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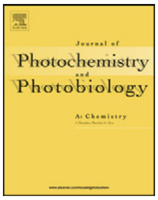

Photocatalytic oxidation of 2,4,6-trinitrotoluene in the presence of ozone under irradiation with UV and visible light

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ABSTRACT

The photooxidation of 2,4,6-trinitrotoluene (TNT), catalysed by nanosized photocatalysts: TiO_2, WO_3/TiO_2, Au/TiO_2 and $Au/WO_3/TiO_2$ was studied under irradiation with UV or visible light in the presence of O_2 or O_2–O_3 mixture. The photocatalysts were characterized by the BET, XPS, TEM methods and adsorption of the model pollutant. The effectiveness of the processes of under UV-A, UV-C and visible light irradiation destruction in the presence of O_3, photocatalysed by the WO_3/TiO_2, Au/TiO_2 and $Au/WO_3/TiO_2$ samples is considerably higher than that registered in process, occurring with pure TiO_2. Thus in the presence of O_3 the rate constants of 2,4,6-trinitrotoluene photooxidation under UV-A, UV-C and visible light irradiation catalysed by $Au/WO_3/TiO_2$ are respectively 2.1, 1.4 and 6.2 times higher than that registered with pure TiO_2. On the other side the ozone rate constants of 2,4,6-trinitrotoluene photooxidation under UV or visible light irradiation are also much higher than those, registered in the presence of O_2 only. Thus under UV light irradiation the O_3 rate constants of 2,4,6-trinitrotoluene photooxidation, catalysed by $Au/WO_3/TiO_2$ are 6 times higher, while under visible light they are 11 times higher than those with oxygen only. Under irradiation with UV-A, UV-C and visible light in the presence of ozone a synergistic effect has been registered, expressed most strongly in the case of TNT destruction, photocatalysed by $Au/WO_3/TiO_2$. Doping of the semiconductor materials with gold nanoparticles increases 1.4–2.2 times the rate constants of 2,4,6-trinitrotoluene mineralization, compared to the undoped samples, which is due to more efficient separation of the electron–hole charges generated upon irradiation.

1. Introduction

Among advanced oxidation processes (AOPs), heterogeneous photocatalysis has proved to be of real interest as an efficient tool for degrading both aquatic and atmospheric organic contaminants [1]. Heterogeneous photocatalysis with TiO_2 nanosized photocatalysts has been the subject of numerous investigations in the last 30 years [2–9]. Upon band gap excitation of TiO_2, the photoinduced electrons and positively charged holes can respectively reduce and oxidize the species, adsorbed on the semiconductor particles. A major disadvantage of most semiconductor materials is the high degree of recombination between the photogenerated charge carriers, which ultimately decreases the photocatalyst effectiveness in the redox process. One of the approaches to increase the efficiency of the processes of destruction of contaminants in water, catalysed by semiconductor photocatalysts, is to carry out these processes in the presence of ozone [10].

The subject of the study is the photooxidation process of 2,4,6-trinitrotoluene (TNT) in the presence and in the absence of ozone. TNT is one of the most stable and recalcitrant explosives and it does not occur naturally in the environment. TNT has contaminated groundwater and soil at numerous sites that are located in explosive manufacturing plants, packing, storage and military-related facilities [11,12]. TNT is toxic, mutagenic and a suspected carcinogen, with an EPA lifetime health advisory of 2 μg/L [13]. In addition to the toxicity of TNT, it has been known that its metabolites are equally or even more toxic than the initial contaminant [14]. Therefore, TNT degradation has attracted the attention of many scientists in the last decade. The application of advanced oxidation processes such as Fenton process, Fenton-like processes, the UV/H_2O_2 process and UV/O_3 process aimed at the degradation of TNT have been discussed in a review paper published recently [15]. In all of these AOPs processes there occurs generation of strong oxidants, such as hydroxyl radicals, assisting the destruction of TNT. Among the studies on the AOPs processes significant attention has been focused on the oxidative photocatalytic destruction of TNT, catalysed by TiO_2-based photocatalytic materials in the presence of O_2 [16–18] or TiO_2 photocatalysis combined with the presence of H_2O_2 [19].

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The UV/TiO_2/O_3 version of the TiO_2 photocatalytic processes is based on attractiveness of using ozone for organic contaminant removal, which includes a relatively higher scavenging effect provided by the ozone, capability to decrease the rate of de-excitation of electrons and the elimination of residues. The combined ozonation–photocatalysis process provides a double benefit, comprising both disinfection and removal of persistent organic contaminants [10,20,21]. As far as the photocatalytic destruction of TNT in the presence of ozone is concerned the studies until now have been focused mainly on the TiO_2 photocatalyst under UV-light irradiation [15,22,23]. It has been shown that in the presence of ozone the processes of destruction are accelerated and this effect is dependent on a series of parameters in the realization of the photocatalytic process: the ratio between the contents of TNT and the photocatalytic material, the pH factor of the medium, the concentration of ozone in the O_2–O_3 mixture, etc. Synergistic effect has been registered upon coupling photocatalysis with ozonation in a series of cases of organic contaminants [24]. The study on other kinds of photocatalytic materials having semiconducting properties, as well as the option to carry out the photocatalytic process of TNT destruction in the presence of ozone using visible light has received little attention so far in the literature.

The purpose of this work was to check the occurrence of a synergistic effect upon coupling photocatalysis and ozonation process in the case of TNT both under UV and visible light irradiation. Several photocatalytic samples have been prepared and tested with respect to their photoactivity: pure TiO_2, WO_3/TiO_2 as well as the corresponding gold (Au^0) modified materials, Au/TiO_2 and Au/WO_3/TiO_2. The basic task of this investigation was to juxtapose the process effectiveness with the above samples in the presence of O_3 with that of the process over pure TiO_2 and to elucidate the option to accomplish these processes upon visible light illumination.

2. Experimental

2.1. Materials and preparation of photocatalysts

TiO_2 (Degussa, P25) was used as the starting photocatalytic material. Tungstic acid, H_2WO_4 (Aldrich), hydrogen tetrachloroaurate(III) $HAuCl_4·3H_2O$ (Aldrich) and TNT, obtained from the High Military College "G.S. Rakovski", Bulgaria were used as received, without any further purification. Before being used, the TNT was dried for 24 h in desiccators. 120 mg/L of TNT stock standard solution was prepared by dissolving 120 mg of dried TNT into 1 L of deionized water at moderate heating for 8 h.

TiO_2 was coated with nanosized WO_3 particles (4 wt%) following the method in reference [25] with further modifications. Aqueous ammonia solution was initially added to a mixture of 0.216 g H_2WO_4 in 10 ml of water until the tungstic acid was completely dissolved. Further 5 g of TiO_2 were added under continuous stirring. The obtained mixture was stirred for 30 min and then acidified down to pH 4 using 0.5 M hydrochloric acid (Aldrich). 10 ml of an aqueous solution of oxalic acid (0.1 M) was then added to the mixture and stirred for another hour at 40 °C. The role of oxalic acid was to prevent the aggregation of WO_x particles in the precipitate – to obtain more uniform distribution of smaller amorphous WO_x particles on the TiO_2 surface [25]. Finally, the solid product was dried at 383 K for 2 h and calcined at 693 K for two further hours.

The gold-loaded semiconductor materials (0.4 wt% noble metal loading on the supports) were synthesized by the photoreduction method [8,26]. The method was accomplished as follows. For each metallized sample, 5 g of TiO_2 or WO_3/TiO_2 composite were dispersed into 500 ml solution of $HAuCl_4·3H_2O$ (0.1 mmol) in bi-distilled water. Upon anchoring the Au onto TiO_2 and WO_3/TiO_2, methanol was added as a sacrificial donor at a molar ratio of methanol to noble metal salts equal to 500:1. The pH of the suspensions was adjusted to 7 by adding a buffer solution (Fixanal, Fluka). Varying the pH, it has been reported that the Au^0 nanoparticle size was the smallest in the case of photoreduction at pH 7, whereupon the activity of the photocatalyst was the highest [26,27]. The reaction system was stirred continuously at room temperature under nitrogen bubbling (100 ml/min) to remove oxygen from the solution. Bubbling was carried out for a short time interval (15 min) to avoid undesirable consecutive reactions at these pH values [26,28,29]. The suspension under continuous stirring was irradiated for 3 h by a UV-C lamp (Philips, TUV 4 W) emitting radiation at 253.7 nm, to reduce Au^{3+} to its metallic state Au^0. Finally, the precipitate was washed with bi-distilled water and then dried at 383 K for 12 h.

2.2. Characterization of the photocatalysts

BET specific surface areas of specimens were measured by nitrogen adsorption at the liquid nitrogen boiling temperature using a Micromeritics FlowSorb II 2300 apparatus based on adsorption data in the partial pressure (P/P_0) range of 0.05–0.35.

The adsorption of TNT on the pure TiO_2, composite WO_3/TiO_2 and gold modified semiconductor materials was measured at pH 7, the pH used during the photocatalytic experiments. In each experimental run, 350 mg of photocatalytic material was added to 350 ml of an aqueous TNT solution (5.3×10^{-4} mol/L). The suspension was then stirred magnetically for 60 min at 293 K, in the dark and in the absence of oxygen to reach adsorption/desorption equilibrium. The photocatalytic material was then separated by filtration (Whatman, Grade 42). The residual TNT concentration in the filtrate was measured by using a total organic carbon (TOC) analyzer (Shimadzu VCSH) to calculate the amount of TNT adsorbed on each catalyst sample. The measurements have been carried out using the high-sensitivity Shimadzu catalyst, calibrated for the 4 ppb–50 ppm range (2% experimental error, based on the coefficient of peak variation).

X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG ESCALAB MK II spectrometer under UHV conditions (base vacuum: $\sim 10^{-8}$ Pa). Mg Kα radiation was used as the X-ray source. The carbon 1 s line (with binding energy of 284.8 eV) was used to calibrate the binding-energy scale of the XPS.

The WO_3 crystallite size in WO_3/TiO_2 composite and the size distribution of Au nanoparticles on the photocatalysts were examined with a HRTEM (JEOL JEM-3011) operated at 300 keV, equipped with a PGT energy-dispersive X-ray (EDX) solid-state detector making use of Excalibur software. The average size of WO_3 crystallites and metal particles were determined statistically based on the sizes of at least 100 particles.

2.3. Photocatalytic experiments

The photodegradation of TNT was studied in a well mixed bubble semi-batch cylindrical photoreactor (100 mm internal diameter, 120 mm height) containing aqueous suspensions of the semiconductor materials at a concentration of 1 g/L. Each catalyst was dispersed in the aqueous solution in advance by sonication for 20 min and then transferred to the reactor vessel and stirred magnetically. TNT from a stock solution was then added to achieve an initial concentration of 5.3×10^{-4} mol/L, equivalent to 38 ppm TOC. The pH of the suspensions was adjusted to 7 by adding a buffer solution (Fixanal, Fluka). The initial volume of the irradiated reaction mixture was 350 ml. Finely dispersed oxygen or oxygen-ozone feed flow mixture were bubbled continuously through a diffuser at the bottom of the reactor during the direct ozonation and the photocatalytic process at a flow rate of 12 $dm^3\ h^{-1}$, at 293 K, pH

Table 1
Physical properties of the photocatalyst samples and pseudo-first order reaction apparent rate constants (k_{app}).

Catalyst sample	BET surface area (m^2/g)	Adsorption of TNT (μmol/g catalyst) ± 2%	Experimental conditions	k_{app} ($\lambda = 254$ nm) (min^{-1}) ± 5%	k_{app} ($\lambda = 365$ nm) (min^{-1}) ± 5%	k_{app} ($\lambda > 400$ nm) (min^{-1}) ± 5%
None	–	–	O_2	No[a]	No[a]	No[a]
None	–	–	O_2–O_3	0.0019[a]	0.0019[a]	0.0019[a]
None	–	–	O_2–O_3	0.058	0.0080	–
TiO_2	50	280	O_2	–	0.0061	0.0002
TiO_2	50	280	O_2–O_3	0.0898	0.0241	0.0024
Au/TiO_2	48	251	O_2	–	0.0124	0.0002
Au/TiO_2	48	251	O_2–O_3	–	0.0333	0.0036
WO_3/TiO_2	45	317	O_2	–	0.0109	0.0007
WO_3/TiO_2	45	317	O_2–O_3	–	0.0411	0.0066
Au/WO_3/TiO_2	43	290	O_2	0.0225	0.0202	0.0013
Au/WO_3/TiO_2	43	290	O_2–O_3	0.1285	0.0510	0.0148

[a] –No UV or visible light irradiation.

7 and atmospheric pressure. The concentration of ozone in the feed O_2–O_3 was 6.7×10^{-4} mol/L. The ozone concentration at the reactor inlet and outlet was analyzed by means of an ozone analyzer BMT 964 based on the absorption of ozone at 254 nm. It has been ascertained that during the whole period of ozonation and photocatalytic oxidation in aqueous phase dissolved O_3 is contained in the water, whereupon its content has been evaluated on the basis of the reactor outlet concentrations by using values of Henry's constants [30] as it has been described in details in a previous investigation [31]. Thus the O_3 consumption during the direct ozonation and in the photocatalytic process with the studied photocatalyst samples, measured 5 min after the beginning of the process of TNT destruction is between 15% and 52%. The concentration of the ozone, dissolved in the water phase, was measured by the indigo method [32] again at the 5th minute after the beginning of the process of TNT destruction is 0.8–1.4 mg/L. This interval of values of the dissolved ozone concentrations shows that its content in the water phase depends on the rate constants of the processes occurring on the studied photocatalyst samples involving the participation of O_3. The photoreactor was equipped with a halogen lamp (Tungsram, 500 W) for visible light irradiation and with a 9 W UV lamps (Philips PL-S 2P or TUV PL-S) for UV-A or UV-C irradiation. The UV lamps were located inside a quartz tube, situated horizontally and immersed in the middle of the reactor suspension. The visible light lamp was located 12 cm above the surface of the liquid in the reactor. A 400 nm cut-off glass filter (Schott) was used to remove the radiation in the UV region emitted by the halogen lamp. The photon flux in the visible light region at the surface of the liquid was 38 mW/cm^2, determined with a YSI 9100 Photometer (Thermo Fisher Scientific). The photon flux in the UV light region at the external wall of the quartz tube was 10 mW cm^{-2} (UV-A) and 14 mW cm^{-2} (UV-C), determined with a Microprocessor-Controlled Radiometer (Cole Parmer, 97503-00) fitted with 254 and 365 nm sensors. Samples collected at regular time interval during the dark period and during irradiation were filtered and the degree of mineralization of TNT was assessed by means of a TOC analyzer, as described above.

3. Results and discussion

A number of authors have investigated coupled WO_3/TiO_2 systems under illumination with UV [33–36] or visible light [37–39] with the purpose of promoting the photonic efficiency of TiO_2 and extending the photonic absorption range of the material in the decomposition of water and air contaminants when the oxidant is only O_2. The photocatalytic activity is a counterplay of two main factors acting in the opposite directions – the mutual screening effect deteriorates the activity, while at the same time the charge separation in the composite WO_3/TiO_2 is improved. So an optimal ratio between the contents of the two components WO_3 and TiO_2 has to be found experimentally for each specific case of the different organic pollutants. Such optima have already been reported in [27,33–37,39,40] and the activity of WO_3/TiO_2 photocatalysts, under UV or visible light irradiation, was found to be the highest at 3–5 wt% optimal WO_3 content in the composite material during photooxidation of various pollutants including aromatics. For this reason 4% WO_3–TiO_2 sample was prepared in the present work and its photoactivity was tested with UV and visible light for the specific case of TNT destruction.

The gold content loaded onto semiconductor materials (0.4 wt% noble metal loading on the supports) was selected, based on previous investigations [8], which reported it to be optimal. It is generally accepted that the increase in the metal content leads to increase in the metal particle size [27] and reduction of the photocatalytic activity, which is undesirable. A number of authors have found values close to 0.4% for the optimal gold content in various cases of photooxidation of different pollutants including aromatics [29,41,42].

It is well known that the catalyst specific surface area, degree of crystallinity and size of metal clusters on the catalyst surface can affect significantly the efficiency of photodestruction of water contaminants [7,8,29]. The specific surface areas of the prepared semiconductor materials prepared are shown in Table 1. The surface area of WO_3 (10 m^2/g) reported in previous article [27] was five-fold less than the area of TiO_2 (50 m^2/g) and the surface area of the composited material WO_3 (4%)/TiO_2 (96%) (45 m^2/g) corresponded to the contribution of the two phases in accordance to their respective loading. In spite of the lower specific surface area of the WO_3/TiO_2 composite the adsorption of TNT (in the dark) (Fig. 1)

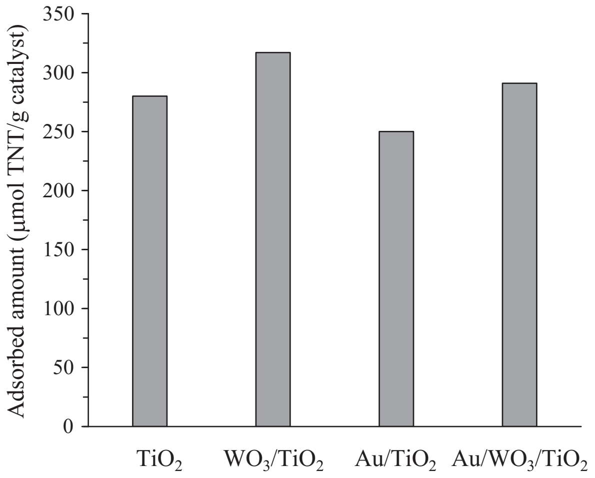

Fig. 1. Total amount of 2,4,6-trinitrotoluene adsorbed on the photocatalysts at pH 7.

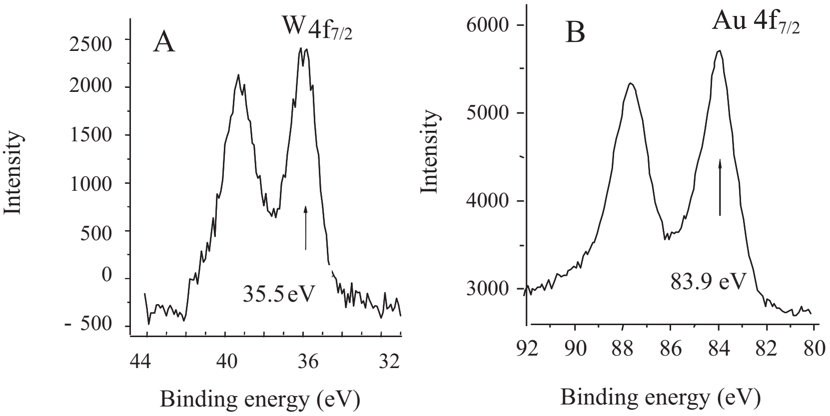

Fig. 2. XPS spectra of: (A) WO_3 in WO_3/TiO_2 composite; (B) Au modified WO_3/TiO_2.

is with 13% higher than that on pure TiO_2. The greater adsorption capacity of the pollutant on WO_3/TiO_2 can be attributed to the increased Brønsted and Lewis type of surface acidity of the composite [33,44,45]. The gold modified (0.4 wt% Au^0) materials, Au/TiO_2 and $Au/WO_3/TiO_2$ showed negligible change in the specific surface areas compared to the parent oxides (Table 1). However, gold doping affected the adsorption of TNT (in the dark) significantly, with a reduction of 9% to 11% of the equilibrium adsorption capacity with respect to the un-doped oxides (Table 1). This effect has been associated with a reduction of the external surface area of TiO_2 or WO_3/TiO_2 available for adsorption of TNT as demonstrated in previous works for the case of adsorption of another organic contaminant in water [7,8,27].

The crystalline structure of the WO_3 component and the presence of WO_3 phase in the synthesized WO_3/TiO_2 material were confirmed by the XRD studies of the samples in previous investigation [27]. The XRD pattern of the single component WO_3 photocatalyst proved monoclinic WO_3 phase [27]. In view of the same synthesis method and conditions for the composite WO_3/TiO_2 photocatalytic material we could suppose that probably the same WO_3 phase is also present in the composite.

The presence of WO_3 in the WO_3/TiO_2 material is evidenced also by the XPS peaks characteristic of the WO_3 (W $4f_{5/2}$, W $4f_{7/2}$) (Fig. 2A). The binding energy of W $4f_{7/2}$ (35.9 eV) corresponds to that specific of WO_3 (W^{6+} coordinated by oxygen atoms) [47]. The XPS spectra of Au modified TiO_2, reported in our previous studies [8,26], showed that the $AuCl_4^-$adsorbed on the surface of the TiO_2 was photoreduced into metallic Au^0 nanoparticles attached on the surface of the oxide. In the composite WO_3/TiO_2 the binding energies of Au XPS peaks (Au $4f_{5/2}$ and Au $4f_{7/2}$) positioned at 87.6 eV and 83.9 eV, demonstrate that the superficially attached gold was also completely reduced to metallic Au^0 (Fig. 2B). It has been found out in our previous investigation [27], that the Au particles were deposited both on the TiO_2 particles as well as on the WO_3 particles in the composite material and no other additional XPS peaks have been registered and no broadening of the existing lines has been observed.

TEM picture of the composite semiconductor material (Fig. 3A) gives evidence that the average size of the WO_3 crystallites, comprised in the WO_3/TiO_2 material, was 20 nm. In the case of photoreduction of $HAuCl_4$ on the surface of TiO_2, the pH of the medium exerts a remarkable influence on the size and on the quantity of gold nanoparticles, deposited on the support [26,28]. In this work, the deposition of Au nanoparticles on the surface of the supports by photoreduction of the precursor $HAuCl_4{\cdot}3H_2O$ was carried out at pH 7, for the reasons explained previously [26]. The average size of the Au nanoparticles (0.4 wt%) on the TiO_2 surface, evaluated by TEM analysis in our previous work [8], was 5 nm. The TEM analysis proves that the average sizes of the Au particles on the surface of composite WO_3/TiO_2 materials were 6 nm (Fig. 3B). Such a small difference in Au particles size was insignificant and it falls within the magnitude of the experimental errors and therefore it should not exert substantial influence on the efficiency of the photocatalysts.

The reduction-oxidation potential of TNT of about - 0.3 V vs NHE [48] made it a suitable model pollutant for investigating the properties of the obtained photocatalyst samples. Typical kinetic curves of degradation of TNT in the presence of UV or visible

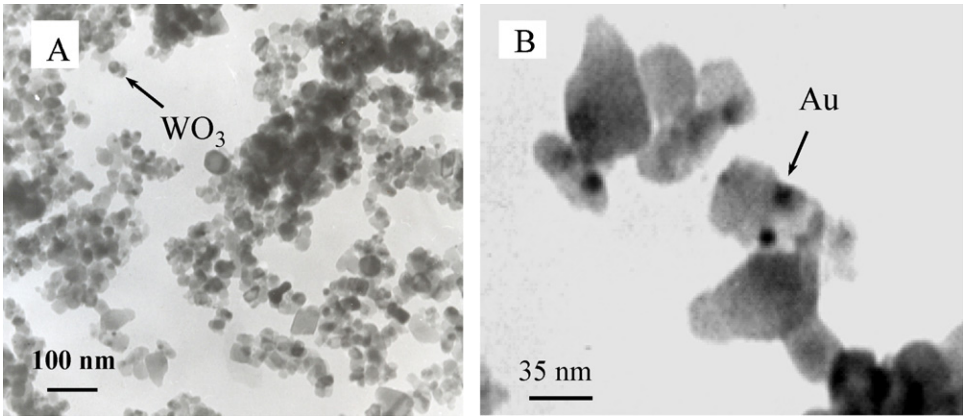

Fig. 3. TEM images of: (A) WO_3/TiO_2 composite; (B) 0.4 wt% Au on WO_3/TiO_2 composite.

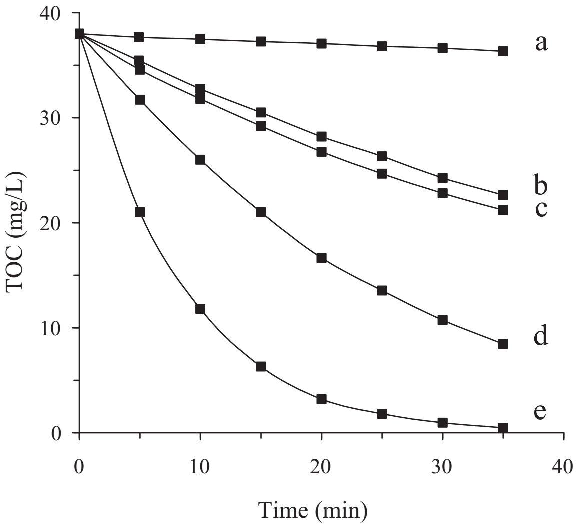

Fig. 4. Total degree of mineralization of 2,4,6-trinitrotoluene (5.3×10^{-4} mol/L) at pH 7 catalysed by $Au/WO_3/TiO_2$. Irradiation with visible light: (a) in the presence of O_2; (b) in the presence of O_2–O_3, irradiation with UV light: (c) in the presence of O_2 ($\lambda = 365$ nm); (d) in the presence of O_2–O_3 ($\lambda = 365$ nm); (e) in the presence of O_2–O_3 ($\lambda = 254$ nm).

light irradiation are presented in Fig. 4. The photocatalytic degradation process of TNT (Fig. 4) can be interpreted based on the Langmuir–Hinshelwood kinetic model [7,45,46]. Under the present experimental conditions of low concentration of TNT and constant UV or visible light flux, the Langmuirian kinetic expression [46] is reduced to a pseudo - first kinetic order with respect to the pollutant (Eq. (1)). The rates are therefore dependent on the TNT adsorption coverage and its concentration is:

$$\ln\frac{C_0}{C} = k_{\mathrm{app}}t \qquad (1)$$

where $k_{\mathrm{app}} = k_{\mathrm{r}}K$ and k_r is the limiting step rate constant of the reaction at maximum coverage under the given experimental conditions, K is the reactant adsorption–desorption equilibrium constant, C_0 is the initial concentration of the TNT and C is the concentration at a given moment of time in the course of the photocatalytic reaction.

The processes of photocatalytic oxidative destruction with TiO_2 are accomplished under irradiation with UV light, due to the wide band gap of the anatase form of TiO_2 (3.2 eV). WO_3 is a semiconductor photocatalyst with a smaller band gap of 2.8 eV, which is activated by visible light illumination. Under irradiation with UV light, the simultaneous excitation of both TiO_2 and WO_3 phases is accomplished in the coupled WO_3/TiO_2 and $Au/WO_3/TiO_2$ materials since the photon energy $E_{h\nu}$ is higher than the band-gap energies of the semiconductors [27]. In the cases of coupled WO_3/TiO_2 and $Au/WO_3/TiO_2$ catalysts under UV irradiation the registered rate constants of the photocatalytic mineralization of TNT in the presence of O_2 or O_2–O_3 mixture (Fig. 5) are much higher than those measured under visible light. This is due to the lower specific surface area of the WO_3 [27] and its small amount in the composite catalyst (4 wt%). Irrespective of the low specific surface area and the small quantity of WO_3 in the composite WO_3/TiO_2 catalyst the rate constants of TNT destruction under irradiation with UV or visible light are higher than those registered in the presence of TiO_2 only (Fig. 5). Under irradiation with UV or visible light two factors exert influence on the photocatalytic destruction rate of TNT, catalysed by the composite WO_3/TiO_2 material: increased adsorption capacity of the composite with respect to TNT and species with unpaired electrons, such as $O_2^{\bullet -}$, H_2O and $HO^-$and more efficient separation of the electron–hole pairs in the photo-activated composite.

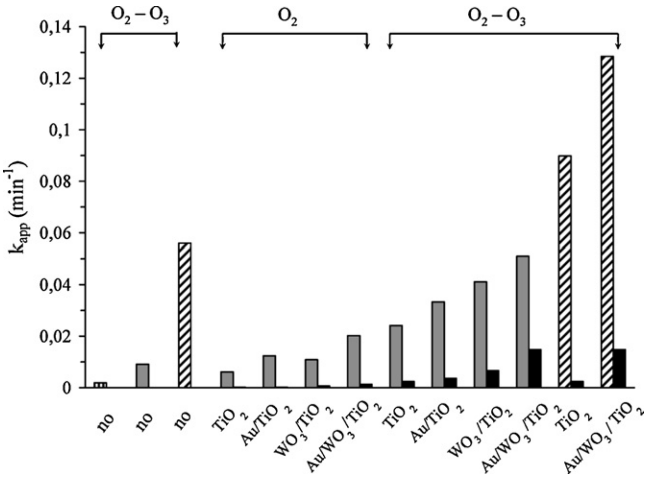

Fig. 5. Dependence of the rate constants of photocatalytic degradation of TNT under the experimental conditions. Type of irradiation: (▥) no irradiation; (▒) UV-light (365 nm); (▨) UV-light (254 nm); (■) visible light.

The promoted adsorption capacity of the WO_3/TiO_2 composite in regard to TNT and species with unpaired electrons, such as $O_2^{\bullet -}$, H_2O and HO^-can be attributed to the increased Brønsted and Lewis types of surface acidity of the composite. It has already been reported [39,43] that the formation of a monolayer of WO_x species on TiO_2 can significantly increase the surface acidity, as WO_3 is 15 times more acidic than TiO_2. Because of this increased acidity WO_3/TiO_2 can adsorb on its surface more species with unpaired electrons, such as $O_2^{\bullet -}$, H_2O and $HO^-$and simultaneously more organic reactants. The enhanced adsorption capacity of WO_3/TiO_2 with respect to TNT with some ~13% compared to that of the pure TiO_2 (Fig. 1) leads to an increase in the local concentration of TNT in the vicinity of their surface, which influences the efficiency of the photocatalytic process. The increased adsorption of $O_2^{\bullet -}$, H_2O and HO^-species on the surface of the photocatalyst, established in refs. [27,34,39,43,44], favours the generation of $HO^{\bullet}$ radicals on the valence band and the reduction of O_2 and O_3 on the conduction band of the WO_3/TiO_2 composite, and as a result of this the photonic efficiency of destruction of the TNT is promoted additionally.

At optimal WO_3 loading (4 wt%), the increase in the rate constant of TNT mineralization with the composite WO_3/TiO_2 catalyst can been explained in terms of an increased degree of charge carrier separation in the photoexcited composite catalyst as the dominating kinetic factor. A detailed explanation of the charge separation mechanism in the WO_3/TiO_2 composite photocatalyst has been reported [27,33,34,40]. The essence of the charge separation mechanism in the WO_3/TiO_2 photocatalyst consists in electron transfer from the conduction band of TiO_2 to the WO_3 conduction band, accompanied by consecutive W^{6+} reduction into W^{5+}, occurring on the surface of the WO_3 crystal lattice [34]. The electron transfer from the photoactive TiO_2 to WO_3 leads to an increase in the lifetime of the photogenerated pairs and as a consequence to a promotion of the photonic efficiency of the photocatalytic degradation of organic substrates (Fig. 6).

The rate constants of TNT destruction increased in all cases (under UV or visible light irradiation) when the photocatalysts were doped with gold nanoparticles (Fig. 5). The effect of gold content and size of Au nanoparticles on the photocatalytic activity of Au/TiO_2, and $Au/WO_3/TiO_2$ in the case of conducting the photocatalytic process in the presence of O_2 has been reported in our previous works [8,26,27]. An optimal quantity of gold, attached to the surface of the catalyst, has been selected (0.4 wt%), as the adsorption properties of the catalysts and the noble metal content

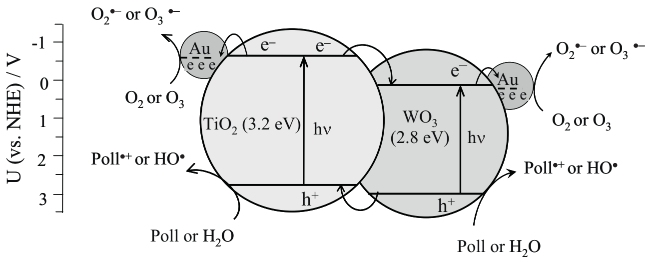

Fig. 6. Schematic representation of charge carrier separation in the photoexcited $Au/WO_3/TiO_2$ photocatalyst.

on the surface of the support are factors acting in the opposite directions, influence the efficiency of the photocatalytic process [8,26]. It can be seen in Fig. 1 that when gold is deposited on the surface of the catalysts their adsorption capacity in regard to TNT is decreased.

In the case of band gap excitation of oxide semiconductor photocatalysts, a major rate-limiting factor, controlling the photocatalytic efficiency [49,50], is the high degree of recombination between photogenerated electrons and holes. On the other hand, the deposits of nano-sized gold particles on the surface of the photocatalysts lead to an efficient charge separation of the photon generated electron–hole pairs in semiconductor photocatalysts (Fig. 6) and, therefore, to an increase in the lifetime of the photogenerated pairs. This allows longer time intervals for the charges to migrate to the surface and to enable redox processes on the valence band and on the conduction band of the photocatalysts [50–52]. Noble metal nanoparticles are highly effective traps for the electrons due to the formation of a Schottky barrier at the metal–semiconductor interphase.

The destruction of TNT occurs both in the case of direct ozonation as well as in the case of photocatalysis in the presence of O_2 or a mixture of O_2–O_3 (Fig. 5). The values of the rate constants of TNT destruction in the presence of O_2 or a mixture O_2–O_3 depend on the type of the studied photocatalyst samples. The mechanism of the photocatalytic destruction of organic substrates in the presence of O_2 and the differences in the activities of TiO_2, WO_3/TiO_2 and photocatalysts modified superficially with noble metals have been discussed in refs. [7,27,29,49]. The enhancement of the photocatalytic activity of Au/TiO_2, WO_3/TiO_2 and $Au/WO_3/TiO_2$ samples with respect to that of the pure TiO_2 is explained by the increase in the lifetime of the photogenerated electron–hole pairs in photoexited semiconductor photocatalysts. The charge separation in the photoexcited catalysts increases the probability of oxidation of the water molecules upon the valence band, whereupon the quantum yield of the generated $OH^\bullet$ radicals is promoted. With all the studied photocatalysts in the case of O_2–O_3 mixture the rate constants of TNT destruction are considerably higher than those registered in processes occurring in the presence of pure TiO_2 (Table 1). Thus in the presence of O_2–O_3 mixture the rate constants of TNT photooxidation catalysed by $Au/WO_3/TiO_2$ are respectively 2.1, 1.4 and 6.2 times higher under irradiation with UV-A, UV-C and visible light irradiation than those registered with pure TiO_2 (Table 1). This substantial increase of the TNT destruction rate constants on the studied samples (Table 1) is attributed to the appearance of a synergistic effect, already registered by other authors with other contaminants [24]. The strongest synergistic effect in the TNT photocatalytic destruction is registered with the $Au/WO_3/TiO_2$ sample (Fig. 5) both under UV-A and UV-C irradiation. In case of UV-A the apparent rate constant ($k_{app} = 0.051\ min^{-1}$) for the $Au/WO_3/TiO_2/UV/O_3$ process is 1.79 times higher than the sum of that $Au/WO_3/TiO_2/UV/O_2$ ($k_{app} = 0.0202\ min^{-1}$), direct ozonation ($k_{app} = 0.0019\ min^{-1}$) and UV/O_3 ($k_{app} = 0.008\ min^{-1}$) process (Table 1). In case of UV-C the apparent rate constant ($k_{app} = 0.1285\ min^{-1}$) for the $Au/WO_3/TiO_2/UV/O_3$ process is 1.56 times higher than the sum of that $Au/WO_3/TiO_2/UV/O_2$ ($k_{app} = 0.0225\ min^{-1}$), direct ozonation ($k_{app} = 0.0019\ min^{-1}$) and UV/O_3 ($k_{app} = 0.058\ min^{-1}$) process (Table 1).

Under visible light illumination in the presence of O_3 there is a great difference between the rate constants with the TiO_2 and with the $Au/WO_3/TiO_2$ photocatalysts. It is due to the presence of 25% rutile only in Degussa P25 TiO_2 (band gap 3.0 eV), which is activated by the visible light and an additional amount of $HO^\bullet$ radicals is being generated by the adsorbed ozone on the conduction band of rutile. On the other hand it can be seen (Fig. 5) that upon feeding O_3 the values of the rate constants of TNT destruction with all the studied photocatalytic materials are quite higher than those registered in processes occurring in the presence of oxygen only. Thus under irradiation with UV light in the presence of O_2–O_3 mixture the rate constants of TNT photooxidation catalysed by $Au/WO_3/TiO_2$ are 6 times higher, while under irradiation with visible light they are 11 times higher than those, registered in the case of the processes, carried out in the presence of oxygen only. Under irradiation with visible light in the presence of O_3 synergistic effect has been registered only with the WO_3 containing photocatalyst samples, excited by photon energy $E_{h(} < 3$ eV, (Fig. 5). During TNT destruction, catalysed $Au/WO_3/TiO_2$ the synergistic effect is most strongly expressed whereupon the rate constant ($k_{app} = 0.0148\ min^{-1}$) is 11 times higher than those, registered in the case of the process, carried out in the presence of oxygen only ($k_{app} = 0.0013\ min^{-1}$) (Table 1). Therefore in the cases of photooxidation over Au/TiO_2, WO_3/TiO_2 and $Au/WO_3/TiO_2$ samples, occurring in the presence of O_3, the effectiveness of the processes of mineralization of TNT is promoted substantially, compared to that catalysed by TiO_2, as well as juxtaposed with the processes occurring in oxygen medium.

The promotion of the rate constants of TNT destruction in the presence of O_2–O_3 mixture shows that some additional processes, connected with the presence of O_3, are combined with the photocatalytic processes occurring in the presence of only O_2 [7,49,50], leading to increase in the rate of pollutant destruction. Data reported by a number of authors [20,21,53] show that in the course of photooxidation of different organic pollutants in water, occurring in the presence of O_2 only or O_2–O_3 mixture, the processes of mineralization of the substrates is associated mainly with the option to generate $HO^\bullet$ radicals under the effect of the photocatalysts. For this reason during the investigation of TNT destruction, especially in the case of O_3 presence, our basic attention was directed to the possibilities of $HO^\bullet$ radicals generation both in the case of direct ozonation of the substrate, as well as in the case of carrying out the catalytic processes under irradiation in the presence of the studied photocatalysts.

Upon direct ozonation of TNT at pH 7 (Fig. 5) complete mineralization of the substrate is observed, whereupon the rate constant $k_{app} = 0.0019\ min^{-1}$ is comparable to that, registered in the case of its destruction, photocatalyzed by pure TiO_2 in the presence of oxygen only. Ozone is a powerful oxidizing agent ($E^0 = 2.08$ V) and it can react with several classes of compounds through direct or indirect reactions. In the absence of light, ozone can react directly with an organic substrate, through slow and selective reactions of electrophilic substitution or dipolar cycloaddition. At the same time it is known that in alkaline or neutral medium ($7 < pH < 10$), upon continuous feeding of O_2–O_3 mixture, as a result of the slow decomposition of O_3 and intermediate formation of H_2O_2, $HO^\bullet$ radicals can be formed [10,21,54]. The destruction of TNT during direct ozonolysis at pH 7 (Fig. 5) is owing to the parallel occurrence of the above – described processes, while the final degree of mineralization can be attributed to the intermediate products from the interaction with the $HO^\bullet$ radicals in the reaction system.

On the other hand it is known [55], that under irradiation with UV-C light ($\lambda = 254$ nm) a direct photolysis of the ozone is occurring in aqueous medium, accompanied by formation of $HO^\bullet$ radicals, which is realized according to the following principle scheme:

$$O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D) \tag{2}$$

$$O(^1D) + H_2O \rightarrow 2HO^\bullet \tag{3}$$

where $O_2(^1\Delta_g)$ is singlet oxygen and $O(^1D)$ is excited oxygen atom.

It is known that the molecule of ozone is adsorbed on the acidic sites of metal oxides [21,56]. Under irradiation with UV (UV-A or UV-C) and visible light (observed only with the WO_3 containing photocatalyst samples) an additional amount of $HO^\bullet$ radicals is generated by the adsorbed ozone on the conduction band of the semiconductors: TiO_2, WO_3/TiO_2, Au/TiO_2 and $Au/WO_3/TiO_2$ (Fig. 6), which is realized according to the following principle scheme [57]:

$$O_{3(ads)} + e^-{}_{cb} \rightarrow O_3{}^{\bullet-} \tag{4}$$

$$O_3{}^\bullet + H^+ \rightarrow HO_3{}^\bullet \tag{5}$$

$$HO_3{}^\bullet \rightarrow HO^\bullet + O_2 \tag{6}$$

Our results can be interpreted in view of the mechanisms, responsible for the appearance of synergistic effect in photocatalytic processes coupled with ozonation, reported in [24,58]. In our specific case of TNT photocatalytic destruction in the presence of ozone we could suppose that the synergistic effect is mainly due to generation of $HO^\bullet$ radicals by the ozone on the conduction band of the studied photocatalyst samples (Eqs. (4)–(6)). Only to a smaller extent it is due to generation of $HO^\bullet$ radicals by the ozone in case of direct ozonation or by the interaction of the dissolved ozone and $O_2{}^{\bullet-}$ radicals with the H_2O_2 being formed in aqueous medium, described in [24,58]. The strongly expressed synergistic effect with the $Au/WO_3/TiO_2$ sample in the presence of ozone is due to increase in the quantum yield of generated $HO^\bullet$ radicals as a result of the efficient charge carrier separation in this photocatalyst.

Therefore the higher rate constants of TNT decomposition in the case of photocatalytic experiment in the presence of O_3 could be explained by the occurring of the additional parallel processes, not existing when only O_2 is applied. These are leading to destruction of the substrate: (i) direct destruction of substrate by the ozone under the effect of the generated $HO^\bullet$ radicals; (ii) direct photolysis of the ozone in aqueous medium (Eqs. (2) and (3)) under irradiation with UV-C light ($\lambda = 254$ nm) accompanied by formation of $HO^\bullet$ radicals and (iii) additional generation of $HO^\bullet$ radicals by the ozone on the conduction band of TiO_2 (Eqs. (4)–(6)).

The direct interaction of the substrate with O_3 and the additional generation of $HO^\bullet$ radicals by the ozone, according to Eqs. (2)–(6), is the reason for the substantial growth of the rate constants of destruction of the TNT in comparison to the processes, occurring in the presence of O_2 only. The hydroxyl radicals are among the most reactive free radicals and probably the strongest oxidants capable of decomposing organic compounds.

4. Conclusions

The effectiveness of the processes of TNT destruction in the presence of O_3, catalysed by the WO_3/TiO_2, Au/TiO_2 and $Au/WO_3/TiO_2$ samples is considerably higher than that registered in process, occurring in the presence of pure TiO_2. Thus in the presence of O_3 the rate constants of TNT photooxidation catalysed by $Au/WO_3/TiO_2$ are respectively 2.1, 1.4 and 6.2 times higher under irradiation with UV-A, UV-C and visible light irradiation than that registered with pure TiO_2.

In the presence of ozone the rate constants of TNT photooxidation under irradiation with UV or visible light are much higher than those, registered in the case of the process, carried out in the presence of O_2 only and they are dependent on the energy of UV light source. This is due to the direct destruction of substrate by the ozone and additional generation of $HO^\bullet$ radicals by the ozone on the conduction band of TiO_2 or as a result of O_3 photolysis under irradiation with UV-C light. Thus under irradiation with UV light in the presence of O_2–O_3 mixture the rate constants of TNT photooxidation, catalysed by $Au/WO_3/TiO_2$ are 6 times higher, while under irradiation with visible light they are 11 times higher than those for the processes, carried out in the presence of oxygen only. The considerable increase in the rate constants of TNT destruction in the presence of O_3 under irradiation with UV-A, UV-C or visible light is attributed to the synergistic effect, involving the participation of the ozone molecule in the photocatalytic process.

The higher rate constants of TNT decomposition under UV or visible light irradiation with the Au/TiO_2, WO_3/TiO_2 and $Au/WO_3/TiO_2$ catalysts, compared with those measured with the individual oxide photocatalysts, are due to the more efficient separation of the electron–hole charges generated upon irradiation. In the presence of WO_3/TiO_2 the effectiveness of the photocatalytic processes increased additionally as a result of the enhanced adsorption of TNT and that of intermediately formed species with unpaired electrons and ozone.

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