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Pr-DOPED TIO$_2$. THE EFFECT OF METAL CONTENT ON PHOTOCATALYTIC ACTIVITY

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Abstract: Pr-TiO$_2$ nanoparticles were prepared by using a sol-gel method. As-prepared samples were characterized by BET measurements, X-ray powder diffraction analysis (XRD) and UV-Vis spectra. Visible and ultraviolet light photocatalytic activity of the sample was studied by photodegradation of phenol, while considering the influence of the dopant concentration. TiO$_2$ doped with 0.25 mol% of praseodymium showed the highest photocatalytic activity under visible light irradiation. Pr-TiO$_2$ had anatase structure. The surface area was higher for powders with higher content of rare earth metal ion, and ranged from 121 to 150 m^2/g. Red shifts of absorption edge toward the visible region were observed for the doped samples compared to pure TiO$_2$.

Keywords: *photocatalysis, rare earth metal, praseodymium, modified TiO$_2$, phenol*

Introduction

Phenols are generally considered to be one of important organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water (Grabowska et al., 2012a). Phenol is toxic even at low concentrations, and also its presence in natural waters can lead further to formation of substituted compounds during the disinfection and oxidation processes (Busca et al., 2008). In response, it has become a challenge to achieve an effective removal of persistent organic pollutants from wastewater effluent to minimize the risk of pollution problems from such toxic chemicals and to enable its reuse. TiO$_2$ is a commonly used photocatalyst in water purification, wastewater and gas streams treatment (Gorska et al., 2008; Zielinska-Jurek et al., 2010; Grabowska et al., 2012b; Nischk et al., 2013). However, utilization

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of pure TiO_2 is significantly constrained because of its wide band gap, low efficiency of sunlight utilization, low quantum efficiency, and high recombination rate of electrons-holes. Therefore, it is of great interest to improve the photocatalytic activity of TiO_2 in order to enlarge practical applications of TiO_2-based photocatalysts (Shi et al., 2012). Rare-earth ion doped materials have played an important role in the development of optical communication technology during the past few decades (Shang et al., 2008). Lanthanide ions are known for their ability to form complexes with various Lewis bases (e.g., acids, amines, aldehydes, alcohols, thiols, etc.) in interaction of these functional groups with the f-orbitals of lanthanides (Ranjit et al., 2001). Titania doping with lanthanides is a method to shift the maximum of absorption as well as enhance the photocatalytic activity (Hassan et al., 2012). Rare earth metals could be introduced to the surface of TiO_2 by various methods such as: sol-gel (Sheng et al., 2011; Tang et al., 2012), hydrothermal (Pedroni et al., 2012; Li et al., 2013), electrospinning (Cacciotti et al., 2011; Hassan et al., 2012) and surface impregnation (Parida and Sahu, 2008).

In our previous paper (Reszczynska et al., 2012) the sol-gel method to synthesize Er and Yb modified TiO_2 nanoparticles was presented. It was observed that the dopant amount affected photocatalytic activity of semiconductor. The presence of erbium was found more beneficial for visible light activation of TiO_2 doped photocatalysts than ytterbium.

In this work, a series of Pr-doped TiO_2 nanoparticles were synthesized using the sol–gel technique with various Pr concentrations. The photocatalytic activity of as-prepared Pr-doped TiO_2 was evaluated using degradation of phenol in aqueous solutions under UV and Vis irradiation. The BET surface area, X-ray powder diffraction analysis (XRD) and UV-Vis spectra were evaluated.

Experimental

Materials and instruments

Titanium(IV) isopropoxide (97%) was purchased from Sigma-Aldrich Co. and used as titanium source for the preparation of TiO_2 nanoparticles. $Pr(NO_3)_3{\cdot}5H_2O$ (99.99%), from Sigma– Aldrich Co. was used as rare earth metal source in the preparation procedure. Acetic acid and ethanol (POCH S.A. Poland) were used without further purification. Deionized water was used for all reactions and treatment processes. A commercial form of TiO_2 (P25, crystalline composition: 80% anatase, 20% rutile) from Evonik, Germany was used for the comparison of the photocatalytic activity.

The nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature (77 K) on a Micromeritics Gemini V (model 2365) and the specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method in a relative pressure (p/p_0) range of 0.05–0.3 Pa. All the samples were degassed at 200 °C prior to nitrogen adsorption measurement.

DRS UV–Vis spectra of synthesized materials were recorded in a scan range 350–700 nm using a UV–Vis spectrophotometer (UV-Vis Thermo model: Nicolet Evolution 220 with ISA-220 integrating sphere) equipped with an integrating sphere and $BaSO_4$ was used as the reference. X-ray diffraction patterns (XRD) were recorded on a X-ray diffractometer (Xpert PRO-MPD, Philips) with Cu target K_α-ray (λ=0.15404 nm) in the range 2θ=20-68°. The patterns were analyzed by the Rietveld refinement method using LHPM program (Hill and Howard, 1986). The crystallite size was estimated by Scherrer equation. The accuracy of the grain size analysis was estimated to be about 20%.

PREPARATION OF Pr DOPED TiO_2 PHOTOCATALYSTS

For the preparation of photocatalyst the sol-gel method was used. TiO_2-based photocatalysts were obtained according to the procedures presented by a simplified block diagram in Fig. 1. The sample of 15 cm^3 titanium isopropoxide was added to the mixture of 3.0 cm^3 acetic acid and 60 cm^3 ethanol. The sol was stirred for 1 h, then 20 cm^3 of $Pr(NO_3)_3$ water solution, with pH adjusted to 3.5 (with 65 % HNO_3), was added dropwise. The obtained solution was stirred for 2.5 h. The prepared gel was filtered and washed four times with water using a centrifugal and dried at 80 ˚C. The heat-treatment of 400 ˚C for 2.5 h in the air was applied to the sample (heating rate of 5 ˚C/min). The concentration of metal precursors, which varied from 0 to 1.5 mol%, was related to the concentration of TIP in the sol-gel system.

MEASUREMENTS OF PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of Pr-TiO_2 powders in the visible and ultraviolet lights were estimated by measuring the decomposition rate of phenol in an aqueous solution. A 25 cm^3 of photocatalyst suspension (125 mg) in 0.21 mM phenol aqueous solution was placed in a quartz photoreactor. After 30 min aeration (5 dm^3/h) the suspension was irradiated with a Xenon 1000 W lamp. The optical path included water filter to cut off IR irradiation. For the test of visible-light-induced activity the light beam was passed through a GG420 filter to cut-off wavelengths shorter than 420 nm. One milliliter aliquots of aqueous suspension were collected at regular time periods during irradiation and filtered through the syringe filters (Ø = 0.2 mm) to remove the photocatalyst particles. The temperature of suspension was maintained at 10 ˚C using a thermostatically controlled water bath. Phenol concentration was estimated by the colorimetric method (λ = 480 nm) after derivatisation with diazo-pnitroaniline using the UV-Vis spectrophotometer (DU-520, Beckman).

Results and discussion

The sample labels, BET surface areas, crystal size and photoactivity for praseodymium-doped TiO_2 photocatalysts were listed in Table 1. For all the doped samples prepared by the sol-gel method, the BET surface area was higher than for the commercially available P25 (50 m^2/g). The surface area was higher for powders with higher content of rare earth metal ion, and ranged from 121 to 150 m^2/g. The Pr-doped sample has larger BET surface area than the undoped sample, indicating that the Pr-doping increases the thermal stability of mesoporous framework. Based on the literature data, it is likely that lanthanides ions are not incorporated into the matrix of TiO_2 but rather form rare-earth oxides, RE_2O_3 (Yang et al., 2011).

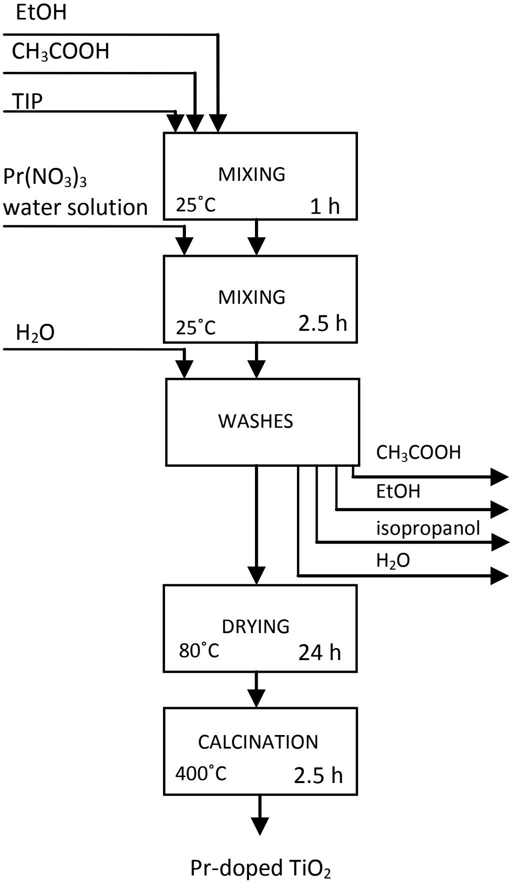

Fig. 1. Block diagram of Pr-doped TiO_2 prepared by the sol-gel method

The melting point of Pr_2O_3 is 2138 °C is higher than that of TiO_2. The surface coverage of metal oxide with higher melting point probably hampers the adjustment of matrix particles and rearrangement of crystal. Consequently, the Pr-doping improves the microstructural properties of TiO_2. Similar observation was made for Yb/N-TiO_2 photocatalysts (Yan et al., 2013). Rare earth ions doping can reduce the crystallite size but increase the surface area of TiO_2, which also contribute to the enhancement of adsorption capacity of TiO_2 for organic pollutants (Liang et al., 2006; 2009).The exceeded surface area for lanthanoid doped TiO_2, in comparison with the pure one, was also reported by Bingham and Daoud (2011).

Table 1. Surface characteristics and photocatalytic activity of Pr-TiO_2 photocatalysts

Photocatalysts type	Amount of metal precursor (mol%)	S_{BET} (m^2/g)	Average crystallite size (nm)	Phenol degradation rate under Vis irradiation (λ> 420 nm) ($\mu mol/dm^3 \cdot min$)	Phenol degradation rate under UV-Vis irradiation ($\mu mol/dm^3 \cdot min$)
TiO2_Pure	none	130	11.1	0.42	2.80
TiO2_Pr(0.1)	0.1	121	11.2	0.69	2.77
TiO2_Pr(0.25)	0.25	146	11.0	1.01	2.55
TiO2_Pr(0.5)	0.5	135	10.0	0.77	2.84
TiO2_Pr(0.7)	0.7	139	9.6	0.56	3.17
TiO2_Pr(1.0)	1.0	148	9.7	0.54	1.48
TiO2_Pr(1.5)	1.5	150	9.6	0.75	3.12
P25	none	50	not measured	0.34	3.19

To study the optical absorption properties of as-prepared samples, the UV-Vis absorption spectra in the range 350–700 nm were investigated, and the results are shown in Fig. 2. It can be seen that modification of titania with praseodymium significantly affected the light absorption property of photocatalysts. Red shifts of

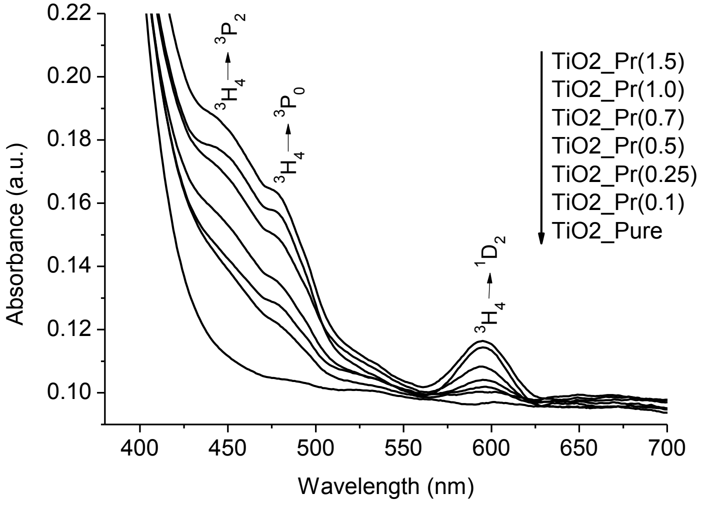

Fig. 2. Absorption properties of Pr-TiO_2 prepared by the sol-gel method

absorption edge toward the visible region were observed for the doped samples compared to pure TiO_2. The correlation between the amount of rare earth metal and the absorption edge shift to a longer wavelength was observed. Furthermore, it can be seen that there are three typical for praseodymium absorption peaks located at 446, 480 and 595 nm and they are attributed to transitions of $^3H_4$ to $^3P_2$, $^3P_0$ and $^1D_2$ (Su et al., 2008; Yang et al., 2011). The intensity of rare earth ion absorption bands was found to increase with increasing in the rare earth ion content.

The X-ray diffraction analysis (XRD) was used to verify the crystalline phase of synthesized doped TiO_2 and to estimate the crystallite size. The XRD patterns of examined samples are shown in Fig. 3. In all prepared photocatalysts, Fig. 3 presents a group of lines at 2θ values of 25.3°, 37.8°, 48.0°, 53.9°and 55.1°,which are attributed to anatase phase (El-bahy et al., 2009). However, no peaks related to the presence of praseodymium or praseodymium oxides were detected for Pr-TiO_2 photocatalysts. Thus, it indicates that the dopant nanoparticles at the TiO_2 surface are very small and highly dispersed (Zhou and He, 2012) or the concentration of rare earth metal was too low for the XRD to reveal (Wu et al., 2011). In our data the average particle size, determined on the base of Scherrer equations, ranged from 9.6 to 11.2 nm for TiO2_Pr(1.5) and TiO2_Pr(0.1), respectively. For undoped TiO_2 the particle size was 11.2 nm (Table 1). The particle size was found to decrease with increase in metal ion dopant concentration in TiO_2.

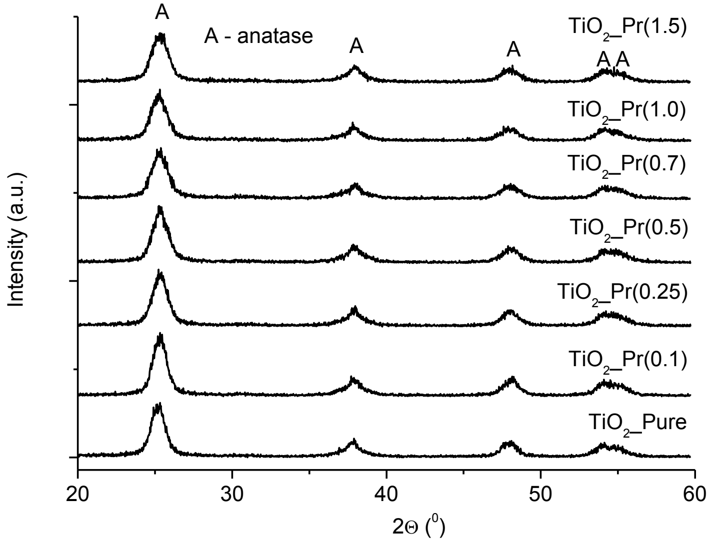

Fig. 3. XRD pattern of Pr-TiO_2 photocatalysts prepared by sol-gel method

The photocatalytic activity of obtained TiO_2 powders was estimated by measuring the decomposition rate of phenol in the aqueous solution in the presence of UV-Vis or visible light irradiation (λ > 420 nm). No degradation of phenol was observed in the absence of photocatalysts or illumination. The pure TiO_2 synthesized by the sol-gel method without any dopant and P25 were used as the reference system. Kinetics of phenol photodegradation in aqueous solution under Vis/UV-Vis light irradiation in the presence of Pr-doped TiO_2 nanoparticles is shown in Figs. 4a,b, respectively. The observed rate constants are listed in Table 1.

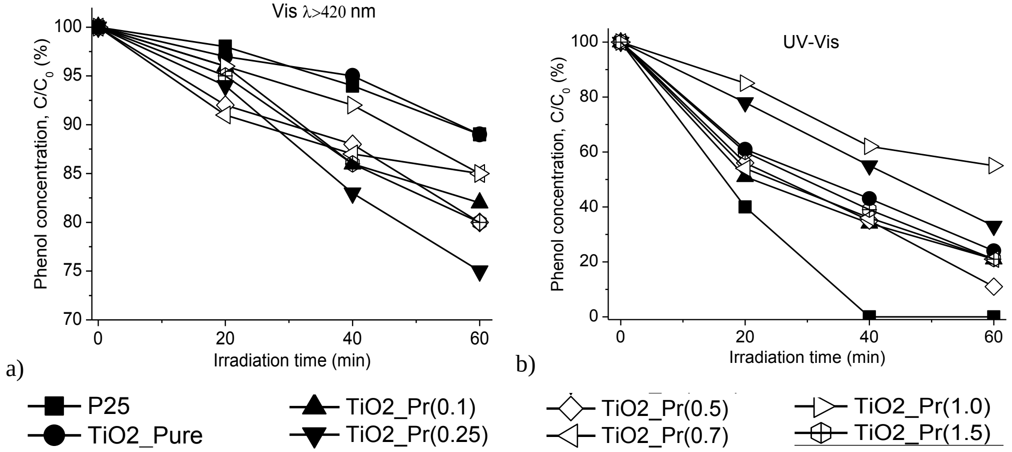

Fig. 4. Efficiency of phenol photodegradation in the presence of Pr-doped TiO_2 during irradiation light: a) Vis (λ > 420 nm), b) UV/Vis

Phenol degradation under visible light irradiation with the participation of praseodymium doped TiO_2 is presented in Fig. 4a. The highest photoactivity was observed for the sample prepared with 0.25 mol% Pr. After 60 min irradiation of aqueous suspension initially containing 20 mg/dm^3 of phenol, 25 % of those was degraded. All rare earth metal-doped photocatalysts had better photocatalytic activity than the undoped ones and P25 under visible light irradiation. The phenol degradation rate under UV-Vis irradiation increased from 2.55 to 3.17 μmol/dm^3·min for 0.25 to 0.7 mol% praseodymium-doped TiO_2, respectively. Praseodymium and nitrogen co-doped titania (Pr/N-TiO_2) photocatalysts, which could degrade Bisphenol A (BPA) under visible light irradiation, were prepared by the modified sol–gel process by Yang et al. (2011). It was found that Pr doping inhibited the growth of crystalline size and transformation from anatase to rutile. For the best photocatalytic activity, the optimal dopant amount of Pr was 1.2 mol% and the calcination temperature was 500 °C. Pr doping could slow the radiative recombination of photogenerated electrons and holes in TiO_2. The improvement of photocatalytic activity was ascribed to the synergistic effects of nitrogen and Pr co-doping.

Chiou and Juang (2007) prepared the Pr-doped TiO_2 nanoparticles with a composition of $Ti_{1-x}Pr_xO_2$(x= 0.018–0.22) using the acid-peptized sol–gel method. The Pr-doped TiO_2 showed high activity for photocatalytic degradation of phenol.

Light absorption reached the maximum for the particles with 0.072 mol% Pr, which was consistent with the trends of phenol photodegradation efficiency.

It is presumed that rare earth doping can lead to defects in the TiO_2 lattice and these defects act as electron traps. The doping may also favor separation of charge carriers efficiently and enhance the photocatalytic activity. It is suggested that rare earth oxides are located on the surface of titania, but more detailed studies about the mechanism of its photoexcitation is required (Wang et al., 2010).

Conclusion

In summary, the Pr-TiO_2 nanoparticles were prepared by the sol-gel method and had the anatase structure. Photocatalysts based on TiO_2 and doped with praseodymium caused an increase of photocatalytic activity under visible light irradiation. It was observed that the dopant affects the surface area and crystal size of TiO_2 powder samples. The photocatalytic activity depends on rare earth ion precursor concentration used during preparation. TiO_2 doped with 0.25 mol% of praseodymium showed the highest photocatalytic activity under visible light. After 60 min of irradiation, 25 % of phenol was degraded. The absorption spectra of Pr-TiO_2 samples show stronger absorption in the UV–Vis region than pure TiO_2.

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