



Photocatalytic activity of silver-modified titanium dioxide at solid–liquid and solid–gas interfaces

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Abstract

Silver-modified titania samples (Ag–TiO₂) with varying silver content (0.1–1.0 wt%) were prepared. Silver-modification of titanium dioxide was examined by TEM, XRD, XPS and DR–UV–vis spectroscopy. Ag or AgO_x particles on TiO₂ surface could not be observed by XRD and TEM investigation, however the color of the Ag–TiO₂ samples varied between light rose and purple–brown. XPS measurements revealed that silver exists mainly in oxide form. The photocatalytic activity of pure and Ag–TiO₂ samples were compared both in solid–liquid and in solid–gas interfaces. In the liquid phase the 2,2′-thiodiethanol was used as test molecule. Ethanol photodegradation was examined in gas phase at dry initial condition. It was shown that the rate of photooxidation of organic compounds significantly enhanced by silver-modification of titania.

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1. Introduction

Among numerous semiconductor materials TiO₂ is the most widely used photocatalyst nowadays due to its optical and electronic properties, chemical stability, low cost and non-toxicity. Forasmuch as the TiO₂ utilizes only a very small region of the solar spectrum due to its band-gap energy, the improvement of the response to the visible light (i.e. photosensitization) resulting in enhanced photocatalytic activity is one of the most important aspects of heterogeneous photocatalysis. Deposition of different metals (like Pt, Pd, Au, Ag, Fe, Nb and Cu) [1–16] or oxides such as WO₃ [17] onto titanium dioxide has been widely used as a technique to extend the light absorption to the visible region.

The usual methods for modification of TiO₂ with noble metals or oxides are impregnation and photodeposition. The altering of the physical and chemical properties of titanium dioxide can

be realised also by fixing it on different support materials (clay minerals, silica, etc.) [18–20]. Among the large number of publications in the literature Carp et al. give an excellent review on the synthesis, characterization and photoinduced reactivity of titania [21]. The effect of the doping agent in the degradation efficiency is not evident. Positive effect of additives in the decomposition of different organic compounds has been published [2–9], but opposite results have been also reported [1,7,9]. This miscellaneous behaviour can be explained by the difference in the morphology, crystal structure, specific surface area and the surface density of the OH groups of the studied TiO₂ catalysts, due to the various preparation methods applied in their synthesis [22].

The positive effect of metal deposits has been explained by the improved separation of electrons and holes on the surface of the photocatalyst. There was also observed, that some metals on TiO₂ surface can have no influence or even a detrimental effect on the photocatalytic degradation of investigated organic pollutants [1,7]. According to a possible explanation for this negative impact presented in the literature metal deposits may

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occupy the active sites on the TiO₂ surface at higher loadings causing the photocatalyst to lose its activity.

The importance of pollutant's adsorption on the catalyst surface was stated for Pt, Pd and Ag doped titania/silica samples by Hu et al. [2]. They found that the silver-modified samples showed almost the same photocatalytic activity as the pure support material. In contrary silver loaded titania catalysts were found to be more effective in azo dye decomposition than the bare TiO₂ sample [23]. Miscellaneous behaviour was observed in the case of Ag–TiO₂ samples, silver enhanced the rates of sucrose oxidation due to the improved charge separation, however it poses similar activities to bare titania for salicylic acid and phenol decomposition [24]. Natural oestrogen's decomposition revealed no effect of silver addition, which also supports the theory on substrate and metal specificity in the organic compound's degradation [7].

In this paper we report a brief study on structural characterization of Ag-modified TiO₂ samples. The photooxidation rate of 2,2'-thiodiethanol in liquid phase and ethanol in the vapour phase on the modified samples with various silver loading was investigated.

2. Experimental

2.1. Sample preparation

The amounts of Ag loading were 0.1; 0.5 and 1.0% (w/w) with respect to the TiO₂ amount. For each Ag-modified sample a 1 g amount of TiO₂ was dispersed into 500 ml of AgNO₃ (Molar, Hungary) solution in distilled water, with a respective concentration to ensure 0.1, 0.5 and 1% (w/w) Ag on the supports. In the photoreduction of Ag onto the TiO₂ 2-propanol was added as a sacrificial donor. The suspension was then irradiated with the UV-light using a 300 W of Xe-lamp (Hamamatsu L8251, Japan) for about 1 h with continuous stirring. The precipitate was washed with distilled water, centrifuged, dried at 60 °C and meshed.

2.2. Sample characterization

X-ray photoelectron (XP) spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer operated in the FAT mode. The excitation source was the K α radiation of a magnesium anode ($h\nu = 1253.6$ eV). The X-ray gun was operated at 225 W power (15 kV, 15 mA). The pass energy was set to 20 eV, the step size was 25 meV, and the collection time in one channel was 100 ms. Typically five scans were added to get a single spectrum. The C 1s binding energy of adventitious carbon was used as energy reference; it was taken at 285.1 eV. For data acquisition both manufacturer's (SpecsLab2) and commercial (CasaXPS, Origin) software were used.

CHEM2000UV-VIS (Ocean Optics Inc.) spectrophotometer equipped with an integrated sphere was used to record the diffuse reflectance spectra (DRS) of the Ag–TiO₂ samples.

The particles were characterized using a Philips CM-10 transmission electron microscope with an accelerating voltage of

100 kV. The microscope was equipped with a Megaview II digital camera.

X-ray diffraction patterns were collected on a Philips PW 1830 diffractometer, using Cu K α -radiation ($\lambda = 0.1542$ nm). The average crystallite sizes were calculated from the XRD peak broadening using Scherrer's equation.

The specific surface area of the different samples was determined by the BET method from N₂ adsorption isotherms at 77 ± 0.5 K (Micromeritics Gemini 2375 Surface Area Analyzer).

The photocatalytic test in gas phase, i.e. the photooxidation of ethanol, was performed in a reactor with a volume of ca. 700 ml at room temperature (25 ± 0.1 °C). The photoreactor is constructed of two concentric tubes, with 15 W low-pressure mercury lamp (GCL307T5L/CELL LightTech, Hungary) with characteristic emission wavelength at $\lambda_{\text{max}} = 254$ nm, placed in the centre as shown in Fig. 1a. The material of the inner tube was quartz and of the outer tube was Pyrex glass. The catalyst was sprayed onto the outer side of the inner quartz tube from 30% (m/v) aqueous dispersion using N₂ stream. The surface area of the catalysts layer on the glass cylinder (see the cross-sectional view of the reactor in Fig. 1b) was 44.8 cm², the catalyst mass per unit surface was 0.490 ± 0.045 mg/cm² and the calculated thickness of the films was 1.48 ± 0.1 μ m. Prior to catalytic test reactions the films were conditioned, the detailed procedure was described elsewhere [25]. The composition of the gas phase (containing ethanol, water, CO₂ and organic intermediate products) was analyzed at given time intervals in a gas chromatograph (Shimadzu GC-14B) using a thermal conductive (TCD) and a flame ionization detector (FID). The initial concentration of ethanol was 6000 ppm at relative humidity of 0%. The photocatalytic experiments were repeated three times and their reproducibility was better than 3%.

Photocatalytic experiments at solid–liquid interface were carried out in a 400 ml batch reactor, thermostated at 25 °C. For sample irradiation a 150 W power, immersion type high-pressure mercury lamp (Heraeus TQ 150) was used, surrounded with a glass filter in order to the high-energy photons ($\lambda < 310$ nm) to be filtered out. 0.1% (w/v) of the catalysts were dispersed in 400 ml of 1 mM aqueous 2,2'-thiodiethanol solutions. The chemical structure of this test molecule (Fig. 2a) is highly similar to that of bis(2-chloroethyl) sulfide, the chemical warfare agent known as sulfur mustard (see Fig. 2b). The suspensions were saturated with oxygen during UV-irradiation. Sample aliquots were withdrawn for analysis after 30 min without irradiation ($t = 0$ min) and at $t = 30, 60, 90, 120, 150$ and 180 min after starting the irradiation.

3. Results and discussion

3.1. Surface and optical properties

The specific surface area of the samples was determined by N₂ sorption measurements. The results varied within the experimental error and were independent of the silver content of the samples, i.e. the value measured was 51 ± 2 m² in all cases.

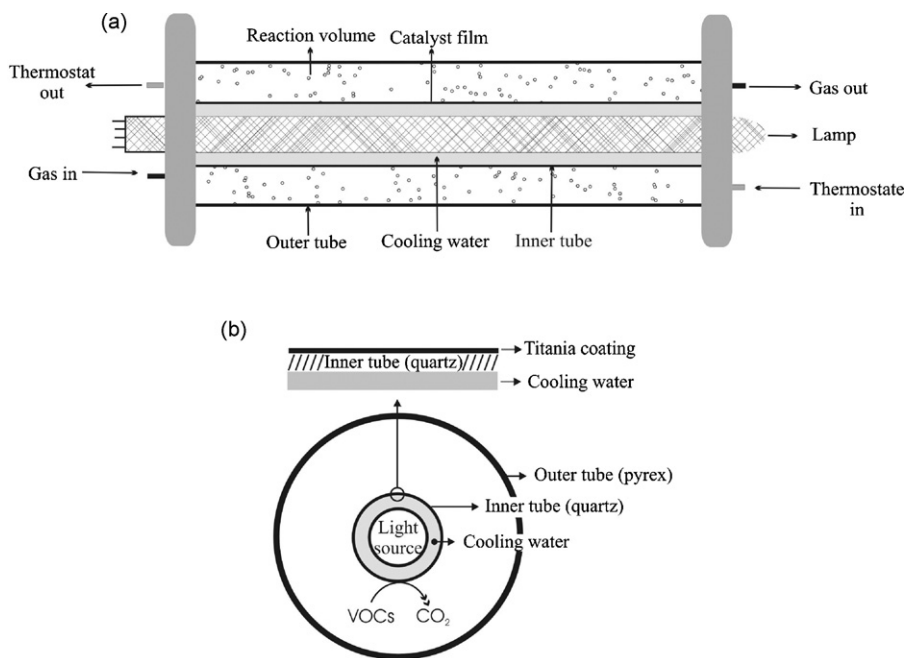


Fig. 1. Schematic drawing of the cylindrical photoreactor (a) and its cross-sectional view (b).

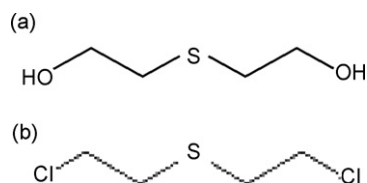


Fig. 2. (a) Chemical structure of 2,2'-thiodiethanol and (b) bis(2-chloroethyl) sulfide (sulfur mustard).

To characterize the optical properties of photocatalysts, the diffuse reflectance UV–vis spectra of pure and Ag-modified titania samples are compared in Fig. 3. In the case of Ag–TiO₂ samples with 0.5 and 1% (w/w) loading, a new, broad absorption band appears in the visible range with a maximum of

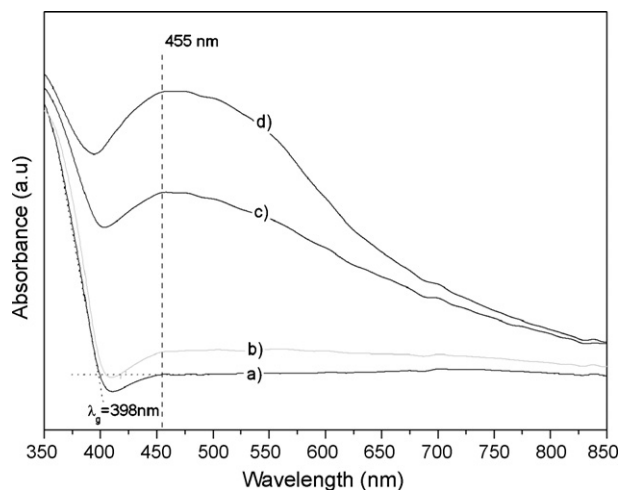


Fig. 3. Diffuse reflectance UV–vis spectra of unmodified TiO₂ (a) and different Ag-modified titania samples: Ag–TiO₂/0.1 wt% (b), Ag–TiO₂/0.5 wt% (c), and Ag–TiO₂/1.0 wt% (d).

$\lambda_{\max} = 455$ nm. The position of the absorption edge characteristic of titania was 400 ± 3 nm, independently of the Ag content of the samples. Although the color of the Ag–TiO₂ gradually turned from light rose to purple-brown as the amount of silver loading was increased, even in the sample with 1% (w/w) loading TEM images only showed particles of sizes and morphologies characteristic of Degussa TiO₂. Nor did X-ray diffraction measurements reveal crystalline silver or silver oxide; the anatase/rutile contents of the pure and modified samples were identical, namely 87% anatase/13% rutile, just like in Degussa TiO₂.

Fig. 4 shows the Ti 2p, O 1s and Ag 3d regions of the high-resolution XP spectra of pure and Ag-modified titanium dioxide. The surface compositions of the samples are summarized in Table 1. After Ag-modification of titanium dioxide, the binding energy of the Ti 2p doublet (Ti 2p_{3/2}, 2p_{1/2}) is unchanged, its shape is symmetrical both before and after the photodeposition of silver, indicating a single chemical state in a chemical environment of the Ti–O–Ti type. The position of the Ti 2p_{3/2} components at 458.7 eV corresponds to a +4 oxidation state in titanium dioxide [25,26].

O 1s spectra are asymmetric; they have a low-intensity shoulder at the high binding energy side. The positions of the higher-energy, but lower-intensity oxygen components obtained by deconvoluting the spectra are 532.2 eV and 531.6 eV, whereas

Table 1
Surface composition of pure and Ag-modified TiO₂ samples

Sample ID	Atomic concentration (%)			
	Ti	O	Ag	C
Degussa P25	27.99	60.87	–	11.14
Ag–TiO ₂ /1 wt%	23.33	62.11	0.238	14.33

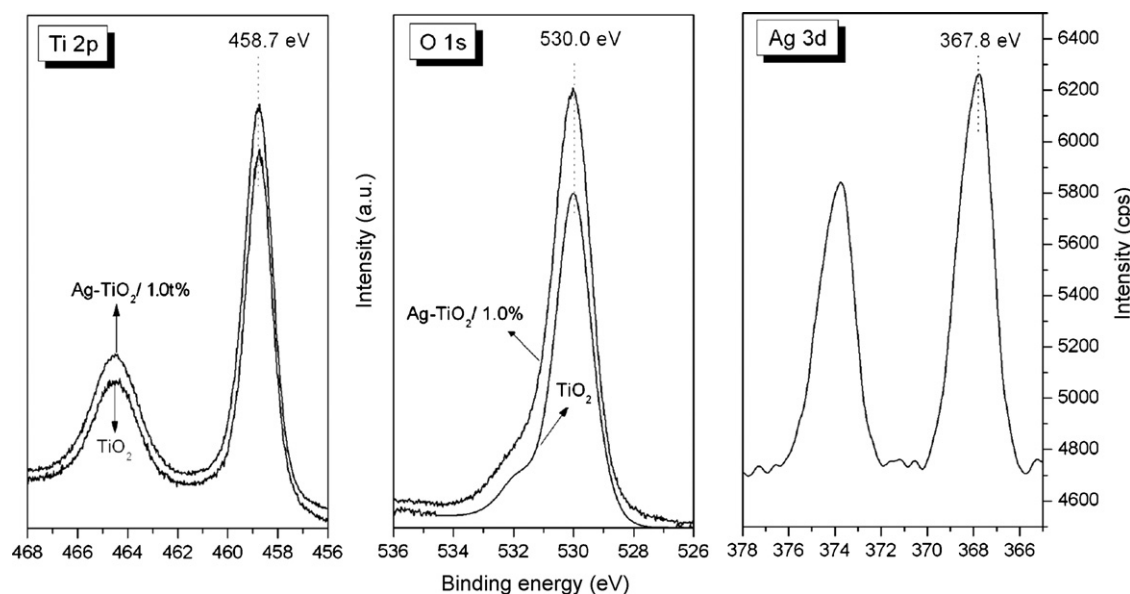


Fig. 4. High-resolution XPS spectra of the Ti 2p, O 1s and Ag 3d region taken on Degussa TiO₂ and Ag-TiO₂/1.0 wt% sample.

the maximum of the main component is at 530.0 eV. The peak at 532.2 eV is assignable to C–O bonds and the peak at 531.6 eV can be attributed to O–H– groups on the surface of titania. The presence of bonds of the C=O or C–O–C type is probably due to the adsorption of carbon-containing compounds (adventitious carbon).

The spectrum of the Ag 3d region of the Ag-modified sample is also symmetrical; the 3d_{5/2} component is positioned at 367.8 eV, indicating the presence of silver oxides. [27]. The silver content of the Ag–TiO₂/1 wt% sample determined by XPS analysis is 0.238 at%, a value sufficiently close to the calculated silver content (0.249 at%) (Table 1). Silver oxide detected on the Ag–TiO₂ samples was presumably formed on the titania surface in the course of the oxidation of photoreduced silver. Based on our XRD measurements, the silver oxide phase detected by XPS on the surface of titania is amorphous, which may be explained by the fact that, in the course of synthesis, the samples were dried at 60 °C rather than calcined.

3.2. Photocatalysis

3.2.1. Photocatalysis at the solid–gas interface

The photocatalytic activity of titanium dioxide samples with or without silver loading was tested in the photodegradation of ethanol at the solid–gas interface, under dry initial conditions. Considering that the surface of the samples was contaminated by adventitious carbon (see XPS measurements), the samples

were first irradiated with high-energy ($\lambda = 180$ nm) UV-light, while simultaneously flushing dry synthetic air over the samples. Pre-treatment of the titania samples and the experimental setup are described in detail in our previous publication [25]. Ethanol photooxidation was also performed in the absence of titania; in this case the concentration of the test molecule decreased only negligibly (<2%).

Ethanol consumption as a function of adsorption time (the negative range of the diagram) and irradiation time (the positive range of the diagram) is shown in Fig. 5. Amounts of ethanol adsorbed by pure and surface-modified samples in 30 min are compared in Table 2. The amount of adsorbed ethanol only slightly increases with increasing the silver content of the samples, whereas the rate of photooxidation is significantly accelerated starting from 0.5% silver content (Table 2). The rate of ethanol conversion on the 1% (w/w) sample was three-fold higher than on pure titanium dioxide. The kinetic curves clearly demonstrate that the entire amount of ethanol is degraded within 15 min on the samples with 0.5 and 1% (w/w) content, whereas on unmodified TiO₂ and on the 0.1% (w/w) sample 100% conversion of ethanol takes 50 min.

The main intermediate of ethanol photooxidation is acetaldehyde. The time course of acetaldehyde concentration is presented in Fig. 6. These kinetic curves have maxima, which are shifted towards shorter reaction times with increasing silver content. In other words, both the formation and the subsequent consumption of acetaldehyde are considerably faster on samples

Table 2
Amount of adsorbed ethanol and photocatalytic activity of pure and Ag-modified TiO₂

Sample ID	a_{Ethanol}^s (mg g ⁻¹)	Ethanol conversion after 5 min (%)	Total mineralization after 60 min (%)
TiO ₂	18	24	38
Ag–TiO ₂ /0.1 wt%	20	24	57
Ag–TiO ₂ /0.5 wt%	24	67	77
Ag–TiO ₂ /1.0 wt%	26	77	94

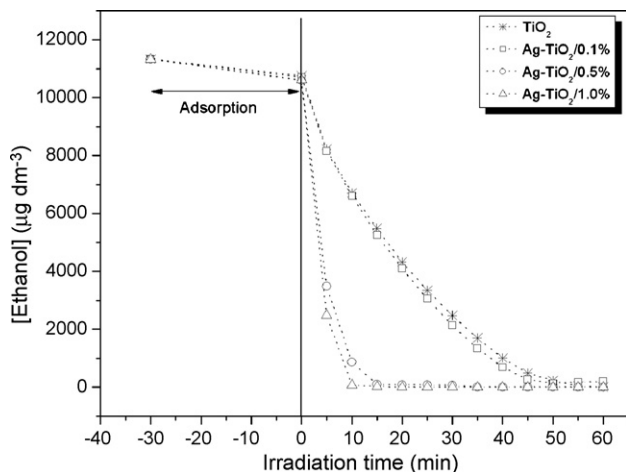


Fig. 5. Photodegradation of ethanol on unmodified (Degussa P25) and Ag-modified titania samples at dry initial condition.

with increasing silver contents than on pure titania. In the initial phase of photooxidation a large proportion (60–90%) of ethanol is converted to acetaldehyde, indicating that total mineralization is not significant at this stage. Additional intermediates such as formaldehyde, acetic acid and formic acid were also identified. These observations adequately fit in with the effect of alcohol adsorption and the mechanism of ethanol photooxidation described previously [25,28,29].

In addition to water and carbon dioxide, methane was also identified among the final products of the reaction. Kinetic curves of methane and carbon dioxide formation are presented in Figs. 7 and 8, respectively. In the case of the Ag–TiO₂ samples of higher photoactivity (0.5 and 1.0 wt% silver loading), all these curves are of the saturation type: after 20–25 min the concentration of CH₄ in the reaction chamber becomes constant. This time corresponds to the duration of the total conversion of acetaldehyde, and after that no additional significant methane formation is observed. In the samples with lower activities such as pure titania and the Ag–TiO₂/0.1%, where acetaldehyde is present throughout the entire reaction time, methane formation is continuous (Figs. 6 and 7).

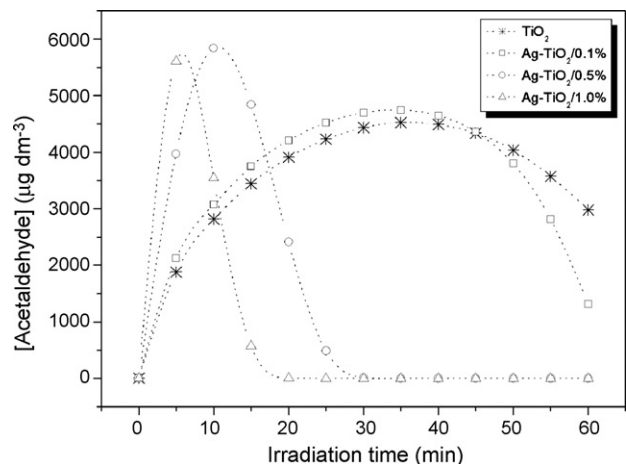


Fig. 6. Changes of acetaldehyde concentrations as a function of irradiation time using unmodified (Degussa P25) and Ag-modified titania samples.

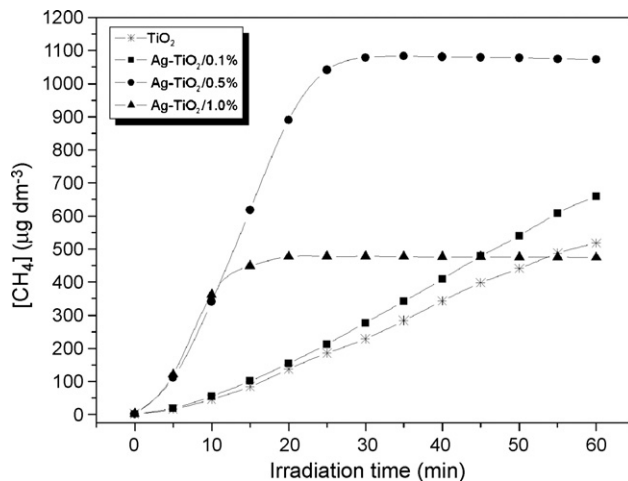


Fig. 7. Formation of CH₄ as a function of irradiation time using unmodified (Degussa P25) and Ag-modified titania samples.

The kinetic curves of CO₂ formation on the Ag–TiO₂ samples with 0.5 and 1% (w/w) silver contents (Fig. 7) are also of the saturation type. Mineralization on the Ag–TiO₂/1.0% (w/w) sample after 60 min is 94%, whereas the same parameter is only 38% on pure P25 TiO₂ (see Table 2).

Photooxidation experiments on the solid–gas interface revealed that silver-modification of titania significantly increases the photooxidation rate of both ethanol and the intermediates formed in the course of the reaction (Figs. 6–8). The samples with 0.5 and 1% silver content showed significant improvement.

3.2.2. Photocatalysis at the solid–liquid interface

Photooxidation of 2,2'-thiodiethanol in aqueous suspensions containing 0.1% (m/V) TiO₂ was studied at the solid–liquid interface at 25 °C. The concentrations of the test molecule and of the intermediates formed were monitored by UV–vis spectroscopy. The first panel of Fig. 9 displays spectra recorded at various time points of the photooxidation of the test molecule on unmodified TiO₂. In the course of photooxidation, the maximum

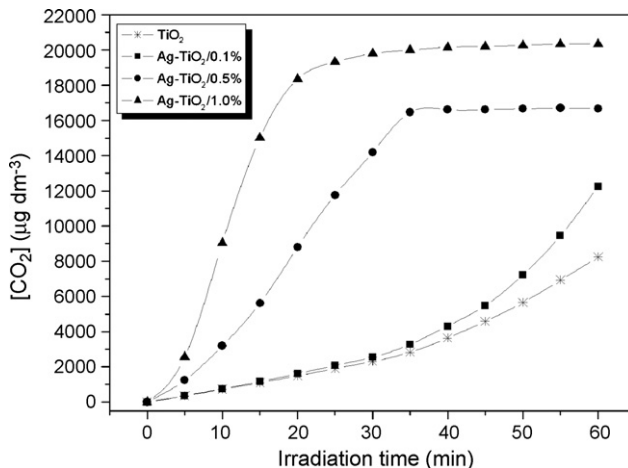


Fig. 8. Formation of CO₂ as a function of irradiation time using unmodified (Degussa P25) and Ag-modified titania samples.

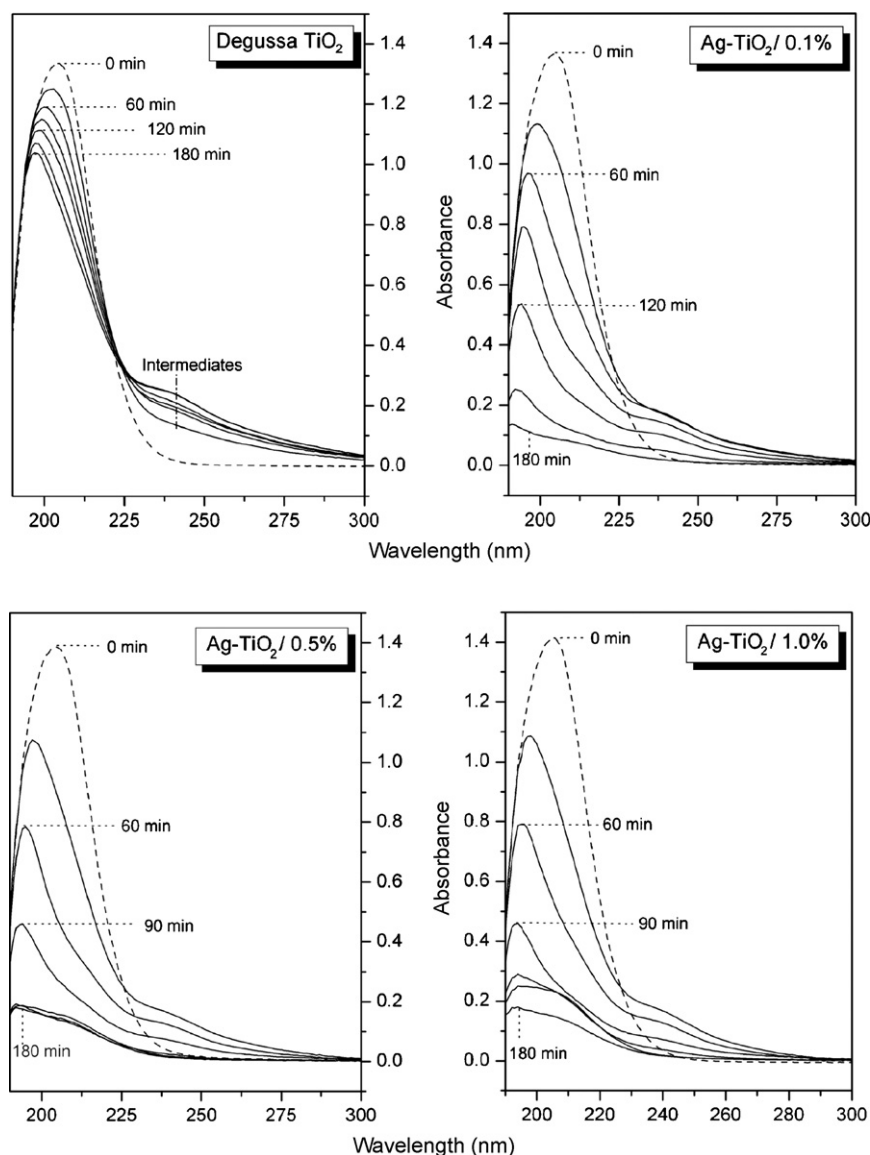


Fig. 9. Photodegradation of 2,2'-thiodiethanol using unmodified TiO₂ (Degussa P25) and different Ag-TiO₂ samples.

of the absorption spectrum of the pure test molecule ($\lambda = 204$ nm) is shifted towards the shorter wavelengths. At an irradiation time of 30 min, a new absorption band appears in the range of $\lambda = 225$ –300 nm, which also indicates the formation of various intermediates. The intensity of this band decreases after 30 min, i.e. intermediate concentration as a function of irradiation time has a maximum. When pure titanium dioxide is used, the absorbance of the organic components (at the wavelength of maximum absorption) decreased only by 14% after 60 min (Table 3).

The Ag-modified samples displayed significantly larger decreases in absorbance (Table 3). The sample with 0.1% (w/w) silver content already achieved more degradation than did pure TiO₂. The samples with 0.5 and 1% (w/w) silver contents were found to be the most active at the S/L interface, just like at the S/G interface. A decrease in absorbance in excess of 60% was recorded in these samples after 1 h.

To sum up, it was established that silver-modification significantly increased the rate of the photooxidation of both test molecules; at the same time, however, there was no detectable difference between the specific surface areas of the pure and modified samples. We therefore assume that the improved

Table 3

Photocatalytic activity of pure and Ag-modified titania for 2,2'-thiodiethanol decomposition

Sample ID	$(1 - A_{\lambda_{\max}}^{60 \text{ min}})/A_{204 \text{ nm}}^{0 \text{ min}}$
Degussa P25 TiO ₂	0.14
Ag-TiO ₂ /0.1 wt%	0.45
Ag-TiO ₂ /0.5 wt%	0.64
Ag-TiO ₂ /1.0 wt%	0.62

$A_{204 \text{ nm}}^{0 \text{ min}}$ is the absorbance at $\lambda = 204$ nm and $t = 0$ reaction time. $A_{\lambda_{\max}}^{60 \text{ min}}$ is the absorbance at λ_{\max} after 60 min reaction time at λ_{\max} in the UV-range on Fig. 9.

photoactivity observed is due to charge transition processes favorably affected by silver oxide. Silver oxide deposited on the surface of titania may inhibit the recombination of photo-generated charge carriers (electron, hole). The probability of the reaction of the charge carriers, whose lifetime is thereby increased, with the substrate (or the adsorbed species) is therefore enhanced.

4. Conclusion

The structural and photocatalytic properties of pure TiO₂ and Ag–TiO₂ samples prepared by photodeposition were compared. The surface region of titania was shown to contain silver oxide, classified as amorphous by XRD. There was no detectable difference between the specific surface areas of the Ag–TiO₂ samples with different silver contents; at the same time, however, Ag-modification of titania significantly increased the rate of ethanol photooxidation in gas phase and that of 2,2'-thiodiethanol photooxidation in aqueous phase. The improved photoactivity of Ag–TiO₂ samples may be due to a decrease in the recombination rate of photogenerated charge carriers.

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