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Proc. of "4th Balkan Conference on glass science and technology & 16th Conference on glass and ceramics", 27 September – 01 October, Varna, Bulgaria, Volume 2, "Ceramics" (2011)

SOL-GEL PURE AND S-DOPED TiO_2 POWDERS WITH ECOLOGICAL APPLICATIONS

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Abstract

The photocatalytic degradation of pollutants using TiO_2 nanopowders or TiO_2 thin films is very attractive for applications to environmental protection, as a possible solution for water depollution. The impurity doping represents one of the typical approaches in order to extend the spectral response of a wide band gap semiconductor to visible light. The aim of the present work was to establish the influence of the S-dopant on the photocatalytic properties of the TiO_2 nanopowders. The relationship between the synthesis conditions and the properties of the un-doped and S-doped TiO_2 materials, such as thermal stability, phase composition, crystallinity, morphology, and size of particles, and the influence of the dopant were investigated. The influence of S on TiO_2 crystallization was also studied (lattice parameters, crystallite sizes, internal strains). The photocatalytic activities of the prepared TiO_2 based nanopowders were determined by testing them in the degradation of different chloride organic compounds from aqueous solutions. It was established that the presence of S dopant in the TiO_2 powders has improved their photocatalytic activities.

Keywords: *sol-gel, TiO_2 powders, S-dopant, photocatalytic activity, environmental protection*

Introduction

TiO_2 represents one of the most studied oxides, due to its high photocatalytic activity, excellent functionality, high chemical stability, thermal stability and non-toxicity. These properties make it useful in different fields, ranging from optics via solar energy to gas sensors. The photocatalytic degradation of pollutants using TiO_2 nanopowders or TiO_2 thin films is very attractive for applications to environmental protection, as a possible solution for water depollution. All the mentioned properties are improved in the case of nanostructured TiO_2, which could be easily obtained by the sol-gel method. Concerning the improvement of the photocatalytic properties, the impurity doping represents one of the typical approaches in order to extend the spectral response of a wide band gap semiconductor to visible light [1-3]. Very few data could yet be found regarding the S-doping of TiO_2 that refer to the preparation of thin coatings [4]. The aim of the present work was to obtain sol-gel S-doped TiO_2 powders with photocatalytic properties which make them useful in one of the most important field of our life: the environmental protection.

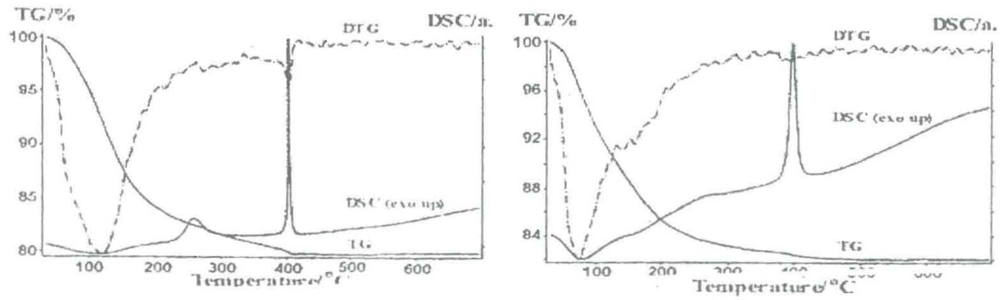
Experimental

Pure and S-doped sol-gel TiO_2 nanopowders have been prepared by controlled hydrolysis-condensation of tetraethylorthotitanate (Merck), $Ti(OC_2H_5)_4$. Absolute ethanol (Riedel de Haën) C_2H_5OH has been used as solvent. The hydrolysis of the Ti alkoxide proceeded with a water excess and in un-catalyzed conditions. The molar ratios were: water/alkoxide = 5 and alcohol/alkoxide = 85. The pH value was 4 and the reaction progressed at 25°C. For the S-doped TiO_2 nanopowders the thiourea (Alfa Aesar), H_2NCSNH_2, has been used as source of dopant. It was introduced in the reaction mixture dissolved in the corresponding quantity of alcohol. The content of S dopant related to TiO_2 was of 5 wt. %.

The prepared un-doped and S-doped sol-gel TiO_2 powders have been dried at 80°C. They have been analyzed from point of view of their thermal behavior, in order to establish the thermal schedule for the subsequent investigations. The thermal analysis was performed using a STA 409 PC Luxx simultaneous DSC and TG/DTG equipment (Netzsch). The structural and morphological characterization of the samples has been accomplished using the following methods: (a) X-ray diffraction with a Shimadzu XRD 6000 diffractometer and (b) TEM with JeolCX equipment. The photocatalytic properties of the prepared powders have been tested in a laboratory installation containing an UV reactor, using a synthetic chlorobenzene solution.

Results and discussion

The thermal behavior of the prepared un-doped and S-doped sol-gel TiO_2 powders in static air atmosphere is presented in Figure 1. The DSC curves of both powders show sharp crystallization effects of TiO_2 anatase at 403.5°C for pure TiO_2 and at 398°C for the doped sample. More details concerning the thermal behavior of the sol-gel prepared powders are presented in our previous paper [5]. Based on thermal analysis results, thermal treatments at 300°C, 400°C and 500°C, respectively, has been establish to be applied for both prepared samples. The heating rates were of 1°C/min. and the plateaus were of 1 hour in all cases.



(a) (b)

Figure 1. Thermal behavior of pure TiO_2 (a), and of S-doped TiO_2 nanopowders (b)

The structural evolution of pure and S-doped sol-gel TiO_2 powders with the temperature is presented by XRD results in Table 1.

Table 1. Calculated values of microstructural factors obtained from computerized analysis of XRD spectra

Sample	Identified phases	Lattice constants*			Microstructural factors	
		a [Å]	c [Å]	u.c.v. [Å^3]	<D>[Å]	10^{+3}x<S>
TiO_2 - 300°C	Anatase	3.7752	9.4973	135.36	74	10.0
TiO_2 - 400°C	Anatase	3.7815	9.4709	135.43	178	1.4
TiO_2 - 500°C	Anatase	3.7750	9.4828	135.14	346	0.3
S-TiO_2 300°C	Anatase	3.7812	9.4778	135.51	172	1.6
S-TiO_2 400°C	Anatase	3.7783	9.4735	135.24	247	1.2
S-TiO_2 500°C	Anatase	3.7676	9.4561	134.23	302	1.5

*a, c- lattice parameters; u.c.v. –unit cell volume; D –crystallite size; S – internal strain

The XRD analysis supplied valuable informations regarding the study of the influence of S as dopant on TiO_2 crystallization by means of lattice parameters, crystallite sizes and internal strains determinations. The presented calculated values from Table 1 have been obtained from the computerized analysis of XRD spectra with a proper XRAY5.0 program [6]. The phase composition shows the presence of anatase as single crystalline phase for both types of sol-gel prepared powders: pure and S-doped TiO_2, respectively and for whole temperature range (from 300°C to 500°C). From the XRD presented data one can establish that: (a) for the pure TiO_2 sample the evolution of the anatase lattice with the temperature is the expected one, that is the lattice becomes more and more structured as the temperature increases, so the lattice strains quickly decreases; (b) for the S-doped TiO_2 powder the effect of dopant interferes with the effect of temperature which arranges the lattice, the rate of crystallite growth being smaller in the presence of S; (c) for both cases and in agreement with <D> and <S> evolution, the geometry of the elementary cell tends to evolve towards the most stable state, which in this case corresponds to a slightly contraction with temperature (lower for the pure TiO_2 sample, compared to the S-doped one).

A supplementary characterization of the sol-gel prepared nanopowders refers to the size distributions, which was obtained from the statistical processing of the TEM images presented in Figure 2.

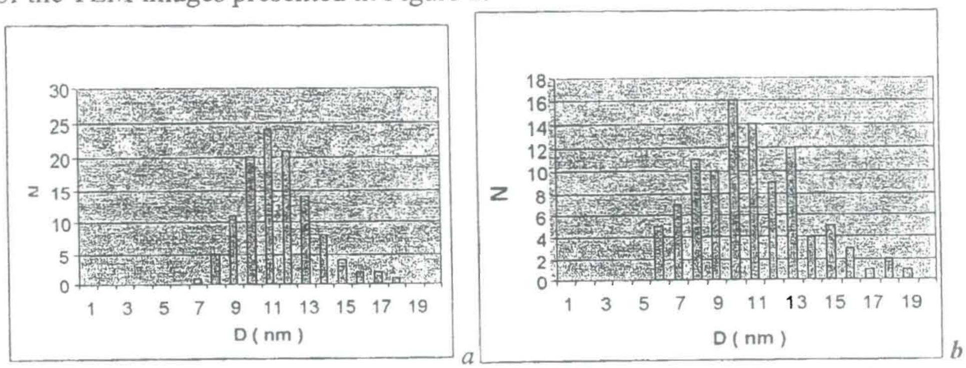


Figure 2. Size distributions from the statistical processing of the TEM images for the un-doped (a) and S-doped TiO_2 nanopowders (b)

In order to establish the photocatalytic properties of the prepared samples, having ecological purposes regarding their applications, they have been tested in a water depollution process. Table 2 presents the obtained results for the chlorobenzene photodegradation.

Table 2. The influence of the temperature of thermal treatment and of the presence of dopant for the sol-gel TiO_2-based photocatalysts on the chlorobenzene (CB) photodegradation and on the mineralization of organic chloride in the water depollution process

Photocatalyst	T (°C)	CB and Cl content in contaminated water				$\square_{CB}$ (%)	$\square_{Cl^-}$ (%)
		[CB]		[Cl⁻]			
		mg/l	$Mx10^3$	mg/l	$Mx10^3$		
TiO_2	300	0.34	0.0030	2.56	0.072	96.7	79.1
S-TiO_2	300	0.23	0.0020	2.27	0.064	97.8	70.3
S-TiO_2	400	0.18	0.0016	2.49	0.070	98.2	77.0
S-TiO_2	500	0.11	0.0010	2.66	0.075	99.0	82.4

As it can be seen from Table 2, the presence of sulfur as dopant in the TiO_2 powders led to the improvement of their photocatalytic activities, so to better cholorobenzene removal yields than for the un-doped samples. In the same time, one can see that the temperature has the same effect on the sol-gel prepared materials: the removal yields increase as the temperature rises.

Conclusions

Pure and S-doped TiO_2 sol-gel nanopowders have been prepared by controlled hydrolysis-condensation of tetraethylorthotitanate.

The influence of the dopant and of the thermal treatment on the nanopowders structure was established.

In order to prove the fact that the prepared materials could have ecological applications, they have been tested for the degradation of chlorobenzene as contaminant chloride organic compounds of aqueous solutions.

The presence of S as dopant in the TiO_2 powders, together with the effect of temperature, improved their photocatalytic activities and led to better chlorobenzene removal yields than for un-doped samples.

Acknowledgments

This work was supported by the GAR No. 56/2008.

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