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SYNTHESIS AND CHARACTERIZATION OF TiO_2 THIN FILM ON FLY ASH CENOSPHERES

Titanium dioxide (TiO_2) thin films obtained on quartz glass and fly ash cenospheres were studied. Titanium(IV) butoxide ($Ti(OBu)_4$), diethanoloamine (DEA), ethanol and deionized water were used as the starting materials. A layer of TiO_2 nanoparticles was coated on the surface of the substrates using the sol-gel method. The thickness of the TiO_2 coatings and the influence of the annealing temperature on the formation of TiO_2 crystallites were studied. The dried gels were treated for 90 min in the temperature range of 400÷640°C to obtain crystallized anatase and rutile. Additional nanopowder TiO_2 samples were prepared and their crystallinity was determined using X-ray diffraction (XRD). It was successfully shown that the anatase crystalline phase is formed when the TiO_2 gel is heated to 480°C, while the rutile phase is obtained at 640°C. Changes in film thickness were studied using an atomic force microscope (AFM). The profound effect of gel viscosity on the thickness of the film was noticed. UV-Vis absorption spectroscopy, performed on the sample treated at 480°C (containing anatase phase only), showed strong ultraviolet light absorption below 400 nm. The estimated band-gap value was 3.2 eV. Transmission scanning microscopy (TEM) examination of the powders revealed agglomerated nanoparticles. A uniform, continuous layer on the surface of the treated microspheres was observed under a scanning electron microscope (SEM). The study shows that the annealing temperature has a profound effect on the phase composition and crystallite size of the sol-gel synthesized TiO_2 nanopowders.

Keywords: **TiO_2 thin film, titanium(IV) butoxide, sol-gel method, fly ash cenospheres**

SYNTEZA I CHARAKTERYSTYKA CIENKIEJ WARSTWY TiO_2 OSADZONEJ NA MIKROSFERACH Z POPIOŁÓW LOTNYCH

Badaniom poddano warstwy z dwutlenku tytanu (TiO_2), które zostały osadzone na powierzchni szkła kwarcowego i mikrosfer z popiołów lotnych. Wyjściowymi substratami były butanolan tytanu(IV) ($Ti(OBu)_4$), dietanoloamina (DEA), etanol i woda dejonizowana. Warstwy z nanocząstkami TiO_2 przygotowano, wykorzystując metodę zol-żel. Zbadano grubość otrzymanych warstw oraz wpływ temperatury wypalania na powstawanie krystalitów TiO_2 syntetyzowanych w zol-żelu. Wysuszone żele poddano obróbce termicznej w zakresie temperatur 400÷640°C przez 90 minut w celu uzyskania krystalicznych form anatazu i rutylu. Za pomocą dyfrakcji rentgenowskiej (XRD) określono skład fazowy nanoproszków TiO_2. Udało się wykazać, że krystaliczny anataz otrzymywany jest podczas ogrzewania żelu w temperaturze 480°C, natomiast krystaliczna faza rutylowa w 640°C. Zmianę grubości warstwy obserwowano z wykorzystaniem mikroskopu sił atomowych (AFM). Zaobserwowano duży wpływ lepkości zolu na grubość otrzymywanych powłok. Przeprowadzona przy użyciu spektroskopii absorpcyjnej UV-Vis analiza próbki poddanej obróbce termicznej w 480°C (w której jedyną występującą fazą był anataz) wykazała silną absorpcję promieniowania ultrafioletowego o długości fali poniżej 400 nm. Szacowana wartość energii pasma wzbronionego wynosiła 3,2 eV. Obrazy z transmisyjnego mikroskopu skaningowego (TEM) ukazały zaglomerowane nanocząstki, a obrazy ze skaningowego mikroskopu elektronowego (SEM) pokazały jednorodną warstwę na mikrosferach. Wykonane badania pokazują, że temperatura wypalania ma ogromny wpływ na skład fazowy i rozmiar krystalitów nanoproszków TiO_2 syntetyzowanych metodą zol-żel.

Słowa kluczowe: **cienkie warstwy TiO_2, tetrabutanolan tytanu, metoda zol-żel, mikrosfery z popiołów lotnych**

INTRODUCTION

Photocatalysis, a technique qualified as one of the advanced oxidation processes, shows potential for environmental detoxification of organic and inorganic pollutants through their degradation and mineralization. Titanium dioxide (TiO_2) is one of the most frequently used photocatalysts due to its nontoxicity, chemical stability and high oxidizing capability [1]. Crystalline TiO_2 has three main polymorphs, varying in band-gap energy: anatase, rutile and brookite. The photocatalytic ability of anatase is superior to that of rutile due to a lower recombination rate of electron-hole (e^-/h^+) pairs, but a large band-gap of 3.2 eV limits its photosensitivity to the ultraviolet (UV) spectrum, which accounts for about 5% of solar energy. The rutile phase (characterized by a band-gap of 3.0 eV) can be excited by visible light, but it has a fast charge recombination rate [2]. Thus, it seems reasonable to produce a mixed-phase photocatalyst to increase the total efficiency [3-6]. The photocatalytic properties of TiO_2 are affected by many factors, e.g. the type of crystalline phase, band-gap energy, thermal treatment conditions, crystallite size and structure, specific surface area degree of crystallinity and the recombination rate of (e^-/h^+) [7]. Various other semiconductors have band-gap energies sufficient to promote photocatalytic activities, for example WO_3 (2.7 eV), α-Fe_2O_3 (2.2 eV), ZnO (3.2 eV), ZnS (3.6 eV) and CdS (2.4 eV) [8]. However, none of these materials is used as commonly as TiO_2.

There are several methods to obtain thin TiO_2 films, including chemical vapor deposition, reactive sputtering and the sol-gel process [9]. Sol-gel synthesis has many advantages over the other techniques - the process is shorter, carried out at a relatively low temperature and requires simple and inexpensive equipment. It also provides homogeneity, high purity, faster nucleation and control over the formation of crystalline phases, as well as the crystallite size and growth rate. The solvent/ precursor type, solution viscosity and water content, together with drying conditions and treatment temperature affect sol-gel synthesized TiO_2 films. The annealing process influences the phase composition and size of TiO_2 nanocrystallites [10, 11]. Different substrates like activated carbon, zeolites, silica or fly ash cenospheres can be coated with a TiO_2 film. Fly ash cenospheres are lightweight, hollow aluminosilicate particles recovered from coal fly ash, used among others as a filler [12].

In this study, TiO_2-coated fly ash cenospheres, with a potential for water and air purification, were prepared via the sol-gel method using titanium(IV) butoxide. The influence of the solution viscosity on the thickness of the TiO_2 layer and the effect of thermal treatment on its phase composition and crystallite size were investigated.

MATERIALS AND METHODS

The experiment used fly ash cenospheres and quartz glass as the substrates. Cenospheres, with a particle diameter of 63 to 200 μm, were obtained from Cenospheres Trade & Engineering S.A. All the reagents used were analytical grade and purchased from Sigma-Aldrich. Deionized water was used to prepare all the solutions.

Following initial cleaning in a surfactant solution, the substrates were washed first with deionized water, then with ethanol and dried at 105°C in an oven for 1 h. Titanium(IV) butoxide ($Ti(OBu)_4$) was chosen as the titanium source for the TiO_2 coating. Diethanoloamine (DEA) was used as a deflocculant to avoid precipitation. A thin TiO_2 film was synthesized on the surface of the substrates via a simple sol-gel method. DEA (5 ml) was mixed with 17 ml of $Ti(OBu)_4$ under magnetic stirring for 30 min at room temperature, yielding a homogenous solution. 1 ml of H_2O mixed with ethanol was then added to the titanium-DEA solution. Stirring was continued for another 90 min to complete the reaction. Five mixtures, containing different amounts of ethanol, were prepared under the conditions shown in Table 1.

TABLE 1. **Preparation conditions of: a) nanopowders (ethanol/($Ti(OBu)_4$ + DEA) = 0.91), b) coatings (thermal treatment: 480°C, 90 min)**

TABELA 1. **Warunki przygotowania: a) nanoproszków (etanol/($Ti(OBu)_4$ + DEA) = 0,91), b) powłok (obróbka termiczna: 480°C, 90 min)**

(a)

Sample	Thermal treatment
1	400°C, 90 min
2	440°C, 90 min
3	480°C, 90 min
4	560°C, 90 min
5	640°C, 90 min

(b)

Sample	Ethanol/ ($Ti(OBu)_4$ + DEA)
1	0.50
2	0.91
3	1.36
4	1.82
5	2.27

To obtain thin TiO_2 films, the solution was aged at room temperature for 2 h, then the substrates were coated using the immersion technique and left to dry for 48 h. The as-prepared samples were annealed at 480°C for 90 min.

Aside from the coatings, TiO_2 nanopowders were obtained to determine the phase composition of samples treated at different temperatures. To form the nanopowders, the solution was aged at room temperature until the gelation process was completed. Afterwards, the prepared gel was dried at room temperature for 48 h and subsequently treated by heating the samples at the rate of 100°C/1 h until the target temperature (400, 440, 480, 560, 640°C) was reached, then maintaining them at the target temperature for 90 min.

RESULTS AND DISCUSSION

The TG curve of the acquired TiO_2 gel, presented in Figure 1, shows a five-stage weight loss, which can be attributed to the evaporation of absorbed water and volatilization of low-molecular-weight organic compounds. The loss of about 11 wt.% in the range of 400÷600°C might be a result of combustion and decomposition of residual organic matter. Figure 2 shows the XRD patterns of TiO_2 powders annealed at various temperatures. All the samples are crystalline. The XRD pattern of the powder formed at 400°C is characteristic of anatase. As the temperature increases, the peaks become sharper. Upon reaching 560°C, rutile phase peaks start to appear, suggesting that there is a phase transition from anatase to rutile occurring around this temperature. Residual anatase peaks are still present in the sample treated at 640°C [13].

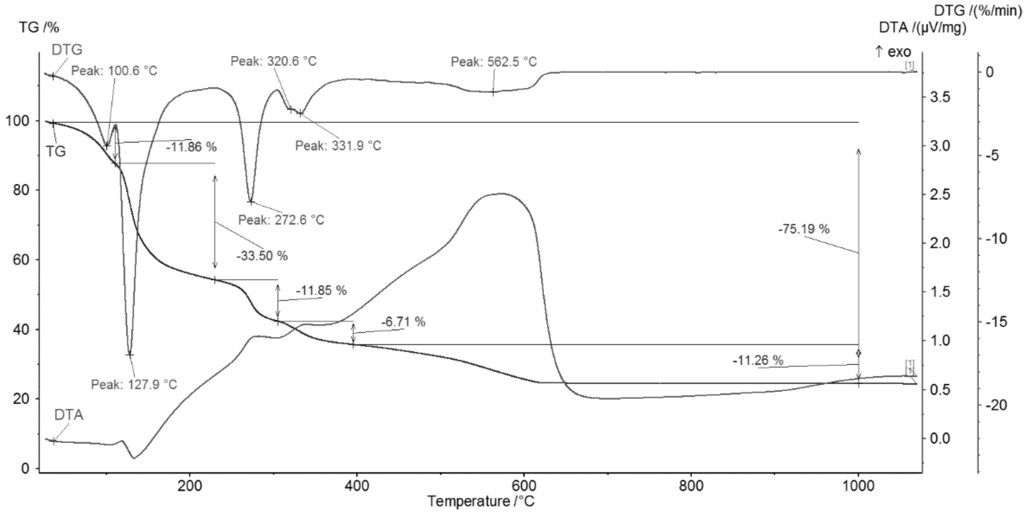

Fig. 1. Thermal analysis of TiO_2 gel

Rys. 1. Analiza termiczna żelu TiO_2

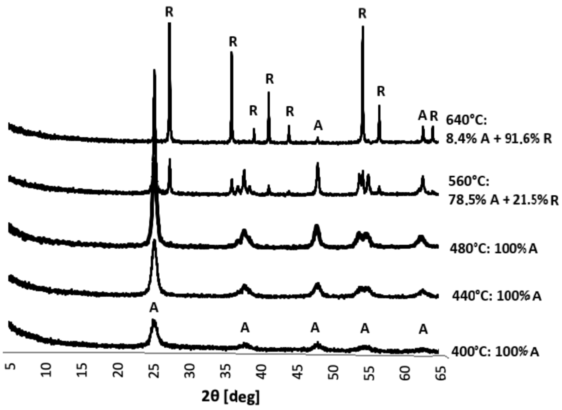

Fig. 2. XRD spectra of TiO_2 powders annealed at different temperatures (A - anatase, R - rutile)

Rys. 2. Widma XRD proszków TiO_2 wygrzewanych w różnych temperaturach (A - anataz, R - rutyl)

The crystallinity of the TiO_2 powders annealed at different temperatures was studied. The crystallite size of the TiO_2 particles was estimated by means of the Debye-Scherrer equation using XRD line broadening. The (101) plane diffraction peak was used for anatase and the (101) peak was used for rutile. As seen in Figure 3, the size of anatase crystallites rapidly increases with annealing temperature. When the temperature exceeds the onset point of phase transition, some anatase crystallites grow and gradually transform into the rutile structure, while others remain in form, but also enlarge rapidly.

The TEM investigations (Fig. 4) performed on TiO_2 powders annealed at 480 and 560°C indicate the formation of small, well-crystallized nanoparticles, which exhibit a tendency to form close-packed, spherical aggregates. The presence of residual organic matter caused difficulties in determining the average crystallite size of TiO_2 in both samples. Therefore, the authors were only able to roughly estimate the particle size to be in the range of 20÷30 nm for the TiO_2 powder treated at 480°C and above 100 nm for the powder annealed at 560°C. The particle sizes estimated from the TEM micrographs are very close to the average size of the crystallites calculated from the XRD data, proving the single-crystal nature of these particles.

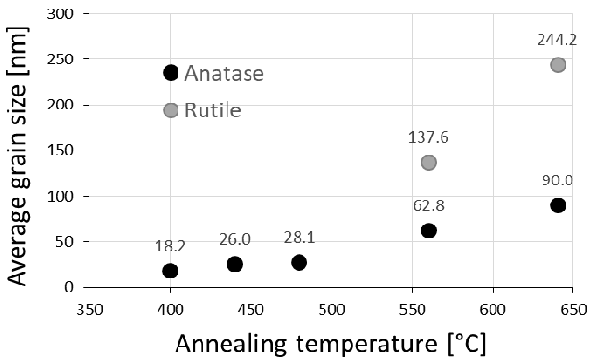

Fig. 3. Variation of crystallite size of TiO_2 powders annealed at different temperatures for 90 min

Rys. 3. Zmiana wielkości krystalitów TiO_2 z proszków wypalanych w różnych temperaturach przez 90 min

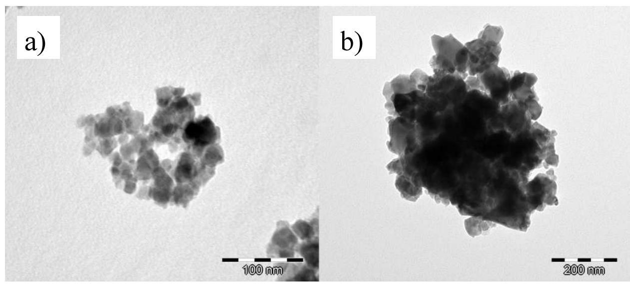

Fig. 4. TEM micrographs of: a) sample N_{480}, b) sample N_{560}

Rys. 4. Obrazy TEM: a) próbki N_{480}, b) próbki N_{560}

Figure 5 shows the surface morphology of the TiO_2 thin film treated at 480°C, obtained through AFM imaging. The thickness of the TiO_2 coatings deposited at various viscosities was determined using Step analysis (by measuring the difference in height between the uncoated and coated regions of the sample). It was observed that the film thickness decreases with the viscosity of the sol. The thickness of the thin film decreased from 400 nm to 170 nm with increasing the ethanol content of the prepared solutions.

SEM micrographs of uncoated and coated cenospheres are presented in Figure 6. The surface of the control sample is smooth and clean (Fig. 6a). A uniform, continuous layer formed on the treated fly ash cenosphere (Fig. 6b$_1$), indicating that the sol succesfully coated the surface. Titanium and oxygen were found in the EDX analysis presented in Figure 6b$_2$, proving that the film consists of TiO_2.

Figure 7 shows the UV-Vis spectrum of the TiO_2-coated glass (annealed at 480°C) and the band-gap energy (E_g) estimation from the Tauc plot. The spectrum indicated absorption in the UV region with the E_g value of about 3.2 eV, which corresponds to anatase TiO_2 nanoparticles.

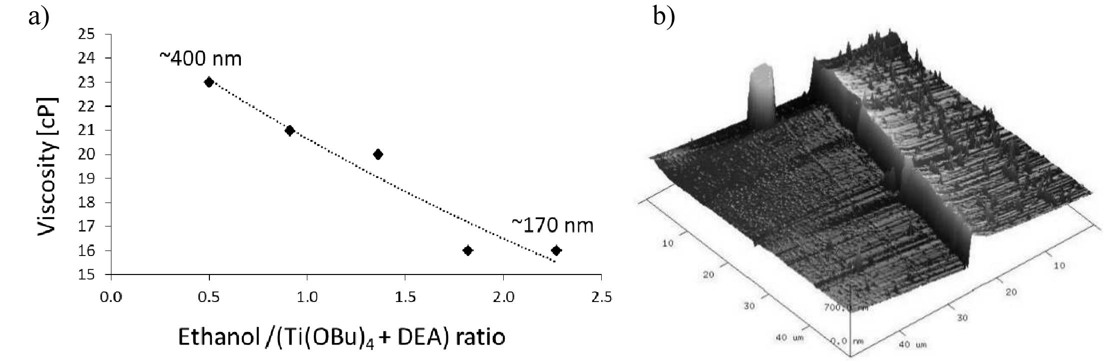

Fig. 5. Sol viscosity and layer thickness as function of ethanol content (ethanol/($Ti(OBu)_4$+DEA) ratio) (a), typical AFM image ofTiO_2 thin film after annealing at 480°C for 90 min (Ethanol/($Ti(OBu)_4$ + DEA) = 0.91) (b)

Rys. 5. Lepkość zoli i grubość warstwy w funkcji zawartości etanolu (stosunek etanol/($Ti(OBu)_4$+DEA)) (a), przykładowy obraz AFM cienkiej warstwy TiO_2 po procesie wypalania w 480°C przez 90 min (Ethanol/($Ti(OBu)_4$ + DEA) = 0,91 (b)

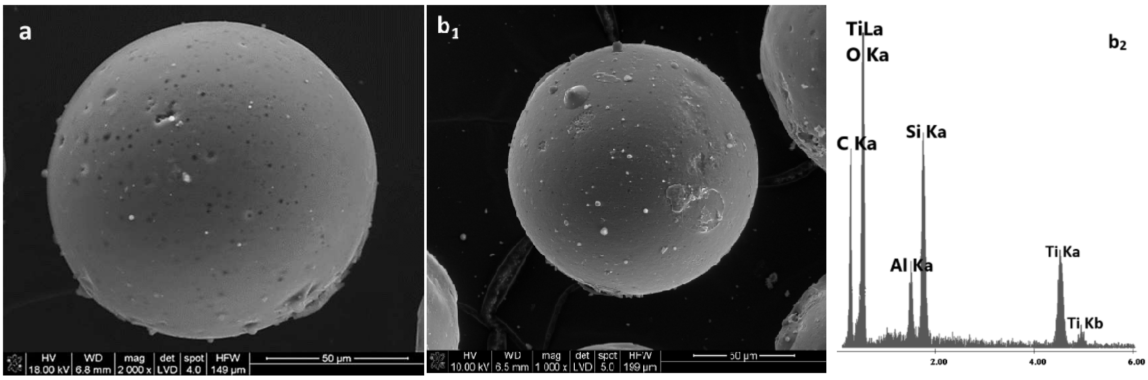

Fig. 6. SEM micrographs of: a) untreated fly ash cenospheres, b) TiO_2-coated cenospheres

Rys. 6. Obrazy SEM: a) niepowleczone mikrosfery, b) mikrosfery pokryte TiO_2

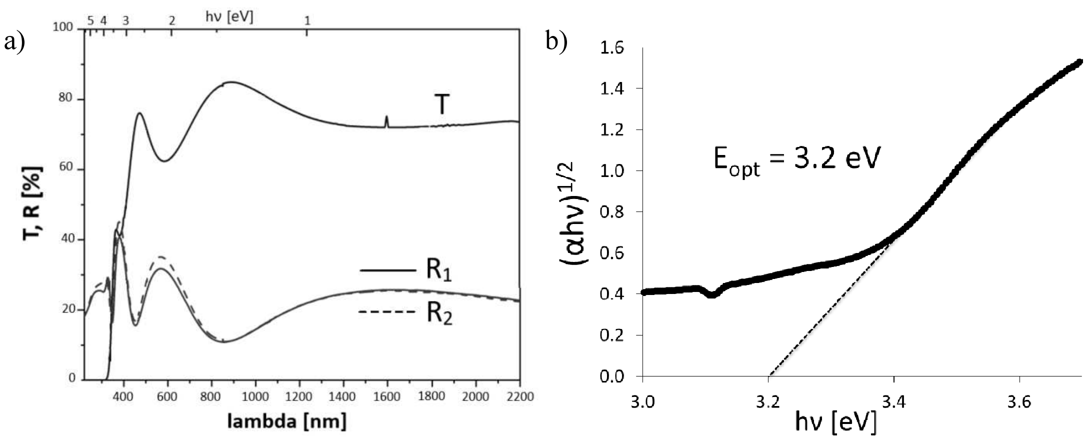

Fig. 7. UV-Vis spectra of TiO_2 thin film applied on microscope glass (a). The band-gap energy of TiO_2 (b)

Rys. 7. Widma UV-Vis powłoki TiO_2 na szkle mikroskopowym (a). Energia pasma wzbronionego TiO_2 (b)

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CONCLUSIONS

Nanopowders were obtained to determine the influence of annealing temperature on the phase composition and crystallite size of TiO_2. Then, the optimal treatment conditions were selected and thin TiO_2 films were coated on the surface of quartz glass substrates to establish the correlation between the coating thickness and ethanol content of the solutions. In the last and most important part of the study, a photocatalytic composite with a buoyant ability was synthesized by coating the fly ash cenospheres with TiO_2 nanoparticles. It is possible to deposit a thin, homogeneous and well adherent layer of TiO_2 on the surface of the microspheres using the sol-gel method with subsequent thermal treatment. Annealing at temperatures below 600°C produces a mixed-phase photocatalyst with increased total efficiency. The layer thickness can be modified, to a large extent, by changing the viscosity of the sol without any deterioration in quality. The annealing temperature influences the phase composition and crystallinity of TiO_2.

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