conductivity should be proportional to the number of free charge carriers:

\[
\Delta \sigma = qN(\mu_{\text{e}} + \mu_{\text{h}}) \tag{5}
\]

where \( N \) is the number of adsorbed photons (if equal reflectivities and short penetration depths are assumed among the samples). The data of Fig. 5 are consistent with the prediction of eqn. (5) that the strength of the conductivity signal increases with the mobility of the charge carriers (\( \sum \mu_{\text{HZO}} = 380 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), \( \sum \mu_{\text{HCA}} = 300 \text{ cm}^2 \text{ s}^{-1} \), and \( \sum \mu_{\text{TiO}_2} = 1.25 \)). From eqn. (3) we see that

\[
\Delta V = (qNV/A)n(\mu_{\text{e}} + \mu_{\text{h}}) \tag{6}
\]

Eqn. (6) predicts a linear correlation between the post-pulse conductivity, \( \Delta V \), and the sum of the mobilities with a corresponding slope of \( (qNV/A)n(\mu_{\text{e}} + \mu_{\text{h}}) \). Using this relationship, our specific apparatus constant, \( A \), can be evaluated. A linear fit applied to the data in Fig. 5 yields a slope of 0.28 mV/(cm² V⁻¹ s⁻¹) and \( A = 1.1 \times 10^3 \text{ S}^{-1} \). Since \( r^2 < 1 \), there is a high probability that localization (i.e. recombination or interfacial charge transfer) has taken place during the laser pulse. Thus, we consider the above \( A \) value to be a lower estimate.

**Photoelectrochemical Mechanisms**

We propose the following four processes for charge-carrier recombination:

\[
\text{TiO}_2 + h\nu \xrightarrow{k_n} e_{\text{cb}}^+ + h_{\text{hb}}^+ \tag{II}
\]

direct and indirect charge-carrier trapping

\[
e_{\text{cb}}^- + T_e^- \xrightarrow{k_m} e_T^- \tag{III}
\]
\[
h_{\text{hb}}^+ + T_h^+ \xrightarrow{k_v} h_T^+ \tag{IV}
\]

carrier recombination

\[
e_{\text{cb}}^- + h_{\text{hb}}^+ \xrightarrow{k_v} \text{TiO}_2 \tag{V}
\]
\[
e_{\text{cb}}^- + h_T^+ \xrightarrow{k_{\text{hv}}} \text{TiO}_2 + T_h^+ \tag{VI}
\]
\[
h_{\text{hb}}^+ + e_T^- \xrightarrow{k_{\text{hv}}} \text{TiO}_2 + T_e^- \tag{VII}
\]

interfacial charge transfer

\[
e_{\text{cb}}^- + O \xrightarrow{k_{\text{hv}}} O^- \tag{VIII}
\]
\[
e_T^- + O \xrightarrow{k_{\text{e}}} O^- + T_e^- \tag{IX}
\]
\[
h_{\text{hb}}^+ + R \xrightarrow{k_u} R^+ \tag{X}
\]
\[
h_T^+ + R \xrightarrow{k_{\text{hv}}} R^+ + T_h^+ \tag{XI}
\]

where \( e_T^- \) is a trapped electron, \( h_T^+ \) is a trapped hole, \( T_e^- \) is an empty electron trap, \( T_h^+ \) is an empty hole trap, \( O \) is an electron acceptor (oxidant) and \( R \) is an electron donor (reductant). At present, we believe that the electron is trapped in a surface Ti site while the hole is trapped in a surface hydroxy group. In a surface hydroxy group, \( e_T^- \) and \( h_T^+ \) have been localized.

Based on this mechanism we can write an equation for the change in microwave conductivity as follows:

\[
\frac{d\sigma}{dr} = \mu_{\text{e}}\frac{d[e^-]}{dr} + \mu_{\text{h}}\frac{d[h^+]}{dr} + \mu_{\text{e}}\frac{d[e_T^-]}{dr} + \mu_{\text{h}}\frac{d[h_T^+]}{dr} \tag{7}
\]

For ZnO, \( \mu_{\text{e}}\frac{d[e^-]}{dr} \) and \( \mu_{\text{h}}\frac{d[h^+]}{dr} \) can be omitted from eqn. (7) owing to the high mobility of the free charge-carriers. However, in the case of TiO₂, these terms must be included since shallowly trapped and free electrons have comparable mobilities. Even though the observed microwave conductivity signal is due to a mixture of species and mobilities, we believe that the observed conductivity as shown in Fig. 8 and 10 can be assigned primarily to electrons.

\[
\left. \begin{array}{l}
\left( \mu_{\text{e}}\frac{d[e^-]}{dr} \right) \text{ and } \mu_{\text{h}}\frac{d[h^+]}{dr} \\
\left( \mu_{\text{e}}\frac{d[e_T^-]}{dr} \right) \text{ and } \mu_{\text{h}}\frac{d[h_T^+]}{dr}
\end{array} \right)
\]

In order to explain the timescales for the microwave conductivity decays shown in Fig. 8 and 10, a mechanism that includes interfacial charge transfer must be invoked because the competition is complete in ca. 100 ns in the absence of interfacial charge transfer. In order for the kinetics of the charge transfer to compete with recombination processes internal to the TiO₂ particle, interfacial charge transfer of at least one carrier should occur within several ns. Therefore, only one charge-carrier type (i.e. holes or electrons) should be present in the particle after 100 ns. Because hole transfer often takes place within ns while electron transfer takes place over the timescale of ns to ms, we conclude that electrons give rise to the measured TRMC conductivity.

The overall quantum efficiency for interfacial charge transfer is determined by two critical processes: the competition between carrier recombination and trapping (ps to ns) followed by the competition between carrier recombination and interfacial charge transfer (µs to ms). The measurement of the
conductivity at 100 ns gives information on fast recombination while the measurement at longer timescales yields information on interfacial charge transfer. The fall-off in the remaining charge carriers at 100 ns with increasing injection level is shown in Fig. 7. The apparent discontinuity at 6 mJ suggests that a higher-order channel is opened with fewer residual charge carriers at 100 ns. These results are consistent with the inverse relationship observed between quantum efficiency for CHCl₃ oxidation and light intensity shown in Fig. 6.18,24 Based on these results, we believe that the recombination lifetime of charge carriers is inversely proportional to the conductivity at 100 ns.

An increase in either the recombination lifetime of charge carriers or the interfacial electron-transfer rate constant is expected to result in higher quantum efficiencies for CW photolysis. The samples S7–P25 are observed to follow this relationship in Fig. 9(a). The linear transformation of the contour plot in Fig. 9(b) makes the correlation more apparent. Fig. 9(a) suggests S21 owes its high photoreactivity to a fast interfacial electron-transfer rate constant whereas P25 has a high photoactivity due to slow recombination. Bickley et al. have suggested that the anatase–rutile structure of P25 promotes charge-pair separation and inhibits recombination.4,5 The different recombination lifetimes and interfacial electron-transfer rate constants may be due to the different methods of preparation of the samples that result in different crystal defect structures and surface morphologies.

A conduction band electron is thermodynamically capable of reducing H⁺, NO₂⁻, O₂ and oxidized trans-decalin radicals (T⁺) while a valence band hole is sufficiently powerful to oxidize trans-decalin. The signal strength observed in Fig. 10(a) for P25-A in the presence of HNO₂ is reduced relative to the uncoated P25-A. This relative change may be due to a similar number of defects are present in each material. In general, the time-dependent changes summarized in Fig. 10 indicate that electrons undergo interfacial charge transfer more slowly for Q-TiO₂ (k = 0.052 ms⁻¹) than for P25-A (k = 0.065 ms⁻¹). This result is consistent with the observed lower steady-state quantum yields (Table 1).

However, the conductivity signal at 100 ns is weaker for the Fe³⁺-doped sample than for the undoped sample. The mobility of the electrons in Fe³⁺-doped Q-TiO₂ may be significantly reduced because Fe³⁺ is present at a concentration of 2.9 × 10⁵ cm² V⁻¹ s⁻¹. For example, the mobility of an electron in silicon drops from 1100 cm² V⁻¹ s⁻¹ to 100 cm² V⁻¹ s⁻¹ in a similar doped lattice.71 The net effect is a lower initial microwave conductivity for Fe³⁺-doped Q-TiO₂.

In summary, we believe the hole, which is trapped at an Fe³⁺ site, is transferred to an adsorbed substrate on a sub-millisecond timescale while the interfacial electron transfer occurs on the ms scale [eqn. (VIII) and (IX)]. As a result, we predict higher steady-state quantum efficiencies for Fe³⁺-doped Q-TiO₂. This prediction is supported by results shown in Fig. 4.

Conclusions

After pulse laser excitation of charge carriers, holes which escape band-gap recombination are transferred to the sorbed electron donor trans-decalin within ns. The TRMC conductivity signals are due to electrons remaining in the semiconductor lattice after hole transfer. The resultant interfacial electron transfer takes place over ms and appears to be faster for P25 than for Q-TiO₂. The slower electron-transfer rates observed for Q-TiO₂ are consistent with the lower steady-state quantum yields. Fe³⁺ doped into the Q-TiO₂ matrix serves to trap holes as Fe⁴⁺ and thus reduces charge-carrier recombination, which in turn results in increased quantum efficiencies. The correlations observed between quantum efficiencies and charge-carrier dynamics emphasize the importance of the interfacial charge-transfer rate constant and the charge-carrier recombination lifetime as contributing factors to TiO₂ photoreactivity.

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