

# Influence of the size of gold nanoparticles deposited on TiO<sub>2</sub> upon the photocatalytic destruction of oxalic acid

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## Abstract

The commercially available TiO<sub>2</sub>-photocatalyst (Degussa P25) was modified with nanosized gold particles by the photoreduction method at four different values of the pH factor of the medium. The characterization of the synthesized catalysts was carried out by the BET method, X-ray photoelectron spectroscopy (XPS), TEM and the adsorption of the model pollutant. A remarkable influence of the pH on the particle size of Au was registered upon investigating the catalysts by XPS and TEM methods. The size of the gold nanoparticles on the TiO<sub>2</sub> surface decreases with increase in the pH of the medium. The degradation of oxalic acid has been studied in aqueous solution photocatalyzed by band-gap-irradiated TiO<sub>2</sub>, modified with nanosized gold particles. The photocatalytic activity of TiO<sub>2</sub>, modified with gold, was found to increase with the decrease of the size of the gold nanoparticles on the surface of the photocatalytic material. The maximal value of the photocatalytic activity (twice higher than that of the semiconducting support) is registered in the case of gold photoreduction at pH 7. The adsorption properties of the catalysts, as well as the size of the noble metal nanoparticles on the surface of the support, influence the efficiency of the photocatalytic process. The reaction rate of photocatalytic degradation of the oxalic acid follows a zero kinetic order according to the Langmuir–Hinshelwood model. The increase of the quantum yield of the photodestruction reaction of the studied model pollutant is due to the formation of Schotky barriers on the metal–semiconductor interface, which serve as efficient electron traps, preventing the electron–hole recombination.

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**Keywords:** Gold nanoparticles; TiO<sub>2</sub>; Photocatalytic decomposition; Oxalic acid; XPS; TEM

## 1. Introduction

TiO<sub>2</sub> heterogeneous photocatalysis has been the subject of numerous investigations recently as it is an attractive technique for the complete destruction of undesirable contaminants both in aqueous [1–4] and gaseous phase [5–7] by using solar or artificial light illumination. Titania photocatalysis advantages, such as strong resistance to chemical and photocorrosion, low operational temperature, low cost, significantly low energy consumption, have led the relevant applications to the stage of commercialization [1,8]. Upon band-gap excitation of TiO<sub>2</sub>, the photoinduced electrons and positively charged holes can respectively reduce and oxidize the species, adsorbed on the semiconductor particles. The high degree of recombination between photogenerated electrons and holes is a major rate-limiting factor controlling the photocatalytic efficiency [9]. The improvement

of the photocatalytic activity of TiO<sub>2</sub> is one of the most important aspects of heterogeneous photocatalysis. Attempts to increase the TiO<sub>2</sub> efficiency have been made by doping and coating with transition metals or noble metals [10–16], combining the effect of two semiconductors or covering the surface with dye microcrystallites to increase the optical absorption in the visible range [17–24]. The usual methods for the modification of TiO<sub>2</sub> with noble metals are deposition–precipitation [12,13] and photodeposition [10,11,15,16,25–30]. The latter technique was reported to yield more active photocatalysts [25]. The photodeposition process involves the reduction of noble metal ions by the conduction band electrons, the anodic process being the oxidation of water by valence band holes [11,16,26,27,31]. Some oxidizable additives (sacrificial electron donors) such as acetate, formaldehyde, methanol, 2-propanol or oxalic acid are generally added to improve the rate of photodeposition [15,29,32,33].

The photocatalytic destruction of oxalic acid has been studied in the presence of gold modified TiO<sub>2</sub>. The modifying with the noble metal at different pH values of the medium was accomplished by the photoreduction method upon irradiation of the

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sample with UV-light. The aim of the study was to investigate the influence of pH of the medium on the size of the Au nanoparticles, deposited on TiO<sub>2</sub> and how this factor is reflected upon the quantum yield of the redox process photocatalyzed by the metallized samples. The photocatalytic activity of the samples, modified with gold, prepared by the photoreduction method has been compared to that of the samples, obtained by the deposition–precipitation method.

## 2. Experimental

### 2.1. Materials and preparation of photocatalysts

TiO<sub>2</sub> (Degussa, P25) was used as a starting photocatalytic material. Hydrogen tetrachloroaurate(III), HAuCl<sub>4</sub>·3H<sub>2</sub>O and oxalic acid (Aldrich) were used without any further purification. The TiO<sub>2</sub>, modified by gold particles was prepared by two different methods—the photoreduction method [29,33] and the deposition–precipitation method [12,13]. The amounts of Au loaded was 1.0 wt.% with respect to the TiO<sub>2</sub> amount.

The procedure of photoreduction method is as follows. For each metallized sample a 5 g amount of TiO<sub>2</sub> was dispersed into 500 ml of HAuCl<sub>4</sub>·3H<sub>2</sub>O solution in bidistilled water, with a respective concentration to ensure 1% noble metal on the supports. Upon anchoring the Au onto TiO<sub>2</sub> methanol was added as a sacrificial donor (at a molar ratio methanol: noble metal salts = 500:1). The pH values of the suspensions are adjusted prior to the starting of process of photoreduction of the metal salt. The pH 3 of the suspensions was adjusted by adding 0.1N HCl, while the value of pH 5 is achieved by adding a solution of 0.1 N Na<sub>2</sub>CO<sub>3</sub>. At pH 3 and pH 5 values the zeta potential of TiO<sub>2</sub> was positive and it was easy to adsorb AuCl<sub>4</sub><sup>−</sup> anion. In the course of catalyst preparation in these cases the reaction system was being stirred at room temperature for at least 2 h with a nitrogen flow at a rate of 100 ml/min bubbling through it to remove the oxygen from the solution and to achieve maximal adsorption of the metal salt on the surface of TiO<sub>2</sub>. Upon preparing the catalysts at higher pH values (pH 7 or 9) the reaction system was being stirred at room temperature with a nitrogen flow at a rate of 100 ml/min bubbling through it for a short time interval (15 min) as in the case of these pH values there starts a precipitation of Au(OH)<sub>n</sub>Cl<sub>4−n</sub>. The pH values of the suspensions are adjusted by adding of 0.1 N Na<sub>2</sub>CO<sub>3</sub> solution. A 4 W capacity

UV-C lamp (Philips, TUV 4W) located inside a quartz tube, situated horizontally in the photodeposition reactor was used as the light source. The slurry was then irradiated with the UV-light for about 5 h upon continuous stirring and nitrogen bubbling. The precipitate was washed with bidistilled water and then dried at 383 K for 12 h.

The procedure of gold deposition–precipitation on TiO<sub>2</sub> particles is as follows [13]. Five gram of the titania support was added to an aqueous solution of HAuCl<sub>4</sub> (200 ml) with a respective concentration to ensure 1% noble metal on the support. The pH 7 of the suspensions was adjusted by adding 0.1 N Na<sub>2</sub>CO<sub>3</sub> solution. The reaction system was being stirred at room temperature for 3 h. The solid product was washed with bidistilled water until no traces of chloride were detectable by titration with silver nitrate. It was then calcined in air for 5 h at 573 K.

### 2.2. Characterization of the photocatalysts

The BET specific surface area of the unmodified TiO<sub>2</sub>-powder material was reported by the producer to be 50 m<sup>2</sup>/g for Degussa P25. The metallized catalyst samples showed no change in the specific surface area within the accuracy of the measurement (Table 1).

The adsorption of oxalic acid on the pure TiO<sub>2</sub> and on the samples, prepared by modifying TiO<sub>2</sub> with gold at various pH was measured at pH 3. For every experimental run an amount of 600 mg of each photocatalytic material was added to 600 ml of the oxalic acid solution (8.5 × 10<sup>−3</sup> mol/L). The suspension of catalyst was then magnetically stirred for 60 min at 293 K, in the dark and in the absence of oxygen. Afterwards the photocatalytic material was separated by filtering. The residual oxalic acid concentration was measured in the filtrate by TOC analyzer Shimadzu VCSH using high sensitivity catalyst (4 ppb–50 ppm) and regular catalysts (50–1000 ppm) so the amount of pollutant adsorbed on the catalyst sample was evaluated based on the C<sub>0</sub>–C difference (Fig. 1). The adsorption of oxalic acid on all of the studied samples (μmol/g catalyst) is presented in Table 1.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG ESCALAB MK II spectrometer under UHV conditions (base vacuum: ~10<sup>−8</sup> Pa). Mg Kα radiation was used as the X-ray source. The carbon 1s line (a binding energy of 284.8 eV) has been used to calibrate the binding-energy scale for the XPS measurements. The intensity of the

Table 1

Physical properties of the photocatalyst samples, zero-order reaction rate constants ( $k_r$ ) and initial photonic efficiency ( $\xi_0$ ) of photocatalytic decomposition of oxalic acid

Catalyst sample	Au loading pH	Method	BET specific surface area (m <sup>2</sup> /g)	Average metal particle size (nm)	Adsorption of oxalic acid (μmol/g catalyst)	$k_{app}$ (mmol/(L min))	$\xi_0$ (%)
None	–	–	–	–	–	No	–
TiO <sub>2</sub>	–	–	50	–	850	0.028	0.76
1% Au/TiO <sub>2</sub>	3	PR	49	18	590	0.029	0.79
1% Au/TiO <sub>2</sub>	5	PR	49	9	500	0.055	1.49
1% Au/TiO <sub>2</sub>	7	PR	47	5	430	0.069	1.87
1% Au/TiO <sub>2</sub>	9	PR	46	4	450	0.062	1.68
1% Au/TiO <sub>2</sub>	7	PD	48	5	440	0.064	1.74

The gold was loaded on TiO<sub>2</sub> by the photoreduction method (PR) and deposition–precipitation method (PD).

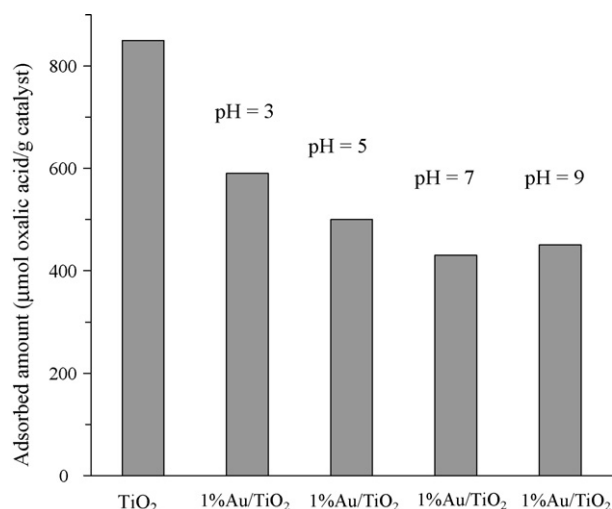


Fig. 1. Total amount of oxalic acid adsorbed on TiO<sub>2</sub> at pH 3 and noble metal modified TiO<sub>2</sub> materials prepared at various pH factor values of the medium.

XPS peaks of gold, attached to the surface of TiO<sub>2</sub> (Au 4f<sub>5/2</sub>, Au 4f<sub>7/2</sub>) is calibrated with respect to the intensities of the XPS peaks of TiO<sub>2</sub> (Ti 2p<sub>3/2</sub>) recorded with each one of the studied samples (Fig. 2A). The XPS peaks of the TiO<sub>2</sub> modified with gold (Au 4f<sub>5/2</sub>, Au 4f<sub>7/2</sub>) and their relative intensity are represented in Fig. 2B.

The surface morphology, roughness and fractality of the gold/titania films were examined with a Transmission Electron

Microscope JEOL JEM 100B. The average metal particle size was determined statistically by counting manually at least 30 particles. The TEM micrograph of noble metal modified TiO<sub>2</sub> photoreduced at pH 3 and 7 are shown in Fig. 3a and b. The average size of the Au nanoparticles, attached to the TiO<sub>2</sub> surface at various pH of the suspension of all the samples are represented in Table 1.

### 2.3. Photocatalytic experiments

A cylindrical Pyrex glass batch reactor was used for the photocatalytic experiments. The initial volume of the irradiated reaction mixture was 600 ml in all the experimental runs. The irradiation source was a 9 W UV-A lamp (Philips PL-S 2P) located inside a quartz tube, situated horizontally in the reactor. The spectral response of the irradiation of the UV lamp, according to the producer, ranged between 350 and 400 nm with a maximum at 366 nm. A light intensity of 7 mW/cm<sup>2</sup> has been determined with a microprocessor-controlled radiometer (Cole Parmer, 97503-00) with 365 nm sensor. The suspension of the photocatalytic material was stirred magnetically and oxygen was being bubbled continuously prior to and in the course of the irradiation at a flow rate of 12 dm<sup>3</sup>/h. Previous experimental runs had shown that increasing the flow rate above this value does not increase the reaction rate with all the studied samples i.e. at this value we reach saturation of the aqueous solution with dissolved oxygen. The catalysts had been treated in advance

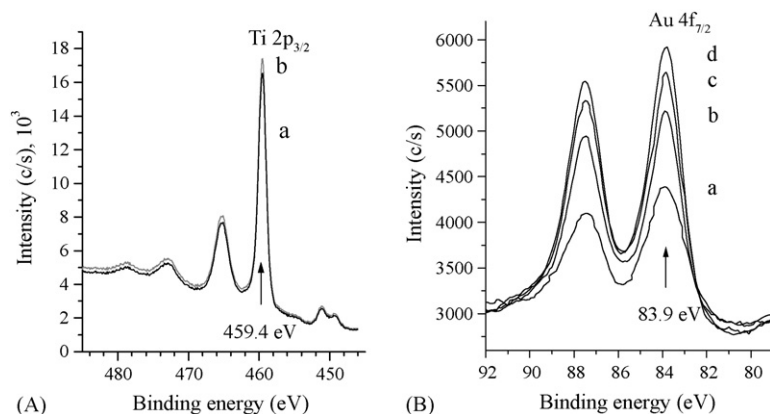


Fig. 2. XPS peaks of Au/TiO<sub>2</sub> samples. (A) Ti 2p photoelectron peaks: (a) Au loaded on TiO<sub>2</sub> at pH 7; (b) Au loaded on TiO<sub>2</sub> at pH 3. (B) Au 4f photoelectron peaks: (a) photoreduction of Au at pH 3; (b) photoreduction of Au at pH 5; (c) photoreduction of Au at pH 7; (d) photoreduction of Au at pH 9.

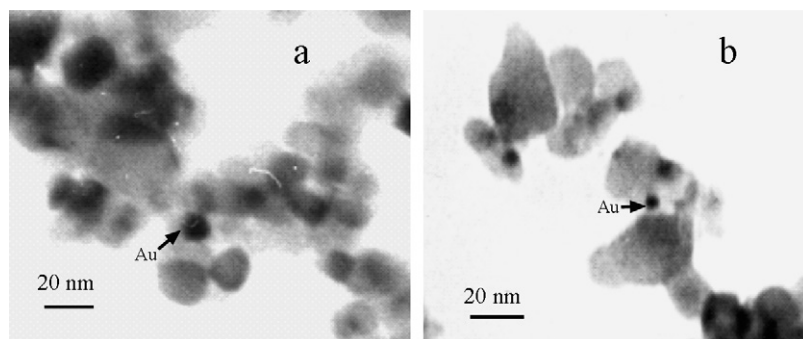


Fig. 3. TEM micrograph of Au modified TiO<sub>2</sub>. Photoreduction of the noble metal at: (a) pH 3; (b) pH 7.

in an ultrasonic bath. The oxidation process was performed at 293 K and pH 3. In all cases the reaction mixture contained 600 mg of the catalyst powder and 600 mL of aqueous oxalic acid ( $8.5 \times 10^{-3}$  mol/L) solution and it was stirred for 30 min in the dark in order to adsorb the substrate. After irradiation with UV-light for specific time intervals samples of the dissolved oxalic acid were withdrawn from the reactor and the mineralization degree of the pollutant was analyzed by means of a TOC analyzer model VCSH (Shimadzu, Japan).

The following equation has been used for calculation of the initial photonic efficiency [2]:

$$\xi_0 (\%) = r_0 I_{hv}^{-1} \times 100 \quad (1)$$

where  $r_0$  is the initial degradation reaction rate (mol/(L min)) and  $I_{hv}$  is the incident photon flux at  $\lambda = 370$  nm (mol photons/(L min) = einstein/min). The results are represented in Table 1.

### 3. Results and discussion

The specific surface area of the catalysts, the degree of crystallinity of TiO<sub>2</sub> and the size of the metal clusters on the surface of the TiO<sub>2</sub> influence substantially the catalyst efficiency in regard to the photodestruction of water contaminants [13,16,29]. In spite of the fact that there is no measurable effect on the specific surface area of TiO<sub>2</sub>, after modifying it with Au, the adsorption of the oxalic acid on the modified sample is lower (Table 1). This is owing to blocking of the adsorption sites of TiO<sub>2</sub> by the Au particles, attached to the surface of the photocatalyst. The adsorption of organic contaminants on the surface of the noble metal is much weaker than that on TiO<sub>2</sub>. The observed lower adsorption rate of oxalic acid on the Au loaded TiO<sub>2</sub> is in accordance with the results, obtained by other authors [16,28,29,34,35].

After preparing the fresh photocatalytic samples, prepared by the photoreduction method, the XPS peaks of the nanosized gold particles, attached to the TiO<sub>2</sub> surface, are registered at 83.9 eV (Au 4f<sub>7/2</sub>) (Fig. 2). The same value of the binding energy for Au 4f<sub>7/2</sub> was registered with the sample, prepared by gold deposition on the TiO<sub>2</sub> surface using deposition–precipitation method. The position of the XPS peaks is not changed after carrying out the photocatalytic degradation reaction of oxalic acid. The XPS peak of Au 4f<sub>7/2</sub> (83.9 eV) indicates that the superficially attached gold is reduced to metallic Au<sup>0</sup>. In the case of photoreduction of a metal salt on the surface of TiO<sub>2</sub>, the pH of the medium exerts a remarkable influence on the intensity of the XPS peaks of Au (4f<sub>5/2</sub>, 4f<sub>7/2</sub>). Upon increasing the pH of the medium the intensity of the XPS peaks of Au grow up (Table 1), which is indirect evidence for a decrease of the size of the metal nanoparticles, attached to TiO<sub>2</sub>. The sampling depth of XPS is between 1 and 5 nm, so the increased Au 4f signal (Fig. 2) indicates that gold is dispersed into smaller Au nanoparticles. This fact is confirmed by TEM measurements of Au/TiO<sub>2</sub> samples, whose average size is listed in Table 1.

The change in the concentration of total organic carbon (TOC) as a function of the illumination time, characterizing

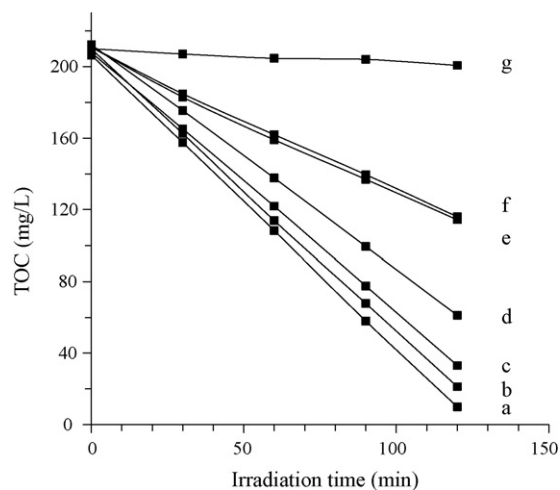


Fig. 4. Total mineralization of oxalic acid ( $8.5 \times 10^{-3}$  mol/L) at pH 3 in the presence of Au/TiO<sub>2</sub> samples. Catalysts: (a) photoreduction of Au at pH 7; (b) Au attached by deposition–precipitation method at pH 7; (c) photoreduction of Au at pH 9; (d) photoreduction of Au at pH 5; (e) photoreduction of Au at pH 3; (f) TiO<sub>2</sub> Degussa P25; (g) absence of catalyst.

the degree of destruction of the oxalic acid in the presence of the studied photocatalytic materials, is represented in Fig. 4. A significant increase in catalytic activity relative to unmodified titania was observed for all samples modified with Au (Table 1). Only the photocatalytic activity of the Au/TiO<sub>2</sub> sample, obtained at pH 3 does not differ from that of TiO<sub>2</sub> Degussa P25 (Fig. 4). The main reasons for the absence of any effect of gold loading on the photocatalytic activity of TiO<sub>2</sub> are both the decrease in oxalic acid adsorption as well as the smaller number of gold nanosized particles on the surface of the photocatalyst due to their bigger size (Table 1). In view of the fact that the photocatalytic process of oxalic acid degradation occurs basically on the TiO<sub>2</sub> surface, where HO• radicals are generated, the adsorption of the contaminant on TiO<sub>2</sub> and its local concentration surrounding the photocatalyst particle, exert a substantial influence on the occurring photocatalytic process. The effect of the pollutant adsorbability and of the noble metal particle size attached to TiO<sub>2</sub> upon the photocatalytic activity have already been discussed in the literature [13,29]. The increase in pH of medium in the case of photoreduction of the golden salt on TiO<sub>2</sub> surface and the respective decrease in the size of the Au nanoparticles result in growing up of the photocatalyst activity (Table 1). In this case, the dominating effect on the photocatalytic activity is based on a more efficient charge separation of the light generated electron–hole pairs in the semiconductor owing to the greater number of metal nanoparticles, which play the role of effective traps for the electrons. The effects of hampered band-gap excitation of TiO<sub>2</sub> and lower adsorption degree of oxalic acid and water, due to the higher degree of covering the TiO<sub>2</sub> surface by Au nanoparticles, acting in opposite direction onto the photocatalytic activity, are not so well expressed. The lower photocatalytic activity for the Au/TiO<sub>2</sub> sample (Fig. 4), obtained after photoreduction of AuCl<sub>4</sub><sup>-</sup> at pH 9 is most probably due to the very fast precipitation of Au(OH)<sub>n</sub>Cl<sub>4-n</sub>, whereupon a part of the reduced gold is not attached to the TiO<sub>2</sub>. An indication for this fact is the promoted adsorption of the oxalic acid on



the catalyst (Fig. 1). The photocatalytic activity of the Au/TiO<sub>2</sub> sample, prepared by the deposition–precipitation method at pH 7 is close to that of the photocatalyst prepared on basis of the photoreduction method at the same pH medium (Fig. 4). This is explicable, taking into account the adsorption properties of the two catalysts, the close size of the golden nanoparticles and the degree of their reduction (Au<sup>0</sup>) on the surface of TiO<sub>2</sub>.

It is known [2,29,34,35] that the rate of photocatalytic degradation of organic pollutants is described by the Langmuir–Hinshelwood kinetic model, modified to describe reactions occurring on the solid–liquid interphase surface:

$$r_0 = \frac{dC}{dt} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \quad (2)$$

where  $r_0$  is the initial rate of disappearance of the organic substrate,  $k_r$  is the limiting step rate constant of reaction at maximum coverage degree under the given experimental conditions,  $K$  is the reactant adsorption constant and  $C_{eq}$  is the equilibrium bulk-solute concentration.

Under the conditions of photocatalytic oxidation of oxalic acid (initial pollutant concentration  $C_0 = 8.5 \times 10^{-3}$  mol/L and photocatalyst content 1 g TiO<sub>2</sub>/L) the photocatalytic degradation reaction rate with all the studied samples is described by a zero order kinetic equation with respect to the pollutant. This is an indication that the photocatalytic degradation reaction rate is independent of the oxalic acid adsorption coverage [29,34]. In the case when  $K C_{eq} \gg 1$  the Eq. (2) is transformed into the following integral form of a zero-order limiting step rate expression:

$$C_0 - C = k_r t \quad (3)$$

where  $C_0$  is the initial concentration of the oxalic acid and  $C$  is the concentration at a given moment of time.

Since the photocatalytic oxidation rate of oxalic acid is described by a zero kinetic order with respect to the pollutant, the evaluation of the amount of pollutant adsorbed upon light irradiation is not possible based on the standard kinetic methods [2,35]. There are reasons to suppose that the tendency of lower adsorption extend of the contaminant in the dark upon decreasing the size of Au nanoparticles, attached to TiO<sub>2</sub> (Fig. 1) is also preserved when photooxidative destruction is proceeding.

Fig. 5 shows a plot of  $C_0 - C$  versus the time for all the experiments of photocatalytic decomposition of oxalic acid. It is seen that a maximum in the photoreaction rate constant  $k_r$  was observed with the samples, for which the photoreduction of the metal salt had been carried out at pH 7 (Fig. 5). In this case, the reaction rate exceeds that of bare titania by a factor of 2 (Table 1).

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

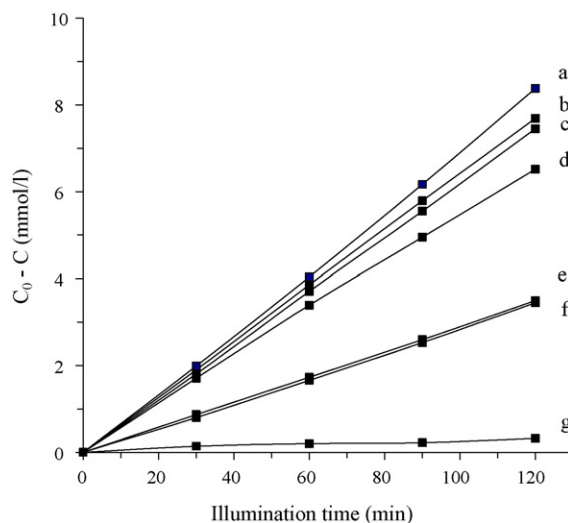
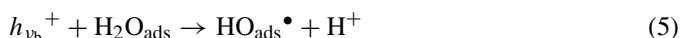
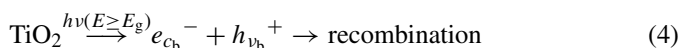
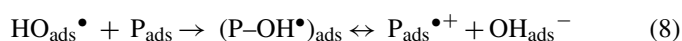
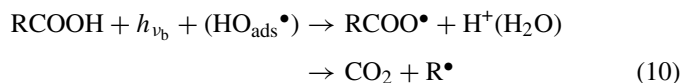


Fig. 5. Zero order kinetics of oxalic acid degradation ( $8.5 \times 10^{-3}$  mol/L) at pH 3 in the presence of Au/TiO<sub>2</sub> samples. Catalysts: (a) photoreduction of Au at pH 7; (b) Au anchored by deposition–precipitation method at pH 7; (c) photoreduction of Au at pH 9; (d) photoreduction of Au at pH 5; (e) photoreduction of Au at pH 3; (f) TiO<sub>2</sub> Degussa P25; (g) absence of catalyst.



where  $c_b$  and  $v_b$  are the conduction band and the valence band of TiO<sub>2</sub>, while P is the 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 of electrons due to the formation of superoxide radical anions according to Eq. (9). Oxidation by holes (Eq. (7)) is favoured by molecules that adsorb easily on the photocatalyst. On the other hand, HO<sup>•</sup> radicals are either able to react on the interface or to diffuse away from the semiconductor particle (Eq. (8)), and to react with organic molecules in solution. The photodecomposition of oxalic acid follows Eq. (7), taking into account the good adsorption of the pollutant on the support, but it can decompose also in the bulk of the solution. The mineralization of the oxalic acid, which proceeds via series of parallel and consecutive reactions, is accomplished simultaneously by the occurring redox processes described by Eqs. (7) and (8).

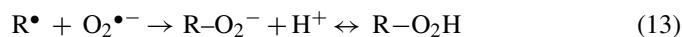
For carboxylic acids [16,32,34] such as oxalic acid, the anodic process leads via Eqs. (7) and (8) to decomposition of the pollutant according to the following principle scheme:



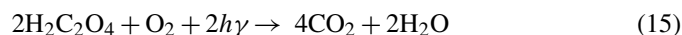
In acidic medium the superoxide radical anion O<sub>2</sub><sup>•−</sup> (Eq. (9)) can also contribute to the degradation of the oxalic acid:



As the mineralization of the oxalic acid proceeds via series of parallel and consecutive reactions it is very probable that the process of photodestruction also involves the occurring secondary interactions between  $R^\bullet$  (Eq. (10)) and  $O_2^{\bullet-}$  leading to formation of peroxides:



The stoichiometry of photocatalytic destruction of oxalic acid following Eqs. (7), (8), (10), (13) and (14) is the following:



The difference in the total rates of oxalic acid photooxidation is due to differences in the rates of the elementary steps in the presence and absence of noble metal. In the case of  $TiO_2$  upon its band-gap excitation the high degree of recombination between photogenerated electrons and holes is a major rate-limiting factor controlling the photocatalytic efficiency [9]. Deposits of nanosized noble metal particles on the surface of the  $TiO_2$  lead to an efficient charge separation of the light generated electron–hole pairs in a semiconductor and to an increase of the lifetime of the photogenerated pairs allowing longer time intervals to diffuse to the surface [16,36,37]. Noble metal nanoparticles are very effective traps for the electrons due to the formation of a Schottky barrier at the metal–semiconductor contact. On the other hand in oxidative photocatalytic reactions in the presence of molecular oxygen the metal doping promotes the rate-limiting cathodic step (Eq. (9)), i.e., reduction of  $O_2$  by conduction band electrons [38]. It could be assumed that upon depositing noble metal nanoparticles on the surface of the  $TiO_2$  the increase of the quantum yield of the photodestruction reaction of the studied pollutant is mainly due to the increased separation of electrons and holes, the higher rate of  $HO^\bullet$  radicals formation and facilitated oxygen reduction, which could be the rate-limiting step of the oxidation reactions (Fig. 6).

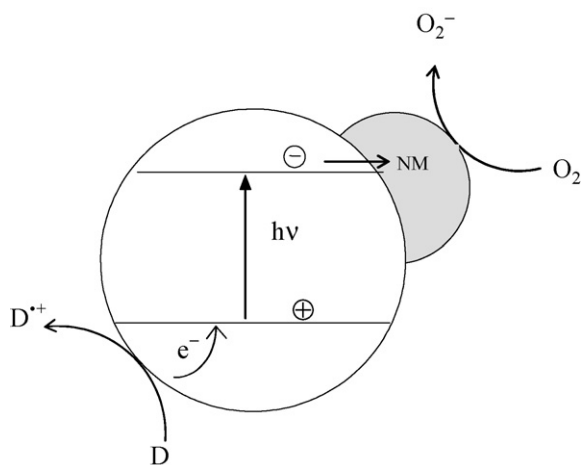


Fig. 6. Schematic representation of electron capture by a noble metal (NM) particle in contact with a semiconductor surface. D: donor molecule ( $H_2O$  or pollutant).

## 4. Conclusions

Upon modifying  $TiO_2$  with Au nanoparticles the rate of photocatalytic destruction of oxalic acid is increased in comparison to that on the pure  $TiO_2$ . Remarkable influence of the pH on the particle size of Au was registered upon attaching gold on the  $TiO_2$  surface by photoreduction. The dimensions of the gold nanoparticles on the surface of  $TiO_2$  decreases upon increasing the pH of the medium. The photocatalytic activity of  $TiO_2$ , modified with gold, was found to increase with the decrease of the gold nanoparticles size on the surface of the photocatalytic material. The maximum in the photocatalytic activity (twice higher than that of the semiconducting support) is registered in the case of gold photodeposition at pH 7. Dominant influence upon the photocatalytic activity of Au/ $TiO_2$  samples is exerted by the more efficient charge separation of the light generated electron–hole pairs in the semiconductor owing to the increased number of metal nanoparticles, which serves as effective traps for the electrons. The effects of the hampered band-gap excitation of  $TiO_2$  and decreased amount of adsorbed oxalic acid and water due to the higher degree of  $TiO_2$  surface coverage by Au nanoparticles act upon the photocatalytic activity in opposite directions and are therefore weakly exressed.

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