TiO_2-Ag Porous Nanocomposites for Advanced Photocatalytic Processes

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ABSTRACT

Porous nanocomposites based on TiO_2 aerogels and silver colloidal particles were obtained by sol-gel method. The samples were heat-treated at 500 ^{0}C for 2h with the aim to obtain a preponderant TiO_2 anatase phase. The photocatalytic performances of the composites were monitored by using salicylic acid as test molecule. The promising results obtained in comparison with the commercial product Degussa P25 directed our attention towards the understanding of the morphological and structural particularities of the composite samples. The morphological data revealed the existence of high specific surface area for the as-prepared samples and of a relatively small one for the heat-treated samples. The influence of the anatase content was found to be insignificant, while that of TiO_2 nanoparticles size was found to be an important parameter besides the presence of silver particles and aggregates inside the TiO_2 porous network.

Keywords: Nanocomposites, TiO_2 aerogels, silver particles, photocatalysis.

1 INTRODUCTION

Titanium dioxide based aerogels are porous solid materials with high surface area, ultra-low density and high homogeneity that make them attractive for diverse applications in solar energy conversion, pigments, electronic devices, etc. [1-4]. Since TiO_2 has a high photosensitivity, non-toxic nature, large band-gap and stability the photo-assisted catalytic decomposition of organic pollutants in water and air, employing titanium dioxide as photocatalysts, is a very promising method. Its photocatalytic performances can be improved by retarding the electron-hole recombination process that is in direct competition with space-charge separation of the electron and the hole. A possibility is the loading of electron accepting species on the TiO_2 surface. It was shown that the contact of Ag nanoparticles with those of the TiO_2 grains influences in a favourable way the energetic and interfacial charge transfer processes and leads to an enhancement of the photocatalytic activity [5]. Thus, the synthesis and characterization of novel heterostructures based on TiO_2-Ag nanoparticles from the structural and morphological point of view with the purpose of improving the photocatalytic activity still remains an imperative challenge.

In the present work, porous nanocomposites based on TiO_2 aerogels and Ag colloidal particles were synthesized by sol-gel method and using the preparation chemical route of the silver colloidal particles. In order to enable the formation of the TiO_2 anatase phase, which exhibits improved photocatalytic performances, the nanoarchitectures were subjected to a thermal treatment and were comparatively characterized from the structural and morphological point of view. In this respect, several complementary investigation techniques like Brunauer–Emmet–Teller (BET), transmission electron microscopy (TEM), Raman spectroscopy and X-ray diffraction were used. The photocatalytic activity tests carried out on the obtained composites revealed exceptional results in comparison with the commercial product Degussa P25. In order to explain the nanocomposites photocatalytic performances the structural parameters have been correlated with the morphological ones.

The heat treatment parameters were settled as those established in a study previously carried out in our laboratory, in which a morphological and structural optimization process was performed with the aim of improving the photocatalytic efficiency of the TiO_2 aerogel [6].

2 EXPERIMENTAL

2.1 Samples preparation

TiO_2 gels prepared by sol-gel method using titanium isopropoxide (TIP), HNO_3, EtOH and H_2O (1/0.08/21/3.675 molar ratio) were allowed to age for a few weeks. The TiO_2 aerogel was obtained after a supercritical drying with CO_2 (T = 40 ^{0}C and p = 1400 psi) was applied [6, 7].

The silver colloidal suspension was prepared in the TiO_2 aerogel presence according to the following procedure [8]: 300 ml $2x10^{-3}$ M $NaBH_4$ kept at ice temperature was added to 100 ml $5x10^{-3}$ M $AgNO_3$ solution under vigorous stirring. The reaction mixture was brought to a boil with vigorous stirring on a magnetic stirring hot plate. The boiling was continued for 60 minutes. The aerogels were filtered from the solution and dried at 100 ^{0}C.

The obtained composites were subjected to a thermal treatment at 500 ^{0}C for 2 hours in order to obtain the desired TiO_2 anatase phase. The as-prepared and heat-treated composite samples will be further denoted as **TiO2@Ag** and **TiO2@Ag-ht**, respectively.

2.2 Samples measurements

The photocatalytic activity of the composites was established from the degradation rate of salicylic acid. The decrease in time of the salicylic acid concentration (C_0 = 5 x 10^{-4} M for all investigated samples) was monitored by using a Jasco V-530 UV-Vis spectrophotometer (λ = 297 nm). The samples immersed in salicylic acid solution were irradiated with UV light from a medium pressure Hg lamp HBO Osram (500 W). The working temperature was 20-22^{0}C and the solution pH 5.3. Before UV irradiation as well as before UV-Vis measurements, the cell with the sample was kept in dark for 15 minutes in order to achieve the equilibrium of the adsorption-desorption process.

The surface area of the samples was determined by the BET method, in a partial pressure range of $0.05 < P/P_0 < 0.3$ by using a home made equipment. The krypton adsorption was carried out at 77 K. Before each measurement the samples were heat cleaned at 333 K for 2 hours.

A Nd-YAG laser (λ = 1064 nm) was employed for the recording of Raman spectra of the prepared composites. The FT-Raman spectra were recorded using a Bruker Equinox 55 spectrometer with an integrated FRA 106 Raman module, a power of 30 mW incident on sample and a resolution of 4 cm^{-1}.

The phase content and the particle dimensions were determined using a DRON X-ray powder diffractometer linked to a data acquisition and processing facility; CuK_α radiation (λ = 1.540598 Å) and a graphite monochromator were used.

A JEOL 200 CX TEM operating at an accelerating voltage of 200 kV was employed to obtain bright (BF) and dark (DF) field images as well as the electron diffraction patterns of the nanoparticles system.

3 RESULTS AND DISSCUSSION

The disappearance of salicylic acid from the solution during the photocatalytic tests was monitored versus time (see Fig. 1); the photodecomposition reaction follows a pseudo-first order kinetics. The apparent rate constant was calculated by plotting $\ln(C_0/C)$ *vs* time. The slope of the plot after applying a linear fit represents the apparent rate constant [9, 10].

The determined apparent rate constants (k_{app}) for the photodegradation of the salicylic acid are presented in Table 1 together with other morphological and structural parameters. One can observe a considerable increase of the apparent rate constant of the **TiO2@Ag** composite in comparison with both Degussa and **TiO2@Ag-ht** samples. However, the improvement of the photocatalytic performances of the heat-treated composite is two times higher than those of the commercial product.

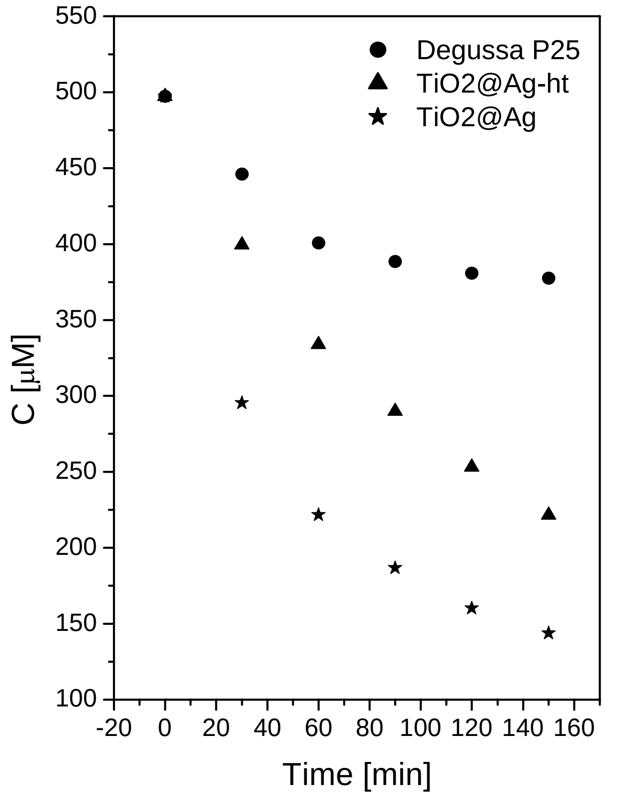

Figure 1: Photodegradation profiles of salicylic acid on nonannealed (**TiO2@Ag**) and annealed (**TiO2@Ag-ht**) nanocomposites as compared to the commercial powder (**Degussa P25**).

Sample	k_{app} x 10^3 [min^{-1}]	BET surface area [m^2/g]	Crystalline phase composition (%)	Average particles size [nm]
TiO2@ Ag	13.46	487	22.3 – A 77.7 – B	10 – A 9 – B 5 ÷ 15 – Ag
TiO2@ Ag-ht	6.62	70	88.5 – A 11.5 – B	13 – A 9 – B 10 ÷ 25 – Ag
Degussa P25	2.5	50	80 – A 20 – R	20 – A 30 – R

Table 1: The apparent rate constant, BET surface area, crystalline phases composition, and average particles size for the investigated samples. Abbreviations: A - anatase, B - brookite, R - rutile and Ag - silver

By looking at the data obtained from the BET analyses of the synthesized composites in comparison with the corresponding value reported [11] for the commercial product (Table 1) one can infer that the specific surface area decisively influence the photocatalytic performances, but only in the situation when it is extremely high, e.g. **TiO2@Ag** composite in comparison with Degussa P25.

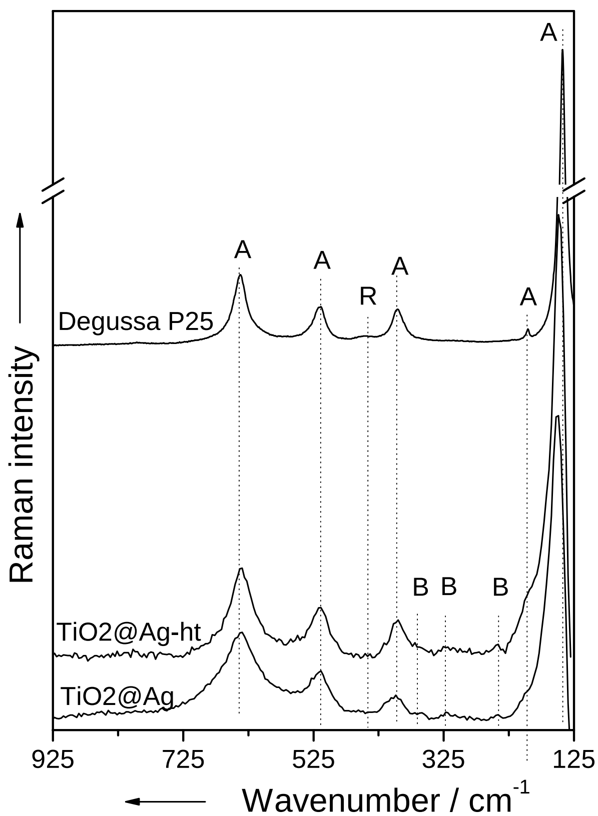

Figure 2: Raman spectra of the synthesized composite samples (**TiO2@Ag** and **TiO2@Ag-ht**) together with the spectrum of the commercial powder (**Degussa P25**). Abbreviations: A - anatase, B - brookite and R – rutile.

The Raman spectra of synthesized composites are displayed in Fig. 2 together with that of the commercial sample. Well-defined bands at 144, 197, 399, 517 and 639 cm^{-1} that correspond to the well-known five fundamental vibrational modes of TiO_2 anatase (denoted with A) with the symmetries of E_g, E_g, B_{1g}, A_{1g} and B_{1g}, respectively [12] can be seen in all recorded spectra. A close analysis of the spectra reveals the presence of other three very small Raman bands around 245, 320 and 365 cm^{-1}, especially in the spectra of the composite samples. Such spectral features were previously observed, when ultrafine TiO_2 powders with grain sizes around 10 nm were investigated, and were attributed to the existence of a little amount of brookite [12-14]. Therefore, the weak intense features from the Raman spectra of the composites can be associated with the presence of brookite phase and are denoted with B. The rutile phase presence can be seen as a band located at 440 cm^{-1}, only in the Raman spectrum of Degussa P25. Unfortunately, no quantitative analysis can be performed on the investigated samples by using Raman spectroscopy. Thus, in order to get further insights into the samples structure X-ray diffraction measurements were done (data not shown). X-ray diffraction patterns confirmed the presence of the anatase phase accompanied by a rather significant fraction of brookite phase. Rietveld refinement reveals an increase of anatase phase content (from 22.3 % to 88.5 %) as a cost of the brookite phase amount (from 77.7 % to 11.5 %) after the heat treatment was applied (see Table 1). As shown by particle dimension calculation (using Scherrer equation) the mean particle diameter of anatase phase is about 10 nm for the as-prepared composite and 13 nm for the heat-treated sample, while the mean size of the brookite nanoparticles are preserved even after annealing (~ 9 nm). By comparing both the crystalline phase composition and average particles size obtained for **TiO2@Ag-ht** sample (88.5 %-anatase, 11.5 %-brookite and 13 nm-anatase, 9 nm-brookite, respectively) with that of the commercial powder (80 %-anatase, 20 %-brookite and 20 nm-anatase, 30 nm-rutile, respectively) one can conclude that the size of the TiO_2 nanoparticles has an important influence on the photocatalytic performances, besides that represented by the presence of TiO_2-Ag nanoparticles contact.

TEM results show that, as compared to the microstructure of **TiO2@Ag**, the **TiO2@Ag-ht** sample presents higher sizes (see Table 1) and more non-homogeneous distribution of silver particles, which can also affect the photocatalytic behavior. Many metallic particles are amorphous in the both samples, but some big particles become monocrystalline.

4 CONCLUSIONS

Porous nanocomposites based on TiO_2 aerogels and silver particles were successfully synthesized by sol-gel method. A major amount of TiO_2 anatase was obtained by applying a heat treatment at 500 ^{0}C for 2h. The photocatalytic performances of the composites were tested by using salicylic acid as test molecule and it was found that both as-prepared and heat-treated composites show a considerable improvement of the photocatalytic activity in comparison with the commercial product Degussa P25. The positive photocatalytic results were completed with information derived from morphological and structural investigations. The morphological data revealed the existence of a huge pores surface area for the as-prepared samples and a relatively small one for the heat-treated samples. The anatase content was found to not decisively influence the photocatalytic performances, while the size of the TiO_2 nanoparticles was found to be an important parameter besides the presence of silver particles and aggregates inside the TiO_2 porous network. The size and distribution of silver particles can also modify the photocatalytic behavior of these nanocomposites.

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