

## PHOTOCATALYTIC OXIDATION OF 4-CHLOROPHENOL IN AQUEOUS SOLUTION OVER $\text{TiO}_2$ - $\text{SiO}_2$ IN A FLOW REACTOR

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**Abstract.** Polycrystalline nano-sized mixed  $\text{TiO}_2$ + $\text{SiO}_2$  powders have been prepared by the sol-gel method. Titanium ethoxide  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  (TETO) has been used as a precursor of titanium, and silicon ethoxide  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (SETO) – as a precursor of silicon. The so prepared mixed  $\text{TiO}_2$ + $\text{SiO}_2$  sol-gel photocatalytic material, as well as commercially available Degussa  $\text{TiO}_2$  P25, have been coated on the outer surface of quartz tubes, comprising a photocatalytic reactor. The activities of these two types of photocatalytic materials have been measured in the reaction of 4-chlorophenol degradation in aqueous solution. The photocatalytic efficiency of our  $\text{TiO}_2$ + $\text{SiO}_2$  material, prepared by the sol-gel method, is twice higher than that of the reference Degussa  $\text{TiO}_2$  P25 photocatalyst, which was ascertained by the apparent rate constant using the Langmuir–Hinshelwood model. The samples have been characterised by bulk and surface techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), specific surface area (BET) and scanning electron microscope (SEM). The higher photocatalytic activity of the sol-gel prepared photocatalyst is due to the fact that our material is pure anatase phase with a smaller size of the crystallites as well as due to the complete removal of the bulk defects during the thermal treatment.

**Keywords:**  $\text{TiO}_2$  preparation, nano-sized titania, silica-modified titania, photocatalysis, 4-chlorophenol photodecomposition.

### AIMS AND BACKGROUND

Photocatalytic reactions on semi-conductor powders are of great interest because of their applicability to the treatment of a large variety of pollutants<sup>1,2</sup>. Different semi-conductor materials have been tested for the degradation of pollutants<sup>3,4</sup>.  $\text{TiO}_2$  has generally been demonstrated to be the most active photocatalyst<sup>5</sup>. The crystalline structure, the size of the  $\text{TiO}_2$  crystallites and the method of preparation are the three most important factors determining the photocatalytic activity. Nanophase titania is prepared frequently by the sol-gel process or by gas-phase synthesis in a flame reactor<sup>3,6,7</sup>. There always exist structural defects on the surface and inside the titania particles<sup>8</sup>. These structural defects have direct influence on the fate of photoexcited electrons. The surface defects promote the photocatalytic activity, as they play the role of active sites, on which the electron donor or acceptor is adsorbed. However, the bulk defects lower the

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photoactivity because they provide sites for the recombination of the photogenerated electrons and holes. Therefore, the number of the bulk defects should be reduced to obtain a high photoactivity. The anatase  $\text{TiO}_2$  is the better photocatalyst, compared to the rutile titania, mostly because of the greater reactive surface area<sup>3,9,10</sup>. Unluckily the anatase phase is converted into rutile at temperature higher than  $500^\circ\text{C}$ , which causes a drastic decrease of the reactive surface area<sup>11</sup>. The removal of the bulk defects in the crystal structure of anatase by high temperature treatment requires selecting a method to suppress the modification transition anatase–rutile.  $\text{SiO}_2$  is one of the widely used dopants, suppressing this transition. It has been established that at a ratio  $\text{TiO}_2:\text{SiO}_2 = 4:1$  a pure anatase phase is observed even at temperatures as high as  $900^\circ\text{C}$  (Ref. 12). For this reason we chose the approach to modify the  $\text{TiO}_2$  with  $\text{SiO}_2$ . A modification of the sol-gel method was chosen here to prepare the  $\text{TiO}_2$ -based photocatalytic materials and to deposit them on the outer surface of quartz tubes in order to test and optimise the construction of a novel 4-tube continuous flow photocatalytic reactor with a popular model pollutant 4-chlorophenol. Industrial dye waste water often contains 4-chlorophenol in addition to a mixture of reactive azo dyes<sup>13,14</sup>.

The aim of this study was to obtain a highly active  $\text{TiO}_2$ - $\text{SiO}_2$  coating on quartz support and to investigate the activity of a semi-conductor photocatalyst in the photodegradation of organic types of pollutants. The activity of the so prepared photocatalysts is compared with that of a standard Degussa P25 photocatalyst widely used as a reference photocatalyst in many studies.

## EXPERIMENTAL

*Chemicals.* 4-chlorophenol, hydrochloric acid, ethanol and isopropanol (Aldrich) were used without further purification. Merck titanium ethoxide  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  and silicon ethoxide  $\text{Si}(\text{OC}_2\text{H}_5)_4$  were used as precursors for Ti and Si, respectively. Degussa P25  $\text{TiO}_2$  was used as a reference photocatalytic material.

*Characterisation.* The photocatalyst samples were characterised by the following methods. The X-ray diffraction patterns of  $\text{TiO}_2$  powder were measured using  $\text{Cu K}\alpha$  ( $\lambda = 0.1506 \text{ nm}$ ) radiation to monitor the degree of crystallinity, the particle size and the anatase/rutile ratio. An X-ray diffractometer (D5000, Siemens) was used with Ni filtered  $\text{Cu K}\alpha$  radiation over the range of  $2\theta$  from  $20^\circ$  to  $80^\circ$ . The specific surface area of the powder material was measured on Micromeritics, USA-Model FlowSorb II 2300 using a mixture of 30%  $\text{N}_2$  in He at a flow rate of 15 ml/min and 77 K. The morphology of the surface was observed and the size of the  $\text{TiO}_2$  particles was evaluated by a scanning electron microscope (SEM) (JEOL model JSM-5300). The X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG ESCALAB MK II spectrometer

under UHV conditions (base vacuum:  $\sim 10^{-8}$  Pa). The photoelectrons were excited with twin anode X-ray source using Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV). The Cl $1s$  photoelectron line at 285.0 eV was used as a reference for calibration.

The sonication of the modified TiO $_2$  material (slurry in isopropanol) prior to the deposition for 1 h at maximum capacity (Ultrasonic Disintegrator UD-20, Poland) was needed to disintegrate the agglomerates.

*Photocatalytic reactor and experimental conditions.* The measurement of the photocatalytic activity was carried out in a batch-circulation reactor. The reactor is a cylinder of diameter 0.09 m and height 130 mm, within which a set of 4 quartz tubes is placed. The reactor was charged with 0.65 l aqueous solution of the model pollutant, which was continuously re-circulated with a Gilson piston pump (Model 302) at 6000 ml/h (ideal mixing reactor). The tubes are coated on their outer surface with catalyst (TiO $_2$  + SiO $_2$ ). The reactor jacket is connected to a thermostat. 4W Philips lamps (TUV G4T5) were used. The TUV lamp emits light at 253.7 nm. The illumination intensity 55.4 mW/cm $^2$  was calculated dividing the lamp capacity 4W by the catalytic coating surface area 289 cm $^2$ . A Matheson mass flow controller was used to feed O $_2$  into the reactor. A Shimadzu TOC VCSH analyser was used to monitor the carbon concentration (mg C/l) and estimate the conversion degree. The batch photocatalytic reactor with water recirculation is operating reliably in the specified interval of parameters and the results are reproducible. The photocatalytic experiments were carried out at room temperature and pH = 3.

## RESULTS AND DISCUSSION

*Synthesis of SiO $_2$ -modified TiO $_2$  photocatalytic materials by the sol-gel method.* Titanium ethoxide Ti(OC $_2$ H $_5$ ) $_4$  (TETO) was used as a precursor of TiO $_2$  and silicon ethoxide Si(OC $_2$ H $_5$ ) $_4$  (SETO) – as a precursor of SiO $_2$ . The ratios between the sum of the two ethoxides (ETO) and the other reagents were as follows: H $_2$ O:ETO=156:1, HCl:ETO=1:5 and C $_2$ H $_5$ OH:ETO=1:1. The ratio between the two ethoxides was TETO:SETO = 25:1.

The first step of the procedure was to add SETO to the H $_2$ O–C $_2$ H $_5$ OH solution of HCl, where the acid plays the role of a catalyst for the prehydrolysis, i.e. the hydrolysis of the tetraethylorthosilicate (molecular solution) to obtain Si-OH groups, which further proceed to polycondensate forming larger nanometer-size colloidal particles. Therefore, silica sol was obtained as a result of this prehydrolysis step. Further in the second step we added slowly TETO stirring continuously for about 24 h. This is the proper hydrolysis of the tetraethylorthotitanate – now Ti-OH groups are being formed and they take part in the polycondensation process. In this way we obtain silica-titania sol. The third step was to evaporate the ethanol at 80°C. Then follows water evaporation at 100°C to ob-

tain the gel. This is not yet the final photocatalytic material as it contains a lot of bulk defects. The calcinations were carried out at 400, 500, 600, 700 or 800°C to remove these bulk defects, which are highly undesirable as they reduce the photonic efficiency through recombination of the photoexcited electrons and positively charged holes<sup>8,11</sup>. A slurry is formed of this powder material in isopropanol, sonicating for 1 h at maximum capacity to disintegrate the agglomerates. Then the suspension is ready for spin coating.

*Coating of the active component on quartz.* The coating of the quartz tubes with the active component has been carried out by the following procedure. A stock standard hydrosol of SiO<sub>2</sub> (40%) was prepared, based on the method of Bechtold and Snyder<sup>15</sup>, and used further as a 10 wt.% SiO<sub>2</sub> working solution after dilution. In order to reduce the content of Na<sup>+</sup>, which plays the role of a stabilising ion with respect to the colloidal particles, an additional purification was made using strongly acidic ion-exchange resin in its H<sup>+</sup> form. It is known that Na<sup>+</sup> 'consumes' photogenerated holes, which is in fact a parasitic reaction in view of carrying out a photocatalytic process and for this reason we have to reduce its content in the final photocatalytic material.

Prior to the silica sol coating a quartz glass tube was immersed in a 2-propanol solution and ultrasonically cleaned. The silica sol solution was poured into a shallow bath and the horizontally positioned quartz tube, immersed partially in it, was rotating slowly, so that the outer surface was thoroughly covered with a silica sol film. The quartz tube stood on one end to remove an excessive liquid by gravitational dropping and then calcined for 1 h in a furnace at 250°C. This procedure was repeated four times under the same conditions. The amount of attached SiO<sub>2</sub> is 1 mg/cm<sup>2</sup>.

The ultrasonically disintegrated Degussa P25 TiO<sub>2</sub> slurry in isopropanol (500 mg/l) was spin coated in the same way, followed by calcination at 350°C on the SiO<sub>2</sub>-coated tubes. The quantity of the deposited TiO<sub>2</sub> (Degussa P25) was 1 mg/cm<sup>2</sup>. The amount was determined gravimetrically with an error of ± 15% .

The SiO<sub>2</sub>-TiO<sub>2</sub> suspension, prepared by the sol-gel method, sonicated in isopropanol, was coated in the same way as the silica sol upon the outer surface of the quartz tubes. This procedure was repeated four times under the same conditions, followed each time by calcination at 350°C. The amount deposited was monitored gravimetrically aiming to obtain a film thickness of 1mg TiO<sub>2</sub> per 1 cm<sup>2</sup>. Prior to the deposition the quartz tubes were subjected to abrasive disk treatment to obtain a rough surface improving in this way the strength of attachment of the deposited coating.

*Characterisation of the photocatalysts.* The characteristic features of Degussa P25 TiO<sub>2</sub> have been described by the manufacturer and they are the following:

particle size varying from 20 to 40 nm (average 30 nm); BET specific surface area BET 50 m<sup>2</sup>/g; ratio anatase-rutile 75:25 (Table 1).

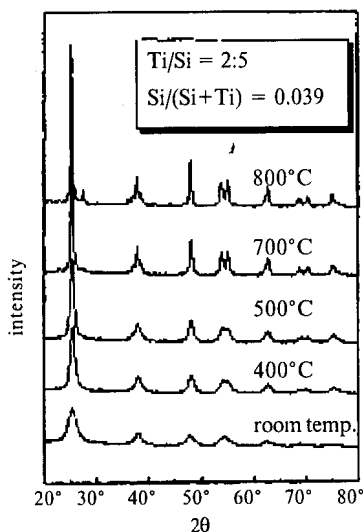
**Table 1.** Physico-chemical properties of the photocatalytic materials and apparent first order rate constants ( $k_{app}$ ) of 4-chlorophenol mineralisation

Catalyst	TiO <sub>2</sub> average particle size (nm)	BET surface area (m <sup>2</sup> /g)	Phase composition	$k_{app}$ (min <sup>-1</sup> )
None	–	–	–	0.2×10 <sup>-3</sup>
TiO <sub>2</sub> (sol-gel)	12	102	anatase	8.4×10 <sup>-3</sup>
TiO <sub>2</sub> (Degussa P25)	30	50	anatase-rutile	4.8×10 <sup>-3</sup>

The TiO<sub>2</sub>-SiO<sub>2</sub> photocatalytic material, prepared from TETO and SETO precursors on the basis of the above described procedure, was characterised by XRD (Cu K $\alpha$ ) (Fig. 1). The rutile reflection at  $2\theta = 27.5^\circ$  appeared only after calcination at 800°C, while at the lower temperatures we had a pure anatase phase with a main reflection  $2\theta = 25.3^\circ$  without any traces of rutile, brookite and crystalline SiO<sub>2</sub> (Table 1). The average particle size of the anatase phase, obtained at 700°C (our best photocatalyst) was estimated to be 12 nm (Table 1). This estimate has been made on the basis of the TiO<sub>2</sub> coating, studied by us using scanning electron microscopy (Fig. 2).

The single point BET specific surface area of the sol-gel prepared photocatalytic material in its powder form was found to be 102 m<sup>2</sup>/g (Table 1).

The attaching of TiO<sub>2</sub> Degussa P25 on the SiO<sub>2</sub> modified quartz flat plates was carried out in the same manner as that on the quartz tubes and the TiO<sub>2</sub>



**Fig. 1.** XRD patterns of titania particles prepared by the sol-gel process from the precursors TETO and SETO

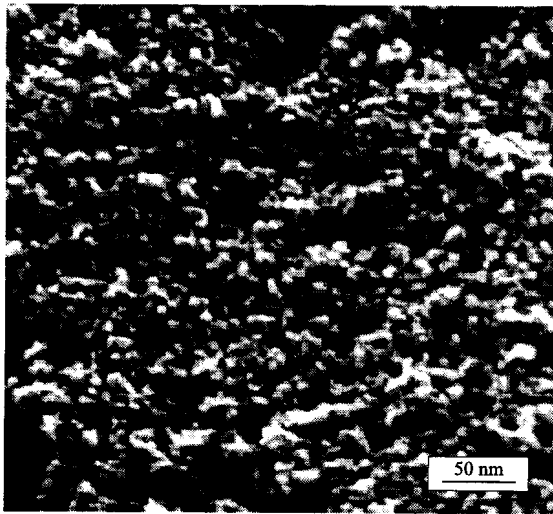


Fig. 2. SEM picture of powder  $\text{TiO}_2\text{-SiO}_2$  prepared by the sol-gel method

distribution on the surface has been evaluated by means of X-ray photoelectron spectroscopy. The X-ray photoelectron spectroscopy allows to discriminate between the oxygen (O1s band), originating from the photocatalytic  $\text{TiO}_2$  coating (binding energy 529.7 eV) and the oxygen of the  $\text{SiO}_2$  doped to the  $\text{TiO}_2$  (or the  $\text{SiO}_2$  of the supporting material or of the intermediate layer, binding the catalytic coating to the supporting material). The latter binding energy is 533.1 eV. The difference between the two binding energies is quite big  $\text{BE} = 3.4$  eV (Fig. 3). Evaluating the peak areas of the two oxygen forms it was estimated that about

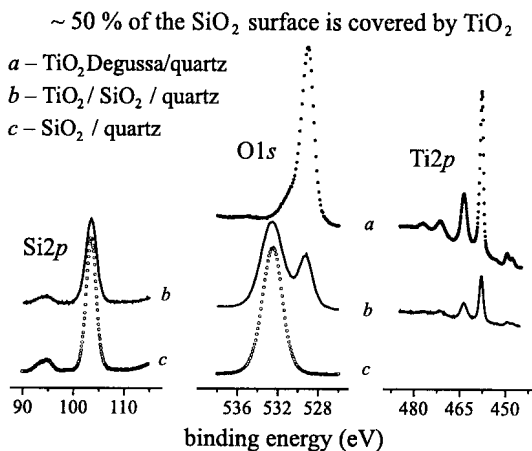


Fig. 3. XPS spectra of  $\text{TiO}_2$  (quartz),  $\text{TiO}_2\text{-SiO}_2/\text{quartz}$  and  $\text{SiO}_2$  (quartz) photocatalysts, prepared by immersion deposition on a piece of flat plate quartz

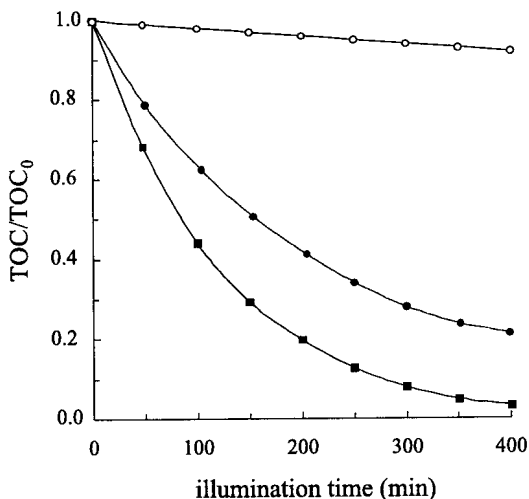
50% of the SiO<sub>2</sub> on the surface of a small piece (~ 1 cm<sup>2</sup>) quartz flat plate is covered by the deposited TiO<sub>2</sub>.

The model contaminant was 4-chlorophenol and the model reaction is described by the following stoichiometric equation:



Samples of 6 ml have been taken at regular 50 min intervals and the total duration of the experimental run was 400 min. The decrease in the concentration of total organic carbon (TOC) is monitored by the TOC analyser. The photocatalytic activity has been measured after selecting the optimal experimental conditions in advance – effect of the O<sub>2</sub> flow rate, the influence of the initial concentration of 4-chlorophenol. The rate of the photocatalytic destruction of the model pollutant (7-60 l O<sub>2</sub>/h) reaches a plateau at 35 l O<sub>2</sub>/h – the solution is saturated with dissolved oxygen. Within the 1-5 mM initial pollutant concentration interval the kinetic curves obey the Langmuir–Hinshelwood type of relationship.

Figure 4 represents the decrease of the TOC/TOC<sub>0</sub> ratio (accepted as a measure of the conversion degree) with the illumination time at constant TUV light intensity, oxygen flow rate and water recirculation rate. The rate of photodestruction of 4-chlorophenol in the presence of the sol-gel prepared TiO<sub>2</sub>-SiO<sub>2</sub> catalysts is higher than that in the case of TiO<sub>2</sub> Degussa P25 coated film. The TUV lamp illumination gives rise to a second mechanism of oxidation (in addi-



**Fig. 4.** Photocatalysed decomposition of 4 CP in the presence of: • – TiO<sub>2</sub> Degussa P25; ◆ – TiO<sub>2</sub> prepared by the sol-gel method; o – no catalyst at 4 mM aqueous solution 4-chlorophenol; 35 l O<sub>2</sub>/h and 55.4 mW/cm<sup>2</sup> intensity of TUV illumination

tion to the photocatalytic oxidation) – direct photolysis, which was evidenced by a blank experiment – illumination in the absence of photocatalysts.

Most of the investigators agree on one point – the expression for the rate of photomineralisation of the organic pollutant upon UV irradiation of  $\text{TiO}_2$  follows a Langmuir–Hinshelwood type of dependence<sup>16-18</sup>. It is considered that the influence of the initial concentration of the pollutant on the photocatalytic degradation rate for most of the organic compounds is described by a pseudo-first order kinetic equation, which is rationalised in terms of the Langmuir–Hinshelwood model, modified to accommodate the reactions, occurring at the solid-liquid interface:

$$r_0 = -\frac{dC}{dt} = \frac{k_r KC_{\text{eq}}}{1 + KC_{\text{eq}}}, \quad (2)$$

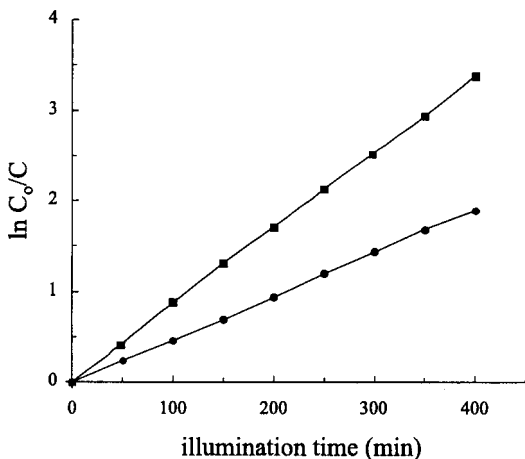
where  $r_0$  is the initial rate of disappearance of the organic pollutant and  $C_{\text{eq}}$  is the equilibrium bulk-pollutant concentration.  $K$  represents the adsorption-desorption equilibrium constant of the organic pollutant onto  $\text{TiO}_2$  and  $k_r$  represents the limiting-step rate constant of reaction at maximum coverage under the given experimental conditions.

The equations can be integrated and when  $C_0$  is very small, the equation can be reduced to:

$$\ln(C_0/C) = k_{\text{app}} t, \quad (3)$$

where  $k_{\text{app}} = k_r K$ .

Figure 5 shows that under the selected experimental conditions the photocatalytic oxidation of 4-chlorophenol follows the Langmuir–Hinshelwood type

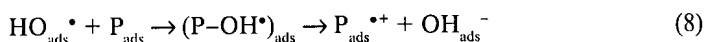
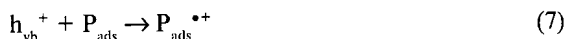
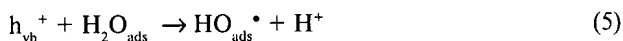
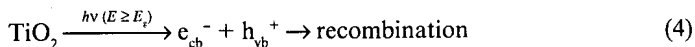


**Fig. 5.** Pseudo-first order kinetics for 4-chlorophenol in photocatalytic decomposition. Catalysts: ● – reference  $\text{TiO}_2$  Degussa P25; ◆ – sol-gel prepared –  $\text{TiO}_2$  at 4 mM aqueous solution of 4-chlorophenol; 35 l  $\text{O}_2/\text{h}$  and 55.4  $\text{mW}/\text{cm}^2$  intensity of TUV illumination



of kinetics. The photocatalytic activity of the sol-gel TiO<sub>2</sub> is twice higher than that of the Degussa reference catalyst (Table 1). The higher photocatalytic activity of our photocatalyst could be due to the fact that our material is pure anatase phase with a smaller size of the crystallites as well as due to the complete removal of the bulk defects during the thermal treatment.

The generally accepted first steps in photocatalytic processes occurring during irradiation of TiO<sub>2</sub> with photons of energy equal or greater than its band-gap (3.2 eV) are:



where the subscripts 'cb' and 'vb' are the valence band and the conduction band of TiO<sub>2</sub>, while P is pollutant. In the absence of electron acceptors (O<sub>2</sub>) the electron-hole recombination is possible. The presence of oxygen prevents this recombination by trapping electrons through the formation of superoxide ions according to equation (9). Oxidation by holes (equation (7)) are favoured for molecules that adsorb easily on the photocatalyst. On the other hand, HO<sup>•</sup> are able either to react in the interface or to diffuse away from the semi-conductor particle (equation (8)), thereby reacting with organic molecules in solution.

## CONCLUSIONS

The sol-gel prepared TiO<sub>2</sub>-SiO<sub>2</sub> mixed material possesses a high thermal stability, thus preventing the anatase-rutile transition. This enables the obtaining of a pure anatase phase, having very good photocatalytic oxidation activity using 4-chlorophenol as a model pollutant at concentrations up to 5 mmol/l in a batch-circulation reactor for water purification.

The rate of photodestruction of the model pollutant 4-chlorophenol in the presence of the coated sol-gel prepared TiO<sub>2</sub>-SiO<sub>2</sub> is twice higher than that of the coated reference Degussa P25 TiO<sub>2</sub>. Apparent rate constants were determined based on the Langmuir-Hinshelwood method.

The higher photocatalytic activity of our photocatalyst could be due to the fact that our material is pure anatase phase with a smaller size of the crystallites as well as due to the complete removal of the bulk defects during the thermal treatment.

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