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Singlet Oxygen Photogeneration at Surface Modified Titanium Dioxide

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Photosensitizers capable of singlet oxygen generation are of significant importance because of the high reactivity of this form of oxygen.[1,2] The role of $^1O_2$ in biology, medicine, and oxidation processes cannot be neglected.[2] Photogeneration of singlet oxygen usually requires a photosensitizer which upon excitation transmits its energy to the O_2 molecule. Most of the known photosensitizers are organic or metalorganic molecules in homogeneous solutions.[2] There are a few reports on $^1O_2$ photogeneration by heterogeneous photosensitizers, that is, semiconductors, like titanium dioxide[3,4] or silicon.[5] In the case of wide-band-gap semiconductors, it may be partially related to difficulties of $^1O_2$ detection in suspensions, but on the other hand the energy transfer from the excited semiconductor to an adsorbed O_2 molecule may be characterized by a low yield owing to competition with other efficient processes including interfacial electron transfer. The singlet oxygen detection problems rise up from low selectivity of indirect methods based on spin trapping[6] or chemical reactivity.[7] Recently Nosaka et al. reported for the first time detection of singlet oxygen photogenerated at TiO_2 surface using the gated photon counting method.[4] This direct method is based on emission properties of singlet oxygen in its $^1\Delta_g$ state.

Although the results of Nosaka prove singlet oxygen generation at TiO_2, it is not clear which conditions favor $^1O_2$ generation at the titanium dioxide surface. In our opinion studies on cyanuric acid (CA) photodegradation may shine some light on this problem. CA is a very stable compound, resistant toward oxidation. It does not undergo degradation either in the presence of neat TiO_2 photocatalyst upon UV-light irradiation or under sonolysis, that is, under conditions where oxygen-centered radicals are formed.[8−10] However, photodegradation of cyanuric acid was observed in the presence of TiO_2 modified with a $[PtCl_6]^{2-}$ complex.[11] There are also reports on photocatalytic degradation of cyanuric acid by fluorinated titanium dioxide ($F-TiO_2$).[12,13] In this photocatalyst, the surface $-OH$ groups were substituted by F^-. The unusual reactivity of $F-TiO_2$ was explained by the generation of “bulk” hydroxyl radicals which are expected to be stronger oxidants than $OH^\bullet$ bound to the surface of unmodified TiO_2.[14,15] Lower efficiencies of interfacial electron-transfer processes—like direct hole oxidation, reduction with electrons from the conduction band, photocurrent generation—were observed for $F-TiO_2$ as compared to neat TiO_2.[13] On the other hand the lifetime of $OH^\bullet$ photogenerated at unmodified TiO_2 is long enough to allow its diffusion to distances of a few micrometers away from the photocatalyst surface.[16] These arguments against the mechanism of CA degradation by “bulk” $OH^\bullet$ led us to check the possibility of singlet oxygen photogeneration in $F-TiO_2$ suspension and to explain its possible role in CA decomposition.

Fluorinated TiO_2, $F-TiO_2$, was prepared by the impregnation method (1 g of Degussa P25 was impregnated in 50 mL of 4% NaF solution for 24 h at room temperature). Highly hydrophobic TiO_2 with $-OH$ surface groups exchanged by silyl groups, $(OR)_3SiO-TiO_2$, is commercially available from Degussa (T805). Suspensions of tested photocatalysts ($0.5\ g\ L^{-1}$) in 2.5×10^{-4} M cyanuric acid solution were irradiated with HBO-500 lamp through the 320 nm cutoff filter. Degradation of cyanuric acid was monitored by determination of formed nitrite/nitrate ions according to Griess’ procedure.[17] Because of the highly hydrophobic surface of $(OR)_3SiO-TiO_2$, it was suspended in aqueous cyanuric acid solution with the addition of 10% ethanol (i.e., ca. 2 M).

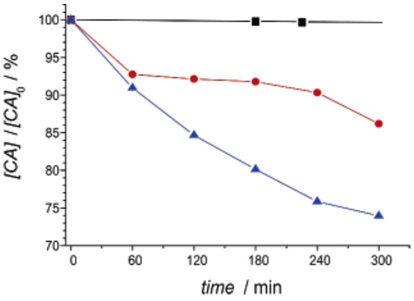

Figure 1. Cyanuric acid degradation (calculated from formed NO_3^- concentration) photocatalyzed by TiO_2 P25 (squares, pH = 6), $F-TiO_2$ (circles, pH = 2), and $(OR)_3SiO-TiO_2$ T805 (triangles, pH = 9).

Photodegradation of CA was not observed in the case of unmodified TiO_2 materials (either Degussa P25 or Kerr-McGee TH0, either in acidic, neutral, or basic medium), which is in agreement with previous reports.[8,9] However, the surface modification with fluoride ions or silyl groups induced UV-light photoactivity of TiO_2 toward CA degradation (Figure 1). Applied pH values were chosen to ensure optimal CA photodegradation rates—the nitrate formation proceeds faster in acidic suspensions of $F-TiO_2$,[13] whereas basic medium is favored in the case of TiO_2 modified with $[PtCl_6]^{2-}$ complex[11] and silyl groups. Photodegradation of CA in deaerated suspensions is suppressed; detailed studies on the influence of oxygen concentration on CA degradation rate are in progress.

To distinguish between the role of hydroxyl radicals and singlet oxygen the photodegradation of CA was followed in the presence of ethanol, the $OH^\bullet$ scavenger. Most of the commonly used $^1O_2$ scavengers (e.g., azide) are also efficient $OH^\bullet$ traps.[1,18] Selection of ethanol as an $OH^\bullet$ trap is justified because rate constants for the hydroxyl radical and the singlet oxygen scavenging by ethanol are significantly different, namely 1.5×10^9 and ca. $10^3\ M^{-1}\ s^{-1}$, respectively.[1,18] For comparison, in the case of sodium azide these numbers are 7.5×10^9 and $5 \times 10^8\ M^{-1}\ s^{-1}$, respectively.[1,18] The CA photodegradation rate in the suspension of $F-TiO_2$ remained practically unchanged when ethanol was added (Figure 2A). Moreover, photocatalytic tests with $(OR)_3SiO-TiO_2$ were done in the presence of 2 M ethanol since this material is very hydrophobic and cannot be suspended in water (Figure 1).

Photodegradation of CA was also achieved in an aqueous solution of rose Bengal. This dye is capable of an efficient singlet oxygen photogeneration (quantum yield 0.75 in water[19] and 0.76−0.79 in methanol[19,20]). However, certain amounts of hydrogen peroxide and

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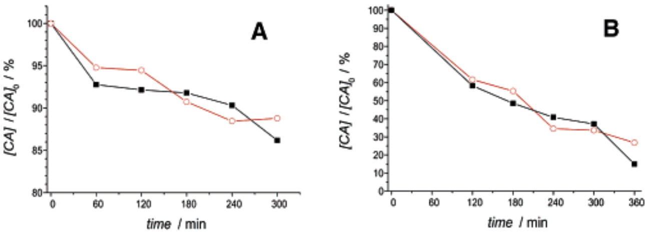
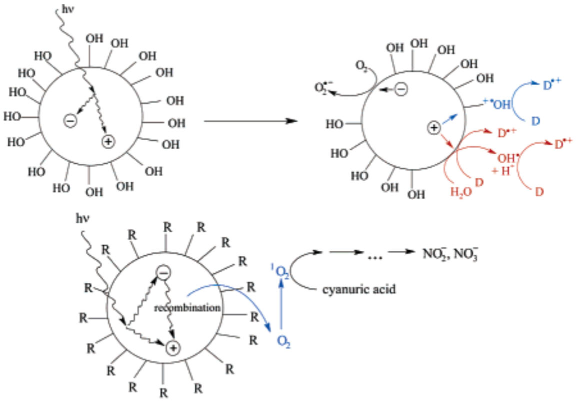


Figure 2. (A) Cyanuric acid degradation (calculated from formed NO_3^- concentration) photocatalyzed by F−TiO_2 in the absence (circles) and presence (squares) of 0.1 M ethanol; (B) cyanuric acid degradation photoinduced by rose Bengal in the absence (circles) and presence (squares) of 0.1 M ethanol.

Scheme 1. Primary Processes at Neat TiO_2 (Upper Scheme) and at TiO_2 with Substituted Surface −OH Groups (Lower Scheme)



$OH^{\bullet}$ can also be formed during the photolysis of rose Bengal solution.[21] Upon prolonged irradiation ($\lambda_{irr} > 455$ nm) the dye decomposes in what results in solution bleaching. The photodecomposition of rose Bengal (containing no nitrogen atoms in its structure) allows application of the Griess' procedure for NO_x^- detection in photolyzed solution. Visible light irradiation of rose Bengal in CA solution induced degradation of cyanuric acid and formation of nitrate ions (Figure 2B). The photodegradation rate was not decreased upon the addition of ethanol.

Photodegradation of CA was also observed in irradiated rutile-TiO_2 (Kerr-McGee Tronox AR) suspension in the presence of ethanol (ca. 15% of degradation after 300 min; data not shown). The rutile structure of TiO_2 is known for its relatively low photocatalytic activity and photocurrent generation as compared to the anatase material.[22] This feature may be related to lower electron mobility and more efficient electron−hole pair recombination.[23,24] In such a situation energy transfer processes rather than the interfacial electron transfer may occur.

Described results do not support the mechanism of CA photodegradation by "bulk" hydroxyl radicals. The hypothesis based on oxidation power of $OH^{\bullet}$ in solution is in contradiction with our results of CA degradation in the presence of the $OH^{\bullet}$ scavenger. In fact, addition of ethanol suppresses the photodegradation of *p*-chlorophenol observed upon UV-light irradiation in the presence of P25 (data not shown), but has nearly no influence on the rate of CA degradation in the presence of tested surface modified titanium dioxide. This observation, together with an efficient CA photodegradation photoinduced by rose Bengal, points at singlet oxygen rather than hydroxyl radicals as an agent responsible for the first steps of CA structure destruction. A kind of endoperoxides may be formed as observed for many other heterocyclic compounds.[1,25]

Considering mechanisms of photocatalytic oxidation at excited TiO_2, two basic processes may be anticipated: the electron transfer and energy transfer (Scheme 1). The first one leads to generation of hydroxyl radical, superoxide radical, and other reactive oxygen species, whereas the second may be responsible for singlet oxygen formation. Modification of the titanium dioxide surface (or its structure) enhances the energy transfer pathway and suppresses the interfacial electron transfer, although a complete inhibition of the latter does not take place. At the surface of unmodified TiO_2, the electron-transfer processes prevail, while singlet oxygen may be formed with lower efficiencies, insufficient for CA degradation. This explains an apparent discrepancy between our results and measurements of Nosaka.[4]

Presented results may shine some light on the mechanism of singlet oxygen generation at the modified surface of titanium dioxide and on cyanuric acid oxidation. On the other hand, cyanuric acid degradation may become a useful, indirect, and selective method of singlet oxygen detection in heterogeneous photocatalytic systems; however, it requires further studies and development.

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