Determination of photonic efficiency and quantum yield of formaldehyde formation in the presence of various TiO$_2$ photocatalysts

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Abstract Illumination of aqueous TiO$_2$ suspensions yields hydroxyl radicals, which can be trapped by methanol producing formaldehyde (HCHO). In this work, the photonic efficiency and quantum yield of HCHO formation in colloidal TiO$_2$ solutions and, P25 and UV 100 suspensions have been determined. Differences in photocatalytic activity of the three photocatalysts have been found and are discussed. The photonic efficiency of HCHO formation in the presence of P25 and UV 100 depends on the concentration of TiO$_2$ and the pH. The critical concentration is 2.5 g/L. Below this, the photonic efficiency with P 25 is higher than with UV 100, and vice versa. Optimum pH values for P25 and UV 100 giving the maximum photonic efficiency are 7.7 and 10.4, respectively. Compared to P25 and UV 100, the true quantum yield of HCHO formation in colloidal TiO$_2$ solution varies a little with pH and virtually does not change with the amount of loading of TiO$_2$. The true quantum yield varies as the inverse square root of light intensity. The quantum yield increases from 0.02 to 0.08 when the absorbed photon flux decreases from $8.1 \times 10^{-7}$ Ein/L s to $4.9 \times 10^{-8}$ Ein/L s. A simple model is presented to explain the experimental observation.

Keywords Concentration and photon flux; effects of pH; formaldehyde; hydroxyl radical; photocatalysis; photonic efficiency; quantum yield; titanium dioxide

Introduction
Photocatalytic detoxification reactions by means of light-absorbing semiconductors have drawn considerable attention in the last 20 years as a possible solution to global environmental problems.1–5 Several oxide and sulfide semiconductors (e.g. Fe$_2$O$_3$, ZnO, TiO$_2$ and CdS) have been employed as photocatalysts, TiO$_2$, however, has proven most suitable for widespread environmental applications because it is highly photoreactive, cheap, non-toxic, chemically and biologically inert, and photostable.3,4

The mechanism of photocatalysis has been an objective of extensive research. Several review articles have been published recently.1–12 Although the detailed mechanism varies for different pollutants, it is commonly agreed that the photodegradation of organics is mainly effected by hydroxyl radicals, which are intermediates produced by the reaction of photogenerated holes with surface adsorbed hydroxide ions or water molecules. Obviously, the production of hydroxyl radicals will directly influence the overall photocatalytic efficiency of catalysts like TiO$_2$. Therefore it is necessary and still meaningful to study the generation of hydroxyl radicals in the system of photocatalyst.

Recently, Sun and Bolton13 proposed a method to determine the quantum yield of hydroxyl radicals in systems containing powdered TiO$_2$ which uses an integrating sphere for measuring the absorbed light intensity. In the present work, our attention is directed to the comparison of different types of TiO$_2$ by determination of the photonic efficiency and quantum yield of formaldehyde generated in photocatalytic oxidation of methanol, which reflects the production of hydroxyl radicals in the reaction systems, and should provide
more insight into the environmental implications and applications of various TiO₂ photocatalysts. The effect of several important factors such as concentration, pH and photon flux on the photocatalytic activity is reported in the present work.

**Experimental section**

Chemicals including TiCl₄ (Merck-Schuchardt), CH₃OH (Merck), HClO₄ (Merck), NaOH (Merck), 2,4-dinitrophenylhydrazine (Aldrich), P25 (Degussa AG), UV 100 (Sachtleben Chemie GmbH) are commercial products which were used without further purification. Water was purified by a Milli-Q/RO system (Millipore). It had a resistivity over 18 MΩ cm.

Colloidal TiO₂ was prepared by controlled hydrolysis of TiCl₄ as reported by Kormann et al. As-prepared TiO₂ comes as a white or slightly yellowish shining, crystal-like powder, which can be resuspended in water, methanol or the mixture of both to obtain transparent colloidal solutions. The particle size was determined to be approximately 2.4 nm by transmission electron microscopy (TEM).

Light was provided by a Xe-lamp, and the wavelength selection was achieved by using band pass filters (Black and WG 320, \( \lambda = 300–400 \) nm). The light intensity could be adjusted through neutral density filters. Photolysis was carried out in 50 mL spherical and 30 mL cylindrical cells with optical grade quartz windows to allow transmission of photons. Determination of incident photon flux by chemical actinometry (Aberchrome 540) was performed in the same cells, thus avoiding the necessity of corrections for any influence of light reflections and reactor geometry. The pH values of the suspensions to be photolyzed were adjusted by HClO₄ or NaOH.

The amount of HCHO formed by photocatalytic oxidation of methanol was determined by HPLC after reaction with 2,4-dinitrophenylhydrazine which absorbs at 360 nm. HPLC employed a Dionex 4500i chromatograph equipped with a reversed phase column Nucleosil-100-10C₁₈, 250 × 4 mm inside diameter (Macherer-Nagel). The eluent for HPLC consisted of CH₃OH, H₂O and CH₃COOH (100:100:1), and the absorbance detector was set at 360 nm. The optical absorption of colloidal TiO₂ solutions and of the band pass filters was measured with an Omega Spectralphotometer (Bruins Instrument). All the experiments were carried out at room temperature unless specified otherwise. The experimental error was found to be within 8% in repeated runs.

**Results**

Illumination of TiO₂ suspensions containing methanol and O₂ leads to the formation of HCHO, which increases with illumination time (Figure 1). From Figure 1 the production rate of HCHO and the photonic efficiency are derived as listed in Table 1. Clearly, the photonic efficiency in case of P25 is much higher than that in cases of UV 100 and colloidal TiO₂. Considering that the photon flux cannot be totally absorbed by TiO₂ at such low concentration, the true quantum yield should be still higher than that listed in Table 1. Unfortunately, it is difficult to determine the light absorption fraction for P25 and UV 100 in our experiment because of the influence of light scattering. So, in cases of P25 and UV 100, only photonic efficiency was determined throughout the work. However, in case of colloidal TiO₂, the light scattering can be neglected because of its extreme small particle size, and the light absorption fraction \((Fₛ)\) can be obtained. The true quantum yield for colloidal TiO₂ can be thereby determined provided that the reaction rate is observed.

Both P25 and UV 100 have been widely used in photocatalysis. They have respective preference in different cases. Figure 1 and Table 1 show that at low concentration (0.1 g/L) P25 appears to be more efficient than UV 100 for the photooxidation of methanol. However, the situation changes with higher loading of TiO₂ (Figure 2).

As shown in Figure 2, the photocatalytic activity of UV 100 is remarkably improved by
increasing the concentration of TiO$_2$, even over that of P25 at a concentration higher than 2.5 g/L. A similar experimental phenomenon has been observed in this laboratory for the photodegradation of dichloroacetic acid (DCA).\textsuperscript{16}

The concentration has a remarkable influence on photocatalytic activity of both P25 and UV 100, particularly for the latter. What is the effect of concentration on colloidal TiO$_2$? As illustrated by Table 2, the concentration of colloidal TiO$_2$ does not change the true quantum yield of HCHO formation. This is in agreement with the finding that reported by Sun and Bolton\textsuperscript{13} who studied powdered TiO$_2$ instead of colloidal TiO$_2$.

In addition, as seen from Table 2, the quantum yield in case of colloidal TiO$_2$ is slightly influenced by the pH. Other than with colloidal TiO$_2$, the effect of pH on the photonic efficiency obtained with P25 and UV 100 appears more pronounced, which is demonstrated in Figure 3. As shown in Table 2 and Figure 3, the extent of the influence of pH on the quantum yield or photonic efficiency is different with types of TiO$_2$. Also, the optimum concentration of TiO$_2$ is 1.0 g/L for P25 and 0.1 g/L for UV 100.

**Table 1** Rate (R) and photonic efficiency (\(\eta\)) of HCHO formation in systems of colloidal TiO$_2$, P25 and UV 100\textsuperscript{*}

<table>
<thead>
<tr>
<th>System</th>
<th>R/10\textsuperscript{-8} M/s</th>
<th>(\eta) Relative to colloidal TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-25</td>
<td>19.1</td>
<td>0.057</td>
</tr>
<tr>
<td>UV 100</td>
<td>2.83</td>
<td>0.008</td>
</tr>
<tr>
<td>Colloidal TiO$_2$</td>
<td>1.62</td>
<td>0.005</td>
</tr>
</tbody>
</table>

\textsuperscript{*} Photonic efficiency is calculated by \(\eta = R/I_0\), where \(I_0\) is the incident photon flux.

Considering that the fraction of light absorbed (Fs) by 0.1 g/L colloidal TiO$_2$ solutions is 0.2376, the true quantum yield (\(\phi\)) of HCHO formation in case of colloidal TiO$_2$ is derived as 0.02 by \(\phi = h/Fs\). Relative values to colloidal TiO$_2$ are calculated by \(\eta/\eta_{\text{colloidal titania}}\) at pH = 3.5.

The concentration is 1.0 g/L for P25 and 0.1 g/L for UV 100. A similar experimental phenomenon has been observed in this laboratory for the photodegradation of dichloroacetic acid (DCA).\textsuperscript{16}

**Table 2** Effect of pH and catalyst concentration on the quantum yield of HCHO formation in the presence of colloidal TiO$_2$, [TiO$_2$] = 100 mg/L, [CH$_3$OH] = 100 mM, O$_2$-saturated, \(V_R = 21\) mL, \(I_0 = 1.425 \times 10^{-6}\) Ein/L s. \(\phi_{\text{HCHO}}\) is calculated by \(R_{\text{HCHO}}/I_0\) and \(I_0 = Fs \times I_0\).

<table>
<thead>
<tr>
<th>pH</th>
<th>0.1 g/L TiO$_2$</th>
<th>1.0 g/L TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fs</td>
<td>(\eta_{\text{HCHO}})</td>
</tr>
<tr>
<td>1</td>
<td>0.3703</td>
<td>0.017</td>
</tr>
<tr>
<td>2</td>
<td>0.5234</td>
<td>0.020</td>
</tr>
<tr>
<td>10</td>
<td>0.4743</td>
<td>0.024</td>
</tr>
</tbody>
</table>
pH values at which the maximal quantum yield is obtained for P25 and UV 100 are different. The optimum pH-values are 7.7 and 10.4, respectively. Such difference can be explained by their different intrinsic properties.

The true quantum yield of HCHO formation in colloidal TiO$_2$ was determined to be around 0.02 as shown in Table 2. By contrast, Sun and Bolton$^{13}$ determined the quantum yield in the presence of powdered anatase TiO$_2$ as 0.04. One might wonder, why the quantum yield is so low in case of colloidal TiO$_2$? On careful comparison of the respective experimental conditions, one concludes that the difference is caused by the different photon flux. This is verified by the results shown in Figure 4.

Obviously, the quantum yield increases (maximum approximately 0.08) with decreasing photon flux. Figure 4 indicates also that the quantum yield is inversely proportional to the square root of the absorbed photon flux, which is consistent not only with the results reported by Sun and Bolton$^{13}$ but also with those reported by Kormann et al.$^{17}$ in a study of the photocatalytic degradation of chloroform in aqueous suspensions of TiO$_2$

### Discussion

#### Primary photocatalytic processes and kinetic analysis

When an UV photon is absorbed by TiO$_2$, an $e^-/h^+$ pair is generated. The $e^-$ and $h^+$ may migrate to the surface and react with the adsorbed reactants in the desired process, or they may undergo undesired recombination. In order to explain our observations, a simple model is presented as follows:

**Charge carrier generation:**

$$\text{TiO}_2 + hv \rightarrow h^+_{vb} + e^-_{cb} \quad (fs^4) \quad I_a$$  \hspace{1cm} (1)

**Charge carrier recombination:**

$$h^+ + e^- \rightarrow \text{TiO}_2 + \text{heat} \quad (\sim ns^4) \quad k_2$$  \hspace{1cm} (2)

**Production of hydroxyl radical:**

$$h^+_{vb} \rightarrow \text{Ti}^{	ext{IV}}\text{OH} \rightarrow [\text{Ti}^{	ext{IV}}\text{OH}^*] + \text{(simplified as $\cdot$OH)} \quad \text{fast} \quad (10 \ ns^4) \quad k_3$$  \hspace{1cm} (3)

**Interfacial charge transfer:**

$$e^-_{cb} (e^-_{tr}) + \text{O}_2 \rightarrow \text{O}_2\cdot \quad (k_4 = 7.6 \times 10^7 \ M^{-1}s^{-1} \text{ for trapped electrons}^{18})$$  \hspace{1cm} (4)
\[
\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O} \quad k_5 = 5 \times 10^8 \text{M}^{-1}\text{s}^{-1}^{19,20}
\]
\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2^* \quad k_6 = 4.5 \times 10^9 \text{M}^{-1}\text{s}^{-1}^{121}
\]
\[
\text{CH}_2\text{OH} + \text{>Ti}^{IV}\text{OH} \rightarrow \text{>Ti}^{III}\text{OH/e}_{\text{tr}}^- + \text{HCHO} + \text{H}^+ \quad k_7
\]

Considering the above processes 1–7, it is assumed that the overall reaction rate is determined by the reduction of \(\text{O}_2\) with surface trapped electrons (Equation 4)\(^{22}\), and the rate of reduction is given by:

\[
d[\text{O}_2^-]/dt = k_4[\text{e}^-][\text{O}_2]
\]

Standard steady-state analysis for \(\text{e}^-\) yields

\[
I_a - k_4[\text{e}^-][\text{O}_2] - k_2[\text{e}^-][\text{h}^+] = 0
\]

Under the assumption that after absorption of a single photon \([\text{e}^-] = [\text{h}^+]\), Equation 9 becomes:

\[
I_a - k_4[\text{e}^-][\text{O}_2] - k_2[\text{e}^-]^2 = 0
\]

Since the quantum yield is very low, most of the photogenerated charge carriers are consumed by recombination. Therefore:

\[
[\text{e}^-] = (I_a/k_2)^{1/2}
\]

Substituting 11 into 8 yields:

\[
d[\text{O}_2^-]/dt = (I_a/k_2)^{1/2}[\text{O}_2]
\]

Putting \(k_{\text{obs}} = [\text{O}_2]/k_2^{1/2}\)

\[
d[\text{O}_2^-]/dt = k_{\text{obs}}I_a^{1/2}
\]

\[
\Phi = d[\text{O}_2^-]/dt/I_a = k_{\text{obs}}I_a^{1/2}
\]

where \(k_{\text{obs}}\) is the observed reaction rate constant. Equation 15 gives the inverse square-root dependence of the quantum yield on light intensity as is experimentally observed (Figure 4). From Figure 4, \(k_{\text{obs}}\) can be derived as shown in the figure.

It should be noted that, the quantum yield of HCHO formation determined in the present work is comparable to that of hydroxyl radical formation reported by Sun and Bolton\(^{13}\) because the main experimental conditions are comparable. Since the photocatalysis process is really complex, it is possible that hydroxyl radicals might take part in other reactions different from Equation 5, or other intermediates react with methanol producing also HCHO. So, throughout the work the quantum yield is reported for HCHO in order to avoid unnecessary controversy.

**Effect of concentration and absorbed photon flux**

As stated above, the quantum yield increases with decreasing absorbed light intensity. The absorbed light intensity can be changed either by changing the incident light intensity or by
changing the concentration of the photocatalyst. The former is consistent with the experimental results (Figure 4), but the latter is controversial. Hoffmann et al. found that the quantum yield of $\text{H}_2\text{O}_2$ formation decreased with increasing the concentration of ZnO. However, our experiments as well as those of Sun and Bolton do not parallel this.

The experimental results shown in Table 2 indicate that in case of colloidal TiO$_2$ the quantum yield is nearly constant, irrespective of concentration in the experimental range. This means that the quantum yield is also controlled by other factors such as surface sites apart from absorbed light intensity in case of changing concentration of TiO$_2$. Different effects of incident photon flux and concentration of photocatalyst on the quantum yield is understandable also from the point of recombination of photogenerated charge carriers. Under the same incident light, there should be no remarkable change in recombination of charge carriers in a single particle although the concentration of particles is changed.

**Effect of pH**

It is known that the conduction band edge, i.e. the redox potential of the conduction-band electron shifts negative by 59 mV per each unit increase in pH. Thus, at high pH, the driving force for oxygen reduction (Equation 4) should increase, hence increase the overall reaction rate, and the quantum yield is expected to be higher.

In addition, pH influences the existing form of surface bounded hydroxyl groups, which react with photogenerated holes producing hydroxyl radicals. There are following acid-base equilibria in aqueous TiO$_2$ suspensions:

$$\text{TiOH}_2^+ \leftrightarrow \text{TiOH} \quad K_{al}$$
$$\text{TiOH} \leftrightarrow \text{TiO}^- + \text{H}^+ \quad K_{a2}$$

The pH of zero point of charge, pH$_{zpc}$, is therefore given as:

$$\text{pH}_{zpc} = 1/2(pK_{a1} + pK_{a2})$$

which can be determined by titration and other experimental techniques. According to the above equilibria, Kormann et al. proposed a detailed model for the existing surface speciation of TiO$_2$ as function of pH in range of 0–14. There is little doubt that the driving force for different hydroxyl groups reacting with photogenerated holes is different. Considering these, the quantum yield or photonic efficiency is expected to increase with increasing pH, but there should be an optimum pH value, as demonstrated in Figure 3.

**Comparison of colloidal TiO$_2$, P 25 and UV 100**

In order to understand the different photocatalytic activity for colloidal TiO$_2$, P25 and UV 100, it is necessary to have a basic knowledge about the three photocatalysts as listed in Table 4. Obviously, most of the properties shown in Table 3 are related to particle size. So, particle size is often considered as an important parameter in the synthesis of materials.

Undoubtedly, the photocatalytic activity of photocatalyst will be influenced by the particle size of the catalyst. As we know, the quantum yield of photocatalysis is limited by the undesired recombination of photogenerated charge carriers, which can be devided into two categories: volume recombination and surface recombination. Such recombination relates directly with the particle size and surface sites. A decrease in particle size leads to the reduction of volume recombination because the time for photogenerated charge carrier migrating to the surface is proportional to the square of particle size. Also, the surface
active sites increases with decreasing particle size, which results in a higher interface charge carrier transfer rate. Based on these, the quantum yield of photocatalysis should increase with decreasing particle size. However, when particle size turns extreme small, surface recombination becomes an important process. Therefore, there should be an optimum size for photocatalyst arriving at maximum photocatalytic efficiency. This has been experimentally demonstrated by Zhang et al. for TiO_2-based photocatalysts.

However, the photocatalytic activity can not be simply determined by the size. It is also influenced by other factors such as microstructure, composition and surface characteristics, etc. High photoreactivity of P25 may arise from small amount of rutile phase or trace impurity of Fe(III), which facilitates the separation of the photogenerated charge carriers. Therefore, the difference in photocatalytic behavior among colloidal TiO_2, P25 and UV 100 as experimentally verified by the determination of the quantum yield of HCHO formation including the influence of conditions like concentration and pH should be understood by their intrinsic properties.

Conclusions
In summary, quantum yields of HCHO formation in systems of colloidal TiO_2, P25 and UV 100 have been determined in this study. Furthermore, effects of several important factors including concentration, pH and photon flux on the quantum yield were thoroughly explored, and the difference in photocatalytic activity for colloidal TiO_2, P25 and UV 100 were compared in detail. Based on this work, following conclusions are derived.

1. When the loading TiO_2 is 0.1 g/L, the values of photonic efficiency in colloidal TiO_2, UV 100 and P25 are 0.005, 0.008 and 0.057, respectively. In this case, P25 appears much more efficient than colloidal TiO_2 and UV 100.
2. Compared to P25, effect of loading TiO_2 on the photonic efficiency is more pronounced with UV 100. When loading TiO_2 is over 2.5 g/L, the photonic efficiency with UV 100 turns higher than with P25. Therefore, it is understandable that high concentrated UV 100 is often used in most organic photodegradation.
3. For P25 and UV 100, the photonic efficiency of HCHO formation varies with pH. pH has different effects on the photoreactivity of P25 and UV 100. Optimum pH values for P25 and UV 100 reaching maximum photonic efficiency are 7.7 and 10.4, respectively.
4. Amount of loading TiO_2 has no, and pH only a little, influence on the true quantum yield of HCHO formation in colloidal TiO_2. Under 1.425 × 10\(^{-6}\) Ein/L s of incident photon flux and loading colloidal TiO_2 in range 0.1–1 g/L, the quantum yield is around 0.02.
5. The quantum yield in case of colloidal TiO_2 is inversely proportional to square root of light intensity. The quantum yield goes up to about 0.08 as the absorbed photon flux decreases to 4.9 × 10\(^{-8}\) Ein/L s.

As observed in the work, the quantum yield of HCHO formation is relative low with pure TiO_2. In order to improve the quantum yield, it is necessary to perform modification with the catalyst. Further work on modification of colloidal TiO_2 and the determination of corresponding quantum yields will be reported elsewhere.

<table>
<thead>
<tr>
<th>Name of TiO_2</th>
<th>Anatase content (%)</th>
<th>Primary particle size (nm)</th>
<th>BET surface area (m²/g)</th>
<th>Secondary particle size (µm)</th>
<th>pH_zpc</th>
<th>Content of OH (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>80</td>
<td>32</td>
<td>49</td>
<td>1.11</td>
<td>6.6/5.9</td>
<td>1.8</td>
</tr>
<tr>
<td>UV 100</td>
<td>100</td>
<td>9</td>
<td>270</td>
<td>0.7</td>
<td>5.7</td>
<td>6.0</td>
</tr>
<tr>
<td>Colloidal</td>
<td>100</td>
<td>2.4</td>
<td>543</td>
<td>0.002</td>
<td>6.4</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Table 3 Properties of the TiO_2 photocatalysts used in the work

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