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Au-RE-TiO₂ NANOCOMPOSITES. SURFACE CHARACTERISTICS AND PHOTOACTIVITY

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Abstract: Photocatalysts based on TiO₂ co-doped with rare earth metal (RE) and gold nanoparticles have been prepared using a sol-gel method and followed by gold reduction. Specific surface areas of the modified photocatalysts were calculated by the Brunauer-Emmett-Teller method (BET). Diffuse reflectance spectra of the obtained photocatalysts were recorded with a UV-Vis spectrophotometer (DRS UV-Vis). The influence of the type of rare earth metal on photoactivity of Au-RE-TiO₂ nanocomposites in model reaction manifested by toluene photodegradation in a gas phase was investigated. The obtained results showed that photodegradation of toluene in the gas phase is possible over Au-RE-TiO₂ irradiated by UV or Vis light. The Au-RE-TiO₂ photocatalysts relative to undoped TiO₂, did not caused an increase of toluene degradation in the air under visible light. The samples doped with Er³⁺ or Pr³⁺ presented the highest activity in solar light among of Au-RE-TiO₂. It was observed that both metal dopants affected the surface area of TiO₂. The Au-RE-TiO₂ photocatalysts relative to undoped TiO₂ exhibited the absorption properties under Vis light.

Keywords: photocatalysis, modified TiO₂, rare earth metal, Au nanoparticles, toluene degradation

Introduction

Advanced oxidation with the aid of sunlight sensitive photocatalysts may prove to be a solution to environment pollution (Fujishima et al., 2000). Photochemical reactions catalyzed by TiO₂ were investigated in the degradation of dyes, hazardous substances in contaminated air and wastewater streams (Ibhadon and Fitzpatrick, 2013). Titanium dioxide is one of the most promising materials in heterogeneous photocatalytic oxidation due to its effectiveness, chemical stability, cheapness and availability. It also exhibits strong purifying power (Zaleska et al., 2007). Although TiO₂ has a large band gap of 3.3 eV in anatase crystalline phase, it can be activated only by UV light and from 3% to 5% of Vis light, limiting utilization of sunlight as the source in

photocatalytic reactions. The development of modified TiO₂ photocatalysts should exhibit high reactivity under Vis light in the main part of the solar spectrum (Parida et al., 2008). Modified TiO₂ photocatalysts with enhanced activity under sunlight can be prepared by doping metal elements such as rare earth metal (Parida and Sahu, 2008) or noble metal (Boyd et al., 2005; Zielinska-Jurek et al., 2011).

If a metal or non-metal is used as a doping agent for TiO₂, these energy levels can be incorporated into the band gap of TiO₂. A new energy levels can either accept electrons from the valence band or donate electrons to the conduction band. Owing to less energy separation between the new energy levels and the valence band or conduction band, visible light becomes energetic enough to facilitate the above mentioned electron transitions (Bingham and Daoud, 2010). Reducing the size of the band gap by introducing energy levels between the conduction band and valence band allowed TiO₂ to be active under visible light. This is the main idea of metal and non-metal doping.

Doping can be achieved through the sol-gel process, hydrothermal synthesis, electrospinning and magnetron sputtering (Diamandesceu et al., 2008; Yang et al., 2011). The sol-gel is one of the wet chemistry method used in non-metal or metal doping TiO₂. The wet chemistry methods usually involve hydrolysis of titanium precursor in a mixture of water and other reagents followed by heating (Chen and Mao, 2007). The benefits of sol-gel method are compositional control, homogeneity on the molecular level due to mixing liquid precursors and low preparation temperature. However, the influence of organic traces on the optical quality of the material might be noticeable. Furthermore, the traditional sol-gel techniques might not be applicable to complex-shaped surfaces (Kanarjov et al., 2008). It can be inferred that the sol-gel method conditions can allow for either lanthanide ions to form oxides dispersed on the exterior of the semiconductor or incorporation in the titania matrix (Su et al., 2004).

Noble metal nanoparticles (gold, silver, platinum, et cetera) were used to enhance photocatalytic activity of TiO₂ (Chuang and Chen, 2009). Gold nanoparticles possess ability to absorb visible light, due to a localized surface plasmon resonance (LSPR). The samples of Au-TiO₂ nanoparticles showed plasmon absorption bands at about 550 nm. The activity of Au-TiO₂ photocatalysis depends on the preparation method and on the size and shape of gold nanoparticles (Kowalska et al., 2010). The gold nanoparticles less than 5 nm in size are the most active catalysts (Haruta et al., 1993).

A rare earth metal (RE) was doped TiO₂ in an attempt to achieve visible light photocatalysis. The rare earth metal established complexation with RE-O-Ti bond on the inner sphere surface, which inhibited the transformation from anatase to rutile (Liu et al., 2012). The best photocatalytic properties in visible light were the TiO₂ doped with Nd³⁺ (Stengl et al, 2009), and Gd³⁺ (Xu et al., 2002) due to their the lowest band gap, particle size, highest surface area and pore volume. The RE-doped TiO₂ nanomaterials usually showed large surface area and high porosity. A larger surface area provided more surface active sites for the adsorption of reactants molecules,



which make the photocatalytic process more efficient (Hassan et al., 2012). Co-doping TiO₂ with different elements showed different absorption and photocatalytic properties to those doped individually (He et al., 2008).

In this paper, we present a novel approach for obtaining RE-doped TiO₂ loaded with Au nanoparticles. The influence of rare metal type (Ho, Nd, Er, Eu and Pr) on Au-TiO₂ surface properties and photoactivity in the gas phase reaction was investigated.

Experimental

Materials and instruments

Titanium isopropoxide (97%, Sigma Aldrich) with acetic acid (99 %, POCH S.A.) and ethanol (96 %, POCH S.A.) were used for the preparation of TiO₂ nanoparticles. The precursors of rare earth metal as salts: Ho(NO₃)₃·5H₂O, Nd(NO₃)₃·6H₂O, Er(NO₃)₃·5H₂O, Eu(NO₃)₃·5H₂O and Pr(NO₃)₃·6H₂O were provided from Sigma Aldrich. Hydrogen tetrachloroaurate (III) (99%, Sigma Aldrich) was used as the precursor for preparation gold nanoparticles. Ammonium hydroxide (25%, Sigma Aldrich) was exploited to adjust the pH above 8.5 of the solution. Sodium borohydride (99%, Sigma Aldrich) was used to reduce the gold nanoparticles. Deionized water was exploited for all the reactions and treatment processes.

Specific surface areas of the modified photocatalysts were determined by the Brunauer-Emmett-Teller method (BET). Nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) on a Micromeritics Gemini V, model 2365 PC. Prior to analysis, the samples were degassed at 200 °C for 2 h.

Diffuse reflectance spectra (DRS) of the obtained photocatalysts were characterized using a UV-Vis spectrophotometer Thermo Evolution Nicolet, model 220 equipped with ISA 220 integrating sphere accessory. The UV-Vis DRS spectra were recorded in the range of 300–900 nm using sulfate barium as the reference standard.

Preparation of Au-RE-TiO₂ photocatalysts

The preparation of Au-RE-TiO₂ photocatalysts is presented in a block diagram in Fig. 1. In the first step RE-modified TiO₂ was prepared using the sol-gel method. The sample of 15 cm³ titanium isopropoxide was added to the mixture of 3 cm³ acetic acid and 60 cm³ ethanol. The sol was stirred for 10 min. Then rare earth nitrate was dissolved in 2 cm³ water, added dropwise to the solution, and stirred for 2 h. The gel was dried at 80 °C for 24 h to remove the solvents and then calcined in air at 400 °C for 4 h at the heating rate of 2 °C/min in an oven. Calcination is used to transform TiO₂ amorphous form to anatase or rutile crystal structure. Enhancing the photocatalytic activity of TiO₂ can be achieved by calcination at temperature of 400 °C allowing TiO₂ to receive anatase crystal structure. The temperature of anatase



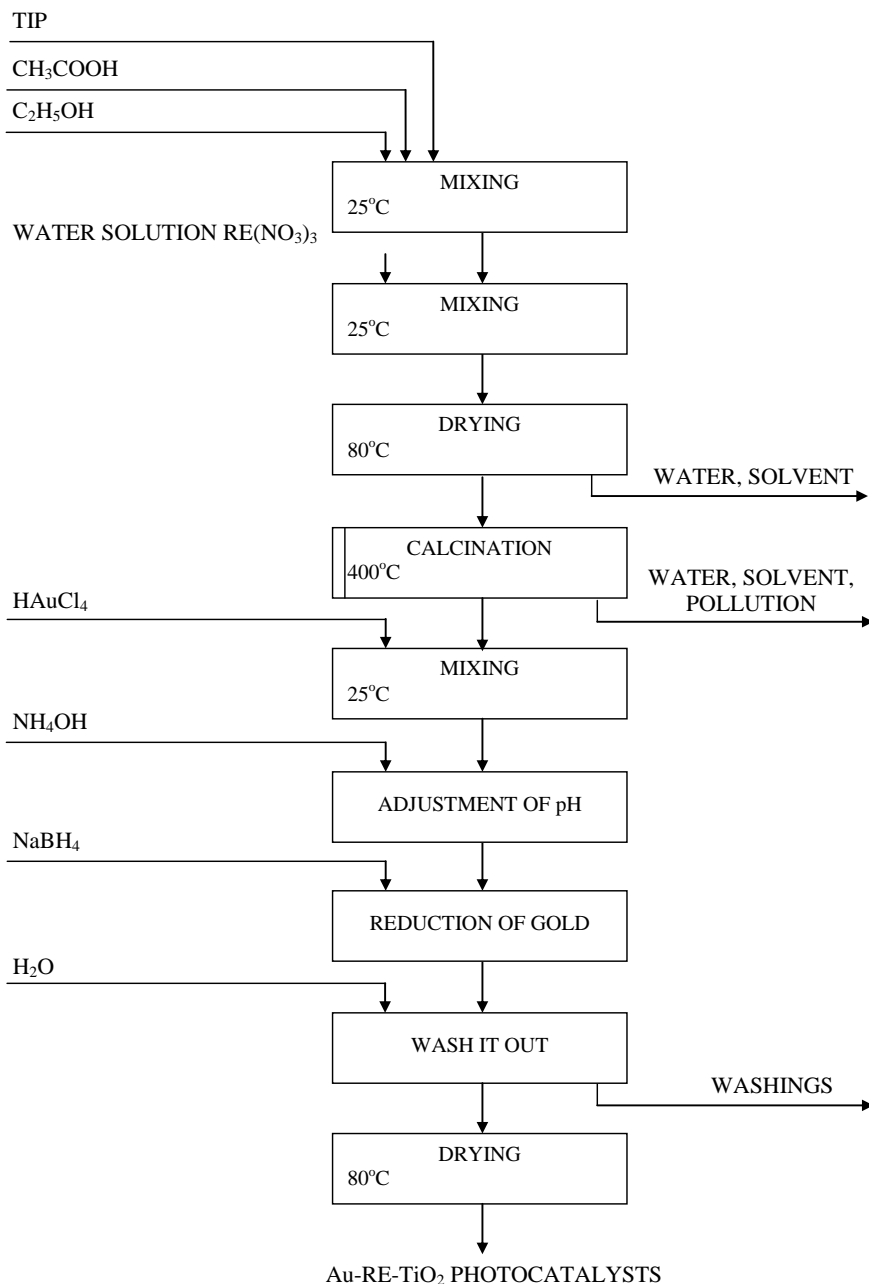


Fig. 1. Block diagram of preparation of Au-RE-TiO₂ photocatalysts

to rutile transformation is estimated to be over 500 °C (Chen and Mao, 2007). The obtained sample was milled into powder. In the second step Au-modified RE-TiO₂



was prepared by the reduction method. Hydrogen tetrachloroaurate (III) as the gold precursor was added to water suspension of RE-TiO₂ powder. The pH 8.5 of dispersion was adjusted with 25% ammonium hydroxide. The gold nanoparticles were reduced by sodium borohydride. The solution turned from transparent to violet color due to reduction of Au ions. The gel was dried again at 80 °C for 12 h. In modified TiO₂ the concentration of rare earth metal was permanently 0.5 mol.% and the concentration of gold nanoparticles were 1 or 2 mol % related to the concentration of TIP. Pure TiO₂ and Au-TiO₂ were prepared in the same way.

Measurements of photocatalytic activity

The photocatalytic activity of Au-RE-TiO₂ powders in visible light was estimated by a model photodegradation toluene in the air. Photochemical reactions were carried out in a custom-made photoreactor with replacements, two sets of 25 LED lamps in range UV light (wavelength 375 nm) or Vis light (wavelength 415 nm). Gases from the reactor were analyzed using an on-line gas chromatography, PerkinElmer, model Clarsus 500 (Nischk et al., 2014).

Results and discussion

Table 1 summarizes the measured BET surface area, total pore volume, pore diameter and photocatalytic activity results for TiO₂ co-doped with selected rare earth metal (holmium, neodymium, erbium, europium or praseodymium) and gold nanoparticles. The TiO₂ as a reference material has the lowest BET surface area and pore volume of about 115 m²/g and 0.1 cm³/g. The 2 % Au-0.5 % Pr-TiO₂ and 2 % Au-0.5 % Eu-TiO₂ have the highest surface area equal to about 139 m²/g. For other Au-RE-TiO₂ samples containing from 1 to 2 mol % of gold and 0.5% rare earth metal the surface areas varied from 134 to 139 m²/g. The 2% Au-0.5% Nd-TiO₂ had the lowest pore diameter of about 1.91 nm. The pure TiO₂ showed well-crystallized anatase structure. Despite having a higher BET surface area, Au-RE-TiO₂ have not caused an increase photocatalytic activity relative to undoped TiO₂. It could be considered that pore accessibility of TiO₂ is constrained by rare earth metals. On the other hand it might be a consequence of remaining carbon deposits on the nanocomposites, which came from titanium isopropoxide. Xu et al. (2002) reported that the rare earth metal salts can be changed into rare earth oxides during the calcinations process. Therefore, it can be inferred that the rare earth ions were dispersed on the surface of TiO₂ in the form of small clusters, which inhibit TiO₂ amorphous structure transform to the anatase crystal structure.

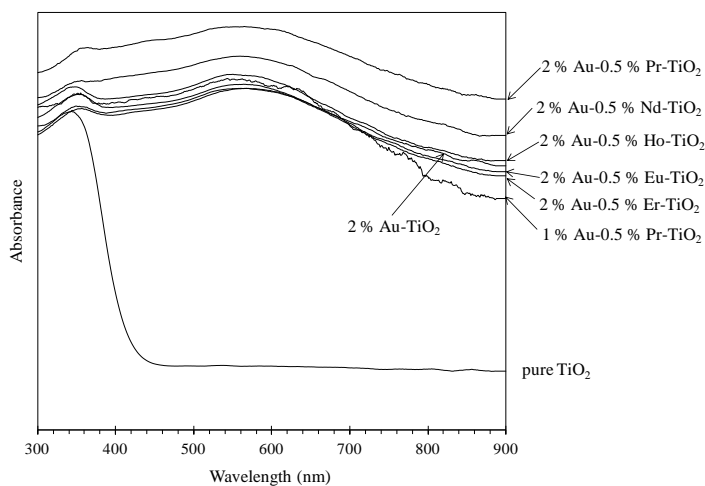
The light absorption properties of prepared Au-RE-TiO₂ photocatalysts, DRS UV-Vis absorption spectra in the range of 300-900 nm were investigated and the results are shown in Fig. 2. The spectrum of DRS UV-Vis showed that the undoped TiO₂ decreased by light reflection at a wavelength of about 380 nm, what proved that it



Table 1 Surface properties and photocatalytic activity of Au-RE-TiO₂ samples

Photocatalysts type	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (4V/S _{BET}) (nm)	Photocatalytic activity (%)	
				UV light	Vis light
2 % Au-0.5 % Ho-TiO ₂	135	0.1	1.92	31	46
2 % Au-0.5 % Nd-TiO ₂	137	0.1	1.91	38	47
2 % Au-0.5 % Er-TiO ₂	137	0.1	1.95	63	99
2 % Au-0.5 % Eu-TiO ₂	139	0.1	1.95	52	76
2 % Au-0.5 % Pr-TiO ₂	139	0.1	1.95	44	99
1 % Au-0.5 % Pr-TiO ₂	134	0.1	1.93	38	88
2 % Au-TiO ₂	122	0.1	1.95	39	97
TiO ₂	115	0.1	1.95	100	100

absorbs only UV light. Other photocatalysts Au-RE-TiO₂ had the highest absorption properties under Vis light in typical absorption peaks located at about 550 nm, which is characteristic for gold plasmon. The maximum absorbance under Vis light exhibited 2% Au-0.5% Pr-TiO₂. It proved that a redshift in the band gap transition of TiO₂ is due to the presence of the rare earth metal and gold. It could be achieved by a charge transfer transition between the lanthanide f electrons and the conduction or valence band of the TiO₂ (Hassan et al., 2012).

Fig. 2. Diffuse reflectance spectroscopy spectra of Au-RE-TiO₂ photocatalysts

The photocatalytic activity of Au-RE-TiO₂ photocatalysts was checked by measuring the decomposition of toluene in the air under UV or Vis light. The efficiency of toluene photodegradation after 30 min of exposure to visible light in the presence of Au-RE-TiO₂ photocatalysts is reported in Table 1 (efficiency of photodegradation toluene in one cycle of photocatalytic reaction) and Figs. 3 and 4



(efficiency of toluene photodegradation under UV or Vis light in four subsequent cycles). All photocatalysts based on TiO₂ co-doped with the rare earth metal and gold nanoparticles showed lower photocatalytic activity than pure TiO₂. The highest activity in solar light from among Au-RE-TiO₂ presented the sample doped with Er³⁺ or Pr³⁺ as the rare earth metal, which received about 50% efficiency degradation of toluene. It indicates that the presence of 2% Au-0.5% Er-TiO₂ and 2% Au-0.5% Pr-

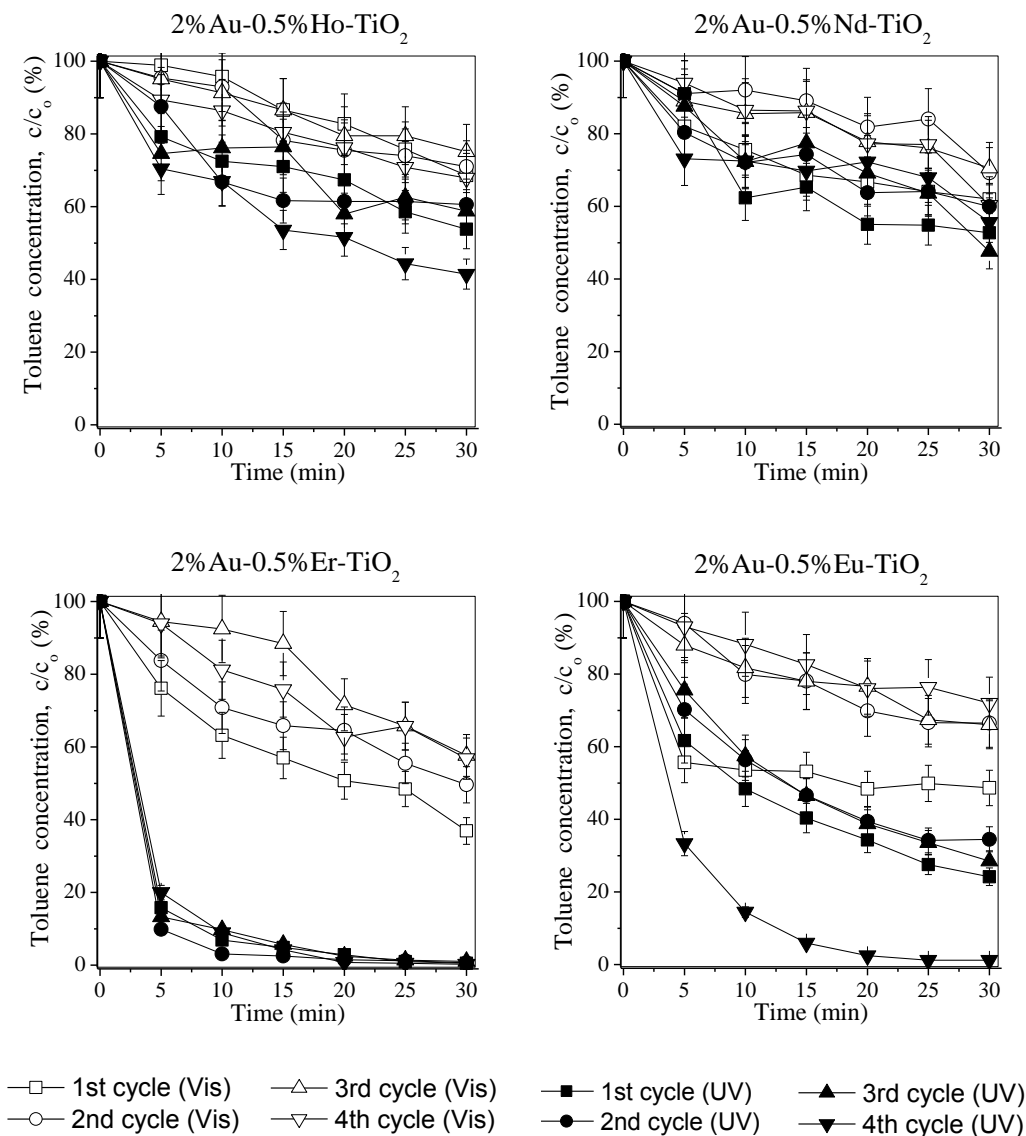


Fig. 3. Efficiency of toluene removal from gas phase in four subsequent cycles in the presence of Au-RE-TiO₂ under UV or Vis irradiation

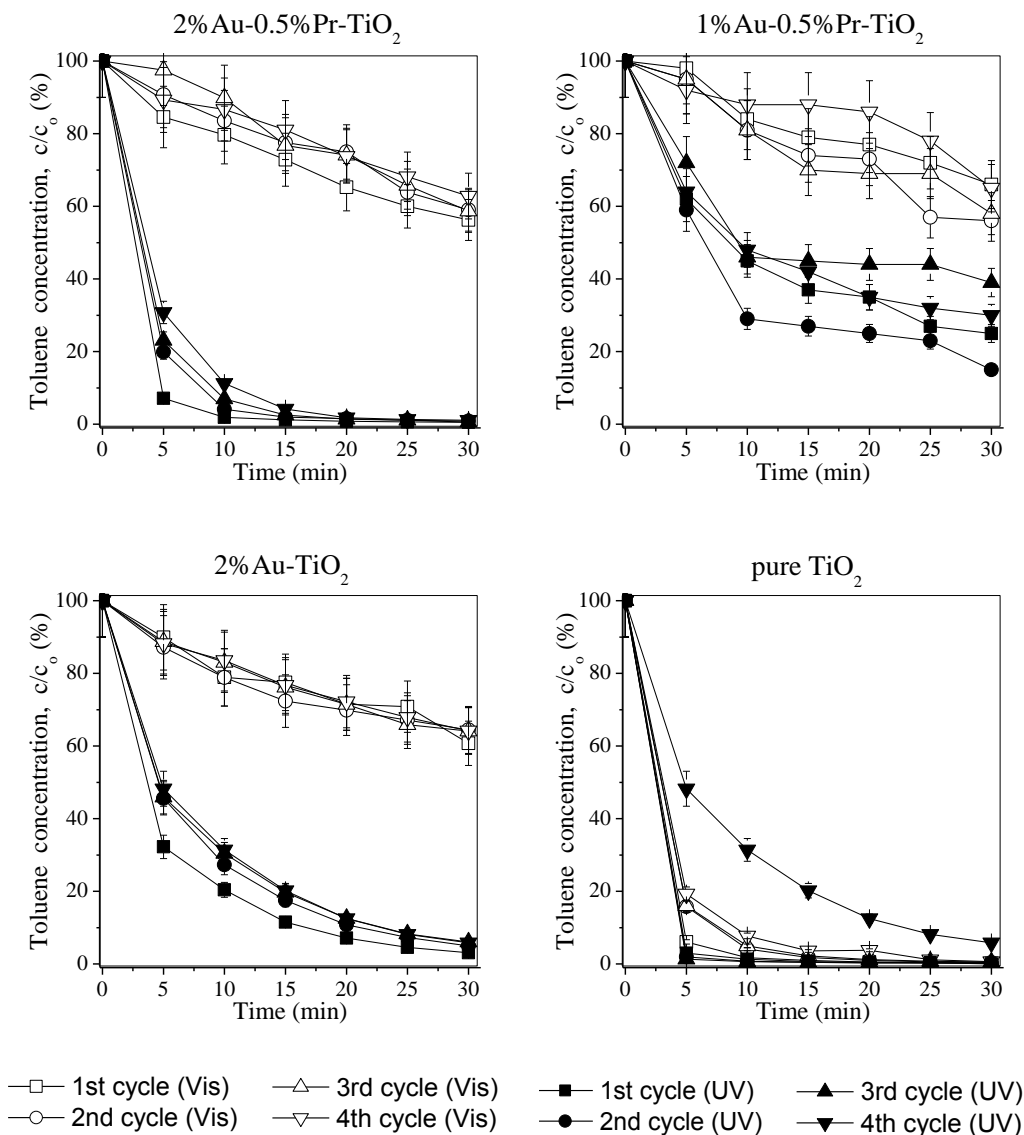


Fig. 4. Efficiency of toluene removal from gas phase in four subsequent cycles in the presence of Au-Pr-TiO₂, Au-TiO₂ and pure TiO₂ under UV or Vis irradiation

TiO₂ were close for UV light activation to undoped TiO₂, where the maximum efficiency of toluene degradation was almost 100%. Other photocatalysts Au-RE-TiO₂ based on TiO₂ co-doped with Ho³⁺, Ne³⁺ or Eu³⁺ and gold nanoparticles showed lower activity in UV and Vis light compared to unmodified TiO₂. As can be seen in the investigations that toluene photodegradation efficiency did not decrease in fourth

cycles photocatalytic reactions. The photocatalytic activity of Au-RE-TiO₂ under UV light is always higher than under Vis light due to physico-chemical properties of TiO₂ and energy of light. The curtailment amount of gold from 2% to 1% wt % in the photocatalysts Au-Pr-TiO₂ under UV light causes reduction in toluene photodegradation activity. To the best of our knowledge no one has previously reported photocatalyst activity of Au-RE-TiO₂ powders and it cannot be compared to results from literature data. Xu et al. (2002) reported that results of photodegradation conversion of nitrite over RE-doped TiO₂ (RE: Er³⁺, Pr³⁺, La³⁺, Nd³⁺, Ga³⁺) and UV-Vis light show higher photoreactivity than pure TiO₂. Zielinska-Jurek et al. (2011) investigated impacts in decomposition of aqueous phenol solution by Au-TiO₂ and Au/Ag-TiO₂ powders under Vis light. The Au/Ag-TiO₂ samples show higher photocatalytic activity than Au-TiO₂.

Conclusion

Our preliminary results showed that photodegradation of toluene in the air over Au-RE-TiO₂ using light emitting diodes is possible. However, it was found that co-doping of TiO₂ with the rare earth metal and gold nanoparticles inhibited photoactivity both under UV and Vis irradiation compared to pure TiO₂. The highest activity under visible light from among Au-RE-TiO₂ was observed for the sample doped with Er³⁺ or Pr³⁺. Reducing the concentration of gold precursor from 2 to 1 mol.% during synthesis, resulted in decrease of photocatalytic activity. It was observed that TiO₂ surface modification with the rare earth metal and gold nanoparticles caused decrease of the surface area of modified TiO₂ powders. Since plasmon band near 550 nm typical for gold nanoparticles was observed, the sol-gel preparation method followed by chemical reduction of gold ions did not enhance photoactivity under visible light. On the basis of the analysis, it is suggested that more detailed studies into the mechanism of Au-RE-TiO₂ photoexcitation is required.

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