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Experimental arrangements for determining the photocatalytic activity of Au/TiO_2 in air and wastewater purification

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Photocatalytic material, representing 0.5wt% Au/TiO_2, has been synthesized using the deposition-precipitation method (DP), on the basis of the commercially available TiO_2 (Degussa P25), modifying it with nanosized gold nanoparticles. The single point BET specific surface area has been found to be 52 m^2/g. The Au/TiO_2 slurry has been deposited on an Al TLC sheet pre-coated with SiO_2 and characterized by SEM revealing uniform thin film coating. The TPR profile proved the presence of oxidic species around the nanosized gold particles and transformation of some Ti^{4+} to Ti^{3+} enhanced by gold in close vicinity. The photocatalytic activity in air purification from ethylene has been measured in a continuous flow flat-plate gas-phase photocatalytic reactor (illumination intensity of 0.14 W/cm^2). The reactor configuration was improved with gas circulation pump and air splitter. The efficiency of the Au/TiO_2 suspension has been tested in model wastewater purification from 4-chlorophenol in a semi-batch slurry reactor (illumination intensity of 0.05 W/cm^2). Both photocatalytic experiments proved that the gold-doped TiO_2 is superior in its performance to the Evonik TiO_2 P25 commercially available photocatalyst due to charge separation and prevention of the electron-hole recombination.

Key words: titania photocatalyst, gold doping, air/water decontamination

INTRODUCTION

4-chlorophenol is a popular model pollutant, selected in photocatalytic studies, as it often appears in industrial wastewaters from the production of diazo dyes or pesticides [1, 2]. Chlorophenols are of special interest due to their high toxicity and low biodegradability [3]. Different semiconducting metal oxides have been studied in the photocatalytic oxidation of organic contaminants [4, 5] and TiO_2 is generally accepted to be the most active photocatalyst among them all [6]. Ethylene (C_2H_4) is the most widely manufactured petrochemical, which causes air pollution in industrial sites, [7, 8] and for this reason C_2H_4 and its chlorinated derivatives (applied as solvents) are often selected as model air pollutants in photocatalytic decontamination studies [9- 16].

There is debate in the current literature about modifying TiO_2 with noble metals, whose clusters possibly separate the charge carriers (capturing the photoexcited electrons) and leaving behind the positively charged holes to act as active sites for oxidation reactions [2, 4, 6, 8, 15]. This supposition is based on the existence of Schottky barriers on the metal/semiconductor oxide inter-phase boundary, preventing the return of the photoexcited electrons to the oxide phase (recombination) [17, 18]. In order to test this hypothesis we chose to deposit gold nanoparticles on commercially available TiO_2 Degussa P25. If it is correct one can expect increase in the photocatalytic activity of the Au/TiO_2 composite in view of the fact that longer life-time of holes will result in generation of larger number of hydroxyl radicals on this type of active sites. It is known, in fact, that these hydroxyl radicals are the active particles in a radical-chain type of oxidation reaction mechanism. Increasing the gold content, however, decreases the adsorption capacity of TiO_2 and reduces the reaction rate, i.e. too high metal content could be an unfavorable factor [17]. There are studies, which claim that metal clusters can cause photon absorption in the visible range, which would considerably increase the utilization of a larger portion of the solar light spectrum and this would make the photocatalysts applicable on an industrial scale [18]. Details about the optimal reactor configurations are to be found in [25, 26].

EXPERIMENTAL

Synthesis of Au/TiO_2 photocatalytic composite material

Photocatalytic material has been synthesized using the deposition-precipitation method (DP), on

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the basis of commercially available TiO_2 (Degussa P25), modifying it with nanosized gold nanoparticles. The deposition was aimed at achieving an optimal gold loading of 0.5% by weight preserving to a great extent the high adsorption capacity of TiO_2. First, the TiO_2 was suspended in deionized water by sonication (Ultrasonic Processor Hielscher UP200S, Germany) aimed at disintegration of the agglomerates and obtaining a stable slurry. Then an aqueous solution of $HAuCl_4$ and K_2CO_3 was added to the suspension and the interaction process was carried out at constant pH of 6.8 and reaction temperature of 60°C. After ageing for 1 hour the precipitate was carefully washed until complete elimination of chloride traces was achieved. Then it was dried first in vacuum at 80°C and then calcined in air at 400°C for 2h. The entire synthesis procedure was carried out with high degree of reproducibility using computer-controlled laboratory reactor Contalab (Contraves AG, Switzerland) under complete and precise control of all reaction parameters: reaction temperature, pH factor of the medium, stirrer speed, reactant feed flow rate.

Single point BET measurements

The standard reference photocatalyst TiO_2 Degussa P25 (80% anatase, 20% rutile), had a specific surface area of $50 m^2/g$, measured using $30\%N_2$ +70%He mixture in order to obtain adsorbed N_2 monolayer at the boiling temperature of liquid nitrogen (77 K). The obtained value for the gold modified sample was $52 m^2/g$ – the difference between the two values is of the order of the experimental error so it can be accepted to be practically the same.

Deposition of thin film coating on TLC sheet

The powdered photocatalytic material, representing 0.5%Au/TiO_2 Degussa 25, was tested in regard to its photocatalytic activity in air purification from ethylene. The color of the powder material is grayish-violet. An amount of 56 mg of the material was weighed on an analytical balance Precisa XB 220A (Switzerland) in order to obtain a thin film coating of $1 mg/cm^2$ on a flat sheet of geometric area of $56 cm^2$. The piece of sheet has dimensions 13.4 cm × 4.2 cm with rounded up corners – it was cut out of TLC foil (thin layer chromatography aluminum sheet 20 cm × 20 cm Merck, Art.5554). It is commercially available pre-coated with silica gel 60 F_{254} having layer thickness of 0.2 mm. TiO_2 suspensions form thin film coatings on silica gel having very good adhesion properties (high sticking coefficient) because of the similar chemical nature of TiO_2 and SiO_2. The sample amount was transferred into a 5 ml volumetric flask and deionized water was filled up to the mark. Then the suspension was treated in ultrasound bath for 15 min to disintegrate the agglomerates using Hielscher Ultrasonic Processor UP200S (Germany) under the following conditions: 24 kHz ultrasound, impulse regime of cycle 0.5, intensity 70% of the maximal amplitude. After the sonication the suspension was deposited drop-wise on the TLC sheet using a capillary with a directing air stream to obtain uniform coating. The coating was dried using an air-drier and left to stay overnight before the photocatalytic activity testing. Then the TLC sheet with the so obtained thin film coating of 0.5%Au/TiO_2 Degussa 25 ($1 mg/cm^2$) (Figure 1) was mounted in the reactor nest of a POLITEF gas-phase flat-plate continuous flow photocatalytic reactor reported in our previous paper [19].

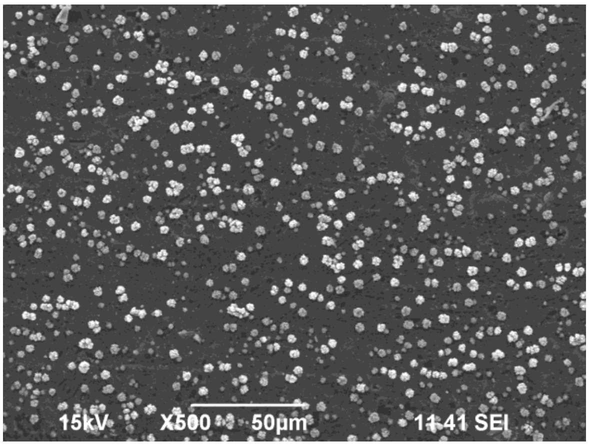

Fig. 1. Secondary electron image of uniform coating of Au/TiO_2 deposited on SiO_2 pre-coated TLC alumina sheet at magnification x 500 and 15 kV acceleration voltage.

RESULTS AND DISCUSSION

TPR Measurements

Titania is among the nonreducible bulk oxides, the standard free energy change (ΔG^o) for reduction has a high positive value of about 200 kJ mol^{-1} [20]. The TPR profile of an Au/TiO_2 sample containing 3 wt% of Au is shown in Figure 2. The detector sensitivity is not enough concerning the samples on TiO_2 with lower Au content. The two registered peaks are with very low intensity. The small LT peak at about 50 °C (HC of only 0.003 mmol/g) can be assigned to the oxidic species around the nanosized gold particles [21]. The peak in the temperature interval 400-500 °C (0.01 mmol/g) could be connected to the transformation of some Ti^{4+} to Ti^{3+} enhanced by gold in close vicinity.

There are literature data for TiO_2 concerning the possibility of Ti^{3+} existing. Since Ti^{3+} ions are not characteristic of anatase, they are assumed to be the places of localization of the hydroxyl groups [22]. Hadjiivanov et al. [23] have reported about anatase reduction with hydrogen at 400 °C (100 Torr of H_2 for 1 h) leading to the formation of some Ti^{3+}ions. Supplementary to the main anatase phase, small quantities of Ti_2O_3 and Ti_4O_7 have been registered by XRD in the case of titania supported on activated carbon. The existence of these Ti^{3+} ion-containing phases were explained by the reducing effect of the carbon [24].

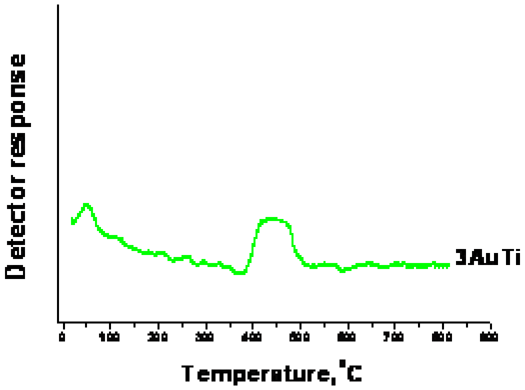

Fig. 2. TPR profile of 3%Au/TiO_2 composite photocatalyst sample.

Continuous flow /flow-circulation photocatalytic reactor

The construction of the POLITEF flat-plate gas-phase continuous-flow photocatalytic reactor (Figure 3), reported previously [19], has been improved by creating a circular contour: reactor-gas pump [20]. Thus the reactor is transformed from plug-flow type PFG reactor [21] into an ideal-mixing type of reactor, when the gas circulation rate inside the circulation contour is more than 50 times greater than the feed flow rate at the reactor inlet [20]. The conversion degree of ethylene, used as a model air contaminant, this time was measured under heavy-duty conditions for the catalyst (in the present study 5% = 50 000 ppm CxHy) – much higher than the concentration used previously (1000 ppm) [19]. The feed concentration of ethylene at the inlet of the reactor is the same as that at the outlet of the reactor when there is no illumination - the reaction is not occurring at room temperature in the dark. In both cases – with illumination and without illumination the LANCOM III gas analyzer (England) is connected to the reactor outlet, measuring feed concentration (the light is off) or converted mixture concentration (the light is on). Multiple flow controller MATHESON model 8249 (Belgium) was used to feed the reactants to the reactor. There are two N_2 flow rates: 30 ml/min dry N_2 (directly into the reactor), while 15 ml/min moist N_2 passes first through a deionized water saturator. The temperature of the saturator was maintained constant using a thermostat set at 25°C. The concentrations of the feed mixture at the inlet of the reactor were 84% N_2, 11% O_2, 5% C_2H_4. All the experimental runs were carried out at one and the same contact time 4.5 min (highest possible contact time) to obtain the highest conversion.

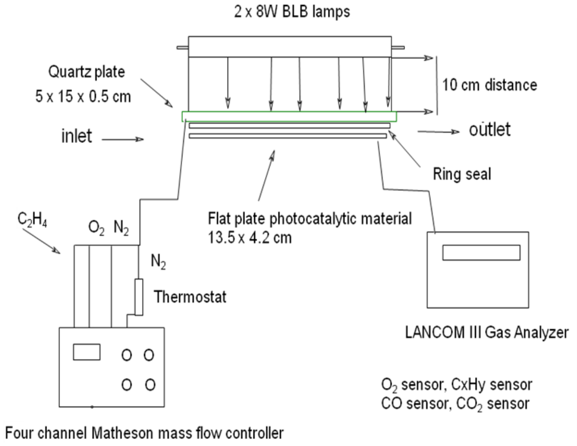

Fig. 3. Gas-phase flat-plate continuous flow photocatalytic reactor, equipped with mass-flow controller and multi-sensor gas analyzer.

The ethylene contact time was calculated as the time interval within which a volume of ethylene equal to the volume of the reactor is passing through the reactor (residence time) – the reactor volume is 11.2 cm^3 and ethylene feed flow rate is 2.5 ml/min. All other conditions were preserved the same – oxygen/ethylene feed ratio and optimal relative humidity of 30%. The relative humidity is calculated as the feed flow rate of moist N_2 (15 ml/min) related to the total feed flow rate (53.5 ml/min). As a result of the transition from the diffusion region to the kinetic region of operation and elimination of concentration gradients and the dead zones, existing previously [19], the performance was improved considerably. The performance of this new photocatalytic material is to be compared with the standard reference photocatalyst TiO_2 Degussa P 25 (75% anatase + 25% rutile with average anatase particle size 25 nm). The small nanometer size of both types of photocatalyst particles excludes in advance the pore diffusion retardation effect and so there is no need of grinding the catalyst and collecting specific sieve fraction, as is the case with classical catalysis and industrial catalysts, tested under laboratory conditions. A sheet of desired dimensions (13.4×4.2 cm) is cut out and accommodated in the reactor nest, giving an illuminated surface area of

56 cm^2. The illumination window was a flat plate quartz glass, enabling the use of two UV light lamps Philips TUV 4W/G4 T5 (Holland), achieving illumination intensity of 0.14 W/cm^2 at illumination distance 0 cm. The use of non-gradient external gas circulation catalytic reactor simplifies to a great extent the mathematic task of calculating the reaction rates [19]. In this specific case the reaction rate R (mol/h.g-cat) is calculated simply by dividing the conversion degree of the substrate (in our case – ethylene as a model air pollutant) by the contact time τ (h.g-cat/mol).

The use of a circulation contour: reactor-gas pump and the creation of ideal mixing conditions do not affect, however, the depth of the kinetic region. As in our previous work [19] the optimal thickness of the TiO_2 film coating remains about 1 mg of photocatalyst per 1 square centimeter. When this film thickness is increased the lower layers suffer from C_2H_4 diffusion limitations. The highest conversion degrees were achieved with the gold-doped sample and UV-C light at the highest contact times of ethylene (4 min) and optimal relative humidity of 28% - Table 1. It can be seen from the data in Table 1 that with all the three different types of illumination the performance of the gold-doped sample is superior to the non-doped TiO_2 samples. The visible light photocatalytic activity can be attributed to the rutile TiO_2 component of Degussa (band gap 3.0 eV and λ_{max} = 413 nm, i.e. activation by visible light) but it is difficult to explain such a huge promoting effect by gold-nanosized particles, which are supposed only to increase the charge carriers separation and promoting the lifetime of the oxidation sites, i.e. the positively charged holes.

Flow-splitter calibration

The second improvement was the application of a flow-splitter at the reactor outlet to improve the precision of the analyses. The LANCOM III gas-analyzer (Land Instruments Co., UK), used for the analyses of the feed mixture and of the converted reaction mixture, creates a problem as it is equipped with a powerful sucking pump creating under-pressure in a small-scale laboratory reactor. In fact this gas-analyzer is designed for use in industrial chimneys at great gas flow velocities to analyze the flue gas. In order to avoid the under-pressure problem in the photocatalytic reactor we had to use a three-way fitting with a loose end – now the analyzer is sucking in the converted mixture together with laboratory air (Figure 4). The ratio between the two split flow rates was calculated for each case based on the gas-analyzer pump productivity (constant) and the specific outlet mixture flow rate (variable) – the latter is specific for each experimental run. So the ratio is also a variable. This calculation is not sufficiently accurate. We applied precision calibration using a cylinder of standard gas 19.25% CO_2, to determine the ratio between the two split flow rates after the reactor outlet and before the LANCOM III gas-analyzer. The analyzer detected 0.36% CO_2, which is 53.47 times lower than the actual CO_2 concentration. Based on these two values one can calculate that the ratio between the air flow, sucked in by LANCOM and the flow of converted mixture at the outlet of the reactor is:

$$F_{air} : F_{out} = 53.47 : 1$$

Therefore one can calculate the actual CxHy, obtained as a result of the photocatalytic reaction at the reactor outlet by multiplying $\mathbf{C_{measured}}$ by 53.47.

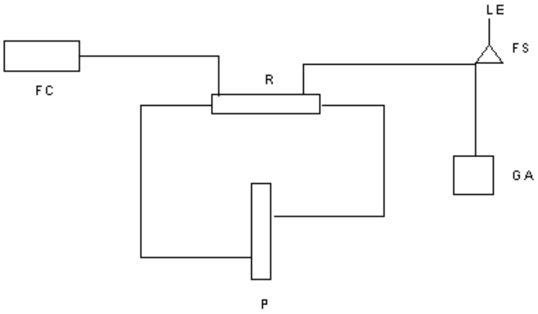

Fig. 4. Block-scheme of a flow-circulation photocatalytic reactor: R-reactor, P –pump, FC – flow controller, FS – flow splitter, LE – loose end, GA – gas analyser

Photocatalytic activity measurements in a semi-batch stirred suspension reactor

The experimental runs for waste water purification were carried out in a semi-batch stirred suspension reactor using 4-chlorophenol as the model contaminant with a concentration of 350 mgC/L. The reactor is "batch type" with respect to the charged amount of photocatalyst (slurry 200 mg in 200 ml 4-chlorophenol solution). At the same time there is continuous air flow through the suspension – it is accepted to denote such combination as "semi-batch reactor". The photocatalytic reactor has a total volume of 300 ml volume (diameter of the reactor 11.2 cm). The reactor is equipped with an electromagnetic stirrer. A sample of the studied photocatalytic powder material is added (200 mg) gradually upon stirring (400 rpm) and bubbling atmospheric air through the suspension, fed by a micro-compressor RESUN AC-2600B at a flow rate of 88 ml/min. The air is fed into the reactor through 2 frits, situated symmetrically on both sides of the UV lamp, dispersing the air flow in very small bubbles to ensure saturation of the aqueous phase with dissolved oxygen in large stoichiometric excess, compared to the model pollutant 4-chlorophenol. The illumination is achieved by means of a Philips UV-C lamp TUV 4W/G4 T5 (4 Watts), which ensures monochromatic illumination at wavelength $\lambda = 253.7$ nm. The lamp is located at a distance of 3 cm from the illuminated suspension. The light intensity is 0.05 W/cm^2. The lamp is covered with an aluminum foil reflector to concentrate the light intensity downwards towards the suspension. In the case of using visible light (Tungsram lamp of 500 Watts) the distance of illumination was 50 cm and the illumination intensity was 8.9 Watts/cm^2.

Table 1. Comparison of C_2H_4 conversion degrees over 0.5%Au/TiO$_2$ and TiO$_2$ Degussa P25 photocatalytic materials (film coating 1mg/cm^2) in continuous flow regime. Conditions: 51 010 ppm feed C_2H_4 concentration, UV-C illumination intensity 0.14 W/cm^2, 56 cm^2 illuminated area, ethylene contact time 4.48 min, 28% relative humidity

Photocatalytic material	Type of illumination	Intensity of illumination	C_2H_4 Conversion
0.5%Au/TiO$_2$	UV-C light	0.14 W/cm^2	88 %
TiO$_2$ Degussa P25	UV-C light	0.14 W/cm^2	63 %
0.5%Au/TiO$_2$	UV-A light	0.14 W/cm^2	87 %
TiO$_2$ Degussa P25	UV-A light	0.14 W/cm^2	40%
0.5%Au/TiO$_2$	Visible light	8.9 W/cm^2	69%
TiO$_2$ Degussa P25	Visible light	8.9 W/cm^2	3%

The photocatalytic activity testing was carried out in the course of 5 hours taking 5 ml samples at regular time intervals (1 hour). The photocatalyst powder is filtered through a double-layer Whatman 42 filter paper (ashless, slow filtering, fine crystalline, Cat. No. 1442 110). The concentration of carbon in the chlorophenol measured with a Total Organic Carbon analyser TOC Shimadzu Model VCSH. Then taking the initial concentration and the concentration at a given moment of time (after switching on the lamp and starting the illumination) i.e. at a given time interval of illumination we evaluated the degree of conversion of 4-chlorophenol, which was accepted as a measure of the photocatalytic activity. The dependence of the chlorophenol conversion degree on the time of illumination for the 2 photocatalytic materials is represented in Table 2.

The dependence is initially almost linear tending to a plateau (4th – 5th hour) indicating probable deactivation that could be due either to some impurities in the chlorophenol or to some kind of polymerization of the chlorophenol on the surface in view of its two functional groups and possible interaction with the surface hydroxyl groups on TiO$_2$.

Table 2. Comparison of the degree of 4-chlorophenol conversion as a function of the time interval of illumination in [mg C/L], measured with total organic carbon analyzer (TOC Shimadzu VCSH) over 0.5%Au/TiO$_2$, Degussa P25 (Spain) at initial concentration 350 mgC/L and Degussa P25 (Bulgaria Conc 63 mgC/L).

Photocatalyst Sample	Degree of conversion of 4-chlorophenol (%) as a function of the time interval of illumination				
	1 hour	2 hours	3 hours	4 hours	5 hours
Sample 1 Au/TiO$_2$ Degussa	11.6%	14.1%	17.7%	23.9%	26.1%
Sample 2 - Spain TiO$_2$ Degussa P25	9.7%	11.3	14.8%	17.1%	20.7%
Sample 3 - BG Degussa P 25	8.9%	10.2%	12.7%	16.3%	19.5%

CONCLUSIONS

The gold-doped photocatalytic material 0.5%Au/TiO$_2$ exceeds TiO$_2$ Degussa P25 in its photocatalytic performance in the reaction of air purification from ethylene in heavy duty experiments (5% feed C_2H_4 concentration) in all photocatalytic activity testing experimental runs – under UV-C, UV-A and visible light illumination in continuous flow experiments (Plug Flow Reactor PFG, operation in the diffusion region). The configuration of the reactor was improved by including gas – flow circulation pump and a GC flow splitter to achieve operation in the kinetic region. The role of the gold nano-particles is to serve as electron traps of photoexcited electrons, preventing their recombination with the positively charged holes in the TiO$_2$. In this way the photonic efficiency (quantum yield) is increased as the holes have longer lifetime - the Schottky barriers at the metal/oxide inter-phase boundary are blocking the return of the photo-excited electrons to the oxide phase. Thus the holes, being the photocatalytically active sites for oxidation reactions, prolong their lifetime and increase their turnover number. It is more difficult to explain the visible light activity – in TiO$_2$ Degussa it is due to the rutile phase having a band gap of 3.0 eV, activated by visible light and it is not very high (3%). The extension of the light absorption band edge to visible light in the presence of gold nanoparticles is yet to be explained.

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ОФОРМЛЕНИЕ НА ЕКСПЕРИМЕНТАЛНАТА КОНФИГУРАЦИЯ ЗА ИЗМЕРВАНЕ НА ФОТОКАТАЛИТИЧНАТА АКТИВНОСТ НА Au/TiO_2 ЗА ОЧИСТКА НА ВЪЗДУХ И ОТПАДЪЧНИ ВОДИ

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(Резюме)

Синтезиран бе фотокаталитичен материал, представляващ 0.5т% Au/TiO_2, с прилагането на метода отлагане-утаяване (DP), използувайки търговски продукт TiO_2 (Дегуса P25) модифицирайки го с наноразмерни златни частици. Прахообразният материал има специфична площ на повърхността 52 м^2/г измерена по едноточковия БЕТ метод. Суспензията на Au/TiO_2 бе отложена като покритие върху Al плака за тънкослойна хроматография, с предварително нанесено покритие от SiO_2. Покритието бе охарактеризирано със сканиращ електронен микроскоп (СЕМ), при което бе наблюдавано равномерно разпределение на TiO_2 върху SiO_2 слой. ТПР профилът показа присъствие на оксидни форми около наноразмерните златни частици и преобразуването на част от Ti^{4+} йони в Ti^{3+} йони, което се подпомага от присъствието на метално злато в непосредствена близост. Фотокаталитичната активност на материала за очистване на въздух, замърсен с етилен, бе измерена в плосък плочест проточен газофазен фотокаталитичен реактор, окомплектован с делител на потока. Ефективността на суспензия от Au/TiO_2 бе тествана за очистване на отпадни води, замърсени с моделен замърсител 4-хлорфенол в полустатичен суспензионен реактор. И двата типа фотокаталитични експеримента показаха, че TiO_2 дотиран със златни частици превъзхожда по своето действие търговския фотокатализатор на фирмата Дегуса (TiO_2 P25) поради разделянето на носителите на заряди, при което се предотвратява рекомбинацията на положително заредени дупки и фотовъзбудени електрони.