Optical Properties of TiO₂ Nanopowder Doped by Silver (Copper) during Synthesis or PVD Method

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Titanium dioxide doped nanopowders were prepared in two ways: (i) by applying a sol-gel method and (ii) by applying the sol-gel synthesis as the first step for pure TiO_2 preparation, and next, doped by using magnetron sputtering technique, that is one of a physical vapour deposition method. Silver and copper (Ag, Cu) metals were used as the dopants. Prepared samples were investigated by scanning electron microscope, X-ray diffraction and UV-Vis spectroscopy. The effect of the dopants' nature and the applied doping method were studied. The results showed that each prepared particles are nanocrystalline materials with particles diameter range from 80 nm to 500 nm (depending on the doping method). From optical experiments, it was possible to observe changes in absorbance spectra, which are probably related to interfacial charge transfer and the localized surface plasmon resonance phenomenon.

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1. Introduction

As a result of their properties, titanium dioxide nanopowders have a potentially wide application in various fields of human activity [1–9]. In recent years, there have been many reports on photocatalytic reactions, which occur in titanium dioxide nanopowders to reduce and convert pollutants from the water and gas phases. Studies on photocatalytic phenomena in TiO_2 have been described in many publications, and have covered: the removal of organic contaminations from water [10]; the oxidation of CO [11], and methyl orange [12]; the degradation of: Congo red, Rose Bengal, Eriochrome black T, and Bromocresol Green [13]; the decomposition of Linuron [14]; the formation of I_3^- [15]; and many others [16-21]. Wider use of the photocatalytic phenomena generated in titanium dioxide materials has been hindered by limitations associated with the low quantum yield of the setting process, as well as the narrow absorption of electromagnetic radiation. The minimum energy needed to excite the electron in the pure TiO_2 nanopowders is approximately 3.2 eV for anatase and 3.0 eV for rutile [22]. In the case of anatase, energy associated with excitation of an electron from the valence to the conduction state corresponds to the quantum lengths of the electromagnetic radiation, about $\lambda = 388$ nm. Since titanium dioxide absorbed only 5% of the electromagnetic radiation, the photocatalytic process in those materials is, therefore, inefficient [23]. In the case of TiO_2 in rutile phase, a lower value of the energy for the excitation of electrons was needed, but photocatalytic processes in

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 TiO_2 were much more inefficient than in the anatase phase. This is related to the rate of recombination of electron-hole pairs. The time recombination of electronhole pairs in the rutile is shorter than the time of their migration to the surface. Furthermore, in rutile a small amount of anatase and active sites of the surface hydroxyl groups have been localized [24]. Also, the high temperature of the transformation process of anatase to rutile causes the agglomeration and sintering of the photocatalyst particle, which leads to particle growth and a reduction in the active surface areas of the material [25]. Obtaining a titanium semiconductor material in the anatase that is structured for photocatalytic activity in the visible range ($\lambda > 400 \text{ nm}$) can contribute to wider applications for industry. To achieve this goal, it is necessary to dope pure TiO₂ with metal ions (Pt, Pd, Au, Ag, Ta, Zr, Cu, Nd, Ni, Fe, Cr, V, Mn, Co, Pb, Ce, W etc.) [26–35].

Metal ions introduced to the TiO₂ nanopowder behave like traps and scatter centres for charge carriers. The introduction of metallic dopants to titanium dioxide leads to the formation of an inhomogeneous electric field in the material, which allows it to obtain more effective quantum efficiency, to change the shape an absorption curve, and to a slight effective modification of the energy band gap. Increasing photoactivity by doping pure TiO₂ material with metals in an anatase form leads to an improvement in the interfacial charge transfer (IFCT) [28]. Also, it is possible to observe such characteristic phenomenon related with interaction of metallic dopants with the light from visible range spectrum as localized surface plasmon resonance (LSPR) [28]. Doped and undoped TiO_2 can be synthesized by several processes including: sol-gel [36-38]; hydrothermal [7, 30, 39, 40]; spray or laser pyrolysis [41, 42]; mechanical alloying [43, 44]; and chemical vapour deposition (CVD) [45, 46].

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In this article, the authors have focused on the optical parameters of TiO_2 nanopowders, undoped and doped with silver and copper during synthesis, or by the pulsed magnetron sputtering method that is one of the physical vapour deposition (PVD) technique [47]. In the magnetron sputtering process, the TiO_2 nanopowder has been covered by Ag or Cu thin film. The implementation of metallic dopants into the TiO_2 structure or on nanopowder surface could lead to improved charge transfer in the material and to appearance of such an effect as localized surface plasmon resonance (LSPR). Obtained and examined effects of TiO_2 :Ag (Cu) nanopowders associated with optical parameters are also highly likely to affect the photocatalytic effects.

2. Experimental

The synthesis of compounds were prepared in two ways:

- Applying only the sol–gel synthesis, for volumetric doping (Sect. 2.1).
- Applying the sol-gel synthesis as the first method, pure TiO₂ nanopowders were prepared, and next, doped with Cu or Ag by using the pulsed magnetron sputtering method [48–51]. This was a surface doping where the titanium dioxide nanopowders were covered by metallic Ag or Cu thin films (Sect. 2.2).

2.1. Volumetric doping of TiO_2 nanopowder

Titanium dioxide doped with Ag (Cu) were obtained by sol–gel technique using two methods of synthesis. In both cases such components as titanium(IV) isopropoxide (TIPO), ethanol, and distilled water were applied and stirred during 4 h. Differences in both methods of synthesis were in the time and order to added AgNO₃ or CuSO₄ to the mixture. In the first method AgNO₃ or CuSO₄ was stirred during 4 h along with other components, while in the second case AgNO₃ or CuSO₄ was added to sol mixture and stirred for 2 h. Details of the TiO₂:Ag(Cu) synthesis are presented below.

First method: 4.5 ml of TIPO and 21 ml of ethanol were mixed with 3.5 ml of distilled water and addition of AgNO₃ or CuSO₄ to the obtaining sol with the molar ratio Ag(Cu)/TIPO equal to 1%, 5%, 10%. The solution was stirred in a plastic flask at room temperature for 4 h. During the stirring the titanium dioxide nanopowder was formed and after filtering dried at room temperature. Obtained sample was finally heated at 500 °C for 1 h. In this case the TiO₂A_{1%}, TiO₂A_{5%}, TiO₂A_{10%} (where A is Ag or Cu ions) samples were obtained.

Second method: 4.5 ml of TIPO and 21 ml of ethanol were mixed with 3.5 ml of distilled water yielding a titania sol. The solution was stirred in a plastic flask at room temperature for 2 h. Next, $AgNO_3$ or $CuSO_4$ were added to the obtained sol with the molar ratio Ag(Cu)/TIPO

equal to 1%, 5%, 10% and mixed for 2 h. During the stirring the titanium dioxide nanopowder was formed and after filtering was dried at room temperature. Prepared $TiO_2A_{1\%-a}$, $TiO_2A_{5\%-a}$ and $TiO_2A_{10\%-a}$ (where A is Ag or Cu ions) samples were finally heated at 500 °C for 1 h.

2.2. Surface doping of TiO_2 nanopowder

In the magnetron sputtering method, 1.8 g of pure TiO₂ nanopowder (prepared by the sol-gel method) was placed in the sample stage, with a distance of 13 cm from the magnetron gun, powered by DPS Power Supply Unit (medium frequency power supply) [52]. The sample stage was vibrated mechanically at 24 rpm during the depositions. High-purity Cu (99.999%) and Ag (99.99%) targets were used. Sputtering processes were carried out in the atmosphere of pure argon (99.999%), under the same pressure of 0.3 Pa. Two values of sputtering power: P = 300, 600 W for Cu and P = 200 and 400 W for Ag and two values of sputtering time ($t_1 = 15$ min and $t_2 = 30$ min) were applied to obtain various amount of metal contents (Table I).

TABLE I

The specific process parameters of doping TiO_2 nanopowders with Cu and Ag by the magnetron sputtering.

Sample no	Sputtering power	Sputtering time		
Sample no.	[W]	[min]		
${\rm TiO}_2:{\rm Cu}_{\rm A}$	300	30		
${\rm TiO_2:Cu_B}$	600	30		
${\rm TiO}_2:\!{\rm Cu}_{\rm A1}$	300	15		
${\rm TiO}_2:\!{\rm Cu}_{\rm B1}$	600	15		
${\rm TiO}_2:{\rm Ag}_{\rm A}$	200	15		
${\rm TiO}_2:{\rm Ag}_{\rm B}$	400	15		
TiO ₂ :Ag _{A1}	200	30		
${\rm TiO}_2:Ag_{\rm B1}$	400	30		

In the case of the Ag target, as previous studies proved, the application of the power exceeding 500 W caused excessive heat on the target and its local melting. This led to replacing the process of sputtering with the process of vaporization. Under such conditions, the target can be destroyed. Therefore, the values of sputtering power were lowered.

Before starting the experiments, the targets were presputtered for 5 min, with a shutter located in between the target and the substrate.

2.3. Analytical procedures

Scanning electron microscope (SEM) (Vega II SBH) equipped with an energy-dispersive X-ray spectroscope (EDS) (INCA PentaFET-x3, manufactured by Oxford Instruments) were used to investigate the morphology and chemical contents. In this case a 30 mm² Li–Si detector area with 133 eV energy resolution was used. In each measurements, the same amount of doped nanopowder was placed on an aluminium table with a diameter of 10 mm. The table had been cleaned with 99.7% isopropanol before the experiments. The distance between the sample and the detector was 23 mm and working voltage was 30 000 V. The investigation occurred at a pressure of 5×10^{-3} Pa. EDS analysis was carried out on an area of 1.00 µm² of prepared powder.

The crystalline phases of prepered samples were examined with X-ray diffraction (XRD) using DRON-2 powder diffractometer with Fe filtered Co K_{α} X-ray beam $(\lambda = 1.7902 \text{ Å})$. The XRD patterns were recorded in 2θ range of 10–70°. The crystal structure of the samples were identified by comparing obtained results with powder diffraction files (PDF) data.

Optical characterizations were performed, using a spectrophotometer JASCO V 670. Relative reflectance (diffusion reflectance) experiments were conducted using snap-reflection, which enabled measurements of intensely light scattering materials to be made. In ordered to realize optical experiments it was necessary to prepare a thick layer of prepared nanopowder in a metal cuvette with a small amount of organic solvent or alcohol, which are neutral for nanopowders and evaporated during the drying process.

3. Results and discussion

Figure 1 shows the SEM images of the undoped titanium dioxide nanopowder obtained at different magnifications. The first image (magnified 30 000×) reveals aggregates consisting smaller particles with a diameter range from 80 nm to 300 nm. The higher magnifications (100 000×) reveal that particles are spherical-like.



Fig. 1. SEM images of undoped TiO₂ nanopowder magnified $30\ 000 \times$ (left) nad $100\ 000 \times$ (right).

The SEM images for the products for samples doped with Cu/Ag by sol-gel method are given in Fig. 2. Compared with the sample shown in Fig. 1 particles are more agglomerated with different shapes and relative larger grain size (up to 500 nm for all doped samples).

Morphologies of TiO_2 nanopowders doped by magnetron sputtering are presented in Fig. 3. The $\text{TiO}_2:\text{Ag}_{A1/B1}$ and $\text{TiO}_2\text{Cu}_{A/B}$ samples are shown. Spherical-like shapes with average size similar



Fig. 2. SEM images of TiO_2 nanopowders doped during sol-gel synthesis.



Fig. 3. SEM images of TiO_2 nanopowders doped by magnetron sputtering method.

to undoped TiO₂ are observed. Aggregates consisting larger particles (up to 500 nm for TiO₂:Cu_{A/B}) can be observed but their amount is quite small. No core-shell structures are observed. In this case further studies with transmission electron microscope (TEM) are necessary.

TABLE II

EDS analysis of the ${\rm TiO_2}$ nanopowders doped with Cu and Ag during the sol–gel synthesis.

Sample no.	Cu contents [wt%]	Sample no.	Ag contents [wt%]
${\rm TiO}_2: {\rm Cu}_{1\%}$	1.16	${\rm TiO}_2:{\rm Ag}_{1\%}$	1.22
$TiO_2{:}Cu_{1\%-a}$	1.26	${\rm TiO_2:Ag_{1\%-a}}$	1.44
$TiO_2{:}Cu_{5\%}$	5.51	${ m TiO}_2:{ m Ag}_{5\%}$	6.31
$TiO_2{:}Cu_{5\%-a}$	4.30	${\rm TiO_2:Ag_{5\%-a}}$	5.39
${\rm TiO}_2: {\rm Cu}_{10\%}$	9.06	${\rm TiO_2:}Ag_{10\%}$	10.72
$TiO_2{:}Cu_{10\%-a}$	5.49	${\rm TiO_2:Ag_{10\%-a}}$	8.70

The specific composition of the obtained phases, identified by the EDS method, are shown in Tables II and III.

Table II shows the experimental data from the EDS experiment, for the samples doped by silver or copper, during the synthesis. A percentage increase in the Ag or Cu during synthesis increases the percentage content of the metallic additives in the titanium dioxide nanopowder.

Table III shows the EDS analysis of the TiO_2 nanopowders doped with Cu and Ag by magnetron sputtering method. It could be noted that in both cases the metal contents increases with the increase in power value. This increase is related to the increase of sputtering yield.

TABLE III

EDS	analysis	of the	TiO_2	nanopowders	doped
with	Cu and A	Ag by n	nagnetr	on sputtering.	

Sample no	${ m Cu/Ag\ contents}\ [{ m wt\%}]$
TiO ₂ :Cu _A	1.42
${\rm TiO_2:Cu_B}$	2.68
${\rm TiO}_2:{\rm Cu}_{\rm A1}$	1.09
$TiO_2:Cu_{B1}$	1.31
$TiO_2:Ag_A$	1.09
$TiO_2:Ag_B$	1.18
$TiO_2:Ag_{A1}$	1.67
${\rm TiO}_2:{\rm Ag}_{{\rm B}1}$	2.60
	•

The power supplied to the magnetron source was controlled through modulation of the pulse quantity. It could be expected that the increase in Ag/Cu contents was caused by the increase of pulse duration; i.e., an increase in the effective sputtering time. It is clearly understandable that using a longer deposition time results in the formation of higher amounts of dopants.

Figure 4 shows the effects of Ag/Cu dopants on the phase compositions of the prepared powders. X-ray diffraction analysis revealed that all obtained samples, independent of the amount of Ag/Cu, have typical peaks of TiO_2 anatase without any detectable peaks of rutile. As shown in the diffraction patterns, a major peak corresponding to (101) reflection is apparent at $2\theta = 29.50^{\circ}$. The crystallite sizes of all samples, as was detected by X-ray, are lower than 20 nm. It indicates that prepared particles are nanocrystalline materials. Small diffraction peak at the angle 57.40° coming from Cu was observed only in the $TiO_2:Cu_B$ and at 52.00° coming from Ag in the TiO_2 :Ag_{10%} and $TiO_2Ag_{10\%-a}$ samples. We believe that it is related to the amount of Ag and Cu dopants, which are the highest in specified samples.



Fig. 4. The XRD patterns of the undoped and selected doped TiO_2 nanopowders.

Optical parameters such as a maximum of absorbance, characteristic peak related to the absorption on copper or silver and an optical band gap were calculated from a Kubelka–Munk function (K–M) which has also been employed in articles [28, 53, 54]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S},$$

where R is the reflectance, K is the absorption coefficient, and S is the scattering coefficient.

To obtain the K-M functions, it was necessary to measure the relative reflectance spectrum in the wavelength range from 250 nm to 1000 nm. Figure 5a (6a) presents K–M spectra for samples with different concentrations of copper (silver) added to titanium dioxide during synthesis process. Optical spectra of TiO_2 nanopowder doped by silver during synthesis have been also published in article [55]. Calculated spectra form K–M function for samples doped by using magnetron sputtering are shown in Fig. 5b (6b). Based on the obtained results it was possible to observe that strong absorption occurred below 350 nm for all samples. However, there can also be noticed an absorption above 675 nm and 600 nm, respectively, for samples doped by copper during synthesis (Fig. 5a), and using magnetron sputtering method (Fig. 5b). A strong absorption in the visible range was also observed for a samples doped by silver (Fig. 6a,b). Based on the obtained results we could conclude that a doping of titanium dioxide by copper or silver during synthesis causes a blue shift of absorbance maximum to pure TiO_2 (see Fig. 5a (6a) and Table IV).



Fig. 5. The Kubelka–Munk function of doped TiO_2 :Cu nanopowders: (a) during synthesis; and (b) using magnetron sputtering method.

However, the main blue shift of maximum absorbance appeared for samples doped by magnetron sputtering method which is related to Ag (Cu) concentration (see Table III). That increase of metal contents is related to specific parameters such as sputtering power and time (see Table I). Maximum content of copper (silver) was obtained for deposition performed in 30 min with 600 W (400 W) and reached accumulation at 2.68% (2.60%). Furthermore, interesting phenomena related to major differences between the intensity of the K–M calculation occurred for samples which were doped using magnetron sputtering method (see Fig. 5b). Probably a variation of Kubelka–Munk function intensity are related to the parameters of the magnetron experiments. It was possible to see that for the highest value of sputtering power one could observe significant changes in K–M function (see Table I and Figs. 5b, 6b) corresponding to the type of metal deposited on the TiO₂ surface.



Fig. 6. The Kubelka–Munk function of doped TiO₂:Ag nanopowders: (a) during synthesis and (b) using magnetron sputtering method.

Moreover, an interesting phenomenon related to the interaction of light with copper or silver incorporated to TiO_2 was observed near the absorption edge. That phenomenon was related to the IFCT between titanium dioxide and copper (silver) (see Figs. 5 and 6). Such a mechanism has been described in articles [28, 29]. In addition, it would probably be possible to observe a trend associated with the localized surface plasmon resonance (LSPR) in obtained TiO₂ nanopowders doped by silver, which might be represented by the peak λ^{Ag} related to absorption on the silver admixture. The LSPR phenomenon was observed in samples made by the sol-gel method when the concentration of silver exceeds 5%. The LSPR effect with a less intensity was also observed for all samples doped by silver using magnetron sputtering method. However, to prove and explore such phenomenon it is necessary to conduct further investigations.

TABLE IV

Optical parameters of nanopowders doped by copper and silver appointed from K–M function.

Sample no.	$\lambda_{ m max}$	$E_{\rm g}^{*}$	Sample no.	$\lambda_{ m max}$	$\lambda_{ m max}^{ m Ag}$	$E_{\rm g}^{*}$
	[nm]	[eV]		[nm]	[nm]	[eV]
$TiO_2{:}Cu_{1\%}$	326	3.22	${\rm TiO}_2:Ag_{1\%}$	326	-	3.13
$TiO_2{:}Cu_{1\%-a}$	322	3.22	$TiO_2{:}Ag_{1\%-a}$	328	-	3.19
${\rm TiO_2:}{\rm Cu}_{5\%}$	318	3.19	${\rm TiO}_2:{\rm Ag}_{5\%}$	332	576	3.07
$TiO_2{:}Cu_{5\%-a}$	318	3.24	${\rm TiO_2:}Ag_{5\%-a}$	323	566	3.10
${\rm TiO_2:}Cu_{10\%}$	314	3.31	${\rm TiO}_2:{\rm Ag}_{10\%}$	332	622	2.97
$\rm TiO_2{:}Cu_{10\%-a}$	315	3.27	$TiO_2{:}Ag_{10\%-a}$	332	609	2.97
${\rm TiO}_2: {\rm Cu}_{\rm A}$	307	3.22	${\rm TiO}_2:{\rm Ag}_{\rm A}$	311	603	3.19
${\rm TiO}_2:\!{\rm Cu}_{\rm A1}$	307	3.22	${\rm TiO}_2:{\rm Ag}_{{\rm A}1}$	314	582	3.19
${\rm TiO_2:Cu_B}$	303	3.06	$TiO_2:Ag_B$	311	614	3.10
${\rm TiO}_2:Cu_{\rm B1}$	307	3.14	${\rm TiO_2:Ag_{B1}}$	311	611	3.15
pure TiO_2	332	3.25	$*E_{\sigma}$ — opti	cal ba	nd ga	p

Also, it has been possible to observe that for titanium dioxide doped by the magnetron sputtering technique, phenomena related with the intensity of the interfacial charge transfer or localized surface plasmon resonance are a function of sputtering power and time of deposition in the used doping method. Such an observable fact has been noticed especially for titanium dioxide doped by silver, using a physical vapour deposition method.

3. Conclusions

In this article experimental data of conducted optical measurements was presented, which conclude that such phenomena, such as interferential charge transfer and/or localized surface plasmon resonance, exist in titanium dioxide doped by silver or copper. Also, the conducted optical experiments permitted the calculation of parameters such as the optical band gaps of doped titanium dioxide, and the maximum absorbance on metallic additives in the studied samples. From the conducted experiments, it was possible to see that increasing the amount silver or copper during synthesis causes insignificant changes in the optical band gaps. However, silver added during synthesis to titanium dioxide has a meaningful influence on the absorption intensity, especially in the spectrum range related to localized surface plasmon resonance. A similar effect was observed for samples doped by silver by the magnetron sputtering method.

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