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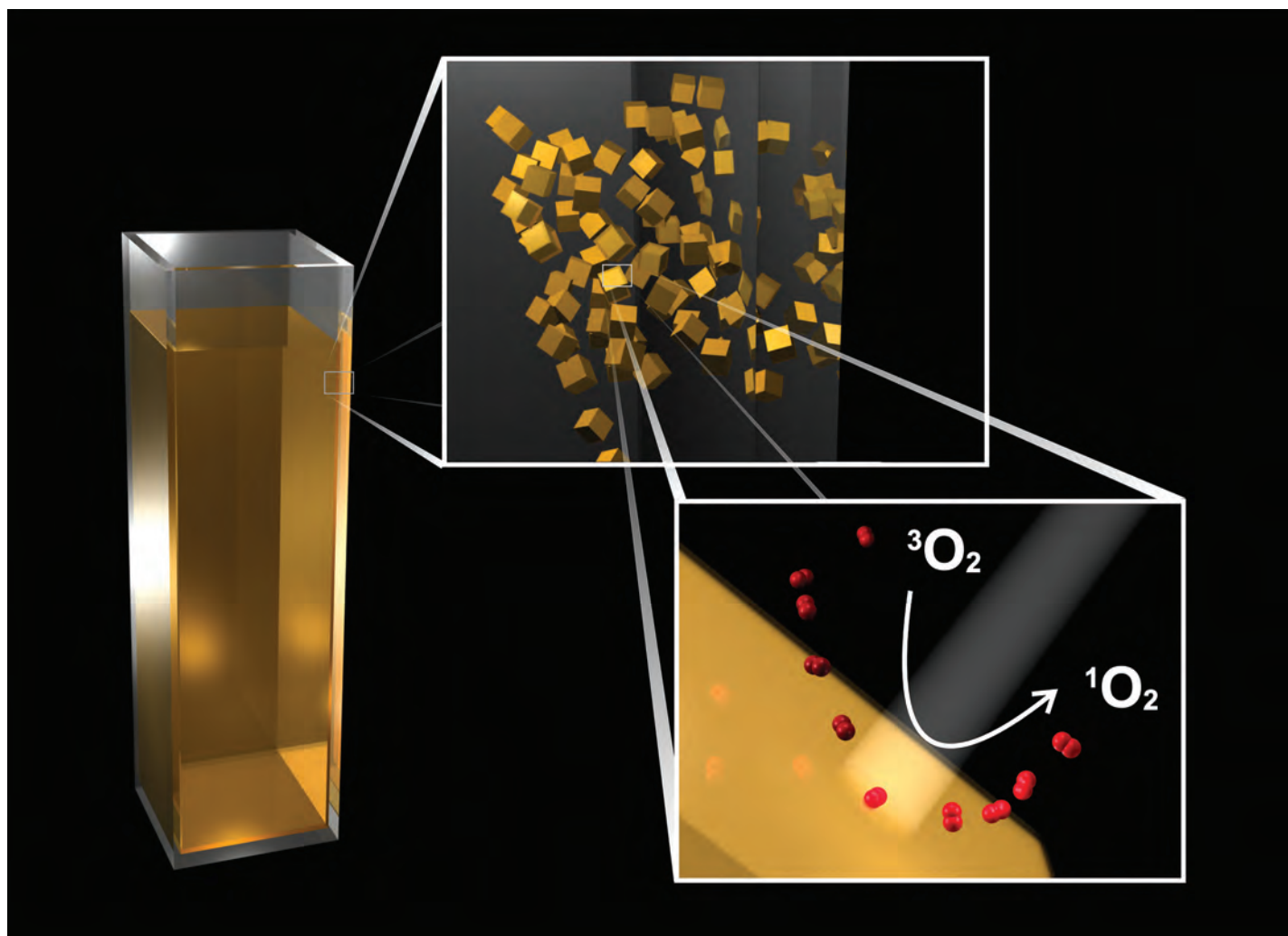


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New insight into singlet oxygen generation at surface modified nanocrystalline TiO_2 – the effect of near-infrared irradiation

Recent studies on singlet oxygen generation in TiO_2 colloids revealed two different mechanisms of this process. In the presence of nanocrystalline TiO_2 photosensitized with titanium(IV) surface complexes $^1\text{O}_2$ results either from superoxide oxidation or energy transfer, involving transient titanium(III) species excited with NIR radiations.

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PAPER

New insight into singlet oxygen generation
at surface modified nanocrystalline TiO₂ – the effect
of near-infrared irradiationCite this: *Dalton Trans.*, 2013, **42**, 9468Marta Buchalska,^a Przemysław Łabuz,^a Łukasz Bujak,^b Grzegorz Szewczyk,^c
Tadeusz Sarna,^c Sebastian Maćkowski^b and Wojciech Macyk^{*a}

The generation of singlet oxygen in aqueous colloids of nanocrystalline TiO₂ (anatase) modified by organic chelating ligands forming surface Ti^{IV} complexes was studied. Detailed studies revealed a plausible and to date unappreciated influence of near-infrared irradiation on singlet oxygen generation at the surface of TiO₂. To detect ¹O₂, direct and indirect methods have been applied: a photon counting technique enabling time-resolved measurements of ¹O₂ phosphorescence, and fluorescence measurements of a product of singlet oxygen interaction with Singlet Oxygen Sensor Green (SOSG). Both methods proved the generation of ¹O₂. Nanocrystalline TiO₂ modified with salicylic acid appeared to be the most efficient photosensitizer among the tested materials. The measured quantum yield reached the value of 0.012 upon irradiation at 355 nm, while unmodified TiO₂ colloids appeared to be substantially less efficient generators of singlet oxygen with the corresponding quantum yield of ca. 0.003. A photocatalytic degradation of 4-chlorophenol, proceeding through oxidation by OH[•], was also monitored. The influence of irradiation conditions (UV, vis, NIR or any combination of these spectral ranges) on the generation of both singlet oxygen and hydroxyl radicals has been tested and discussed. Simultaneous irradiation with visible and NIR light did not accelerate OH[•] formation; however, for TiO₂ modified with catechol it influenced ¹O₂ generation. Singlet oxygen is presumably formed according to Nosaka's mechanism comprising O₂^{•−} oxidation with a strong oxidant (hole, an oxidized ligand); however, the energy transfer from NIR-excited titanium(III) centers (trapped electrons) plays also a plausible role.

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Introduction

The photogeneration of singlet oxygen, mediated by titanium dioxide particles, usually is not considered as a substantial process, compared to the formation of other reactive oxygen species (ROS). This is due to relatively low efficiencies of ¹O₂ photogeneration by these materials. The generation of singlet oxygen in the process of direct energy transfer from photo-excited TiO₂ to oxygen molecule seems to be impossible due to a huge mismatch of the bandgap energy of titanium dioxide and the energy of oxygen excitation. However, some photosensitizers based on TiO₂ appear to be quite efficient generators of singlet oxygen.

Nosaka and co-workers reported singlet oxygen generation in the presence of UV-excited titanium dioxide powders (P25 produced by *Evonik*, composed of ca. 70% of anatase and 30% of rutile).¹ The quantum yield of this process was estimated to be rather high – 0.12–0.38 in water (measured lifetime of 2–2.5 μs¹). The efficiency strongly depends on the particle size² and pH.³ Studies on the mechanism of singlet oxygen generation excluded a possibility of a direct oxygen excitation and suggested alternative pathways of singlet oxygen generation involving superoxide radical oxidation with valence band holes.²

The generation of singlet oxygen in the presence of TiO₂ may proceed *via* two-photon excitation (λ_{exc} = 532 nm).⁴ Li *et al.* concluded that the mechanism of Nosaka operated also in this case. The estimated quantum yields were 0.23 and 0.22 for the same material in chloroform, excited at 532 nm and 355 nm, respectively. Recently, the generation of ¹O₂ at nanocrystalline TiO₂ and other metal oxides was confirmed by Li *et al.*⁵

The efficiency of singlet oxygen generation may be enhanced by a smart TiO₂ surface modification. We have postulated that microcrystalline TiO₂, after exchange of the surface –OH groups with fluoride anions, silyl groups or

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platinum(IV) chloride complexes, may generate singlet oxygen upon UV irradiation ($\lambda > 320$ nm) with a higher efficiency than that observed for neat titanium dioxide.⁶

A surface modification may influence both reaction pathways and spectral properties of TiO_2 . Two main types of photosensitization mechanisms induced by surface modifiers can be distinguished. In the first type, excitation of the surface-bound photosensitizer is followed by an interfacial electron transfer from the excited state to the conduction band. This type of photosensitization is described by the Sakata–Hashimoto–Hiramoto mechanism and is based on a photoinduced electron transfer (PET).⁷ It takes place in the case of TiO_2 with adsorbed metal complexes, e.g. $[\text{PtCl}_6]^{2-}$,⁸ ruthenium dyes.⁹ The second mechanism involves excitation of the surface $[\text{Ti}^{\text{IV}}\text{L}]$ complex. Irradiation within its LMCT band results in the electron transfer directly from the surface modifier (ligand) to the conduction band of titanium dioxide. The ligand should be a good electron donor, which is the case for e.g. catechol derivatives or cyanoferrates.¹⁰ This mechanism, also called the Creutz–Brunschwig–Sutin mechanism,¹¹ involves the optical electron transfer (OET).

The surface modification of titanium dioxide can be described as Lewis and/or Brønsted acid–base reaction. Surface Ti^{IV} sites show a Lewis acid character; therefore O-, N-, S-ligands can efficiently bind to TiO_2 surface.¹⁰ Catechol, salicylic acid, phthalic acid and their derivatives with carboxyl groups belong to this class of ligands. Formed surface charge transfer complexes sensitize TiO_2 through the OET mechanism. The absorption edge of surface Ti^{IV} complexes depends on the ligand structure.^{10,12} Surface modified materials show different spectroscopic and electrochemical properties when compared to neat TiO_2 . Formation of a ligand– TiO_2 complex is associated with a charge transfer absorption band, easily observed for small molecules that absorb only UV light (e.g. alizarin¹³ or caffeic acid¹⁴), since the new band often extends to above 400 nm. The OET mechanism can be achieved also for bigger molecules used as surface modifiers of TiO_2 , e.g. porphyrins,¹⁵ carotenoid dyes,¹⁶ thiophene dyes,¹⁷ ruthenium complexes with the catecholate anchoring group,¹⁸ etc.

The use of organic ligands strongly bound to titanium dioxide should influence not only optical properties of the material, but also electron and energy transfer processes occurring at the surface. In this study we focus on the generation of singlet oxygen and hydroxyl radicals upon irradiation of nanocrystalline TiO_2 colloids (anatase), modified with Ti^{IV} surface complexes. We discuss the influence of irradiation conditions (UV, vis, NIR or any combination of these spectral ranges) on the generation of both singlet oxygen and hydroxyl radicals and use the results to discuss the mechanisms of $^1\text{O}_2$ generation.

Experimental section

Materials and characterization

Photocatalysts were prepared by a modification of nanocrystalline TiO_2 (aqueous anatase colloid from *Nanostructured and*

Amorphous Materials, TiO_2 concentration of 15%, average particle size of 15 nm) with the following compounds: catechol (cat), salicylic acid (sal), *ortho*-phthalic acid (pht), 2,3-naphthalenediol (nd) and 3-hydroxy-2-naphthonic acid (hn). The colloidal solution of nanocrystalline anatase was first diluted with water to a concentration of 0.75% and mixed with the methanolic solution of a modifier (0.1 mol dm^{-3}) in the ratio of 9 : 1 (v/v). In this way yellow and orange colloids of surface modified nanocrystalline TiO_2 were obtained. Within this paper the abbreviations cat@ TiO_2 , sal@ TiO_2 , pht@ TiO_2 , nd@ TiO_2 and hn@ TiO_2 have been assigned to modified colloids.

Zeta potential and hydrodynamic diameter measurements were done with a Zetasizer Nano ZS (*Malvern Instruments*). UV-vis absorption spectra were recorded with the UV/Vis/NIR Lambda 950 (Perkin Elmer) spectrophotometer in a 1 cm quartz cuvette.

4-CP photodegradation tests

The photocatalytic activity of materials was tested in the process of 4-chlorophenol (4-CP) photodegradation ($0.25 \text{ mmol dm}^{-3}$). Samples were irradiated with an XBO-150 xenon lamp. A quartz filter filled with CuSO_4 solution was used as a bandpass filter ($275 \text{ nm} < \lambda < 700 \text{ nm}$). Other *Schott* filters were used for the selection of specific spectral windows: UG2 (a bandpass filter 300–400 nm, denoted here as UV), cut-off 400 nm (vis), cut-off 320 nm (UV-vis) and cut-off 695 nm (NIR).

Tests of photocatalytic activity were done in a cylindrical quartz cuvette, characterized by the diameter of 47 mm and the optical path of 10 mm. 2 ml of TiO_2 or mod@ TiO_2 colloids (mod – a modifier) and 18 ml of a 4-CP solution were placed in the cuvette. The solution was purged with a stream of air during irradiation. Samples (ca. 2 ml) were collected every 5 min. A precipitation of the photocatalyst was achieved by adding 200 μl of a saturated NaOH solution to colloidal samples. After 24 hours sedimentation was finished and UV-Vis spectra of supernatants were recorded with the UV/Vis/NIR Lambda 950 (Perkin Elmer) spectrophotometer in a 1 cm quartz cuvette. In strongly alkaline solutions the 4-CP spectrum is red-shifted by ca. 20 nm, compared to neutral pH. The concentration of 4-CP was calculated taking into account the absorbance at $\lambda = 300 \text{ nm}$.

Tests with SOSG

The efficiency of singlet oxygen generation was monitored using Singlet Oxygen Sensor Green (SOSG) (a solution of 0.5 g dm^{-3} in methanol). All colloids were diluted in methanol to a concentration of $2 \times 10^{-4} \text{ mol dm}^{-3}$. Prior to the measurements equal volumes of SOSG and a colloid were mixed and placed in 3 mm quartz cuvettes (*Hellma*). The first type of measurements involved a single-wavelength excitation provided either by a laser 405 nm, 20 mW (*Crystal Laser*) or by a laser 355 nm, 20 mW (*CryLas*). The generation of singlet oxygen as a result of SOSG excitation is negligible due to low powers of applied lasers. The second mode of experiments involved two lasers exciting the sample simultaneously: at

405 nm, 20 mW together with either 355 nm, 20 mW or 785 nm, 400 mW (*Spectra Laser*). Both laser beams used in the experiment were focused at the same point of the sample using lenses with the focal length of 50 mm.

Emission spectra of samples, recorded in the direction perpendicular to the excitation beams, were collected with a fiber optics CCD spectrometer (*Spectra Laser*) based on a Czerny-Turner monochromator and a CCD line detector (2048 pixels, SONY). The spectrometer enabled measurements within the spectral range of 500–1100 nm with a resolution of 2.5 nm. In order to eliminate the excitation light a bandpass filter centered at 550 nm (20 nm half width, *Chroma*) was used. The samples (modified TiO₂, unmodified TiO₂ and modifiers) were irradiated for 10 min. Within this time the emission spectra were collected every 30 s.

Phosphorescence of ¹O₂

Photocatalysts (a 2×10^{-4} mol dm⁻³ solution in methanol) were excited using 355 nm μ J pulses generated by a microchip Nd:YAG laser (Pulselas-P-1064-300-FC, *Alphas*) operating at 5 kHz. To filter out the first and second harmonics of the laser radiation, a 50 cm water filter and dichroic mirrors (BK7 series, *EksmaOptics*) were used. A luminescence at 1270 nm was measured perpendicularly to the excitation beam in a photon counting mode¹⁹ using a thermoelectric cooled NIR PMT module (model H10330-45, *Hamamatsu*) equipped with a 1100 nm cut-off filter and additional selected narrow-band filters (NB series, *NDC Infrared Engineering*). Data were collected using a computer-mounted PCI-board multichannel scaler (NanoHarp 250, *PicoQuant*). The data collection was synchronized with laser pulses using an ultrafast photodiode (UGP-300-SP, *Alphas*) as a trigger. The data analysis, including the first order luminescence decay fitting by the Levenberg-Marquardt algorithm, was done by custom-written software. Phosphorescence measurements have been done for the solutions of modifiers.

Results and discussion

Materials

Mixing of TiO₂ colloid with ligand solutions resulted in yellow and orange colloids. Only the use of pht did not change the color of the colorless TiO₂ solution. The color of the obtained material depends on the ligand structure. The formation of surface charge-transfer complexes of Ti^{IV} was confirmed by broad bands in absorption spectra, extending to 500–600 nm (Fig. 1). None of the applied modifiers in a methanolic solution absorbs visible light.

Zeta potential values of the synthesized materials at pH \approx 3 were 50 mV for unmodified anatase and *ca.* 45 mV for the surface modified materials. The differences in zeta potential values between modified materials were irrelevant. The adsorption of these organic molecules does not affect significantly the surface charge or stability of synthesized materials.

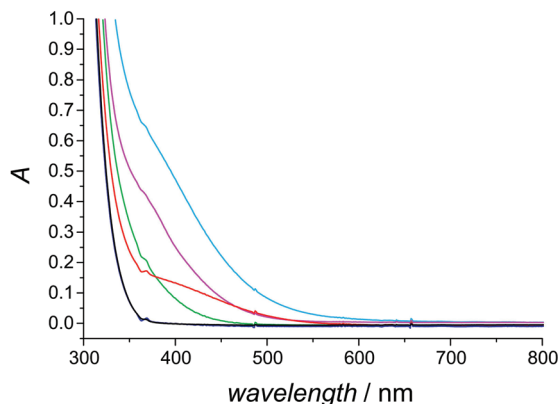


Fig. 1 Absorption spectra of colloidal solutions of the studied materials: TiO₂ (black), cat@TiO₂ (red), sal@TiO₂ (green), pht@TiO₂ (blue), nd@TiO₂ (cyan), hn@TiO₂ (magenta).

All colloidal solutions were stable for several weeks, if kept in the dark at pH \approx 3–4.

A mean hydrodynamic diameter of unmodified anatase was *ca.* 42 nm. No significant differences were noticed after surface modification with sal, pht or nd. The modification of TiO₂ surface with hn and cat caused an increase of the diameter up to 50 and 70 nm, respectively.

4-CP photodegradation

A typical degradation process photocatalyzed by TiO₂ involves the reduction of molecular oxygen to superoxide radical by electrons from the conduction band. Further reduction steps lead to hydrogen peroxide, hydroxyl radicals and water. Hydroxyl radicals can also be generated in a one-step water oxidation with valence band holes.^{20,21} The 4-chlorophenol (4-CP) degradation may give information on hydroxyl radicals generation, since the first steps of this process involve the chlorine or hydrogen substitution by a hydroxyl radical.^{22,23} Chlorophenols can also react with singlet oxygen; however, this process is very inefficient. In the group of monochlorophenols, 4-CP is most inert regarding its reactivity with ¹O₂.²⁴ The efficiency of this process is particularly low in acidic solutions.²⁵ Our recent studies demonstrated negligible rates of 4-CP oxidation in aqueous solutions in the presence of phenalenone (an efficient singlet oxygen photosensitizer).²⁶ Therefore the photocatalytic oxidation of 4-CP can be used to gather information on the OH[•] generation.

The degradation of 4-CP was monitored upon various irradiation conditions. Photodegradation curves for unmodified anatase-TiO₂ and TiO₂ modified with salicylic acid are shown in Fig. 2. Analogous activity was observed for other surface modified materials (except for cat@TiO₂). All materials appeared active in this process pointing at hydroxyl radicals generation.

Efficiencies of 4-CP degradation, expressed as the amount of decomposed 4-CP after 30 minutes of irradiation in the presence of the studied materials, are presented in Fig. 3. Most of the materials show a lower activity than unmodified TiO₂ in

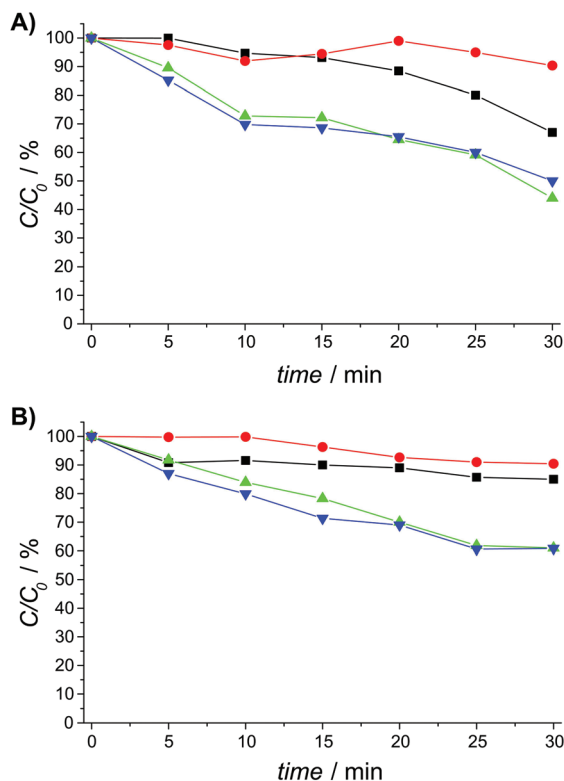


Fig. 2 The photocatalytic degradation of 4-CP upon irradiation with UV (300–400 nm, squares), visible (>400 nm, circles), UV-vis (320–700 nm, triangles) and UV-vis-NIR light (>300 nm, inverted triangles) in the presence of unmodified TiO₂ (A) and sal@TiO₂ (B). Errors: $\pm 5\%$.

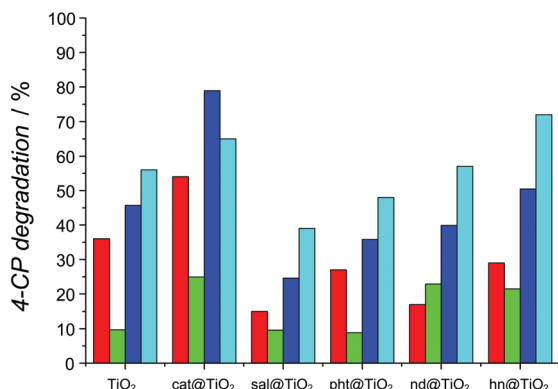


Fig. 3 A degree of 4-CP degradation after 30 min of irradiation in the presence of the studied colloids. Red bars denote the degree of 4-CP degradation upon UV (300–400 nm) irradiation; green bars – upon vis irradiation (>400 nm); blue bars – a mathematical sum of red and green bars; cyan bars – the effect measured upon UV-vis irradiation (320–700 nm).

the process induced by UV light. The only exception is cat@TiO₂, which shows a considerably higher activity under these conditions. It can be expected that hydroxyl radicals are generated in the process of water oxidation upon irradiation with UV light both in the presence of unmodified TiO₂ and at other materials (Fig. 4, processes 1 and 3).

The lower activity of modified materials upon UV irradiation is caused by a partial UV-light absorption by the

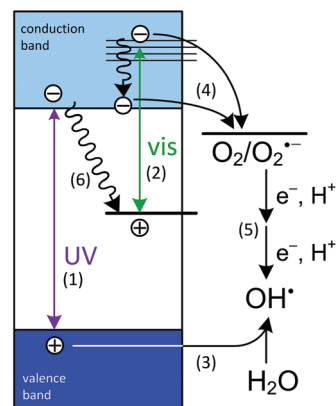


Fig. 4 The mechanism of hydroxyl radicals photogeneration in the presence of surface modified nanocrystalline TiO₂.

sensitizer. Then the less efficient mechanism of OH[·] radicals generation, involving a multistep O₂ reduction, is initiated. Only a fraction of UV light is absorbed directly by TiO₂, leading to a more efficient OH[·] production as a result of a direct water oxidation with photogenerated holes. Therefore, the surface-bound sensitizer acts partially as a UV-light filter for TiO₂ core, lowering the quantum yield of OH[·] generation. This effect was previously reported for TiO₂ modified with the [PtCl₆]²⁻ complex.^{8,27}

Three materials show a relatively high activity upon visible light irradiation (cat@TiO₂, nd@TiO₂ and hn@TiO₂, Fig. 3). Under these conditions only the surface charge transfer complex is excited (Fig. 4, process 2). Water oxidation with the valence band holes is then impossible (Fig. 4, process 3), but irradiation with visible light may induce generation of hydroxyl radicals in a multistep reduction of oxygen with electrons from the conduction band (Fig. 4, processes 4 and 5).

An unexpectedly high photocatalytic activity of all materials was observed upon irradiation with UV-vis light. Degradation rates are higher than the sums of the effects observed separately for ultraviolet and visible light (with the exception of cat@TiO₂, Fig. 3). Under these conditions hydroxyl radicals can be generated either in the process 3 or 5 (Fig. 4). Upon excitation of both, the semiconductor (with UV light) and the surface complex (with visible light), the oxidized form of the ligand can be reduced back by electrons from the conduction band (Fig. 4, process 6). Presumably, this process inhibits to some extent the electron–hole recombination and leads to an increase of the lifetimes of valence band holes and Ti^{III}-centered electrons. Decreased emission intensities of nanocrystalline TiO₂ recorded upon the addition of modifiers supports this hypothesis (data not shown). Increased lifetimes should improve the efficiencies of interfacial electron transfer processes.

This effect is also parallel to the observed enhanced activity of unmodified TiO₂ irradiated with UV-vis light. The influence of “two-color” (UV and visible light) irradiation of TiO₂ on rates of photocatalytic degradation of methyl orange was studied by Liu *et al.*²⁸ A two-color irradiation induced much

faster reactions when compared to irradiations with exclusively UV or visible light. The photodegradation rate was also significantly higher than the sum of rates measured when only ultra-violet or visible light was employed. The authors associated this effect with the d–d excitation of photogenerated titanium(III) ions leading to higher excited states.^{28,29} They concluded that the electron transfer from this excited state to oxygen molecule (the generation of superoxide radicals) was particularly effective.

Singlet oxygen detection – SOSG photooxidation

Singlet Oxygen Sensor Green (SOSG) is a selective sensor used for singlet oxygen detection. This molecule combines a chromophore part and the electron donor fragment, quenching the fluorescence of the chromophore as a result of an intramolecular electron transfer. The electron donor can be oxidized by singlet oxygen to the endoperoxide product, unable to quench fluorescence of the chromophore. Therefore the emission of SOSG is pronounced upon its oxidation with singlet oxygen. The maximum of SOSG emission is localized at 565 nm when excited at 400 nm.^{30,31} The sensor is commonly used for *in vivo* detection of singlet oxygen generated in plant tissues.³² The use of SOSG to detect photogenerated singlet oxygen causes more problems since the sensor may act as a photosensitizer itself. Quantum yields of singlet oxygen generation are 0.006 and 0.18 for the non-oxidized and oxidized forms of SOSG (SOSG-O₂), respectively.³⁰ Therefore whenever SOSG is used to detect photogenerated singlet oxygen, the results have to be compared with the measurements made for SOSG in the absence of any other photosensitizer.

In our measurements the photocatalyst solution in methanol was added to the SOSG solution after measuring the emission spectrum of the sensor solution. At the beginning the recorded emission decreased due to the sensor dilution. Upon irradiation the signal increased as a result of an increasing amount of SOSG-O₂ in the system, reaching a nearly constant value after *ca.* 8–10 minutes. The difference in emission intensity measured after 8 minutes of irradiation and directly after the addition of the analysed solution was a measure of the photogenerated singlet oxygen. An exemplary dependence of the emission intensity on irradiation time is presented in Fig. 5.

The evolution of the emission intensity differs for various photocatalysts (Fig. 6). Upon irradiation at $\lambda = 405$ nm a very pronounced effect was observed for sal@TiO₂, nd@TiO₂ and TiO₂, compared to the reference SOSG solution. No influence of the modifier alone on the fluorescence of SOSG was observed. Upon two-color irradiation (405 + 785 nm) an increase of the intensity compared to that observed for a monochromatic 405 nm irradiation was recorded for a majority of samples, excluding sal@TiO₂. Upon a monochromatic excitation at 785 nm the emission of SOSG was not observed.

The results of this study confirm that singlet oxygen can be photogenerated in the presence of the tested photocatalysts (except for hn@TiO₂). The photoactivity of the materials was

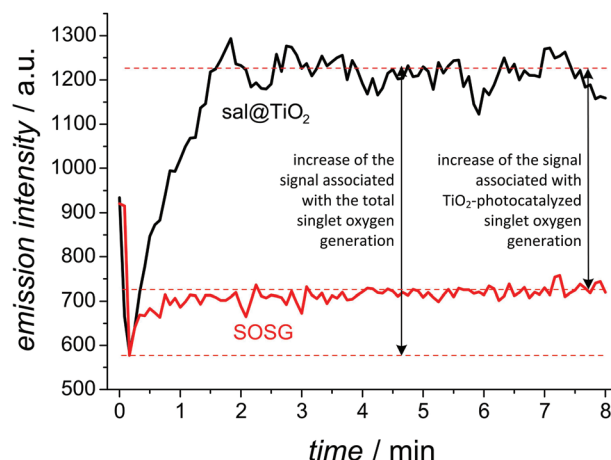


Fig. 5 The development of the emission intensity recorded at 565 nm upon excitation of SOSG at 405 nm in the presence of sal@TiO₂ (black line) and for SOSG alone (red line). Similar curves were recorded for other photomaterials.

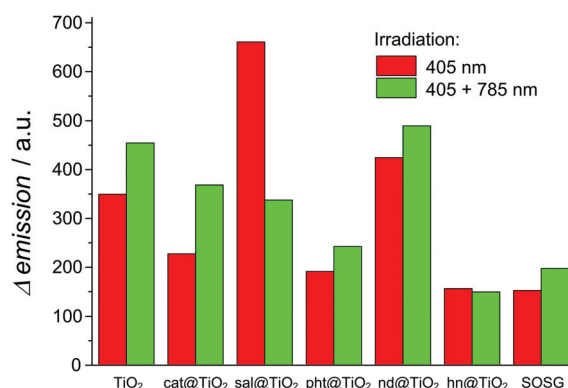


Fig. 6 The emission of the SOSG sensor measured at 565 nm upon irradiation with lasers: 405 nm and 405 nm + 785 nm.

also observed upon irradiation with visible light, providing the evidence for an efficient photosensitization of TiO₂ with selected surface modifiers. In several cases the two-color irradiation of the system enhanced significantly the generation of ¹O₂, although none of the systems absorbs at 785 nm (compare Fig. 1). The mechanisms of singlet oxygen generation are discussed in detail in the following sections.

Singlet oxygen detection – phosphorescence measurements

A singlet oxygen generation was also confirmed in direct measurements of phosphorescence at 1270 nm upon excitation at 355 nm. The signal recorded for all samples consisted of two components: the fast one (from TiO₂ scattering) and the slower one (from singlet oxygen phosphorescence). The measured lifetime of singlet oxygen was 8.5 μs. This value is very close to the literature data (10 μs in methanol³³). Intensities of signals were very small due to a low concentration of photocatalysts and low yields of the process. The concentration of TiO₂ colloid in the experiment could not be increased since

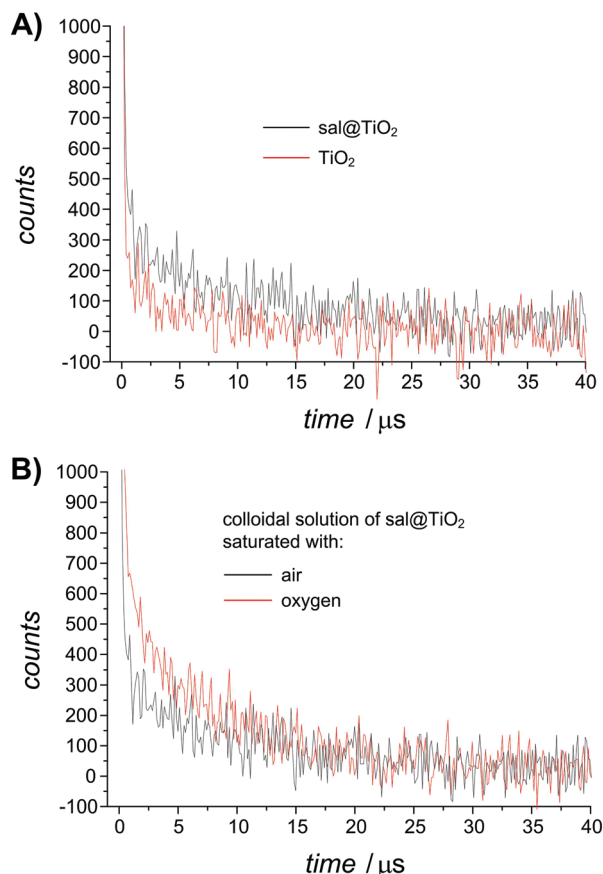


Fig. 7 The phosphorescence of singlet oxygen (1270 nm) generated in methanolic solutions of TiO_2 and sal@TiO_2 in equilibrium with air (A). A comparison of phosphorescence of $^1\text{O}_2$ generated in the solution of sal@TiO_2 saturated with air and oxygen (B).

it would cause a too strong light scattering and a drop of the measured emission intensity.

Only hn absorbs at 355 nm; however, no phosphorescence at 1270 nm was recorded when solutions of modifiers alone were excited. Signals recorded in the presence of surface-modified materials were stronger than those obtained for unmodified TiO_2 (Fig. 7A). The most intense signal was obtained for sal@TiO_2 , in agreement with the results of SOSG photooxidation. After saturation of the solution with oxygen the intensity of the measured signal increased (Fig. 7B), providing an additional support for photogeneration of singlet oxygen in the studied system. For other photocatalysts the intensities of signals were lower, close to the noise level. The quantum yields for singlet oxygen generation in air-saturated solutions were estimated to be at the level of 0.012 ± 0.005 and 0.003 ± 0.003 for sal@TiO_2 and TiO_2 , respectively.

Mechanisms of singlet oxygen generation

As demonstrated by direct measurements of $^1\text{O}_2$ phosphorescence, singlet oxygen can be generated upon UV irradiation (Fig. 8A, process 1). The energy of an excited TiO_2 nanoparticle is too high to be efficiently transferred directly to the oxygen molecule. As reported by Nosaka, under these conditions

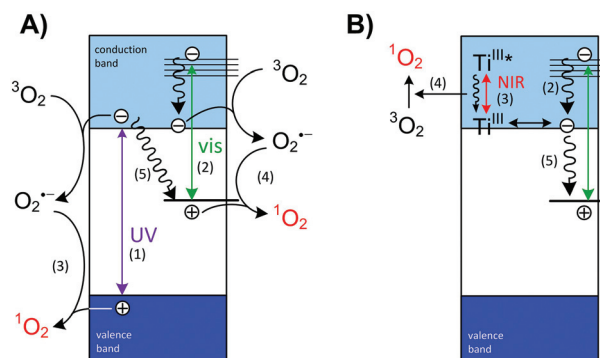


Fig. 8 Mechanisms of the photoinduced singlet oxygen generation at the surface-modified nanocrystalline TiO_2 : Nosaka's mechanism (processes 3 and 4) upon UV-vis irradiation (A); the energy transfer mechanism (process 4) upon vis-NIR irradiation (B).

singlet oxygen can be generated in the presence of unmodified TiO_2 as a result of superoxide oxidation by valence band holes (Fig. 8A, process 3). Since the singlet oxygen generation was also confirmed upon visible light irradiation (excitation at 405 nm) the analogous mechanism can be concluded. Visible light irradiation of the surface modified materials also leads to the superoxide generation, followed either by its further reduction to hydrogen peroxide and hydroxyl radicals or by its oxidation to $^1\text{O}_2$ (Fig. 8A, processes 2 and 4).

Upon a two-color irradiation (UV and visible), the excitation of both, TiO_2 and the surface complex, takes place. The population of electrons in the conduction band is higher and the efficiency of superoxide radical generation increases. Singlet oxygen can be generated in both types of Nosaka's mechanism – when superoxide reacts either with the valence band holes or the oxidized ligand (Fig. 8A). Upon the two-color irradiation the oxidized form of the ligand can be reduced back by electrons from the conduction band (Fig. 8A, process 5; compare also Fig. 4, process 6), diminishing the role of $\text{O}_2^{\cdot-}$ oxidation by the oxidized ligand.

For some materials, particularly for cat@TiO_2 , but also for neat TiO_2 , enhanced generation of singlet oxygen was observed upon simultaneous visible and NIR irradiation (Fig. 6). NIR radiation does not accelerate the process of 4-CP photodegradation (Fig. 2) and therefore it affects neither hydroxyl nor superoxide radicals generation. This effect cannot be explained by Nosaka's mechanism, but rather by an energy transfer process. Upon a simultaneous 405 and 785 nm irradiation the Ti^{III} centers (trapped electrons) can undergo a further excitation (λ_{max} of Ti^{III} is ca. 780 nm; Fig. 8B, process 3) playing the role of an oxygen photosensitizer (Fig. 8B, process 4). This process, however, competes with the relaxation of excited states of titanium(III). Apparently, for sal@TiO_2 the energy transfer process 4 (Fig. 8B) is very inefficient and cannot compete with the relaxation process. Therefore, for this material, an irradiation with NIR light does not improve the generation of singlet oxygen, as demonstrated in Fig. 6. A significant decrease of the efficiency of $^1\text{O}_2$ generation in the presence of this material remains unclear.

Our study proves a competition between two completely different mechanisms of singlet oxygen generation in the presence of TiO₂ colloids, modified with organic ligands forming surface titanium(IV) charge-transfer complexes. The role of photogenerated titanium(III) in the process of energy transfer cannot be therefore neglected.

Conclusions

Stable colloids of surface modified nanocrystalline TiO₂ were synthesized in water. Most of the materials are visible light active due to the OET mechanism operating within the surface charge transfer complex of titanium(IV). The experiments with 4-CP photodegradation prove the generation of hydroxyl radicals in the presence of studied materials upon irradiation with either UV or visible light. Relatively high activities induced by visible light were observed for cat@TiO₂, nd@TiO₂ and hn@TiO₂. A simultaneous irradiation with UV and vis light shows a synergistic effect on 4-CP degradation; however, the NIR light did not influence rates of 4-CP oxidation.

The generation of singlet oxygen was proven for sal@TiO₂ (the most efficient singlet oxygen photosensitizer out of the tested group of colloids) using direct ¹O₂ phosphorescence measurements upon excitation at 355 nm. The measured quantum yield of singlet oxygen formation in the air-saturated solution was 0.012 ± 0.005, *i.e.* 3–4 times higher than values measured for unmodified TiO₂ (0.003 ± 0.003). The photogeneration of singlet oxygen in the presence of other materials was confirmed using Singlet Oxygen Sensor Green (SOSG). Singlet oxygen is presumably formed according to the mechanism of O₂^{•−} oxidation by a strong oxidant, *i.e.* a valence band hole or an oxidized ligand. The analysis of the results of SOSG fluorescence measured upon various modes of irradiation has shown that in some systems a direct energy transfer from the NIR-excited titanium(III) centers plays also a plausible role. This is valid mainly for cat@TiO₂, but also for unmodified TiO₂.

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