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NOBLE METAL MODIFIED TiO_2 FOR PHOTOCATALYTIC AIR PURIFICATION

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Abstract: TiO_2 was surface modified with silver, gold, palladium and platinum ion clusters to improve its photocatalytic activity. The effect of metal content and kind of dopant used during preparation procedure on the photoactivity were investigated. in toluene removal which was used as a model volatile organic compound. Toluene, at the concentration of about 100 ppm, was irradiated over noble metal modified TiO_2 using light-emitting diodes (LEDs) in four subsequent cycles.

Keywords: *photocatalysis, noble modified* TiO_2*, air treatment; toluene*

Introduction

Volatile organic compounds (VOCs) are a group of air pollutants widely present in both indoor and outdoor environments. The main emission sources of VOCs are motor vehicle exhausts and solvent utilization (Zou et al., 2006). Toluene, as one of widespread volatile organic compounds, is found in polluted urban atmosphere. Due to its high toxicity, carcinogenicity, and long environmental persistence, it is regarded as a priority hazardous substance. Therefore, removal of toluene in the contaminated atmosphere has become an increasingly concerned issue in the field of environment protection (Zou et al., 2012).

The use of heterogeneous photocatalysis in the degradation of environment pollutants has aroused intensive attention during the past two decades (Minabe et al., 2000; Hoffmann et al., 1995). Among various semiconductor photocatalysts for environment purification, titania appears to be the most promising and important one due to its stable physical and chemical characteristics, unique electronic properties, strong oxidizing power, non-toxicity and low price. However, the wide band gap of TiO_2 (>3.2 eV) and the high recombination rate of the photoinduced electron–hole

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pairs formed in photocatalytic processes limit the efficiency of the photocatalytic degradation of toxicants (Minabe et al., 2000).

Barraud et al. (2005) investigated the photocatalytic removal of toluene in the gas phase carried out over UV-illuminated sulfated titania materials in a cylinder-like continuous reactor. They have concluded that only CO_2 and H_2O were detected as gaseous reaction products whatever photocatalyst was used. The presence of the adsorbed reaction intermediates such as benzaldehyde and benzoic acid was identified by the FTIR spectra of the sulfated TiO_2 photocatalysts. Keller et al. (2007) compared the photocatalytic behavior of different TiO_2-based photocatalysts for the gas-phase toluene removal under both UV and visible light illumination. They reported that promotion by sulfates and the use of nanosized anatase TiO_2 prepared by sol–gel route did strongly increase the toluene removal efficiency under UV illumination. Sekiguchi et al. (2008) performed the photocatalytic degradation of toluene gas in a mist formed by ultrasonic atomization of slurried TiO_2. They revealed a new effective utilization of ultrasonic mist and TiO_2 photocatalyst over which gaseous toluene could be decomposed and mineralized. Nischk et al. (2013) prepared vertically ordered TiO_2 nanotube arrays and measured photocatalytic activity in the toluene removal. Toluene, at the concentration of about 100 ppm, was irradiated over TiO_2 nanotube arrays using xenon lamp and light-emitting diodes (LEDs) in four subsequent cycles. The results showed that toluene could be mostly removed from the air after 30 min of irradiation over TiO_2 nanotubes (NTs), even using LEDs (375 nm) as a irradiation source. Photoactivity increased with increasing of nanotubes lengths and decreasing of the crystallite size (Nischk et al., 2013).

In this work series of modified TiO_2-based photocatalysts were prepared by the photodeposition of noble metals at the surface of P25 (TiO_2 loaded with Pt, Pd, Ag, Au nanoparticles). Photocatalytic activity of prepared TiO_2 photocatalysts was determined in the process of cleaning air from volatile organic compounds (VOC). Toluene was used as a model air contaminant.

Materials and methods

P25 (70:30% anatase-to-rutile mixture with a BET surface area of 55 ± 15 m^2/g and crystallite sizes of 30 nm in 0.1 μm diameter aggregates) was obtained from Evonik Industries, Germany (Ohno et al., 2001, Ohtani et al., 2010). 98% $KAuCl_4$, 99% H_2PtCl_6, $PdCl_2$ (anhydrous, 60% Pd basis) were purchased from Sigma-Aldrich. 99,9 %$AgNO_3$ was purchased from POCh S.A. (Poland).

Toluene (99.5%, p.a., POCh S.A., Poland) was used as a model air contaminant. All reagents were used without further purification.

All the photocatalysts were obtained by radiolysis reduction of noble metals in the TiO_2 suspension. 70 cm^3 of solution containing TiO_2 P25 (3 g), metal precursor (0.1 or 1 % m/m Au, Pt, Pd and Ag respectively), water (68 cm^3) and isopropanol (2 cm^3) was degassed with nitrogen in dark for 40 min. Then the suspension was illuminated by

1000 W Xe lamp used as an irradiation source for 2 h. Obtained samples were rinsed with deionized water, dried in air (80°C for 24 h) and grinded in the agate mortar.

Light-absorption properties of TiO_2 nanotubes were characterized by recording diffuse reflectance (DR) spectra and converting the data in order to obtain absorption spectra. The measurements were performed on UV-Vis spectrophotometer (Evolution 220, Thermo Scientific) equipped with an integrating sphere. The baseline was determined using barium sulfate as a reference

Total metal content of the samples was determined by X-ray fluorescence spectrometry (XRF). Pressed pellet (diameter 8mm) were analyzed using WD-XRF (Bruker S8 Tiger 1KW). The instrument is equipped with a rhodium tube and a proportional and scintillation detector. Linear intensity range was more than 10 million cps. All analyses were conducted at maximum 50 keV and 50 mA. Standardless analysis was used to determine the concentrations of the measured elements.

The modified TiO_2 samples were examined by transmission electron microscopy (STEM-EDX, FEI Europe, model Tecnai F20 X-Twin). To obtain a suitable sample for TEM characterization metal modified TiO_2 powder was dispersed in ethanol in an ultrasound bath for a few minutes. Some drops of suspension were deposited on carbon covered microgrid.

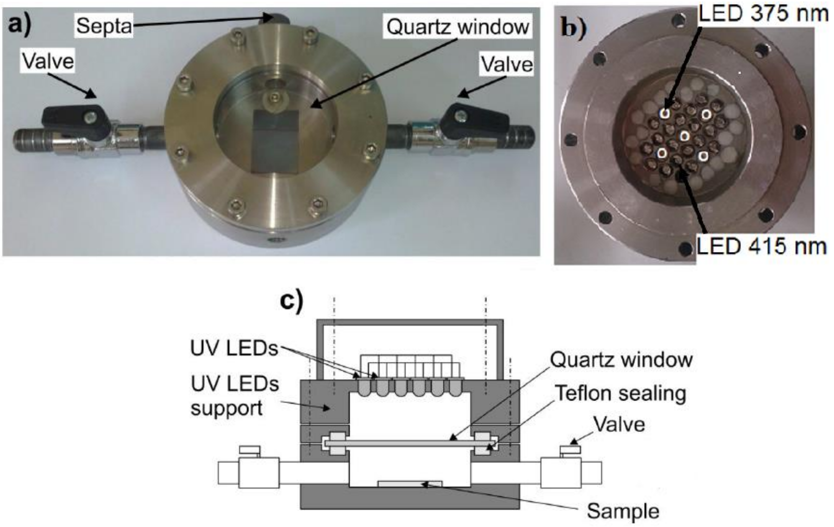


Fig. 1. Photocatalytic set-up for gas phase reaction: (a) image of gas phase photoreactor; b) image of UV-Vis LEDs array; (c) scheme of photoreactor equipped with UV-Vis LEDs as an irradiation source

Photocatalytic activity of prepared TiO_2 photocatalysts was determined in the process of cleaning air from volatile organic compounds (VOC). Toluene was used as a model air contaminant. The photocatalysts activity tests were carried out in a flat stainless steel reactor with the working volume of about 30 cm^3 (see details in Fig. 1) equipped with a quartz window, two valves and a septa (Fig. 1a). An array of 20 UV LEDs ((λ_{max} = 375 nm, 63 mW per diode) and 5 VIS LEDs (λ_{max} = 415 nm) was used as an irradiation source. Glass plate covered by noble metal modified TiO_2 was placed at the bottom side of the reactor followed by closing the reactor with a quartz window. Subsequently, the gaseous mixture was passed through the reaction chamber for 2 min. After closing the valves, the reactor was kept in dark for 10 min in order to achieve equilibrium. A reference sample was taken just before starting irradiation. The analysis of toluene concentration in the gas phase was performed using gas chromatograph (Clarus 500, PerkinElmer) equipped with flame ionization detector (FID) and Elite-5 capillary column (30 m × 0,25 mm, 0,25 μm). Details of GC analysis are reported by Nischk et al., 2013.

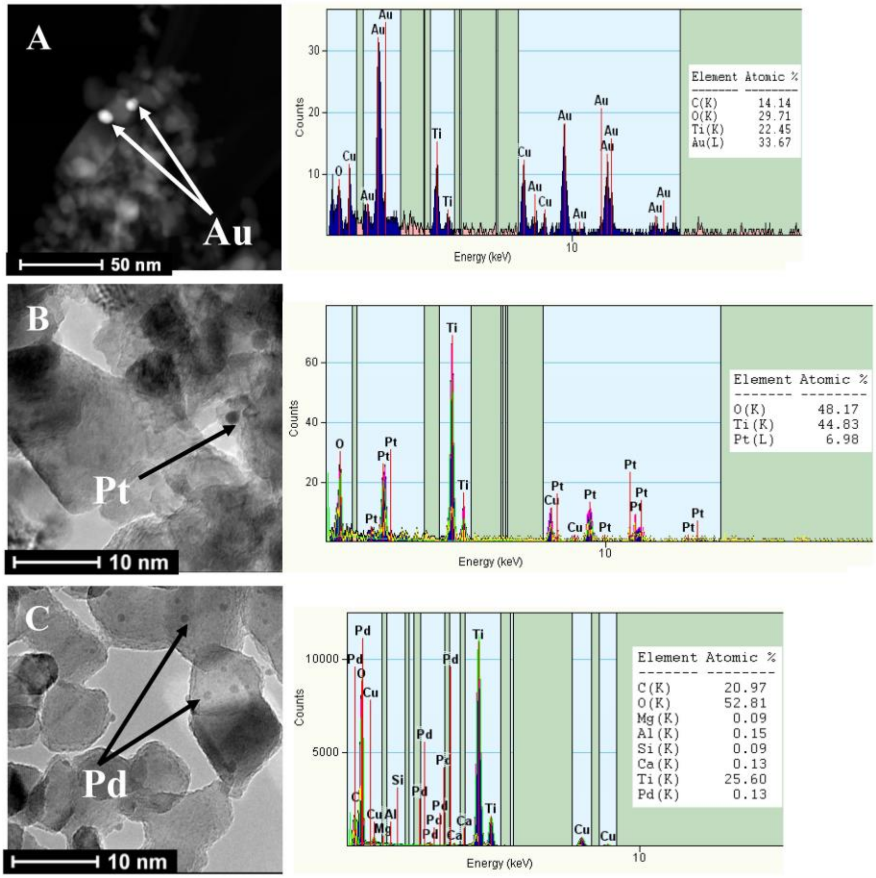
Result and discussion

Sample labeling and coloration of the samples after metal modification are given in Table 1.

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

Sample label	Metal precursor	Concentration of metal precursor used during photodeposition % (m/m)	Metal amount based on XRF analysis % (m/m)	Sample color
P25_Au(0.1)	$KAuCl_4$	0.1	0.1	violet
P25_Au(1)		1	0.8	
P25_Ag(0.1)	$AgNO_3$	0.1	0.1	light pink
P25_Ag(1)		1	0.71	
P25_Pt(0.1)	H_2PtCl_6	0.1	0.1	light grey
P25_Pt(1)		1	0.9	
P25_Pd(0.1)	$PdCl_2$	0.1	0.1	grey
P25_Pd(1)		1	0.65	
P25	–	–	–	white

Microstructures of the selected samples and their surface morphologies were examined by TEM equipped with EDS. TEM images and EDS mapping of gold, platinum and palladium nanoparticles deposited at the surface of P25_TiO_2 are given in Fig. 2. TEM observations show small metal nanoparticles homogeneous in size. Metal nanoparticles with mean sizes 20, 4 and 1.5 nm were obtained for the P25 samples loaded with gold, platinum and palladium, respectively. As it can be observed from Fig. 2B and C, photodeposited Pt and Pd particles are always found to be spherical in shape. It can be also observed that the photodeposited gold and platinum show poor homogeneity and dispersion of deposits with some areas of the TiO_2 surface having a high density of Au or Pt particles and others being relatively empty.



Element	Atomic %
C(K)	14.14
O(K)	29.71
Ti(K)	22.45
Au(L)	33.67

Element	Atomic %
O(K)	48.17
Ti(K)	44.83
Pt(L)	6.98

Element	Atomic %
C(K)	20.97
O(K)	52.81
Mg(K)	0.09
Al(K)	0.15
Si(K)	0.09
Ca(K)	0.13
Ti(K)	25.60
Pd(K)	0.13

Fig. 2. EDS mappings of 1 % (m/m) (A) gold- (B) platinum (C) palladium-modified TiO_2

This results are in correlation with literature data. Zielinska et al. (2011) obtained Au-TiO_2 nanoparticles using a water-in-oil microemulsion system of water/AOT/cyclohexane and water/Triton X-100/cyclohexane. They obtained gold nanoparticles on the surface of TiO_2 in the range of 10-69 nm. Silva et al. (2010) obtained Pt nanoparticles on Ce-Ti-O support by photochemical deposition. They identified Pt particles ranging in size from 2.5 to 4 nm. A comparative study of the photodeposition of Pt, Au and Pd under the same experimental conditions onto pre-sulfated and non-sulfated TiO_2 was performed by Maicu et al. (2011). They observed that for the nonsulphated TiO_2 most of the Pt deposits have diameters ranging from 3 to 6 nm, while for the pre-sulphated material the average particle size is smaller, having more than 50% of the platinum particles an average diameter in the range of 2–4 nm. In case of Au particles deposited via this method are irregularly sized, varying from around 10nm to more than 100 nm in diameter. The estimation of Pd average particle size shows that Pd particles deposited on non-sulfated TiO_2 have diameters ranging from approximately 3 to 7 nm while on the pre-sulfated sample the average size is higher with particles ranging from 4 to 10 nm (Maicu et al., 2011).

The optical properties have been studied in details by Diffuse Reflectance Spectroscopy (DRS). Figure 3 shows the absorption spectra of pure and metal modified TiO_2-based photocatalysts. The measurement of the samples was made at the wavelength of light in the range from 300 to 750 nm. The absorbance in the visible region is always higher for the modified than for pure TiO_2. It should be pointed out that the DRS of the modified samples shows a shift in the band-gap transition to longer wavelengths for all kinds of surface-modified photocatalysts.

The DR spectra of gold-modified titanium dioxide nanoparticles are shown in Fig. 3A. In the visible region the absorption spectrum for Au-TiO_2 nanoparticles is characterized by a pronounced plasmon band, whose maximum location depends on the gold nanoparticles size.

The P25_Au- TiO_2 nanoparticles show plasmon absorption bands at about 560 nm. Au doping has a significant effect on the absorption properties of TiO_2 and that the absorption of light by TiO_2 in the visible region increases when particles size decreases.

In the case of Ag-modified samples (Fig. 3B), a wide absorption is observed with a maximum at 450 nm. Silver nanoparticles are known to exhibit a plasmon band with a maximum at around 400 nm in water. This plasmon band is sensitive to the environment and can be shifted depending on the stabilizer or on the substrate.

The spectra of the Pt and Pd-loaded samples show a slight shift in the band gap transition to longer wavelengths (Fig. 3C and D). The red shift in the band gap transition revealed by diffuse reflectance spectra can be explained by the introduction of energy levels of the metal ions into the band gap of TiO_2. The absorbance in the visible region for the metallised systems shows that lower-energy transitions are possible. This is because the metal clusters give rise to localised energy levels in the bandgap of TiO_2 into which valence band electrons of TiO_2 are excited at wavelength longer than 400 nm (Sakthivel et al., 2004).

The effect of kind and amount of metal precursor on the photocatalytic activity of modified TiO_2 as well as their stability in four measurements cycles under UV-Vis LEDs irradiation were presented in Fig. 4. In the case of pure TiO_2 P25 (Fig. 4a) all toluene was removed from gas phase after 20 min irradiation in three subsequences cycles. Only in the last cycle toluene removal efficiency reached about 86% after 30-min process.

Definitely, the highest photocatalytic activity was observed in the case of P25_Pd(1) and P25_Pt(0.1) sample. In both cases all toluene was removed after 20 min irradiation in three subsequences cycles. Only in the last cycle toluene removal efficiency reached about 100% (the final toluene concentration was below detection limit) after 25-min process.

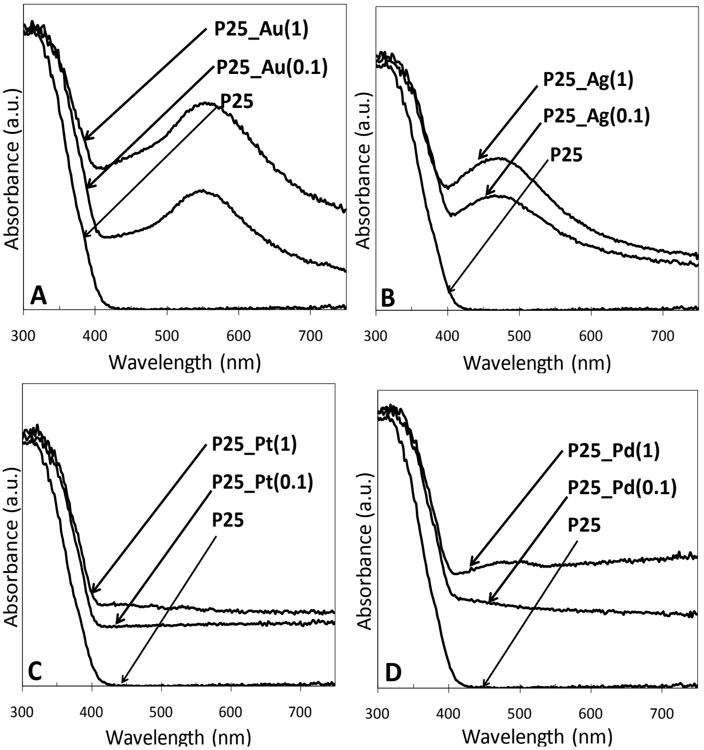


Fig. 3. Diffuse reflectance spectra of pure and: (A) gold- (B) silver (C) platinum (D) palladium-modified TiO_2

In the case of all samples the photocatalysts' activity decreased in subsequent measurement cycles which suggests that active sides of TiO_2 may have been blocked by toluene partial decomposition products. The lowest photoactivity was observed for samples modified with silver. Even in the first cycle of toluene degradation in the presence of P25_Ag(1) sample toluene removal efficiency reached only 67% after 30-min process and decreased to about 34% in the last cycle.

Conclusions

In summary, photocatalytic acitivity of noble metal modified TiO_2 in the gas phase reaction depends on the kind of metal and noble metal precursor concentration used during synthesis.

Generally, TiO_2-P25 surface modified with silver, gold, palladium and platinum clusters exhibits high efficiency in toluene removal. 30-min of irradiation by twenty five UV-LEDs (λ_{max} = 375 nm, 63 mW per diode) was enough to complete removal of toluene (C_0 = 100 ppm) from the gas phase in four subsequent cycles in the presence of almost all samples (except P25_Pt(1), P25_Ag(1) and P25-Pd(0.1)). The same photoactivity was observed in four subsequent cycles for P25_Au(0.1) and P25_Pd(1) samples.

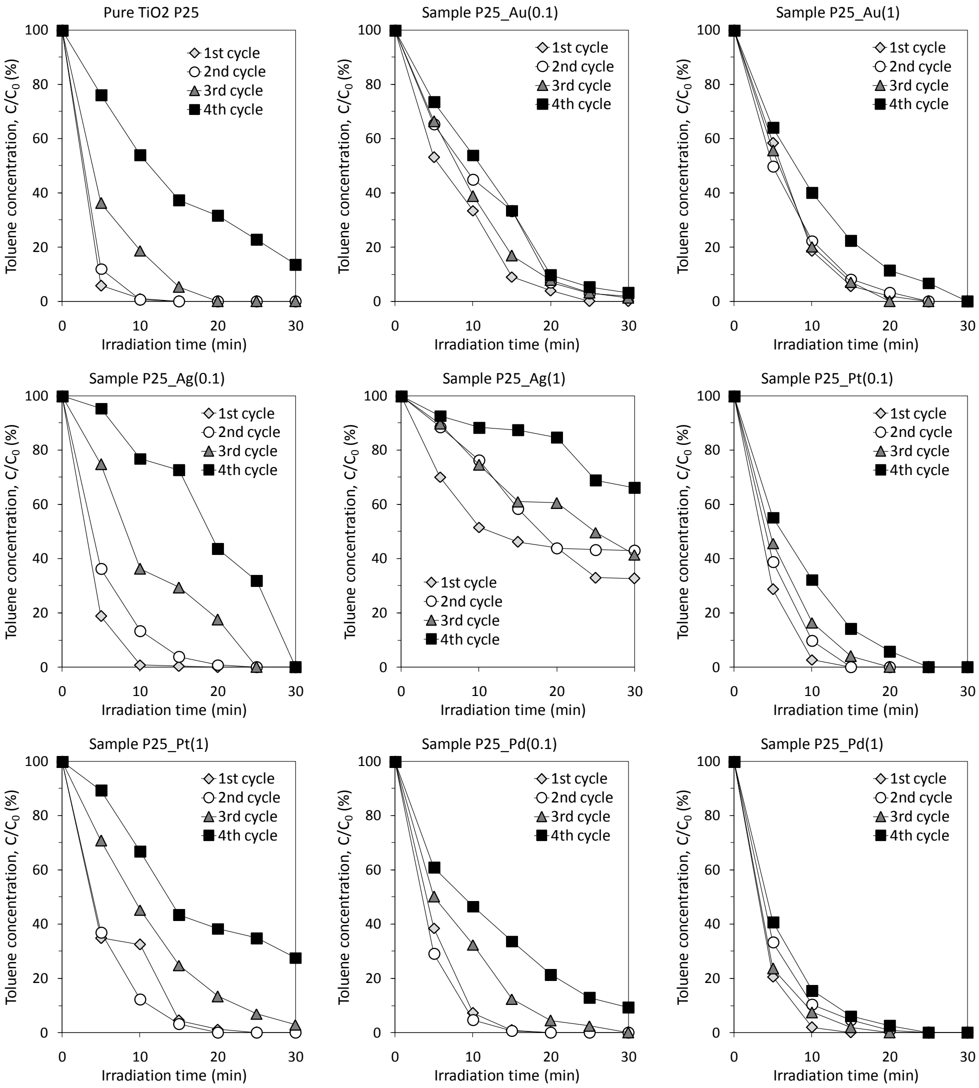


Fig. 4. Toluene photodegradation efficiency as the function of irradiation time. The influence of kind and amount of metal precursor on the initial photocatalytic activity of TiO_2 nanotubes and their stability in four measurement cycles under UV-Vis LEDs irradiation

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