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PHOTOCATALYTIC ACTIVITY OF TiO₂ LOADED WITH METAL CLUSTERS

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TiO₂ was surface modified with silver, gold and platinum ion clusters to improve its photocatalytic activity. The effect of metal content, the kind of dopant and titanium dioxide source (commercial – P25 and ST-01) used during preparation procedure on photoactivity were investigated. The photocatalytic activity was estimated by measuring the decomposition rate of 0.21 mM phenol aqueous solution under UV-Vis and visible ($\lambda > 400$ nm). The highest photoactivity was observed for TiO₂ loaded with silver (2%Ag on P25), gold (1%Au on P25) and platinum (0.5% Pt on ST-01) clusters. After 60 min. of irradiation under UV light phenol solution was degraded in 91%, 49% and 91%, respectively

keywords: photocatalysis, metal clusters, modified TiO₂

1. INTRODUCTION

Photodegradation of various pollutants using semiconductors has been intensively studied in recent years for its wide application in environmental protection. TiO₂ is a very promising photocatalyst due to its strong oxidation capacity, high photochemical and biological stability, non-toxicity and low cost [1]. Addition or doping with noble metal, such as platinum [2], palladium [3], silver [4] and gold [5] ions allow to extend

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the light absorption of band gap semiconductors to the visible light. Noble metals could be introduced to the surface of TiO_2 by various methods such as: electrolysis, chemical reduction, UV photoreduction, γ -reduction deposition from colloids or adsorption of metal clusters [6-10].

It was proved that doping with $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n=3-10$) clusters could enhance the photoconversion yield by inhibition of the electron hole recombination [11-13]. Kowalska et al. [14] modified titania with platinum ions (Pt(II) or Pt(IV)) or clusters ($[\text{Pt}_3(\text{CO})_6]_6^{2-}$). TiO_2 was modified with noble metals by direct surface adsorption of Pt(IV) (PtCl_6^{2-}) or Pt(II) (PtCl_4^{2-}) in aqueous or mixed alcohol-water solutions (metal/ $\text{TiO}_2 = 1-2\%$ w/w). Pt salts or clusters were put into contact with TiO_2 under stirring for several hours. Pt(IV) was introduced from aqueous solution (10^{-3} M) and stirred in the dark for 3 h. Pt(II) surface adsorption was carried out during stirring in the dark. Platinum clusters $[\text{Pt}_3(\text{CO})_6]_6^{2-}$ were used as surface adsorbates. These clusters were synthesized by radiolytic reduction (using a ^{60}Co γ -source of 3000 Ci, dose of 800 grays) of Pt(II) in water/2-propanol solutions (10^{-3} M) under 1 atm of CO. The samples obtained by Pt clusters and Pt(II) deposition at the surface of P 25 exhibited a visible light activity for phenol and Rhodamine B degradation [14].

Here, we report the preparation method and characteristics of silver, gold and platinum modified TiO_2 photocatalysts. Metal clusters with controlled nuclearity had been deposited at the TiO_2 surface by radiolytic reduction (using a ^{60}Co γ -source of 3000 Ci, dose of 800 grays) of metal precursors (Au(III), Ag(I) and Pt(IV)) in water/alcohol solutions in the presence of ligands (such as CO), surfactants or polymers.

2. MATERIALS AND METHODS

TiO_2 ST-01 powder having anatase crystal structure was obtained from Ishihara Sangyo, Japan (surface area $300 \text{ m}^2/\text{g}$, particle size 7 nm) and P25 (70:30% anatase-to-rutile mixture with a BET surface area of $55 \pm 15 \text{ m}^2/\text{g}^{-1}$ and crystallite sizes of 30 nm in $0.1 \mu\text{m}$ diameter aggregates) from Degussa GmbH, Germany. 98% KAuCl_4 , 99.5% AgClO_4 and 99% H_2PtCl_6 from Aldrich Chem. Co were used as gold, silver and platinum source.

TiO_2 -based photocatalysts were obtained according to procedures presented by a simplified block diagram in Figure 1. Silver and gold modified TiO_2 was prepared by one-pot method. Ag- TiO_2 and Au- TiO_2 were prepared by radiolytic reduction (using a ^{60}Co γ -source) of Ag(I) and Au(III), in the presence of suspended TiO_2 in methanol under N_2 atmosphere. Platinum modified titania was synthesized by a two-step method. In the first step, platinum clusters were synthesized by radiolytic reduction (using a ^{60}Co γ -source) of Pt(II) in water/methanol under 1 atm of CO. Obtained platinum

clusters were adsorbed at the TiO₂ surface. The modified TiO₂ photocatalysts were separated by centrifugation and dried at 60°C.

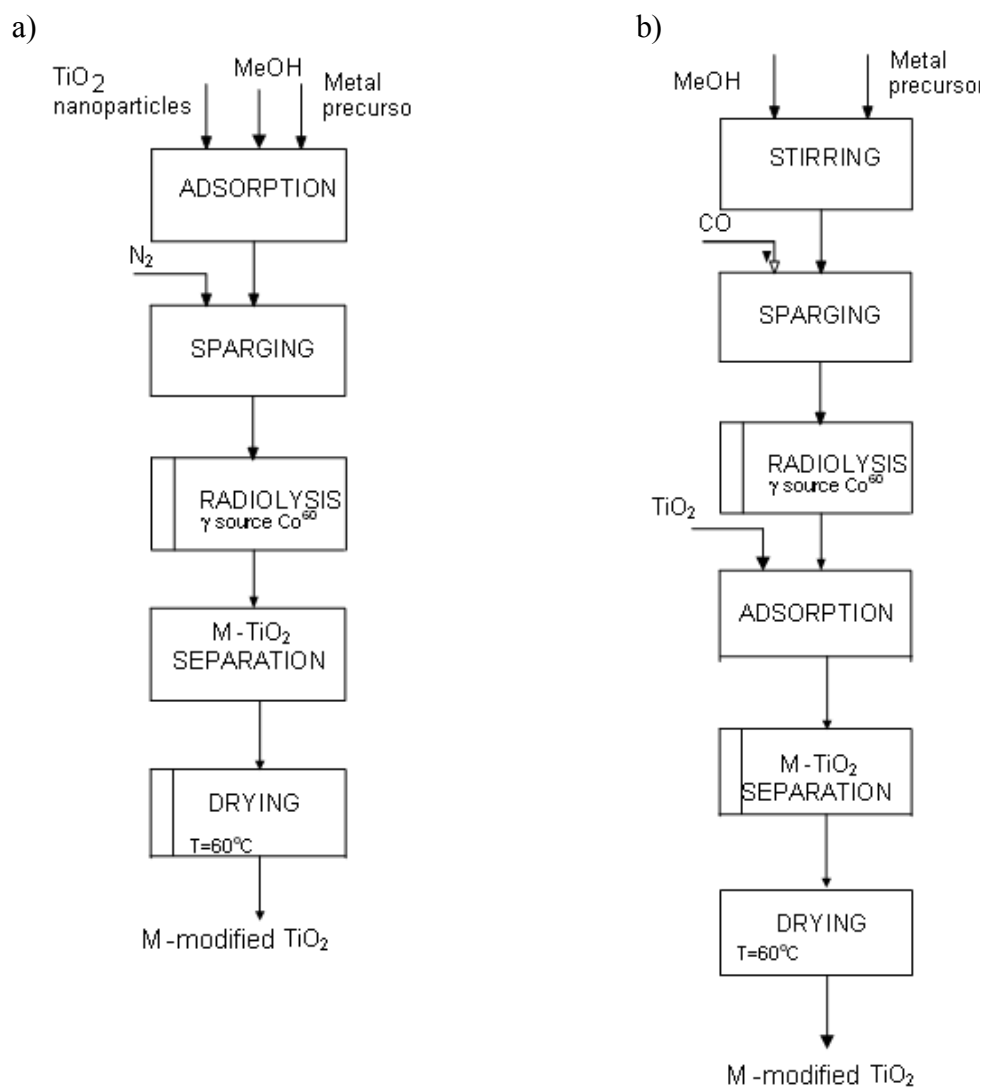


Fig. 1. Block diagram of Me-doped TiO₂ prepared by radiolysis method: (a) one-pot method (metal clusters are reduced directly at the surface of TiO₂ nanoparticles, and (b) two-step method (metal cluster reduction are followed by adsorption at the TiO₂ surface)

The photocatalytic activity of the obtained powders in ultraviolet and visible light was estimated by measuring the decomposition rate of phenol (0.21 mmol/dm^3) in an aqueous solution. Photocatalytic degradation runs were preceded by blind tests in the absence of photocatalyst or illumination. 25 cm^3 of catalyst suspension (125 mg) was stirred using magnetic stirrer and aerated ($5 \text{ dm}^3/\text{h}$) prior to and during the photocatalytic process. Aliquots of 1.0 cm^3 of the aqueous suspension were collected at regular time periods during irradiation and filtered through syringe filters ($\text{Ø}=0.2 \text{ }\mu\text{m}$) to remove catalyst particles. The suspension was irradiated using 1000 W Xenon lamp (Oriol), which emits both UV and Vis light. To limit the irradiation wavelength, the light beam was passed through GG400 filter to cut-off wavelengths shorter than 400 nm. Phenol concentration was estimated by colorimetric method using UV-VIS spectrophotometer (DU-7, Beckman).

3. RESULT AND DISCUSSION

All photocatalysts obtained by radiolytic reduction of AgClO_4 (0.5; 1; and 2 wt.%) at the surface of ST-01 or P25 were pinky to violet. The samples prepared by modification of ST-01 or P25 with KAuCl_4 (0.5; 1; and 2 wt.%) were pinky-violet or light grey, respectively. The samples prepared by γ -radiation of H_2PtCl_6 (0.5; 1; and 2 wt.%) followed by adsorption at the ST-01 and P25 surface were creamy-grey. It was reported that surface modification with Pt clusters caused the grey color of the sample, possibly due to the presence of Pt^0 or PtO_2 [15]. Sample labeling, preparation method and coloration of the samples after metal modification are given in Table 1. For selected samples, the size of metal aggregates was confirmed by microscopy analysis (STEM) and equaled about 2 nm.

The photocatalytic activities of metal loaded TiO_2 samples were quantified in terms of the oxidative degradation of phenol in aqueous solution under UV-Vis irradiation. The observed reaction rate with various metal loaded TiO_2 , which were prepared at metal ion concentration from 0.5 to 2 wt.%, are listed in Table 2. Under UV-Vis light irradiation, the rate of phenol degradation in the presence of pure ST01- TiO_2 was estimated to be $0.82 \text{ }\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$. The observed rate was increased slightly to 1.02, 1.05 and $1.2 \text{ }\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ in the presence of ST01 loaded with silver and gold clusters prepared by γ -reduction of the solution containing 0.5 wt.% of Ag(I), 2 wt.% of Ag(I) and 0.5 wt.% of Au(III), respectively. However, the increase in Au(III) concentration from 0.5 to 2 wt.% during radiolytic preparation, resulted in the decrease on photoactivity of the obtained photocatalysts, see details in Table 2. Platinum modified ST01 showed significantly enhanced photocatalytic activities under UV-Vis irradiation as compared to pure ST01. Phenol degradation rate was

3.15 $\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for the sample Pt-ST01(0.5).

Table 1. Preparation method and coloration of the samples after metal modification

Sample label	Metal precursor	TiO ₂ matrix	Content of metal precursor [wt. %]	Preparation method	Sample color
Au-ST01(0.5)	KAuCl ₄	ST-01	0.5	one-pot	pink/ violet
Au-ST01(1)		ST-01	1	one-pot	pink/ violet
Au-ST01(2)		ST-01	2	one-pot	pink/ violet
Au-P25(0.5)	KAuCl ₄	P25	0.5	one-pot	light grey
Au-P25(1)		P25	1	one-pot	light grey
Au-P25(2)		P25	2	one-pot	light grey
Ag-ST01(0.5)	AgClO ₄	ST-01	0.5	one-pot	light pink
Ag-ST01(1)		ST-01	1	one-pot	pink
Ag-ST01(2)		ST-01	2	one-pot	pink
Ag-P25(0.5)	AgClO ₄	P25	0.5	one-pot	pink
Ag-P25(1)		P25	1	one-pot	pink
Ag-P25(2)		P25	2	one-pot	violet
Pt-ST01(0.5)	H ₂ PtCl ₆	ST-01	0.5	two-step	creamy-grey
Pt-ST01(1)		ST-01	1	two-step	green
Pt-ST01(2)		ST-01	2	two-step	creamy-grey
Pt-P25(0.5)	H ₂ PtCl ₆	P25	0.5	two-step	grey
Pt-P25(1)		P25	1	two-step	grey
Pt-P25(2)		P25	2	two-step	deep grey
Pt-P25(1a)	(NH ₃) ₄ PtCl ₂ ·H ₂ O	P25	1	one-pot	green-grey
P25	-	P-25	0	-	white
ST-01	-	ST-01	0	-	white

Figure 2 shows the results of phenol degradation under UV-Vis irradiation in the presence of TiO₂ modified with platinum. All powders, prepared by radiolytic reduction of H₂PtCl₆ followed by adsorption of platinum clusters at the ST01 surface, exhibited higher photoactivity than pure ST-01 TiO₂. The highest photoactivity was observed for lower dopant amount (0.5 wt. %). In the presence of the sample Pt-ST01(0.5), phenol

was degraded in 91% after 60 min of irradiation.

Table 2. Photocatalytic activity of pure TiO₂ and samples prepared by metal modification

Sample label	Rate of phenol degradation [$\mu\text{mol dm}^{-3} \text{min}^{-1}$]	
	UV-Vis	Vis
Au-ST01(0.5)	1.2	-
Au-ST01(1)	0.75	0.08
Au-ST01(2)	0.27	-
Au-P25(0.5)	1.25	0.5
Au-P25(1)	1.94	0.54
Au-P25(2)	1.53	0.52
Ag-ST01(0.5)	1.02	-
Ag-ST01(1)	0.58	-
Ag-ST01(2)	1.05	-
Ag-P25(0.5)	2.69	0.33
Ag-P25(1)	2.28	0.78
Ag-P25(2)	3.14	0.27
Pt-ST01(0.5)	3.15	1.07
Pt-ST01(1)	2.15	0.44
Pt-ST01(2)	3.09	0.19
Pt-P25(0.5)	3.45	1.42
Pt-P25(1)	3.71	0.85
Pt-P25(2)	3.64	1.15
Pt-P25(1a)	3.43	-
P25	2.0	0.55
ST-01	0.82	0.25

Degussa P25 is highly photoactive in phenol degradation under UV-Vis light. After 60 min of irradiation, 52% of phenol was degraded. The same time of irradiation resulted in 22% of phenol degradation under visible light. P25 modified with gold clusters revealed lower photoactivity than pure P25 both under UV-Vis and visible light



irradiation. However, deposition of silver or platinum clusters at the surface of P25 nanoparticles resulted in higher photoactivity. Phenol degradation rate was 2.69, 2.28 and 3.14 $\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for the samples obtained by radiation of P-25 suspension containing 0.5, 1 and 2 wt.% of AgClO₄, respectively.

All photocatalysts obtained by radiolytic reduction of AgClO₄ in the presence of P25 showed higher photoactivity than the samples prepared with ST01. From all the samples prepared by radiolysis reduction of platinum salts in the presence of P25, the highest photoactivity was observed for the samples obtained by γ -irradiation of 1 wt.% H₂PtCl₆ and 1 wt.% (NH₃)₄PtCl₂·H₂O solution followed by adsorption of metal cluster at the P25 surface. Phenol decomposition rate was 3.71 and 3.43 $\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for the sample Pt-P25(1) and Pt-P25(1a), respectively. It was observed

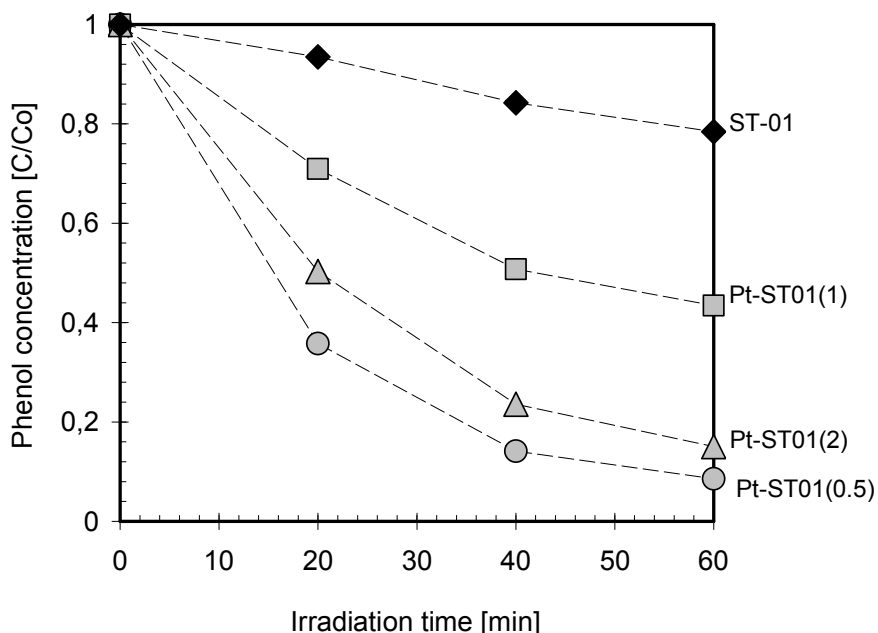


Fig. 2. Photoactivity under UV-Vis light of ST01-TiO₂ modified with platinum clusters deposited by radiolytic reduction of H₂PtCl₆. Experimental conditions: C₀=0.21 mM; m (TiO₂) = 125 mg, T=10°C, Q_{air}=5 l/h

Figure 3 shows the comparison characteristics of the most photoactive metal-modified P25 samples prepared using three types of metal precursors: KAuCl₄, AgClO₄ and H₂PtCl₆. All photocatalysts revealed the highest photoactivity under UV-Vis light comparable to that of pure TiO₂. Phenol degradation rate was 3.14 $\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for

the Ag-P25(2) sample, $3.15 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for the Pt-ST01(0.5) sample, and $1.94 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for the AuP25(2) sample.

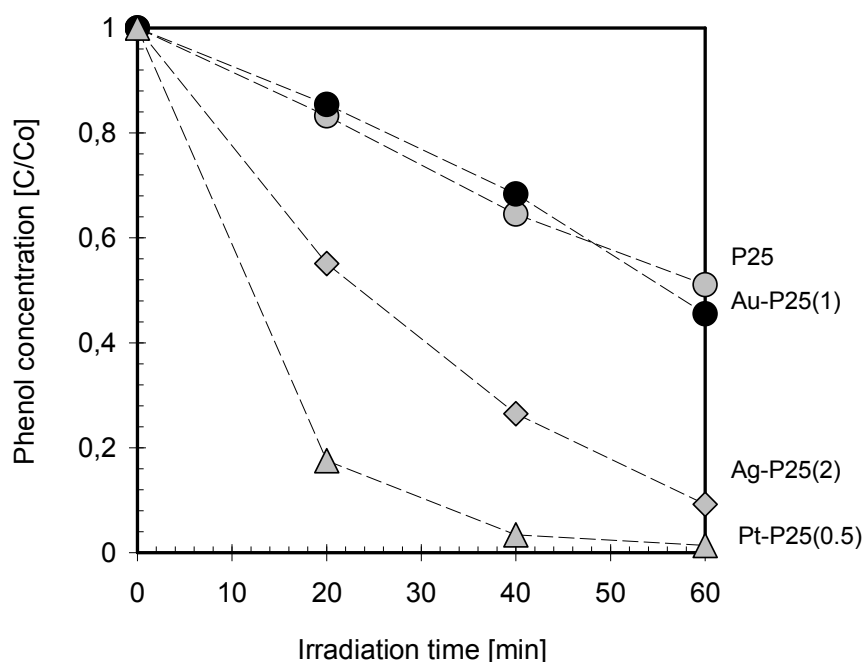


Fig. 3. Photoactivity under UV-Vis light of Au, Ag, Pt-TiO₂ photocatalysts. Experimental conditions: C_o=0.21 mM; m (TiO₂) = 125 mg, T=10°C, Q_{air}=5 l/h

Visible light activity was measured only for the samples revealed high photoactivity under UV-Vis light. The highest photoactivity was observed for the sample prepared by reduction Ag(I) (1 wt.%) on P25 and Pt(IV) (0.5% wt.) on ST-01 nanoparticles. Phenol degradation rate equaled 0.78 and $1.07 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for the sample Ag-P25(1) and Pt-ST01(0.5), while it was 0.55 and $0.25 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$ for pure P25 and ST01, respectively. We did not observe any increase in photoactivity under visible light in the case of gold surface modification of P25. All obtained powders prepared by radiolytic reduction of KAuCl₄ in the presence of P25 had almost the same photoactivity under visible light (about $0.5 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$).

Among all tested Pt-TiO₂ samples, Pt-P25(1) showed the best both UV-Vis and visible light photoactivity for phenol degradation. After 60 min irradiation, phenol was degraded in 99 and 38% under UV-Vis and visible light, respectively. According to the literature data under UV irradiation platinum acts as a charge scavenger hindering

charge recombination. Under visible light irradiation a sensitization mechanism should be considered such as absorption of light by platinum clusters.

4. CONCLUSION

The effect of the metal modification on the photocatalytic activity depends on the type of metal, metal precursor concentration used during synthesis and the origin of titania. Generally, Degussa P25 surface modified with silver, gold and platinum clusters exhibits better efficiency in phenol photooxidation than ST01-based photocatalysts. It was found that titania surface modification with silver and platinum enables the increase of the photocatalytic activity both under UV and visible irradiation.

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REFERENCES

- [1] FUJISHIMA A., RAO T.N., TRYK D.A., (2000) *Titanium dioxide photocatalysis* J. Photochem. Photobiol. C 1, 1-21
- [2] KITANO M., TEKAUCHI M., MATSUOKA M., THOMAS J.M., ANPO M., (2007) *Photocatalytic water splitting using Pt-loaded visible light-responsive TiO₂ thin film photocatalysts* Catal. Today 120, 133-138
- [3] KUMAR S., FEDOROV A.G., GOLE J.L. (2005) *Photodegradation of ethylene using visible light responsive surfaces prepared from titania nanoparticle slurries* Appl. Catal. B 57, 93-107
- [4] DAMM C., IZRAEL G., (2007) *Photoelectric properties and photocatalytic activity of silver-coated titanium dioxides* Dyes Pigments 75, 612-618
- [5] ORLOV A., JEFFERSON D. A., MACLEOD N., LAMBERT R. M. (2004) *Photocatalytic properties of TiO₂ modified with gold nanoparticles in the degradation of 4-chlorophenol in aqueous solution* Catal. Lett. 92 1, 41-47
- [6] HWANG S., LEE M. C., CHOI W., (2003) *Highly enhanced photocatalytic oxidation of CO on titania deposited with Pt nanoparticles: kinetics and mechanism* Appl. Catal., B, 46, 49-63
- [7] CHAO H. E., YUN Y. U., XINGFANG H. U., LARBOT A., (2003) *Effect of silver doping on the phase transformation and grain growth of sol-gel titania powder* J. Eur. Ceram. Soc 23, 1457-1464
- [8] TORIMOTO T., NAKAMURA N., IKEDA S., OHTANI B., (2002) *Discrimination of the active crystalline phases in anatase-rutile mixed titanium(IV) oxide photocatalysts through action spectrum analyses* Phys. Chem. Chem. Phys. 4, 5910-5914
- [9] ZHU Y., QIAN Y., HUANG H., ZHANG M., LIU S., (1996) *Sol-gel γ -radiation synthesis of titania-silver nanocomposites* Mater. Lett., 28, 259-261
- [10] EL-AZAB A., GAN S, LIANG Y., (2002) *Binding and diffusion of Pt nanoclusters on anatase TiO₂(0 0 1)-(1 x 4) surface* Surf. Sci., 506, 93-104

- [11] LONGONI, G.; CHINI, P. (1976) *Synthesis and Chemical Characterization of Platinum Carbonyl Dianions* $[Pt_3(CO)_3(m-CO)_3]n^{2-}$ ($n=10,6,5,4,3,2,1$). *A New Series of Inorganic Oligomers* J. Am. Chem. Soc. 98, 7225-7231
- [12] TREGUER M., REMITA H., BELLONI J., KEYZER R., (2002) *Carbonyl platinum clusters as silver halide dopant for photographic latent image formation.* *J. Imaging Sci. Technol.* 46, 193-199
- [13] BELLONI J., TREGUER M., REMITA H., DE KEYZER R., (1999) *Enhanced yield of photoinduced electrons in doped silver halide crystals* *Nature* 402, 865-867
- [14] KOWALSKA E., REMITA H., COLBEAU-JUSTIN C., HUPKA J, BELLONI J. (2008) *Modification of Titanium Dioxide with Platinum Ions and Clusters: Application in Photocatalysis* *J. Phys. Chem. C* 112. 1124-1131
- [15] BURGETH G., KISCH H., (2002) *Photocatalytic and photoelectrochemical properties of titania-chloroplatinate(IV)* *Coord. Chem. Rev.* 230, 41-47

