TiO₂-Based Nanopowders and Thin Films for Photocatalytical Applications

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TiO₂-based nanopowders are elaborated by flame spray synthesis, FSS from organic precursors of titanium and chromium with the Cr content changing from 0 to 15 at.%. Well-crystallized nanopowders with high specific surface area SSA reaching 107 m²/g for undoped TiO₂ and 177 m²/g for TiO₂ + 15 at.% Cr are obtained. Thin films are deposited by rf reactive sputtering from metallic Ti and Ti-Cr targets in Ar + O₂ flow controlled atmosphere. The adjustable area of Cr/Ti allows to obtain up to 16 at.% Cr in TiO₂ thin films. X-ray diffraction, transmission electron spectroscopy, TEM, atomic force microscopy, AFM and optical spectrophotometry over the ultraviolet UV and visible VIS range of the light spectrum have been performed in order to characterize the nanomaterials. The particle size of nanopowders is within the range of 5–42 nm. Anatase is the predominating polymorphic form while the amount of rutile increases with Cr content to reach of about 25 wt.% at 15 at.% Cr. The post-deposition annealing of thin films in air at temperatures from 770 K to 1280 K modifies the phase composition, leads to irreversible transformation from anatase to rutile and affects the surface roughness. Structural and optical properties of TiO₂-based nanopowders and thin films are compared. The effect of grain size and the level of chromium doping on the band gap E_g is discussed. Photocatalytic activity of the nanopowders is tested for degradation of methylene blue, MB.

Keywords: TiO₂, Nanopowders, Thin Films, Band Gap, Photocatalysis.

1. INTRODUCTION

Titanium dioxide TiO₂ is superior to many other semi-conducting photocatalysts because of its high photoactivity over the ultraviolet range of the light spectrum and stability against photocorrosion. However, its intrinsic wide band gap, i.e., 3.0 eV for rutile and 3.2 eV for anatase prevents TiO₂ from profiting efficiently from the solar radiation as the major part of the visible light is not absorbed in this material.^{1–2} Hence, the conversion efficiency has been found too low for practical applications of materials based on TiO₂.³ The imperative is to extend the optical absorption of TiO₂ towards longer wavelength which can be attained either by red-shifting the fundamental absorption edge or by creating additional absorption features in the visible range of the light spectrum. Different modifications of TiO₂ have been undertaken such as cationic or anionic doping, dye sensitization, incorporation of noble

metals and formation of solid solution^{4–11} but with little or moderate success.

New expectations in the field of photoelectrochemistry and photocatalysis are due to the exceptional progress in nanotechnology and development of emerging nanostructured materials. For the photocatalytic applications, the total surface area is very important, and it can be significantly increased in nanocrystalline powders and thin films.

Among unique properties of nanomaterials, the movement of electrons and holes is primarily governed by the well-known quantum confinement, and the transport properties are largely affected by the size and geometry of the materials. Nanosized TiO₂ particles generally demonstrate higher photocatalytic activity than those with larger particle sizes, partly due to the enhanced redox potential of photogenerated electrons and holes.^{5, 12–14} Compared to the microcrystalline material, nanostructured TiO₂ has unique charge transfer and recombination kinetics due to high absorption cross section, high surface-to-volume ratio, fast

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diffusion of charge carriers to the surface or interface that can reduce charge recombination. The specific surface area, SSA and surface-to-volume ratio increase dramatically as the size of the material decreases. The high surface area is beneficial to many TiO₂-based devices, as it facilitates reaction/interaction between the devices and the interacting media, which mainly occurs on the surface or at the interface. Thus, the performance of TiO₂-based devices is largely influenced by the sizes of TiO₂ grains at the nanometer scale.¹⁵

However, direct application of nanopowders in photocatalysis presents some inconveniences related to the:

- (i) need of separation (filtration) of the photocatalyst from the suspension at the end of the photodegradation procedure,
- (ii) difficulties due to the aggregation of particles, especially at high concentration,
- (iii) problematic use of nanopowders in continuous flow systems,
- (iv) higher risk of possible toxicity and stronger penetration in human body due to decreased particle size.^{16,17}

Different approaches have been reported that aim at solving the problem of separation of photocatalyst from the solution in which the degradation process is carried out. Some of these attempts involve magnetic interaction via immobilization of TiO₂ on ferric oxide.^{18,19} Other methods propose TiO₂-anchoring on supports such as glass beads;²⁰ fiberglass;²¹ zeolites;²² clay;²³ and silica.²⁴ So far, these methods have failed to be efficient because supported TiO₂ shows smaller photoactivity than unsupported TiO₂ nanopowder. Further development of immobilized photocatalysts and thin films is necessary from the technological point of view.

Therefore, in this paper we focused our attention at both nanopowders and thin films of modified TiO₂. In our earlier works that concentrated on microcrystalline powders and thin films, we have shown that it is possible to tailor, to some extent, the optical absorption spectrum of TiO₂⁸ by doping with transition metals. In this paper a study on structural and optical properties of pure TiO₂ and TiO₂ doped with Cr is presented. Nanomaterials in the form of thin films were deposited by rf reactive sputtering while nanopowders were obtained by flame spray synthesis, FSS. The aim of this work is to compare the influence of form of the material, i.e., thin film versus nanopowder of the same material on the modification of the optical spectrum necessary for improvement in photocatalytic performance. The photocatalytic degradation of methylene blue, the test organic compound, is demonstrated for TiO₂ nanopowders prepared by FSS.

2. EXPERIMENTAL DETAILS

The materials under study comprise: nanopowders obtained by FSS and thin films deposited by rf reactive sputtering. Commercial nanopowders from Aldrich

and microcrystalline ceramics elaborated previously by us using sol-gel methods²⁵ are treated as references.

2.1. Elaboration of Powders

Nanopowders of pure and modified TiO₂ were prepared by flame spray synthesis (FSS) as described in Ref. [26]. Pure TiO₂ nanopowders with different specific surface area, SSA were obtained from 2 M solution of titanium tetra-isopropoxide (TTIP; Ti(C₃H₇O)₄, purity > 99%, VWR) in ethanol (EtOH; 99%, Aldrich). The precursor was supplied in a controlled amount by adjusting its flow rate from 0.3 to 0.034 cm³/s into the flame to obtain a desired particle size.

Nanopowders of TiO₂:Cr were obtained from 3.3 M titanium tetra-isopropoxide (TTIP, Ti(C₃H₇O)₄, 99%, VWR) and (0.02–0.04) M solution of chromium acetylacetonate (CHAA, C₁₅H₂₁CrO₆, 99%, ACROS) in *m*-xylene (1,3-Dimethylbenzene, C₈H₁₀, 99.9% anhydrous, ACROS). The precursors and *m*-xylene were mixed in proportions required to reach the chromium concentration range extending from 0.1 to 15 at.%. The total flow rate of precursors was 0.095–0.125 cm³/s. The flow rates of gases were: 583 cm³/s for atomizing oxygen, 217 cm³/s for acetylene and 283 cm³/s for oxygen acting as a burning gas. The composition, particle diameter and specific surface area (SSA) were controlled by the flow rate of the precursors.

2.2. Preparation of Thin Films

Pure and modified thin films of TiO₂ have been deposited by rf reactive sputtering from metallic Ti and Ti-Cr targets in Ar+O₂ flow controlled gas atmosphere. The adjustable area of Cr/Ti of the Ti-Cr mosaic target allowed us to obtain up to 16 at.% Cr in thin films. Different materials such as amorphous silica, Corning glass and Si wafers served as substrates. Each deposition run was carried out under predefined conditions of the total gas pressure, constant oxygen and argon flows, constant input power and voltage as well as the controlled substrate temperature, T_{sub} . Majority of thin films discussed in the paper were deposited at $T_{\text{sub}} = 620$ K. Prior to the sample deposition, the target pre-sputtering in Ar+O₂ atmosphere was performed in order to stabilize the sputtering conditions (voltage, pressure, gas composition) and to equilibrate the oxidized target surface.

The post-deposition annealing in air at high temperatures over the range from 770 K to 1280 K was used to modify the crystallographic structure and the optical band gap of TiO₂.

2.3. Measurement Techniques

Different measurements were performed for nanopowders and thin films.

The specific surface area, SSA and the resulting particle size are the most important parameters for the characterization of nanopowders.

The SSA of nanopowders was calculated from the well-known BET (Brunauer-Emmett-Teller) method with nitrogen, in Beckman-Coulter SA3100 apparatus. Water was desorbed from the surface by low-temperature annealing in nitrogen at 450 K for 2 h.

The particle size, i.e., the so-called BET-equivalent particle diameter D_{BET} was derived from the SSA assuming that the powder consists of uniform, non-porous and spherical grains.

Under these conditions the following, simplified equation can be used:

$$D_{\text{BET}} = \frac{6}{\text{SSA} \times (x_A \rho_A + x_R \rho_R)} \quad (1)$$

where, x_A and x_R represent the volume ratio while ρ_A and ρ_R denote the density of anatase and rutile, respectively.

X-ray diffraction, XRD was performed on X'Pert MPD Philips diffractometer within the range of diffraction angles 2θ from 10 deg to 80 deg with the $\text{CuK}\alpha$ filtered radiation. Crystallographic and phase analysis was carried out by means of a technique of Line Profile Analysis, LPA that uses the shape of X-ray diffraction peak profiles to get information about finite crystallite size or/and microstrains. This technique allows the full width at half maximum FWHM together with the integral breadth β to be estimated from a peak profile recorded as a step scan. The integral breadth β is the peak area divided by the peak maximum and it represents the width of a rectangle with the same area and height as the peak concerned. If the internal breadth of an observed peak profile is only due to finite crystallite size, the volume averaged crystallite size D_{XRD} is calculated from the well-known Scherrer's formula:

$$D_{\text{XRD}} = \frac{\alpha \lambda}{\beta \cos \theta} \quad (2)$$

where, α is a constant with a value close to 1, λ is the wavelength of the radiation used, θ is the diffraction angle.

A mean lattice distortion e can be derived from the following expression:

$$e = \frac{\beta}{4 \tan \theta} \quad (3)$$

The line broadening effects due to each of these factors D_{XRD} and e have different angular dependence and hence can be separated. In this work the contribution from microstrains has been found negligible thus we have used the Scherrer's formula (Eq. (2)) to calculate the crystallite size. The instrumental broadening of diffraction lines was taken into account by analysing the profile obtained from standard reference material, LaB_6 . Single line analysis of (200) diffraction peak of anatase and that of (211) for rutile was performed.

The phase composition comprising the weight contribution of the anatase W_A was estimated from the relation:

$$W_A = \frac{1}{1 + 1.265(I_R(110)/I_A(101))} \quad (4)$$

where I_A and I_R are the intensities of chosen diffraction lines, (101) for anatase and (110) for rutile, respectively.

Transmission electron microscopy, TEM was employed to verify the data concerning the particle size, shape and distribution. The TEM images were recorded with a Philips CM30 operating at 300 kV for samples deposited onto carbon coated copper grids. From these images a mean grain size D_{TEM} and geometric standard deviation σ_g were calculated. The log-normal distribution for aerosol particle size was applied.

For characterization of thin films we have used X-ray diffraction at grazing incidence GID (X'Pert MPD Philips) and atomic force microscopy AFM (NanoScope E, Digital Instruments).

Fundamental information concerning the band gap E_g and positions of impurity or dopant energy levels was obtained from the optical spectra over the wide wavelength range extending from 250 nm to 2200 nm. Perkin Elmer Lambda 19 double beam spectrophotometer equipped with a 150 mm integrating sphere was used for nanopowders and thin films. The basic difference in the way the optical data are taken for nanopowders and thin film comes from the form of these both materials. The granular structure of nanopowders with highly developed surface area results in the enhanced light scattering. Thus, only the diffuse reflectance R_{Diff} can be measured. On the other hand, relatively smooth, mirror-like surface of thin films does not introduce strong light scattering effects and both transmittance T and reflectance R can be analyzed.

For nanopowders, we have used the Kubelka-Munk approach with K-M function $K_M(R_\infty)$ defined as:

$$K_M(R_\infty) \equiv \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \quad (5)$$

where R_∞ is the absolute reflectance of the sample, k is related to absorption while s is due to the scattering. Provided that the scattering is the same over a small wavelength region, the $K_M(R_\infty)$ function follows the changes in the absorption coefficient. Therefore, the appropriate fits of $(K_M h\nu)^{1/2}$ versus photon energy $h\nu$ serve to derive E_g .

These results were confronted with those obtained from the energetic position of the maximum in the first derivative of the diffuse reflectance $dR_{\text{Diff}}/d(h\nu)$. This method gives approximate results without the need to calculate the absorption and is based on the assumption that the onset of the greatest increase in the diffuse reflectance corresponds to the band gap.

For thin films, the wavelength dependences of transmittance and reflectance coefficients have been measured in

specular geometry as well as with the help of integrating sphere, in which case the diffuse and total spectra are recorded. The optical transitions have been analyzed by means of standard methods taking into account interference effects in thin films.⁸ The energy of the band gap has been determined from the Tauc' plots.

The photocatalytic activity (PCA) of the nanopowders was evaluated by the degradation of aqueous solution of methylene blue (MB) under UV ($\lambda_{\text{max}} = 355$ nm) and visible ($\lambda_{\text{max}} = 435$ nm) irradiation in the presence of the suspended photocatalyst. Details of the experiment and photochemical reactor have been reported elsewhere.^{27, 28} In brief, the photochemical irradiation system comprised two half-cylinders, each of which contained six Hg T5 lamps, 8W for the visible light or six Coastwave Blacklight UVA, 8W lamps for UVA irradiation. The reaction vessel was a double-wall 125 cm³ quartz Drechsel bottle with a rubber septum through which the samples were extracted. Thermostated water at 300 K was pumped continuously through the outer jacket of the reaction vessel.

The pollutant liquid consisted of an aqueous solution of 5.15×10^{-5} M methylene blue (deionized water, pH = 5.5). The powder concentration in the solution was adjusted at 0.4 mg/cm³. The reaction dispersion was continuously purged with air (110 cm³/min) and magnetically stirred (300 rpm) throughout the irradiation period. Extracted samples were filtered through 0.2 μ m nylon membrane filters to remove the photocatalyst particles before the optical analysis. Calibration of the absorbance at $\lambda = 664$ nm against MB concentration was carried out for the determination of the photocatalytic activity with concentration derived from the peak intensity.

3. RESULTS AND DISCUSSION

Figure 1 demonstrates X-ray diffraction patterns of pure and modified TiO₂ nanopowders prepared by flame spray synthesis, FSS. The results for commercial nanopowders of rutile TiO₂ from Aldrich and that of P25 Degussa, well-known for its photocatalytic properties, are included for comparison.

Nanopowders of TiO₂ prepared at the different flow rates of precursors varied from 0.3 to 0.034 cm³/s are characterized by the increased specific surface area SSA, e.g., for the flow rate of TTIP of 0.3 cm³/s the SSA = 37.5 m²/g and increases to SSA = 106.8 m²/g with the decreasing flow of 0.034 cm³/s. This results in a change in the particle size as calculated from BET measurements. The values of BET-equivalent particle diameter D_{BET} are given in Table I. There is a clear correlation between the increasing SSA and decreasing particle size as indicated by Eq. (1). The crystallite size, calculated from the XRD patterns with the help of Scherrer's formula (Eq. (2)), is shown in Table I.

X-ray diffraction patterns of TiO₂ nanopowders indicate that, independently of the specific surface area SSA, the

Fig. 1. X-ray diffraction patterns of pure (a) and Cr-modified TiO₂ (c) nanopowders prepared by flame spray synthesis, FSS. XRD patterns for commercial nanopowders (b) are given for comparison; SSA – specific surface area; red lines indicate rutile, blue lines – anatase.

crystallinity of materials prepared by FSS is quite good (Fig. 1(a)).

The anatase polymorphic form constitutes the majority phase (Table I) while rutile is present in a small amount, not exceeding 10 wt.% for pure TiO₂. As compared with P25, we can conclude that the rutile content is smaller for FSS nanopowders.

XRD studies reveal better crystallization of FSS nanopowders than commercial ones (Fig. 1(b)). The crystallite sizes of flame-made pure TiO₂ nanopowders are larger $D_{\text{XRD}} = 7\text{--}27$ nm than those of the commercial rutile $D_{\text{XRD}} = 9$ nm and anatase $D_{\text{XRD}} = 12$ nm as can be seen in Table I.

Doping with 1 at.% of Cr makes XRD peaks slightly wider than in the case of pure TiO₂, but otherwise no significant changes are seen in X-ray diffraction patterns (Fig. 1(c)). Substantial amorphisation is observed at 15 at.% of Cr. Conditions of synthesis are such that the crystallite size can be made as small as $D_{\text{XRD}} = 5$ nm for anatase and $D_{\text{XRD}} = 8$ nm for rutile in the case TiO₂ doped with 15 at.% Cr (Table I).

At low Cr doping levels, neither chromium oxide nor chromium titanates precipitation has been observed. The weight percentage of anatase W_A remains mostly unaffected by Cr doping up to a certain limit at which it decreases to reach 75 wt.% at 15 at.% Cr (Table I).

Table I. Basic morphological parameters of TiO₂-based nanopowders obtained by flame spray synthesis FSS. Data for commercial powders are included for comparison.

Sample and its chemical composition	Specific surface area SSA (m ² /g)	BET-equivalent particle diameter D_{BET} (nm)	Crystallite size D_{XRD} (nm) from XRD		Particle size D_{TEM} (nm) from TEM	Weight percentage of anatase W_A (wt.%)
			Anatase	Rutile		
TiO ₂	106.8	14.5	13.4	6.7	—	96
TiO ₂	86.7	17.8	15.6	8.6	—	91
TiO ₂	63.9	24.2	18.1	8.5	—	91
TiO ₂	54.1	28.7	21.0	10.9	21.1	89
TiO ₂	37.5	41.4	26.8	13.6	—	95
TiO ₂ + 0.1 at.% Cr	48.4	32.1	21.2	9.6	27.7	95
TiO ₂ + 1 at.% Cr	87.1	17.8	13.8	9.3	18.9	91
TiO ₂ + 15 at.% Cr	176.6	8.6	5.0	8.2	7.5	75
Commercial (Aldrich)	150.1	9.4	—	9 ± 3	—	0
TiO ₂ rutile nanopowder						
Commercial (Aldrich)	124.2	12.5	10 ± 2	15 ± 3	—	93
TiO ₂ anatase nanopowder with traces of rutile						
Commercial (Degussa)	50	21.0	19.1	14.6	—	80
P25 powder of TiO ₂						

However, even at 15 at.% Cr no other phases than TiO₂ can be seen. The fact that the solubility limit of Cr in TiO₂ is surpassed for nanopowders is not surprising because it is well known that nanomaterials can be doped at unusually high concentrations.²⁹ The fact that no important distortion of lattice occurs is due to the similarity between the ionic radii of Cr³⁺ (0.0615 nm) and Ti⁴⁺ (0.0605 nm).³⁰

The influence of post-deposition annealing in air at progressively increasing temperature T_a on crystallization of TiO₂ thin films deposited by rf reactive sputtering is illustrated in Figure 2. Evolution of the phase composition is clearly seen. Film deposited even at the elevated temperature $T_{\text{sub}} = 620$ K is largely amorphous with anatase crystallites embedded within. Upon annealing, anatase polymorphic form undergoes the systematic and irreversible transformation to rutile. The transformation is quite clearly observed at about $T_a = 770$ K, the temperature at which the contributions from anatase and rutile are comparable. At $T_a = 970$ K rutile dominates over anatase. From 1170 K to 1280 K the complete transformation to rutile is accomplished. The resulting structure shows a very strong preferred orientation perpendicular to the (110) crystallographic plane. X-ray reflections from the crystallographic planes of Miller indices (hkl) with $l \neq 0$ are almost completely quenched.

The conditions under which the transformation from anatase to rutile takes place are similar to those observed in the literature.³¹ As expected, the anatase content decreases with the annealing temperature above 620 K. The grain size of both disappearing anatase and emerging rutile increases systematically with the annealing temperature as seen in Table II.

Incorporation of Cr in thin films of TiO₂ affects the crystallization process as can be noticed in Figure 2. At the largest content of 16 at.% Cr, the X-ray GID pattern

Fig. 2. Grazing incidence GID X-ray diffraction patterns of TiO₂ thin films deposited by rf sputtering and modified by annealing in air at high temperature T_a ; T_{sub} is the substrate temperature during film deposition. For sample identification see Table II.

Table II. Basic morphological parameters of TiO₂ thin films obtained by rf reactive sputtering.

Sample	Annealing temperature T_a (K)	Phase composition W_A from Eq. (4)	Crystallite size D_{XRD} (nm) from Eq. (2)		Surface roughness (nm) from AFM
			Anatase	Rutile	
R22 TiO ₂ thin film deposited at substrate temperature $T_{sub} = 620$ K	—	Anatase $W_A = 89$ wt.% with traces of rutile in amorphous background	12 ± 3	12 ± 3	3.2–4.2
T500 annealed TiO ₂ thin film	770	$W_A = 37$ wt.%	23 ± 5	21 ± 7	4.8–5.2
T700 annealed TiO ₂ thin film	970	$W_A = 18$ wt.%	60 ± 10	40 ± 10	6.5–7.2
T7 annealed TiO ₂ thin film	1280	$W_A = 0$ well-crystallized rutile	—	95 ± 30	13–20

indicates precipitation of anatase in largely amorphous background with the possibility of formation of Anderson phases.

Figure 3 demonstrates the TEM images from TiO₂ nanopowders prepared by FSS that show typical particle morphology which can be expected from flame spray synthesis of metal-organic titanium precursors.

The particles in the representative overviews are mainly spherical-shaped, non-aggregated and do not possess any interstitial particle necking, what is typical for such a kind of process under these conditions. However, hexagonal (1) and square-shaped (2) grains are also present. Moreover, giant (3) granules are also formed. Particles visible in TEM images are probably composed of smaller crystallites as can be inferred by comparing their dimensions with those derived from XRD results as shown in Figure 4.

Fig. 3. TEM images of pure TiO₂ and TiO₂ doped with Cr nanopowders with different specific surface area, SSA; (1) hexagonal, (2) square-shaped, (3) giant grains.

Figure 4 illustrates particle size determined from BET and TEM as compared with the crystallite size found from XRD. Comparison of data from BET and TEM revealed good agreement. Some differences between D_{BET} and D_{TEM} may result from only partially fulfilled assumptions of spherical, uniform and nonporous grains necessary for accurate determination of BET-equivalent particle size (Eq. (1)).

The crystallite size for anatase and rutile D_{XRD} as determined from XRD assumes lower values than the particle size found from BET and TEM (Fig. 4). Thus, the slope of both experimental lines for D_{XRD} anatase and D_{XRD} rutile as a function of D_{BET} is smaller than 1 in the representation chosen in Figure 4. This results from the fact, that XRD data provide rather dimensions of crystallites. The D_{XRD} for anatase is systematically higher than that of rutile which might be explained by the predominance of anatase with better conditions for nucleation in the prepared nanopowders (Table I).

AFM micrographs presented in Figure 5 reveal a distinct change in the surface morphology upon annealing of TiO₂ thin films obtained by rf reactive sputtering. Round-shape nodules are seen at the surface of as-deposited films (Fig. 5(a)). The surface of the film annealed at 970 K

Fig. 4. Juxtaposition of D_{XRD} and D_{TEM} with BET-equivalent particle size D_{BET} for pure TiO₂ and Cr-doped TiO₂ nanopowders prepared by FSS.

Fig. 5. AFM surface images of TiO₂ thin film deposited at the substrate temperature $T_{\text{sub}} = 620$ K by reactive rf sputtering (a) and subsequently annealed at $T_a = 970$ K (b) and $T_a = 1280$ K (c). The images correspond to the samples, the X-ray GID patterns of which are demonstrated in Figure 2.

contains relatively large particles with well-defined facets. When the temperature exceeds 1170 K, a distinct change can be seen. The size of particles increases strongly and steps can be distinguished at $T_a = 1280$ K. Such an effect is due to the transformation from anatase to rutile and remains in agreement with the XRD data. As shown in Table II, the surface roughness, estimated on the basis of AFM images, increases drastically from about 3 nm for

as-deposited thin films to 13–20 nm when the transformation is complete. Large, recrystallized rutile grains of the size of about 100 nm are responsible for this effect.

Diffuse reflectance R_{Diff} , typical for highly scattering samples, as a function of the photon energy $h\nu$, close to the fundamental absorption edge, is presented in Figure 6. The fundamental absorption edge, that is characterized by an abrupt decrease in the diffuse reflectance when the photon energy approaches the value of the band gap energy E_g occurs at higher photon energies $h\nu$, for anatase than for rutile. For the microcrystalline powders obtained by sol-gel in our earlier work²⁵ the values of E_g have been found to be 3.0 eV and 3.2 eV for rutile and anatase, respectively. This remains in agreement with the data reported by other authors both for polycrystalline samples and single crystals.³²

The size of grains being of the order of hundred nanometers in the case of microcrystalline rutile powder makes it a good reference to observe a shift of the fundamental absorption edge towards the UV when the crystallite size decreases to 9 nm (see data for commercial nanopowder of rutile from Aldrich in Table I). Such a blue-shift is observed in Figure 6 and it amounts to about 0.25–0.3 eV for the nanocrystalline rutile.

In the case of nanopowders consisting in majority of the anatase phase such a displacement of the absorption spectrum is more difficult to observe. The fundamental absorption edge changes its slope for nanopowders prepared by FSS (Fig. 6) because there are now two contributions to the electronic transition: one from anatase and another from rutile. This is particularly well-demonstrated in Figure 7, where the first derivative of the diffuse reflectance reveals

Fig. 6. Optical diffuse reflectance R_{Diff} as a function of photon energy $h\nu$ for: sol-gel microcrystalline powder of TiO₂ rutile (blue), commercial Aldrich rutile nanopowder (red) and flame-made TiO₂ nanopowder containing 95% of anatase (green).

Fig. 7. Analysis of the optical transitions from the diffuse reflectance spectra of pure TiO₂ and TiO₂:Cr nanopowders prepared by FSS; first row – Kubelka-Munk spectra $(K_M h\nu)^{1/2}$, second row – the first derivative spectrum $dR_{\text{Diff}}/d(h\nu)$; $h\nu$ – photon energy, K_M – Kubelka-Munk function. The analysis for the commercial P25 nanopowder has been performed for comparison.

two maxima, one corresponding to the band gap of anatase and another to that of rutile.

The results of the application of two methods of analysis of the diffuse reflectance spectra are given in Figure 7. The band gap energy E_g was determined from the appropriate fits of the Kubelka-Munk function K_M calculated directly from the diffuse reflectance spectra as those presented in Figure 6. The calculations were performed according to the Eq. (5).

In most cases, two straight lines of different slopes and cut-off with $K_M = 0$ can be obtained from the fits in Figure 7. The highest value corresponds to the band gap of anatase and the lower one to rutile.

The photon energy at which the $dR_{\text{Diff}}/d(h\nu)$ attains its maximum has been used as well for the band gap determination (Fig. 7). Comparison between the values of photon energies of the optical transitions derived from these two methods indicates that there is no much change between them for pure TiO₂. Two transition energies 3.33–3.35 eV and 3.17–3.19 eV are found for TiO₂ nanopowder, independently of the analysis method used and might be attributed to anatase and rutile band gap, correspondingly. Upon doping with Cr³⁺ the discrepancies between Kubelka-Munk model and the analysis of maximum in the differential reflectance become more profound. The highest transition energy of 3.40 eV obtained from the maximum in $dR_{\text{Diff}}/d(h\nu)$ cannot be fitted with the Kubelka-Munk model. Therefore, when the doping level increases above 1 at.% Cr the energies of optical transitions are not so easy to distinguish and the differences

between two methods of analysis become significant. This might be due to fact that the increased level of doping with Cr³⁺ results in an important deformation of diffuse reflectance spectra in the region close to the fundamental absorption edge. This results from the formation of the additional absorption bands related to the impurities. Above 1 at.% Cr the fundamental absorption edge disappears while the absorption increases substantially within the visible range of the light spectrum, which is seen as a decrease in the R_{Diff} .³³

The fact that the band gap expands with the reducing particle size is usually explained by the quantum confinement. Spatial confinement of charge carriers due to the quantum-size effect has been observed to affect the photoabsorbance of nanometric semiconductors such as CdS, CdSe, ZnO, etc.³⁴ The size-dependent shift in the band gap ΔE_g can be calculated as³⁵

$$\Delta E_g = \frac{\hbar^2 \pi^2}{2\mu \langle R \rangle^2} - \frac{1.786e^2}{\epsilon \langle R \rangle} + 0.284E_{\text{Ry}} \quad (6)$$

where $\langle R \rangle$ is the particle radius, ϵ represents the dielectric constant, E_{Ry} is the Rydberg (spatial correlation) energy. The reduced mass μ of an electron-hole pair is defined as:

$$\mu = \frac{m_e^* m_h^*}{m_e^* + m_h^*} \quad (7)$$

where m_e^* and m_h^* denote the effective mass of electrons and holes, respectively. The parameter μ is very important because if it is too large as in the case of TiO₂ (1.63 m_0 ,

Fig. 8. The effect of crystallite size D_{XRD} (anatase and rutile) determined from X-ray diffraction on the band gap energy E_g for pure TiO₂ and TiO₂:Cr nanopowders prepared by FSS. Experimental results are indicated by points, theoretical simulations for varied reduced mass μ of an electron-hole pair (Eq. (7)) are depicted as lines (solid – rutile, dashed – anatase).

where m_o is the electron rest mass) the blue-shift in E_g becomes significant only at a very low particle diameter ($\langle 2R \rangle = 2.4$ nm for $\Delta E_g = 0.15$ eV).

Taking into account data given in Table I, especially the crystallite sizes determined from XRD for anatase and

rutile grains we did some simulations of the band gap shift predicted by Eq. (6). The results of simulations for different values of the effective mass μ are shown in Figure 8. The experimental data for all nanopowders prepared by FSS are included as well. Simulated curves at $\mu = 1.63 m_o$ or $\mu = 1 m_o$ describe quite well the experimentally observed behavior for pure TiO₂ rutile crystallites. However, the reduced mass should be decreased to $\mu = 0.2 m_o$ for rutile TiO₂ doped with Cr. For the anatase crystallites the observable blue-shift in the band gap seems to require smaller effective masses $\mu = 0.2 m_o$ or $\mu = 0.1 m_o$.

The effect of the high-temperature annealing on the optical properties of TiO₂ thin films is very dramatic as seen in Figure 9. This is due to the structural transformation from anatase to rutile well-documented by XRD data in Figure 2. Upon an increase in the annealing temperature T_a , the total transmittance T_t decreases and becomes strongly modified over the region of the fundamental absorption edge. The same applies to the total reflectance spectra $R_t(h\nu)$. The edge itself shifts towards lower photon energies, which is a direct consequence of the transformation from anatase to rutile. Large differences between the specular and total transmittance/reflectance are due to large diffuse components T_{Diff} , R_{Diff} that appear at high annealing temperatures of 1170 K. The increased level of the diffuse reflectance R_{Diff} is due to the enhanced surface

Fig. 9. Transmittance T and reflectance R spectra of TiO₂ thin films annealed at 970 K and 1170 K; coefficients of: T_t – total transmittance, T_{Diff} – diffuse transmittance, T_s – specular transmittance, R_t – total reflectance, R_{Diff} – diffuse reflectance, R_s – specular reflectance.

Fig. 10. Energy of the optical transitions E as a function of Cr atomic concentration in FSS nanopowders and thin films of TiO₂; E_{dop} is the energy of the transition from the band related to Cr doping that is formed within the band gap E_g of TiO₂.

roughness as seen in Table II while that of the diffuse transmittance T_{Diff} results from the light scattering in the volume.

The evolution of the energy of the optical transitions upon Cr doping of TiO₂ is demonstrated in Figure 10. The energy of the fundamental band gap E_g and that of the impurity band E_{dop} for the nanopowders were found from the analysis of the maximum in $dR_{\text{Diff}}/d(h\nu)$. Nanopowders with the chemical compositions falling within the range of 0–1.0 at.% Cr show two values of E_g . These two fundamental optical transitions disappear at the doping level exceeding 1 at.% Cr.

For thin films of TiO₂ only one energy of the band gap can be determined, in spite of the fact that both rutile and anatase are present. The E_g decreases with the increasing Cr content which can be related to the increased contribution of rutile.

Fig. 12. Kinetics of photodegradation of methylene blue, MB on TiO₂ nanopowder with SSA = 54 m²/g prepared with FSS. The photodegradation was performed under irradiation over the visible range of light $\lambda = 400\text{--}500$ nm ($\lambda_{\text{max}} = 435$ nm). The progress of photodegradation over commercial TiO₂-P25 nanopowder from Degussa is shown for comparison.

The band located at about 2.5–2.6 eV below the bottom of the conduction band CB of TiO₂ nanopowders and 2.3–2.9 eV for thin films is related to impurities and depends upon the Cr composition. This transition energy could be explained by excitation of an electron of Cr impurity band located above the valence band VB into the CB of TiO₂. Comparison between thin films and nanopowders indicates that the impurity band is placed deeper in the forbidden band gap of TiO₂ in the case of thin films doped up to 8 at.% Cr. At higher doping levels the differences in E_{dop} between the nanopowder and thin film of the same composition, disappear. The presence of this additional absorption feature is promising for applications in the photocatalysis.

The progress of the photocatalytic decomposition of the methylene blue (MB) under UVA radiation in the presence of TiO₂ nanopowder (SSA = 54 m²/g) prepared by FSS can be seen in Figure 11. High absorbance over 550–700 nm wavelength range of the MB decreases systematically upon irradiation indicating degradation of MB. Decomposition is completed after 45 min of irradiation, where the frequency of sampling and the irradiation time are indicated in Figure 11. Before the irradiation started (time 0 min) a decrease in the absorption of MB can be observed and it is related to the adsorption of MB at the surface of the photocatalyst. The concentration of the MB was calculated from the peak intensity at $\lambda = 664$ nm and has been used for the evaluation of kinetics of the photodegradation.

The kinetics of degradation of MB under visible irradiation (180 min) in the presence of TiO₂-FSS and TiO₂-P25 are presented in Figure 12. The decomposition of MB under applied irradiation over the wavelength range of 400–500 nm can be assigned to the photocatalytic activity of investigated photocatalysts since the photosensitising effect can be neglected over this irradiation

Fig. 11. Evolution of the optical absorbance A peak of methylene blue, MB, under UVA irradiation at $\lambda_{\text{max}} = 355$ nm in the presence of TiO₂ nanopowder with SSA = 54 m²/g prepared by FSS.

range.^{36,37} Flame-made TiO₂ exhibited much higher photoactivity over the visible range in comparison to the commercial P25 powder. The enhancement of the photoactivity in the case of TiO₂-FSS nanopowder can be related to better crystallinity and bigger size of the crystallites³⁸ what results in a lower number of defects which may act as the recombination centres. Another aspect which can potentially cause high activity of flame made TiO₂ is higher amount of anatase phase as compared to TiO₂-P25. Anatase is known to be a favourable structure for photocatalytic applications due to a convenient position of its conduction band edge CB with respect to the reduction potential of water as well as a better affinity of anatase surface to water and hydroxyl group adsorption.³⁹

4. CONCLUSIONS

Pure and modified titanium dioxide in the form of nanopowders and thin films were successfully elaborated and characterized by means of X-ray diffraction, TEM, AFM and optical spectrophotometry. Nanopowders prepared by flame spray synthesis, FSS were found to be well-crystallized, with the anatase phase predominating over rutile. The crystallite size determined from XRD was found to be smaller than that obtained from BET-measurements of the specific surface area, SSA and from TEM. In the case of thin films the irreversible structural transformation from anatase to rutile occurred upon post-deposition annealing over the temperature range extending from 770 K to 1170 K. This transformation had quite a dramatic effect on the optical properties and film morphology as revealed by AFM images. Relatively high level of the diffuse transmittance and reflectance in the vicinity of the fundamental absorption edge could be traced back to the increased volume and surface scattering at large agglomerated grains. The spectrophotometry over the UV and visible range of the light spectrum allowed us to determine the energy of the optical transitions for pure and Cr-doped TiO₂ in the form of nanopowders and thin films. The effect of quantum confinement in the case of rutile and anatase grains resulted in the increase in the band gap of TiO₂ and TiO₂-Cr. The enhancement of the photoactivity for TiO₂-FSS nanopowder can be related to the better crystallinity and bigger size of the crystallites that leads to lower concentration of defects acting as the recombination centres.

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