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Influence of pH of sol-gel solution on phase composition and photocatalytic activity of TiO_2 under UV and visible light

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ABSTRACT

Nanocrystalline TiO_2 was prepared in the sol-gel method by hydrolysis of titanium (IV) isopropoxide (TIP) at the different pH: autogenic, pH = 10 (with ammonia solution) and pH = 3 (with acetic acid solution). The obtained materials were calcined at 400 °C. Time Resolved Microwave Conductivity (TRMC) analyses showed, that the highest lifetime of charge-carriers was obtained for sample prepared at pH = 10 calcined at 400 °C, which exhibited highly crystallised anatase phase and the lowest value of ς potential. Preparation of TiO_2 with an ammonia solution and its further calcination at 400 °C caused reduction of Ti^{4+} to Ti^{3+} in the bulk, narrowing of the band gap with formation of an extra band above the valence band of TiO_2 assigned to formed NO_2^{2-} species. Such prepared photocatalyst showed extended lifetime of free charges under UV irradiation in comparison with the other prepared samples and activity under visible light.

1. Introduction

TiO_2 is a very popular material used in the large area of photocatalytic processes such as water and air purification, self-cleaning surfaces and microorganisms' deactivation [1–4]. There are many methods of TiO_2 preparation such as hydrothermal, sol-gel, spray-pyrolysis and others. Among all of them the sol-gel seems to be the most convenient, because it is carried out at low temperature with easily-controlled reaction conditions, and it allows to design nanomaterial with demanded surface properties [5–8]. However many factors affect the rate of TiO_2 hydrolysis and polycondensation processes such as type of precursor, pH of solution, the presence and kind of alcohol used, the atmosphere of preparation, temperature, organic additives, mixing conditions, etc. Temperature of calcination has also a high impact on the physico-chemical properties of the final product. In many cases ethanol is added to titanium alkoxide solution, because through that the hydrolysis process of titania can be slowed down and crystallisation is retarded. As a consequence small size crystallites of titania can be obtained. However the presence of ethanol has also a negative effect on titania particles, because it causes that they have tendency to agglomeration. Agglomerated particles exhibit lower BET surface area than the isolated ones [6]. However it was reported, that methanol, which has shorter alkyl chain than ethanol caused lower aggregation of TiO_2 primary particles during sol-gel process [6]. Moreover it was evidenced, that when methanol was added to titanium isopropoxide in sol-gel process, the final product, whih was obtained after calcination of titanium precipitate at 450 °C, was totally crystallised and has quite high BET surface area, 100 m^2/g and an average particle size of 12–15 nm [7].

The other way for controlling the hydrolysis conditions during sol-gel process is using sonication. It was reported, that when titanium tetraisopropoxide was dropwise added to the high quantity of water under stirring and sonication at room temperature then the hydrolysis process was slowed down and formation of TiO_2 agglomerates was avoided [8].

Sol-gel method gives huge possibility of modifying the properties of TiO_2 by changing the pH value of source solution and doping both metals and non-metals. Besides the phase composition of TiO_2, its crystallites size, surface area, morphology and particles shape, there is also another factor, which influences the photocatalytic activity of TiO_2, such as acid and basic character of surface sites.

Chemical character of TiO_2 surface can be modified by some additives used in sol-gel preparation. The acid character of TiO_2 particles can be obtained by its modification with anion-derived

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compounds. High photocatalytic activity of TiO_2 having negatively charged surface was reported [9,10].

The influence of the pH of titania precursor solution on the formation of TiO_2 crystallites, phase composition and the electrokinetic potential of the particles surface was noted [11]. It was experienced, that preparation of TiO_2 at low pH such as pH = 3 caused faster transformation of anatase to rutile during heat treatment process. Value of negative charge of the particles decreased with the increase of the pH of the solution [11].

The other studies showed influence of nitrogen compounds having basic or acidic character on the growth of titania crystallites and its phase formulation. For TiO_2 preparation, titanium tetraisopropoxide with HNO_3 or NH_4OH were used and hydrolysis was conducted under ultrasonic irradiation [12]. The results showed, that HNO_3 enhanced the growth of brookite, while NH_4OH not only delayed phase transformation of the TiO_2 powders from amorphous to anatase and anatase to rutile but also suppressed the growth of brookite [12].

It was also reported, that pH of titania solution could affect not only on the crystallisation and phase transformation, but also on the formation of mesoporous structure of TiO_2 [12].

The crystallinity and phase composition of TiO_2 are essential factors responsible for its photocatalytic activity. It is believed that the most active form of TiO_2 is anatase, while rutile and brookite have relatively less meaning. Calcination of samples causes an increase of crystallites size and reduction of its specific surface area. The low calcination temperature leads to the homogeneity and regularity of the pores, whereas at higher temperatures the phase transformation of anatase nanoparticles to rutile occurs and leads to a significant reduction in the photocatalytic activity of TiO_2 [13]. Porous structure of TiO_2 also affects its photocatalytic activity. It was reported that the prepared mesoporous TiO_2 with anatase crystallites size of 10–15 nm had higher photocatalytic activity than nonporous commercial TiO_2 [14]. However the activity of amorphous TiO_2 was reported to be negligible [15].

The aim of the performed research studies was the preparation of nanocrystalline TiO_2 of high crystallised anatase structure by a sol-gel method. Basic and acidic pH of solution was used in order to increase electrostatic repulsion between primary particles of TiO_2 and suppress their aggregation. One of the aims of these studies was to obtain TiO_2 consisted of small crystallites of anatase and acidic character of surface, because it was already proved, that acidic surface of TiO_2 could enhance its affinity to hydroxyl ions and as a consequence results in generation of high quantity of $^{\bullet}OH$ radicals [16].

Reactivity of the photogenerated holes was controlled by detection of OH radicals' formation on the surface of TiO_2 upon UV–vis and visible light irradiations. Additionally such parameters as BET surface area, zeta potential, micro and mesoporosity, phase composition and an average crystallites size were measured. Mobility of free charge-carriers in TiO_2 after laser excitation and their rate of recombination were measured by Time Resolved Microwave Conductivity (TRMC) method.

2. Experimental

2.1. Chemicals and materials

The synthesized product was obtained from titanium (IV) isopropoxide, ≥97% (Sigma-Aldrich Co., USA) (TIP). Subsequent reagents were used: ethyl alcohol, ≥96% (Chempur, Poland), ammonia solution 25% pure (Avantor Performance Materials Poland S.A., Poland) and acetic acid, ≥99.5% (Chempur, Poland).

2.2. Preparation of TiO_2 photocatalyst

TiO_2 photocatalyst was prepared by a sol-gel method. At first 20 ml of titanium precursor (TIP) was mixed with 5 ml of ethyl alcohol. Then, 50 ml of ultrapure water was slowly added drop by drop into a flask containing precursor and alcohol under magnetic stirring. The other TiO_2 samples were prepared at the same way, but with a revised pH (pH = 3 or pH = 10). The pH of autogenic solution was about 5. Ammonia water was used to increase pH value up to 10 and acetic acid to reduce pH to 3. All the reagents were magnetically stirred for 24 h and then left for the aging process taking one day. The sols were transformed into gels form. The obtained gels were dried in a drier at 100° C for 24 h. Dried solid materials were ground to get a fine powder. In the second step TiO_2 samples were calcined at 400° C for 1 h in a muffle furnace.

2.3. Analytical methods

The prepared TiO_2 photocatalyst**s** were analysed by a few methods, such as X-ray diffraction (XRD), BET measurements, UV–vis/DR, FTIR, EPR (Electron Paramagnetic Resonance) Spectroscopies, zeta potential, and TRMC. Determination of OH radicals formation was measured indirect by the fluorescence technique in the reaction of hydroxyl radicals formed on TiO_2 surface upon UV or visible light excitation with a terephthalic acid solution. This method has been widely described in our previous paper [17].

The X-ray diffraction patterns were measured with X'Pert PRO diffractometer (Philips), using CuKα lamp ($\lambda = 1.54439$ Å, 35 kV, 30 mA). The sizes of the crystallites were calculated using Scherrer's formula, $D = \lambda/(\beta \times \cos\theta)$, where λ is the wavelength of the X-ray radiation ($\lambda = 1.54056$ nm for CuKα), β is the full-width at half maximum (rad) and θ is the reflection angle.

BET surface area was measured by nitrogen adsorption at 77 K in QUADRASORB Si analyzer (Quantachrome, U.S.A.) equipment. Prior to the adsorption measurements the samples were degassed for 12 h at 105 °C under high vacuum. Specific surface area was determined by the BET method.

UV–vis/DR spectra were recorded using UV–vis diffuse reflectance spectrophotometer (Jasco V-650, Japan). The band gap energies were evaluated from the diffuse reflectance data, by plotting of the Kubelka-Munka function, $(F(R)h\upsilon)^{1/2}$ versus $h\upsilon$, where R–reflectance, h–Planck constant, υ–frequency and $F(R) = (1-R)^2/2R$.

FT-IR/DRS spectra presented in this work were measured by reflection technique in the air atmosphere using FT/IR 4200 spectrophotometer (Jasco, Japan). All the spectra were collected with resolution of 4 cm^{-1} and a scanning speed of 1 mm/s.

The electrokinetic potential of the photocatalyst particles was determined in an apparatus Zetasizer Nano ZS of Malvern company. Triton as a non-ionic surfactant was used for dispersion of photocatalyst in an ultra high pure water during determination of electrokinetic potential.

Activity of the prepared samples towards OH radicals formation was measured indirect by monitoring of 2-hydroxyterephthalic acid formation in a reaction of terephthalic acid with OH radicals produced by photocatalyst under both, UV–vis and visible light irradiations. For all tests 0.02 g of photocatalyst was mixed with 100 ml of prepared terephthalic acid solution, and magnetically stirred under UV–vis irradiation. The UV source was a medium P Hg light (six 20 W Cleo Philips lamps with the irradiation intensity of 86 W/m^2 vis and 80 W/m^2 UV). For visible light irradiation, a halogen lamp of 150 W was used, which was equipped in the "hot mirror" filter with cut off the infrared light and UV filter with cut off the light <425 nm. The emission spectra of these lamp were measured by using Ocean Optics USB 4000+ spectrometer. Optical characteristics of these lamps were illustrated in Fig. 1. Every