Synthesis and characterization of Ag nanoparticles and Ag loaded TiO₂ photocatalysts

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Abstract

Ag nanoparticles and Ag-TiO₂ nanostructures were grown on (001) SiO₂ quartz substrates by pulsed laser deposition using a KrF* excimer laser source ($\lambda = 248$ nm, $\tau_{FWHM} \sim 10$ ns, $\nu = 10$ Hz) for the irradiation of Ag and TiO₂ targets. The obtained structures were characterized by atomic force microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and UV-visible absorption spectroscopy. Photocatalytic activity was evaluated under near-UV light illumination by decomposition of methylene blue. The relationship between the laser synthesis process parameters and nanoparticles' chemical composition, crystal structure, morphology, shape and size distribution on the substrate surface were investigated and correlated with their optical properties. The established experimental parameters were used for the synthesis of nanostructures consisting of anatase phase TiO₂ thin films covered by Ag nanoparticles for photocatalytic applications. The optimum experimental conditions were established which ensure significantly improved photoactivity in the presence of Ag nanoparticles as compared to the bare oxide surface.

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1. Introduction

Noble metal nanoparticles represent subject of extensive research due to their potential applications in many key technological areas.¹⁻³ In particular, silver nanoparticles owing to their characteristic strong surface plasmon resonance absorption in the visible range of the electromagnetic spectrum attracted huge interest in the last few years, for development of new type of biomedical,⁴⁻⁷ or nanoscale electronics and photonics⁸⁻¹² devices. Many of these applications require the nanoparticles to be embedded or supported on a solid substrate. Moreover, the extreme sensitivity of the optical properties to the nanoparticles' geometry as size, shape, interparticle distance stands at the basis of all applications mentioned above. Therefore, the investigation of the relationship between the synthesis process parameters and nanoparticles' geometry is necessary to achieve controlled growth.

A large number of methods for the preparation of noble metal nanoparticle colloidal solution have been developed, including chemical processing^{13,14} or laser ablation of noble metal plates immersed in organic solvents.¹⁵⁻¹⁸ Homogeneous noble metal nanoparticle arrays were created on solid substrates by nanosphere lithography,^{6,19} electron beam lithography,²⁰ and laser techniques.^{21,22} Oxide-noble metal nanocomposite thin films were synthesised of by sol-gel method,²³ RF sputtering,^{24,25} atom beam sputtering,²⁶ or pulsed laser deposition.²⁷⁻²⁹

The sequential character of techniques including pulsed laser radiation permits the precise control of the amount of material deposited on the substrate surface. The possibility to grow multistructures consisting of subsequent deposition of different materials by the simple change of the targets submitted to the laser radiation stands also among the advantages of these methods.

Noble metal nanoparticles exhibit strong UV-visible absorption due to their plasmon resonance, which is produced by the collective oscillations of surface electrons.¹⁻³ Their photosensitivity is potentially applicable to the development of new class of photocatalysts or photovoltaic fuel cells to meet the requirements of future environmental and energy technologies, driven by solar energy.

The first objective of our investigations is the study of the evolution of the shape and size of Ag particles grown by pulsed laser deposition on (001) SiO₂ quartz substrates, as a function of increasing laser pulse number, i.e. increasing Ag coverage. We found that changing only this experimental parameter the peak surface plasmon resonance absorption of the nanoparticles can be correlated with their geometrical characteristics and tuned through the UV-visible spectrum. As a second step the established experimental conditions were used to obtain nanostructures consisting of anatase phase TiO₂ thin films covered by Ag nanoparticles. TiO₂ photocatalysis has been extensively studied for environmental protection applications, decomposition of organic pollutants in water and air.³⁰⁻³² However, the large band gap of TiO₂ and quick recombination of the photogenerated charge carriers severely limits practical applications. Addition of metal nanoparticles acting as electron traps could represent a solution to overcome this inconvenience. About the presence of metal particles on the surface of oxide catalysts many controversial results are reported and photocatalytic activity has been found to depend on both the preparation method and the nature of the degraded pollutant.³³⁻³⁵ Development of synthesis methods ensuring the precise control on nanoparticles size and uniform distribution on the catalyst surface, as well as the understanding of the implied photoinduced mechanisms are essential for practical applications. In this study the optimal conditions were determined for the creation of Ag-TiO₂ nanocomposites with improved photocatalytic activity as compared to anatase phase TiO₂ through the established relationship between the Ag nanoparticles morphological characteristics and deposition parameters.

2. Experimental

Ag nanoparticles and nanostructures consisting of TiO₂ thin films covered by Ag nanoparticles have been grown inside a stainless steel reaction chamber. A KrF* excimer laser ($\lambda = 248$ nm, $\tau_{FWHM} \cong 25$ ns, $\nu = 10$ Hz) was used for the irradiation of Ag (99.9 % purity) and TiO₂ (99.8% purity) targets (Aldrich). The oxide targets were prepared from TiO₂ powders by pressing at 3 MPa. The obtained pellets were sintered at 1100 °C for 4 hours. The laser beam incidence angle onto the target was chosen of about 45°. The incident laser fluence on the target surface was set at about 2 J/cm². The

complete PLD workstation was purchased from SURFACE & SURFACE systems & technology GmbH & Co KG, Hückelhoven, DE.

For the growth of the Ag nanoparticles the number of the subsequent laser pulses was varied in the range (20-1000) for each deposition experiment. To avoid piercing, the targets were both rotated with a frequency of 3 Hz and translated in the X-Y surface plane during the multipulse laser irradiation. Before each experiment the reaction chamber was evacuated with a high vacuum installation down to a residual pressure of 10^{-6} Pa. The dynamic ambient gas pressure during the irradiations was kept at 10 Pa by feeding high-purity oxygen (99.999%) into the chamber with the aid of a calibrated gas inlet. An MKS 100 controller was used for the measurement of the gas pressures.

The (001) SiO₂ quartz substrates were placed parallel to the target at a separation distance of 5 cm, and heated during the nanoparticles synthesis process at a temperature value of 500 °C. A ramp of 20 °C/min was chosen for heating the substrates to reach the deposition temperature. Once the nanostructures growth was completed, the cooling down to room temperature was performed in the same reactive ambient gas atmosphere as used for the nanostructures growth, with a ramp of 20 °C/min.

A number of 4500 subsequent laser pulses were used for the growth of the oxide thin film. All experimental parameters, target rotation and translation, SiO₂ substrates temperature and heating regime, target to substrate separation distance, as well as ambient gas nature and pressure were identical to those used for the synthesis of the Ag nanoparticles.

Prior to introduction inside the reaction chamber, the targets and substrates were carefully cleaned in ultrasonic bath with ethanol. Additional target cleaning was achieved with the application of preliminary laser pulses for the elimination of the last contaminants and impurities present on the target surface. During the laser cleaning procedure a shutter was interposed at the mid-distance between the target and the substrate, parallel to them.

The surface morphology and growth mode of the deposited nanostructures were investigated by atomic force microscopy (AFM) in acoustic (dynamic) configuration with an Agilent 5100 apparatus and field emission scanning electron microscopy (FE-SEM) with a Fei Quanta 650 FEG apparatus. The crystalline structure of the deposited thin films was investigated by grazing incidence angle X-ray diffraction (GIXRD). The measurements were performed with a Bruker Advance D-8 system coupled with a Gadds detector ($\text{Cu K}\alpha$, $\lambda=1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) studies were performed with a SPECS EA10P hemispherical analyzer using a non-monochromatized X-ray source ($\text{Al K}\alpha$ line of 1486.6 eV and 300 W), placed perpendicular to the analyzer axis and calibrated using the 1s line of C. The measurements were made in ultra high vacuum (UHV) at residual pressure around 10^{-8} Pa. The optical absorbance measurements were performed with a ThermoSpectronic, Helios Gamma spectrophotometer in the wavelength range of 300-800 nm. The photocatalytic activity of the deposited Ag-TiO₂ nanostructures with 1 cm² surface area was studied by measuring the concentration changes in time of organic methylene blue dye in aqueous solution. A monochromatic 365 nm wavelength, 125 W Hg lamp was used for irradiations. During the photodegradation experiments the absorbance of the solution was measured at 665 nm wavelength which corresponds to the peak absorbance of methylene blue in the UV-visible spectral range, with a ThermoSpectronic, Helios Gamma apparatus. The samples were immersed in 30 ml solutions with 10^{-5} M initial dye concentration. The intensity of the light emitted by the lamp on the sample surface was 0.2 mW/cm². Fig. 1 shows a schematic diagram of the photoreactor consisting of the Hg lamp, water refrigerated vessel, and magnetic stirrer placed in an aluminium housing to prevent interfering of external light in the photodegradation experiments.

3. Results and discussions

Fig. 2a-d contains the AFM images of the Ag nanoparticles obtained with different number of laser pulses applied for the irradiation of the Ag targets. The formation of spherical shape nanoparticles can be clearly distinguished. Both nanoparticles diameter as well as height increase with the increase of the number of laser pulses, i.e. with the

amount of the deposited material. The several bigger, few tens of nm sized particles visible on the surface of the samples are possibly due to the coalescence processes. In order to have a reference we provided the AFM image of an uncovered SiO₂ quartz substrate (Fig. 2e). As can be observed, the surface is smooth, with a local height not exceeding 1.5 nm. The calculated minimum root-mean square (RMS) surface roughness of the SiO₂ substrate is around 0.13 nm.

Fig. 3 shows the profiles corresponding to the uncovered SiO₂ quartz substrate as well as the Ag nanoparticles deposited on the substrate surface with increasing number of laser pulses. As can be observed the height of the nanoparticles increases with the increase of the number of laser pulses. An average height of about 2.4 nm corresponding to the sample obtained with 20 laser pulses and around 10 nm at 200 pulses applied for the ablation of the Ag target were calculated on 500x500 nm² AFM scan areas. The histograms of nanoparticles diameters evaluated on the same AFM scan areas are presented in Fig. 4. The average diameter of the grains increases gradually from about 5 nm corresponding to the samples obtained with 20 pulses (Fig. 4a), to about 23 nm for the sample obtained with 200 pulses (Fig. 4d). Table I summarizes the estimated values concerning particles mean diameter, mean height, density as well as RMS surface roughness as a function of number of incident laser pulses. The density of the particles decreases while the RMS surface roughness value increases gradually due to the formation of larger size particles with the increase the number of laser pulses. At low Ag content the nanoparticles are well separated and have a spherical in-plane shape with a narrow size distribution following a Volmer-Weber growth regime on the substrate surface. However, as reported, their size distribution becomes broader as the Ag content increases due to coarsening and coalescence of the NCs.^{27,36}

The nanoparticles obtained with the low, up to 200 subsequent laser pulses applied for the ablation of the Ag targets are well separated and the average diameter and height could correctly be estimated. However, for higher number of pulses the gaps between the particles are on the order of the AFM tip diameter (~6 nm). Consequently, the AFM tip can not reach the substrate surface between the particles, and therefore the maximum height determined from the images could be underestimated. The real shape and in-plane dimensions of the particles can be observed on the FE-SEM micrographs as a

function of number of laser pulses (Fig. 5). The micrographs confirm a formation of well separated nanoparticles on the substrate surface, with a quite homogeneous size distribution, controlled by the number of subsequent laser pulses. We note that the very small particles obtained with 20 subsequent laser pulses could not be visualised by SEM. Conversely, at higher number of pulses, until 200 the values estimated for the mean diameters of the nanoparticles by AFM corroborates well with those obtained by FE-SEM if the influence of the AFM tip on the measurements is taken into account. In order to reduce the widening effect, much more pronounced in the measurements of the particles in-plane dimensions as compared to their height,³⁷ we used a geometric deconvolution³⁸ considering a spherical tip with a radius of 6 nm. The mean particle diameters after deconvolution are in agreement with the TEM results (Table I). With the further increase of the number of pulses the increase of the coupling between the nanoparticles leads to a gradual change of the reflected color from blue to metallic,³⁹ as occurred in our experiments at number of pulses exceeding 400.

We present in Fig. 6 the GIXRD diffractograms of the Ag nanoparticles obtained with increasing number of laser pulses. The diffractograms reproduce the patterns of polycrystalline cubic Ag phase, with lines at 38.1° corresponding to the most intense (111) and at 44.3° to the (200) lattice plane reflections, as referred to in the JCPDS Card No. 00-004-0783.⁴⁰ As can be seen, the lines intensity increases with the increase of the number of laser pulses due to increase of the Ag coverage.

The XPS spectrum of silver nanoparticles obtained with 100 subsequent laser pulses is presented in Fig. 7. The Ag 3d region consists of two main peaks belonging to the Ag 3d_{5/2} and Ag 3d_{3/2} doublet. The Ag 3d_{5/2} peak position at 368.57 eV is in good agreement with the values of 368.00, 368.26, or 368.40 eV reported in Refs. [41], [42], and [43], respectively for metallic silver. The low intensity satellite at 364.67 eV is typical for non-monochromatized Al K α excitation source.⁴⁴ We note that the shape of the XPS spectrum and peak positions is similar for all samples, independently on the number of subsequent laser pulses applied for the ablation of the Ag targets.

Under visual inspection the aspect of the samples indicated the formation of Ag clusters instead of a continuous metallic Ag layer. Their color was changing from nearly transparent at 20, to light yellow at 60, orange at 100, and finally dark blue at 200 laser

pulses, as a function of their morphology and density on the substrate surface. As known, color variation arises from changes in the size, shape and proximity to each other of nanoparticles.⁴⁵ The UV-visible optical absorption spectra of the Ag nanoparticles obtained with increasing number of laser pulses are presented in Fig. 8. The absorption maximum around 440 nm appearing in the spectrum of the nanoparticles obtained with 60 subsequent laser pulses (Fig. 8b) is associated with the surface plasmon resonance (SPR) absorption band, characteristic to metallic nanoparticles. The absorption is attributed to the conversion of incident photons of this wavelength to surface plasmons as a result of interaction with the free electron distribution on the silver nanoparticles surface.¹ Approximately at the same wavelength an absorption band appears also in the case of the nanoparticles obtained with 20 laser pulses (Fig. 8a). Its very low intensity could be attributed to the reduced number of Ag particulates on the substrate surface. The absorption maximum shifts towards higher wavelengths with the increase of the number of laser pulses. The shift can be associated with the increase of the nanoparticles size, i. e. in-plane diameter, with the increase of the Ag coverage.^{46,47} Moreover, an additional absorption shoulder appears at around 550 nm in the case of the sample obtained with 100 laser pulses (Fig. 8c). The absorption spectrum of the structure deposited at 200 pulses (Fig. 8d) is formed by a broad band in the visible spectral region. The additional absorption shoulder at higher wavelengths and the broadening of the main absorption band could be due to the coalescence of the nanoparticles with the increase of the Ag coverage.^{39,48}

As a second step in our investigations we used the established experimental conditions for the synthesis of Ag nanoparticles to obtain nanostructures consisting of TiO₂ thin films covered by Ag nanoparticles, for photocatalytic applications. The diffractogram of a reference titanium oxide thin film in a 2 θ range which contains also the main reflections of the metallic Ag is composed by lines at 37.8° and 38.6° corresponding to the (004) and (112) lattice plane reflections of the tetragonal anatase TiO₂ phase, as referred to in the JC-PDS Card No. 21-1272⁴⁰ (Fig. 9a). The insert shows a scan on a wider 2 θ range, composed by lines at 25.4°, 37.8°, 38.6°, and 55.1° attributed to the most intense (101), (004), (112), as well as (211) lattice plane reflections of the polycrystalline tetragonal anatase TiO₂ phase, with [112] preferred orientation. Stabilization of the metastable anatase crystal structure is essential as it is known that possesses higher photoactivity as compared to the thermodynamically stable rutile

phase TiO₂.⁴⁹ The line at 50.8° corresponds to the (001) SiO₂ substrate. An average size of TiO₂ nanocrystallites of about 25 nm was determined by the Scherrer equation:⁵⁰ $D_{hkl} = 0.9\lambda/\beta_{hkl}\cos\theta_{hkl}$, where λ is the X-ray wavelength, θ_{hkl} is the Bragg diffraction angle, and β_{hkl} is the full width at half-maximum (FWHM) in radian of the diffraction line corresponding to the most intense (112) lattice plane reflection.

In the diffractograms of the oxide thin films covered by Ag nanoparticles the shoulder appearing at 38.1° assigned to the most intense (111) lattice plane reflection was the first indication of the presence of the metallic Ag, for the sample obtained with 100 laser pulses incident on the Ag target (Fig. 9c). With the increase of the number of pulses the lines at 38.1° and 44.3° corresponding to the (111) and (200) lattice plane reflections, as referred to in the JC-PDS Card No. 00-021-1272,⁴⁰ become clearly visible (Fig. 9d-f).

The photocatalytic activity of the TiO₂-Ag nanostructures was examined through the decrease of methylene blue dye concentration, C , of the solution in time. The obtained results are presented in Fig. 10. The reference shown in Fig. 10 represents the methylene blue dye self-degradation process in time. C_0 stands for the initial dye concentration. No significant difference was observed in the photocatalytic activity of the samples containing low Ag loading, obtained with 60 (Fig. 10b) and 100 (Fig. 10c) subsequent laser pulses incident on the Ag targets, as compared to the bare TiO₂ thin film (Fig. 10a). On the contrary, at number of pulses exceeding 200 (Fig. 10d,e) faster photodegradation rate of the organic dye was achieved than in the case of the pure TiO₂ catalyst (Fig. 10a). We would like to note that the bare TiO₂ thin film had a thickness of about 400 nm, as determined by cross-sectional scanning electron microscopy investigations. The corresponding catalytic amount is around 5 mg/l. Moreover, corroborating the AFM and FE-SEM data the Ag amount was calculated and found to be between 0.6 and 1.8 $\mu\text{g}/\text{cm}^2$ for increasing number of pulses from 60 to 200. These values corroborates well with those estimated using the growth rates measured by X-ray reflectometry 0.09 as well as 0.008 nm/pulse for TiO₂ and Ag, respectively.

As known, the photocatalytic reaction takes place on the surface of the catalysts and recombination of photogenerated electrons and holes is very fast. The enhanced

photoreactivity can be explained by the transfer of photogenerated electrons from TiO_2 to the metal particles, inhibiting electron-hole recombination and thus raising the oxidation efficiency of the positive holes generated in the valence band of TiO_2 .^{51,52} Metal nanoparticles can act as electron traps due to the formation of a Schottky barrier at the metal-semiconductor contact.⁵² As a consequence the holes, having strong oxidative power, can decompose organic substances more efficiently. Moreover, the tail of the localized surface plasmon resonance in the near-UV region can have an effect on the photocatalytic activity.⁵³⁻⁵⁵ Surface plasmon resonance absorption is associated with a significant enhancement of the electric near-field in the vicinity of the Ag NPs. It was reported that the enhanced near-field could boost the excitation of electron-hole pairs in TiO_2 and therefore increase the efficiency of the photocatalysis.^{54,55}

Our results demonstrate that there is an optimal loading amount of Ag nanoparticles on TiO_2 . Indeed, at number of pulses higher than 400 the photocatalytic activity of the samples decreased (Fig. 10f). This feature could be attributed to the gradual reduction of the active TiO_2 surface area directly irradiated by the UV light with the increase of the Ag coverage, causing lower photocatalytic efficiency.

Conclusions

Ag nanoparticles and Ag- TiO_2 nanostructures were synthesized by pulsed laser deposition technique. The established dependence between the Ag nanoparticles morphology and SPR absorption permits the continuous tuning of their optical properties in the UV-visible spectral range. The obtained results demonstrate that laser techniques allows for the creation of Ag- TiO_2 nanocomposites with improved photocatalytic activity as compared to bare TiO_2 . The optimum loading amount of Ag nanoparticles was determined. It was found that there exists a maximum threshold for the Ag loading value after which the photocatalytic activity of the Ag- TiO_2 nanocomposites decreases. The sequential nature of the technique including pulsed laser radiation permits the precise control of the size, distribution and amount of noble metal nanoparticles deposited on the oxide photocatalysts surface. It was proposed that two distinct mechanisms can contribute to the enhanced photoreactivity under near-UV irradiation. Ag NPs retard electron-hole recombination by photogenerated electron

transfer from TiO_2 . Moreover, localised surface plasmon resonance absorption of Ag NPs can have positive effect on the photocatalytic activity.

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Table I. Particles mean diameter, mean height, density, and surface RMS roughness calculated from 500x500 nm² AFM scan areas as well as particles mean diameter calculated from FE-SEM micrographs as a function of number of incident laser pulses.

Number of pulses	Mean diameter AFM [nm]	Mean height [nm]	Density [μm^{-2}]	RMS roughness [nm]	Mean diameter FE-SEM [nm]
20	5	2.4	5700	0.6	-
60	16	5.0	3600	1.2	10
100	19	6.0	2900	1.3	14
200	23	10.0	1900	2.2	18

Figure captions

Fig. 1. Experimental set-up used for the photodegradation of organic methylene blue dye.

Fig. 2. AFM images of Ag nanoparticles obtained with (a) 20, (b) 60, (c) 100, and (d) 200 subsequent laser pulses as well as (e) (001) SiO₂ quartz plate used as substrate for the growth of the nanoparticles.

Fig. 3. Surface profiles of (a) (001) SiO₂ quartz plate and Ag nanoparticles obtained with (a) 20, (b) 60, (c) 100, as well as (d) 200 subsequent laser pulses

Fig. 4. Histograms of Ag nanoparticles diameters counted on 25 μm^2 surface areas of samples obtained with (a) 20, (b) 60, (c) 100, and (d) 200 subsequent laser pulses.

Fig. 5. FE-SEM images of Ag nanoparticles obtained with (a) 60, (b) 100, and (c) 200 subsequent laser pulses.

Fig. 6. GIXRD of Ag nanoparticles obtained with (a) 20, (b) 60, (c) 100, and (d) 200 subsequent laser pulses.

Fig. 7. XPS spectrum of Ag nanoparticles obtained with 100 subsequent laser pulses.

Fig. 8. UV-visible optical absorbance spectra of Ag nanoparticles obtained with (a) 20, (b) 60, (c) 100, and (d) 200 subsequent laser pulses.

Fig. 9. XRD of (a) TiO₂ thin film as well as nanostructures consisting of TiO₂ thin films and Ag nanoparticles obtained with (b) 60, (c) 100, (d) 200, (e) 400, and (f) 1000 subsequent laser pulses. The insert shows wider θ -2 θ scan of the TiO₂ thin film.

Fig. 10. Comparison of methylene blue dye degradation process on (a) TiO_2 thin film as well as nanostructures consisting of TiO_2 thin films and Ag nanoparticles obtained with (b) 60, (c) 100, (d) 200, (e) 400, and (f) 1000 subsequent laser pulses, as a function of exposure time. The reference corresponds to the methylene blue dye self-degradation process in time.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.