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Original Scientific Article

Manganese/TiO$_2$ Composites Prepared and Used for Photocatalytic Active Textiles

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Abstract. Manganese/TiO$_2$ composites are prepared by a solvothermal process starting from the precursors titanium propoxide and manganese nitrate. The solvothermal processes are driven at temperatures of 140 °C or 180 °C. The formation of anatase as crystalline TiO$_2$-phase was determined by XRD for preparation conditions at 180 °C. The occurance of crystalline phases in nanometer scale is determined further by TEM. The prepared manganese/TiO$_2$-composites are further investigated as coating onto viscose textile. The photocatalytic activity of those composites was determined by degradation of organic dye stuff under illumination with UV-light. The effect of photocatalytic dye degradation is also investigated in presence of H$_2$O$_2$. The prepared textile coatings exhibit a high capability for dye decomposition under the chosen arrangement of investigations. For this reason, the prepared coated textile materials could be of high interest for industrial applications, for example, as filter material for cleaning waste water from dyeing processes. (doi: 10.5562/cca2097)

Keywords: titania, photocatalysis, H$_2$O$_2$, hydrogenperoxide, Acid Orange

INTRODUCTION

A photocatalytic process is a process which is accelerated in presence of light and a photocatalyst. A photocatalyst is a material, which has no influence on the process under dark conditions. However, in case of illumination, the photocatalyst is able to accelerate a reaction. Most photocatalysts are semiconductors containing an electronic structure with certain bandgap between a valence band and a conduction band.[1–4] The photocatalytic reaction starts with the transport of electrons from valence to conduction band induced by light absorption. To overcome the bandgap in this process, the absorbed light needs to have a certain energy, which is in relation to the wavelength of light. For this, the photoreaction is started by the absorption of light with a certain maximal wavelength determined by the bandgap of the photocatalyst. If light is used with wavelengths larger the maximal wavelength, the photoreaction cannot start, because the light does not contain the necessary energy to transport electrons from the valence to the conduction band.[4]

One frequently reported photocatalytic process is the photooxidation with oxygen. This kind of photooxidation is developed for several applications, e.g. degradation of organic dyes in wastewater, degradation of chlorophenol or oxidation of gaseous benzene.[3,5–7] An interesting topic is also the use of photocatalytic materials as coating on fiber materials to reach self-cleaning fabrics, which eliminate dirt by photooxidative processes. Examples are given for different fiber materials like cotton, keratins or polyester.[8–10] Beside the degradation of dye, toxic compounds or dirt, also bacteria can be degradated and eliminated by photooxi-

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dation. This degradation of bacteria is also defined as antimicrobial effect caused by a photooxidative process.[11,12]

One of the probably best investigated photocatalysts is titanium oxide. TiO_2 can occur in amorphous form or in three different types of crystalline phases as rutile, anatase or brookite. For photooxidation with oxygen the TiO_2 crystalline phase anatase contains the highest photocatalytic activity.[3,13] For photooxidation with other oxidative agents, like hydrogenperoxide and also for the other TiO_2 crystalline phase like rutile, a high photocatalytic activity can be observed.[13] The disadvantage of TiO_2 as photocatalyst is probably that due to the large band gap of 3.2 eV the photocatalytic effect works only with UV light.[1] An application with visible light is with pure TiO_2 not possible, which closes the door for economic daylight applications, *e.g.* for waste water treatment.

For this, many efforts have been done to modify TiO_2 in order to induce a photoactivity with visible light. Beside the general enhancement of photoactivity of TiO_2, the generation of photoactive properties using visible light is in the focus of current research. The modification of TiO_2 is done by combination with other materials to prepare so-called doped TiO_2 or TiO_2 composites. For modification of TiO_2 in order to reach activity with visible light a wide range of different materials are investigated and only a short overview can be given in this introduction. Main modifications of TiO_2 are done by doping with non-metals as nitrogen, fluorine, carbon, boron or sulphur.[14–19] Other groups report that the modification with metal are suitable to reach a photoactivity of TiO_2 for visible light. Examples are given for the doping with cobalt, iron, antimony, chromium or vanadium.[20–23] Beside doping also the use of composites is reported, as for example composites of TiO_2 with silver or silver compounds, manganese oxides, cadmium sulfide or tungsten oxide.[24–27]

Also many efforts have been made to prepare TiO_2 coatings instead of TiO_2 powders in order to improve their usability in technical processes. TiO_2 coatings are prepared on different types of substrates like metal, glass or textiles.[28,33] Especially, the TiO_2 coatings on textiles are of high interest, because textiles are highly flexible, have a large surface areas and can be easily fit to the demands of a photoreactor.[34]

Beside TiO_2 catalysed reactions with O_2 as oxidative agent, also many investigations have been performed with the stronger oxidative agent hydrogenperoxide.[13,35–38] These experiments were done to improve the decomposition rates of toxic or other hazardous compounds.[39–41] With this background also other semiconductor materials like ZnO, ZnS or CdS were investigated with view on their photocatalytic activity in presence of hydrogenperoxide.[42–44]

Under this aspect, manganese oxide is another interesting material to catalyse oxidation reactions, which is able to enhance the degradation of hydrogenperoxide, and by this, accelerate the oxidative reaction.[45–47] Manganese compounds are also reported to act as photocatalysts with oxygen as oxidative agent.[48,49] For this reason, many attempts have to be performed to combine both materials, titanium and manganese oxide, to get a composite material with advantageous catalytic activity.[50–56] However, it is also reported that, by addition of Mn to TiO_2 the photoactivity decreases.[57]

Because manganese oxide is a catalyst for the splitting of hydrogenperoxide, these manganese/titanium oxide composites should be interesting materials for photooxidative reactions with H_2O_2. Nevertheless, in contrast to the strong investigations with oxygen as photoactive agents, the properties of these composites are less investigated in presence of H_2O_2.

Therefore, the aim of this study is first the preparation of photoactive TiO_2 modified with manganese and second the testing of these materials in respect to photocatalytic properties with oxidative agents O_2 and H_2O_2. The preparation is done using a sol-gel process under solvothermal conditions. The resulting TiO_2 sol can be used as coating agent onto textiles or for the preparation of photoactive powders. The photoactivity is tested as function of degradation of dye under illumination.

EXPERIMENTAL PART

Materials and Preparation

A TiO_2-sol is prepared using the following procedure. Into 226 ml ethanol an amount of 2 g Pluronic P123 (blockcopolymer supported by BASF) is dissolved. To this solution an amount of 14 g titaniumtetrapropoxide is given under stirring. At last, under strong stirring 1.8 ml 1N-HNO_3 is added. To combine this TiO_2-sol with manganese an ethanol based solution of $Mn(NO_3)_2 \times 4H_2O$ (4 % *w*/*w*) is used. To 50ml of the TiO_2-sol the manganese nitrate solution is added under stirring in amount of 0.05 ml up to 5 ml. 10 minutes after these solutions are prepared, they are treated in a solvothermal process at 140 °C or 180 °C in a steel autoclave with Teflon vessel (Berghof Instruments GmbH, Germany; Hochdruck-Laborreaktor BR-500). The process duration is set to 2 hours. The annealing to reach the final process temperature took 45 minutes, while for the subsequent cooling at least 2 hours were necessary. All TiO_2-sols were applied onto viscose fabrics by dip-coating. After application the fabrics were dried at room temperature and finally a thermal treatment at 120 °C for 1 hour was done. The viscose fabric was made from multifilament yarn (supplied by

KOB-Wolfstein, Germany) with a weight of 240 g/m^2 and was used for coatings as received. For X-ray diffraction (XRD) investigations and for transmission electron microscopy (TEM) the coating solutions were also dried at room temperature and grinded to powders.

Analytical Methods

Measurements of wide-angle X-ray scattering (WAXS) were performed to identify the crystalline species in the solvothermally prepared materials. These measurements were performed on powders gained from the liquid coating solutions after drying for 48hours at room temperature and an afterwards grinding. For investigations a vertical X-ray diffractometer D8 (Bruker AXS) equipped with a scintillation detector was used. All measurements were performed with Cu-Kα radiation selected by a secondary graphite monochromator. The received diffraction patterns were identified by using the Powder Diffraction File 2 (PDF-2) database.[58] Transmission electron microscopy TEM was used to determine crystalline size and crystalinity of the prepared materials. TEM samples are prepared with 200 mesh copper grids containing a graphite membrane of 20 nm thickness (supported by Plano GmbH). For preparation, the powder materials were dispensed in water and the copper meshs were dipped into this solution. After drying for at least 12 hours at room temperature the TEM measurements were performed. As-prepared samples are investigated using a JEOL JEM 2100F Field Emission Electron Microscope. The photocatalytic activity of the prepared composites is determined for the composites as coatings on textiles. In all cases, the photoactivity is measured by the degradation of the dye Acid Orange 7 in presence of the composites and UV-light irradiation.[59,60] As light source six UV-lamps with a maximum of intensity at 360 nm were used (OMNILUX 18Watt – supplier Eurolite). To evaluate the photoactivity of the coated textiles in case of illumination with visible light a similar set-up is used with 18 Watt white lamps (OMNILUX). These white lamps are used as they are, emitting also a small amount of UV-light. However, experiments are also done after filtering the UV-light from the white-lamp by using a cut-off filter semaSORB PET 400 (sema GmbH, Coswig, Germany). The spectra of the used lamps are described in reference.[34] During 4 hours illumination the lamps are placed in a distance of 45cm from the dye solutions. Reference measurements are performed analogously but without light irradiation. For measurements of textile samples, sample pieces of 1 cm × 5 cm are cut and placed into a 15 ml aqueous solution 0.1 mmol/L of Acid Orange 7. For determination of the dye decomposition in presence of H_2O_2 the same arrangement is used. For this, to 15 ml of the dye solution an amount of 1ml H_2O_2 solution (35 % in water) is added, with the results of a 2.2 % H_2O_2 concentration in the dye solution. The concentration of dye is determined afterwards by measurement of the extinction of the dye solution at 486nm with a UV/Vis spectrometer (MCS 400, Zeiss) in arrangement of transmission. The photoactivity A(%) can be calculated as percentage value by using the relation $A(\%) = 100 \times (C - C_r)/C$ – with C as the final dye concentration in the UV illuminated arrangement and with C_r as dye concentration without light exposure. If this experiment is performed with the analogous uncoated viscose fabric and without the presence of H_2O_2, the determined decomposition of the dye Acid Orange 7 is smaller than 1 %.

RESULTS AND DISCUSSION

Material Properties

To gain information about the crystallinity of the prepared materials, all samples (see Table 1) are investigated by WAXS. From this, it can be clearly seen that

Table 1. Overview on investigated TiO$_2$ samples and their photoactivity against the dye Acid Orange under illumination with UV-light and with a white-lamp

Sample	Amount of manganese as molar ratio to TiO$_2$ / %	Solvothermal process temperature / °C	Photoactivity A / % against Acid Orange	
			UV-light	white-lamp
A1	0	140	3	1
A2	0	180	40	6
B1	0.18	140	1	1
B2	0.18	180	4	1
C1	0.02	140	1	1
C2	0.02	180	18	2

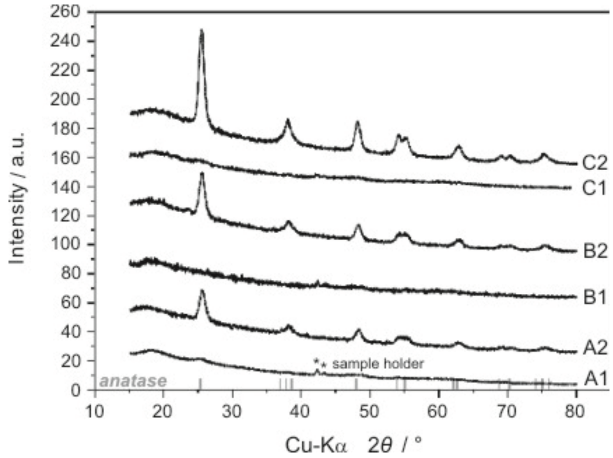

Figure 1. WAXS patterns of the prepared powders obtained from the solvothermally prepared sols. * indicates artefacts of the sample holder. Below the diffraction patterns the positions of reflections of the anatase TiO_2 phase are indicated.

the TiO_2 materials prepared solvothermally under the chosen conditions at 180 °C contain the crystalline TiO_2 modification of anatase (Figure 1). The samples prepared by a lower process temperature of 140 °C do not show reflection, as can be seen from WAXS patterns. So under this reaction conditions, the formation of an amorphous material is suggested. However, also small reflective patterns for samples prepared at 140 °C could give a hint a beginning of crystallisation process also under lower process temperatures. The beginning of anatase formation at temperatures of 140 °C could only be stated for sample A2 and C2 without addition of manganese or with low manganese concentrations. For the sample with highest manganese content, B2, even not a beginning of crystallisation could be proposed from the WAXS patterns. The WAXS patterns of the samples prepared at temperature higher than 180 °C do only show reflection of crystalline anatase, which is independent from the content of added manganese. No crystalline manganese component can be determined for these samples by WAXS.

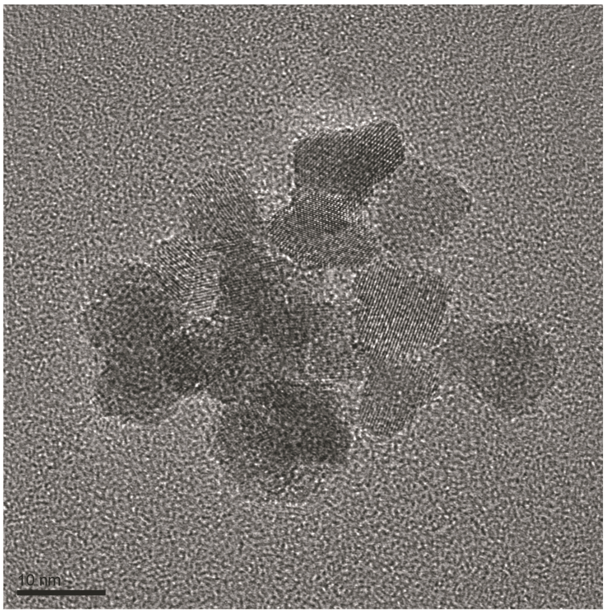

Figure 2. TEM image of sample C2 – preparation with a solvothermal process at 180 °C.

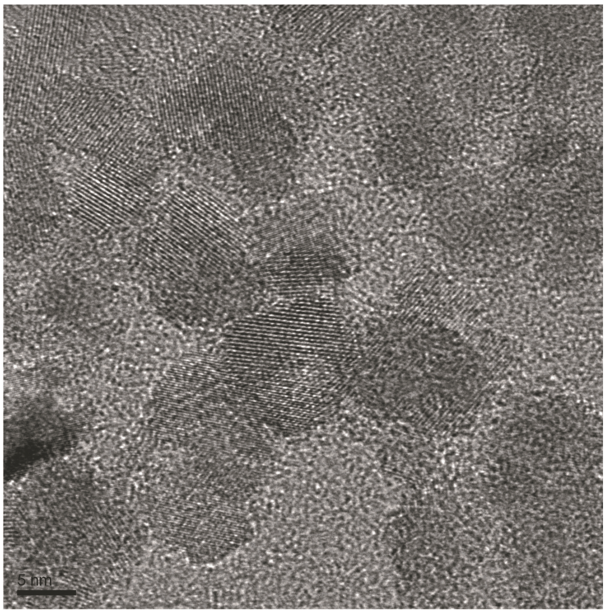

Figure 3. TEM image of B2 – preparation with a solvothermal process at 180 °C.

The WAXS results are comparable with the results gained by TEM investigations (Figures 2 to 4). The crystalline structure of materials formed under preparation conditions of 180 °C can be clearly determined by TEM (Figures 2 and 3). The diameters of these crystallites is smaller than 10nm, so it is stated that under the chosen preparation conditions nanocrystalline anatase is formed. An influence on the structure of these anatase type crystallites by addition of manganese cannot be detected. For sample B1, prepared at 140 °C, no crystalline phases were observed by TEM investigations (Figure 4). This result is congruent with the WAXS results.

Photoactivity of Textile Coatings

The photoactivity is determined for the prepared materials after coating on viscose textiles as the decomposition rate of the organic dye stuff Acid Orange 7. First investigations are done with the coated viscose under illumination with UV light and without further addition of H_2O_2 (Table 1). Also, a testing with a white-lamp was performed. If this determination is performed with uncoated viscose fabric, only an amount of smaller 1 % Acid Orange 7 is decomposed under the chosen set-up.

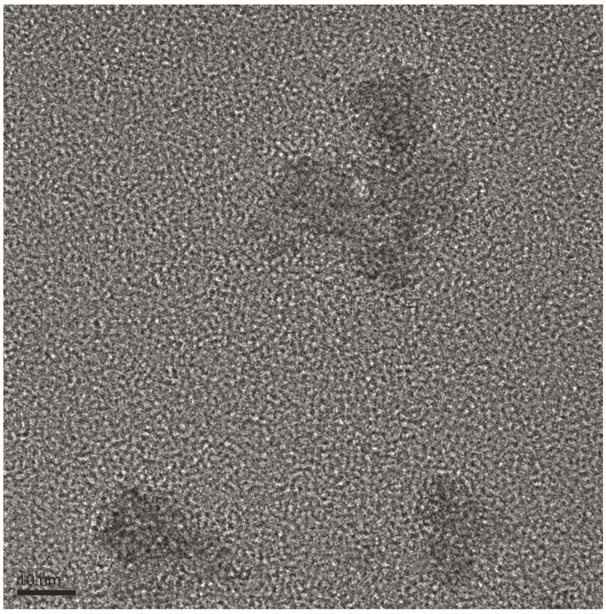

Figure 4. TEM image of B1 – preparation with a solvothermal process at 140 °C.

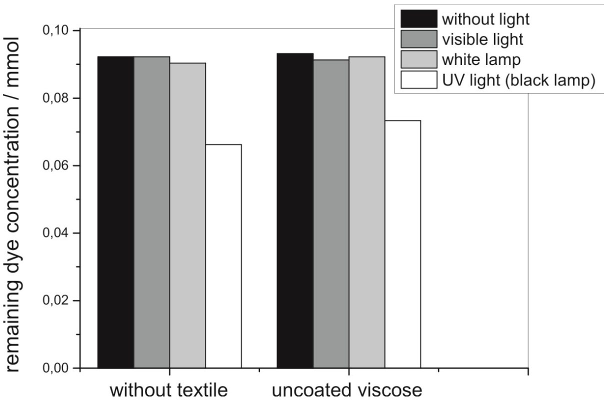

Figure 5. Overview on the reference measurements concerning the decomposition of the dye Acid Orange 7 in presence of 2.2 % H_2O_2 under different regimes of illumination. These measurements are performed without the presence of textiles and in presence of uncoated viscose fabrics.

The samples A2 and C2 prepared solvothermally at 180 °C, which contain crystalline anatase, exhibit a significant photoactivity. All samples prepared at 140 °C, containing only amorphous material, do not lead to a significant photoacive dye decomposition. These results are in good agreement with the literature, which stated that the anatase modification of TiO_2 exhibit higher photocatalytic activity for oxidative reactions with oxygen, compared to other crystalline modifications of TiO_2 or even the amorphous TiO_2.[3,13] It is also clearly indicated that, the addition of manganese to the anatase lead to a decrease of photoactivity and for sample B2 with highest investigated manganese content the photoactivity is nearly diminished (Table 1). Even small amounts of manganese compared to the TiO_2 content in the prepared materials can lead to a significant decrease of photocatalytic dye degradation. Such a decrease of photoactivity is reported in literature by several groups and is for example a useful property for preparation of TiO_2 materials for sunprotective applications.[61–64] This decreased catalytic efficiency is explained by adsorption of Mn^{2+} ions on the surface of TiO_2. By this, the separation of the photogenerated electron and hole is less effective leading to a higher rate of recombination.[63,64] For all investigated samples no significant photoactivity was determined in case of illumination with the white-lamp. It can be stated that, by combination of titania with managanese no sensibilisation of the photocatalyst for visible light was reached.

Because manganese is supposed to catalyse oxidation reactions with H_2O_2, investigations concerning the photoactivity of the prepared materials are also performed in presence of H_2O_2. For this, the decomposition of Acid Orange 7 is determined under analogous conditions but with the addition of 2.2 % H_2O_2 during illumination with UV-light, visible light or a white-lamp containing both visible and UV light, respectively. Reference measurements are performed without any kind of illumination.

Before investigating the coated viscose textile, a dye solution without any textile and with the analogous uncoated viscose fabric is investigated as reference (Figure 5). It can be clearly seen that even if the reactive oxidative H_2O_2 is added to the dye solution, nearly no additional dye decomposition can be observed in case of no illumination or illumination with visible light. A significant dye decomposition is only be observed in case of illumination with UV light. This decomposition is reduced for the reference with the uncoated viscose fabric, probably due to a kind of shadowing of the dye solution by the presence of the textile.

In contrast, a totally different behaviour of dye decomposition is observed, if the TiO_2 coated viscose fabrics are added to the H_2O_2 containing dye solution (Figure 6). In this case the TiO_2 materials solvothermally prepared at lower process temperature of 140 °C lead to a strong decomposition of the dye. This decomposition is even strong, if no illumination is performed. For this, it is stated, that the coated TiO_2 materials do not only work as a photocatalyst for dye oxidation with H_2O_2 but can also catalyse this reaction in the dark. This strong dye decomposition occurs for the sample A1, containing only TiO_2, and for the sample B1 and C1 with the manganese addition to the TiO_2 material. Small amounts of added manganese seem to have a small decreasing effect. It is worth to remark that the addition of TiO_2 materials solvothermally prepared at 180 °C do not lead such a dye decomposition without light expo-

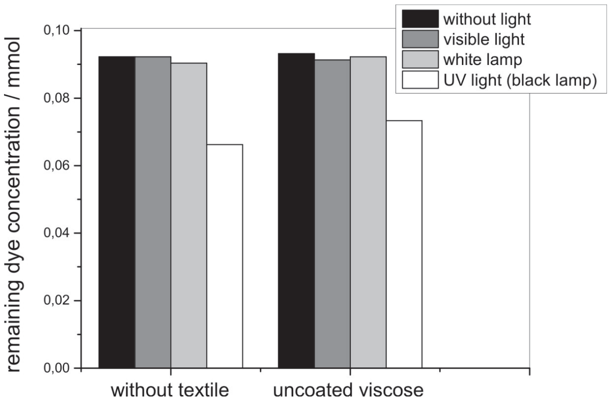

Figure 6. Decomposition of the dye Acid Orange 7 in presence of 2.2 % H_2O_2 under different regimes of illumination. These measurements are performed in presence of viscose fabrics coated with different TiO_2 samples.

sure. With these materials also by illumination with visible light no significant additional dye decomposition is observed. Only in case of UV-light a significant dye decomposition is observed and could be explained by a photocatalysed oxidation of the dye. This behaviour of these anatase containing samples prepared at 180 °C is in good agreement with the photocatalytic behaviour as reported in literature.[3,13]

In contrast, there is no simple explanation, why the amorphous TiO_2 coatings from materials solvothermally prepared at 140 °C exhibit a higher catalytic activity. Such a behaviour may be explained in accordance to the different behaviour of different TiO_2 modifications in presence of H_2O_2 instead of O_2, which is earlier described for a comparison between both TiO_2 modifications anatase and rutile.[13] It was reported that rutile does not cause a photoactive reaction with O_2 which has been explained by a higher stability of O_2^- species adsorbed on the rutile surface. When H_2O_2 is present next to rutile a reactive OH radical is formed leading to further photodecomposition reactions. Such a process may also be an explanation for the strong dye decomposition in presence of solvothermally prepared amorphous TiO_2 and H_2O_2.

CONCLUSIONS

Manganese/TiO_2 composites are prepared by a sol-gel process under solvothermal conditions. A solvothermal process driven at 180 °C lead to the formation of TiO_2 in the crystalline modification of anatase with crystallite sizes of the crystalline areas of smaller than 10nm. Is the process driven at lower temperatures of 140 °C mostly amorphous material is formed. The prepared materials can be applied as photocatalytic active coating onto textile fabrics. If this photoactivity is determined as oxidative degradation of organic dyestuffs with oxygen, especially the anatase containing samples exhibit a strong photoactivity in presence of UV light. In contrast, under reaction conditions with H_2O_2, a stronger oxidative dye decomposition is observed with the amorphous TiO_2 coatings on textiles. This decomposition reaction runs especially under illumination with visible light but also without illumination. Therefore, this materials could be of high interest for the development of cleaning systems for waste water under the use of sun-light without the necessity of an artificial UV source. For applications in waste water treatment it is of especial interest, that the oxidative decomposition with H_2O_2 is also catalysed in the dark, so it should be possible to develop a waste water cleaning plant working for 24 hours a day without the necessity of an artificial light source.

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