Titanium oxide - reduced graphene oxide - silver composite layers synthesized by laser technique: Wetting and electrical properties

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Abstract

Titanium dioxide (TiO₂), TiO₂ / silver (Ag), and ternary TiO₂ / graphene oxide (GO) / Ag nanocomposite coatings were synthesized by matrix assisted pulsed laser evaporation, a laser-based environmental friendly thin film deposition technique. TiO₂ and Ag NPs, as well as GO platelets were used as base materials for the preparation of the composite target dispersions. An UV KrF* excimer laser ($\lambda=248$ nm, $\tau_{FWHM}\sim 25$ ns, $\nu=10$ Hz) was used for the irradiation of the composite targets. The experiments were performed in controlled oxygen atmosphere. The functional, wetting and electrical properties of the layers were investigated as a function of target composition as well as ambient oxygen pressure value. The coatings exhibited hydrophobic character. The lowest electrical resistance value was measured for the ternary TiO₂/GO/Ag coatings with the high Ag NPs loading, deposited at low ambient oxygen pressure.

Keywords: titanium oxide / graphene oxide / silver nanocomposite layers; multifunctional properties; hydrophobic; conductive; laser processing and immobilization;

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1. Introduccion

Titanium oxide (TiO_2) is an extensively investigated semiconductor material owing to its outstanding properties such as nontoxicity, earth abundance, low cost, chemical and biological inertness, thermal stability [1, 2]. Due to its high photoactivity, TiO_2 shows great potential for environmental applications such as solar energy conversion and storage and photocatalytic dissociation of organic compounds for waste-water treatment, disinfection, as well as air purification [3-5]. Moreover, TiO_2 surfaces are hydrophobic. On hydrophobic surfaces the water droplets flow freely and contaminants are carried along, being washed away. Coating of materials surfaces with highly hydrophobic water-repellent layers confer to them valuable self-cleaning properties, required for many application fields as for example windows, microfluidics, photovoltaic, biomedical devices, anti-bacterial surfaces and textiles.

Self-cleaning property was found to be a collective effect between the wetting characteristics of the materials and photocatalytic reactions. Indeed, organic contaminants can be removed from TiO_2 surfaces by UV light induced photocatalytic reactions [6]. When TiO_2 is irradiated with a photon energy higher or equal to its bandgap, electron-hole pairs are generated. However, the photocatalytic activity of TiO_2 is constrained by the fast recombination of the generated charge carriers [7]. Noble metal nanoparticles (NPs), Ag, Au, Pt, or Pd can act as scavengers for the photo-induced electrons improving this way the photocatalytic activity of TiO_2 [7, 8]. Addition of conducting carbon nanomaterials as carbon nanotubes [9] or reduced GO (rGO) [10] is another approach to reduce recombination rate of charge carriers and to promote electron transport. According to our recent investigations [11] the photocatalytic activity of the $\text{TiO}_2/\text{rGO}/\text{Au}$ ternary nanocomposite materials is around 170% higher than that of pure TiO_2 .

Carbon nanomaterials add also additional functionalities for the hydrophilic surface. It is known, that surface electroconductivity is also important in environmental self-cleaning applications [12 - 14]. Previous investigations demonstrate that highly conductive surfaces avoid adsorption of organic contaminants by antistatic effect [13, 14]. Moreover, multifunctional electrically conductive and highly hydrophobic surfaces have many attractive applications such as electrical circuits protecting them from short-circuiting and corrosion in water, electromagnetic shielding, or static charge dissipation, micro-fluidics, electrodes for fuel cells, solar panels, non-fouling surfaces. [15].

In the present work, we report the deposition by matrix assisted pulsed laser evaporation (MAPLE) technique of TiO₂/GO/Ag ternary nanocomposite thin films. The main advantage of MAPLE is that complex multicomponent materials can be synthesised and deposited on practically any type of substrate materials, including flexible organics, in a single technological step. Laser deposition methods have also other advantages over conventional techniques. The chemical composition and quantity of the transferred material can be controlled through the irradiation process parameters as laser pulse energy, number of subsequent laser pulses applied for the irradiation of the targets, as well as nature and pressure of the ambient gas in the irradiation chamber [16, 17]. Moreover, laser deposition methods are characterized by reduced processing time, high reproducibility, and very low risk of cross-contamination due to the use of light as energy source.

In this work we establish a correlation between processing parameters, surface morphology and chemical composition, as well as functional wetting and electrical properties of TiO₂/GO/Ag nanocomposite thin films. Our results demonstrate that both wetting and electrical properties of the TiO₂/GO nanocomposite thin films can be simultaneously engineered through the addition of GO and Ag nanoparticles (NPs). Besides environmental applications conductive layers with improved wetting and antimicrobial properties are of interest for many practical applications as biosensing [18], smart fabric sensors and electronic textile technologies [19, 20], as well as flexible and transparent optoelectronic devices [21].

2. Experimental

The laser transfer and immobilization experiments were performed inside a stainless steel deposition chamber. A pulsed UV KrF* ($\lambda = 248$ nm, $\tau_{FWHM} \leq 25$ ns, $\nu = 10$ Hz) COMPexPro 205 Lambda Physics excimer laser source was used for the irradiation of the composite MAPLE targets. Anatase phase TiO₂ NPs with an average diameter below 25 nm (Sigma-Aldrich, 99.7%), GO platelets with about 1 μm^2 surface area (NanoInnova Technologies, Spain) and Ag NPs with an average diameter below 100 nm (Sigma-Aldrich, 99.5%) were used as base materials for the preparation of the MAPLE targets. Dispersions in distilled water of 1 wt.% TiO₂ NPs, 1 wt.% TiO₂ NPs and Ag NPs with concentrations in the range (1-5) wt.% as well as 1 wt% TiO₂ NPs, 5 wt% GO platelets, and Ag NPs with concentrations in the range (1-5) wt.% were prepared. After

sonication the dispersions were introduced into a special double wall target holder and flash-frozen by circulating liquid nitrogen inside the holder walls. The targets were kept frozen during the irradiation experiments. The laser fluence at the target surface was set at 400 mJ/cm^2 . A number of 10^4 subsequent laser pulses were applied for the deposition of each sample. BK7 glass plates with $1 \times 1 \text{ cm}^2$ surface area were used as substrates, placed parallel to the target at a separation distance of 4 cm. During the experiments the substrates were kept at a constant temperature of 50°C with the aid of a PID Excel temperature controller. Before each experiment the irradiation chamber was evacuated down to a residual pressure of 10^{-3} Pa . The experiments were performed in controlled O_2 atmosphere at 2 and 20 Pa pressure values.

The surface morphology of the deposited films was investigated by scanning electron microscopy (FE-SEM) with a Hitachi S-3400 instrument, operated at 15 kV acceleration voltage and atomic force microscopy (AFM) using a NT-MDT model BL222RNTE equipment with images taken in semicontact mode with Si-tips (NSG10, force constant 0.15 N/m, tip radius 10 nm). The chemical bonds between the elements of the deposited nanocomposite thin films were investigated by X-ray photoelectron spectroscopy (XPS). The XPS studies were performed with the aid of a SPECS XPS spectrometer (SPECS Surface Nano Analysis GmbH, Berlin, Germany), based on Phoibos 150 electron energy analyzer operated in constant energy mode. A non-monochromatic X-ray source (MgK α line of 1253.6 eV) was used for excitation and was run with 12.5 kV anode bias and 20 mA emission current (250W). The measurements were made in an ultrahigh vacuum at a residual pressure of around 10^{-7} Pa . A SPECS FG20 flood gun was used for the charge neutralization. High-resolution spectra were acquired over smaller ranges of 20 eV using 0.05 eV step at 10 eV pass energy. The binding energy scale of the spectra has been corrected using the C1s line. A binding energy of 284.8 eV corresponding to the C=C bonds has been assumed to this purpose. The obtained data were analyzed using SDP32 XPS software (version 7.0; XPS International, Mountain View, CA). Contact angle investigations were performed by the sessile drop method using an OCA-20 contact angle system from DataPhysics Instruments. To this aim a 3 μL volume liquid droplet was placed with 0.5 $\mu\text{L/s}$ steps on the surface of the synthesized thin films. Contact angles were measured during 5 minutes and data were recorded with 1 second step. The electrical properties of the nanocomposite thin films were studied by sheet resistance measurements over $1 \times 1 \text{ mm}^2$ film areas, with a micro-probe station and a Keithley 2612B source-meter system. The micro-probe station was equipped with tips with a diameter of 10 μm .

3. Results and discussion

The FE-SEM micrographs of the TiO_2/Ag as well as $\text{TiO}_2/\text{Ag}/\text{GO}$ composite thin films deposited in 20 Pa O_2 pressure are presented in Fig. 1(a,b). The TiO_2 and Ag NPs as well as GO platelets concentrations in the MAPLE targets were 1, 5, and 5 wt.%, respectively. The surface of the TiO_2/Ag film (Fig. 1a) is composed by large particles with diameters in the several hundreds of nm up to 1 μm as well as smaller NPs with diameters below 100 nm. As it can be observed, significant part of the particles are larger as compared to the starting TiO_2 and Ag NPs used for the preparation of the MAPLE targets, with diameters of around 20 and 100 nm, respectively. The spherical shape of the particles suggests that they are formed in liquid phase through the coalescence of the initial NPs, molten under the action of the laser pulses. On the surface of the film $\text{TiO}_2/\text{Ag}/\text{GO}$ composite film large, micron sized aggregates composed of GO irregular shape platelets, spherical particles, as well as NPs with diameters below 100 nm can be distinguished (Fig. 1b).

Fig. 1. (a) FE-SEM micrograph of TiO_2/Ag nanocomposite thin film obtained by the irradiation of a MAPLE target containing 1 wt.% TiO_2 nanoparticles and 5 wt.% Ag, (b) FE-SEM, (c) AFM images, and (d) local surface height histogram of $\text{TiO}_2/\text{GO}/\text{Ag}$ nanocomposite thin film obtained by the irradiation of a MAPLE target containing 1 wt.% TiO_2 nanoparticles, 5 wt% GO platelets, and 5 wt.% Ag deposited in 20 Pa O_2 pressure.

AFM investigations were performed to further evaluate the surface morphology of the composite films. As Fig. 1c shows, the large irregular shape aggregates and spherical particles are covered by

smaller, tens of nm, up to 100 nm sized NPs, the average local surface height being of around 50 nm (Fig. 1d). The surface morphology of the films was found to not be significantly influenced by the ambient gas pressure value.

Fig. 2 shows the Ti2p (a) and Ag3d (b) XPS doublets of the TiO₂/GO/Ag composite thin film obtained at 2 Pa O₂ pressure. The Ti2p_{3/2} and Ti2p_{1/2} lines are located at 459.4 and 465.1 eV, corresponding to the binding energy values reported in the literature for stoichiometric TiO₂ [22, 23]. The symmetrical shape of the Ti2p_{3/2} and Ti2p_{1/2} lines and their positions indicate that no TiO_{2-x} suboxides, titanium oxides with Ti species of lower oxidation state, or Ti-C bonds were formed during the laser irradiation and transfer processes. As known, the binding energy values of both Ti-O bonds corresponding to TiO_{2-x} suboxides and Ti-C bonds are situated at lower values as compared to Ti-O bond of stoichiometric TiO₂ [22-24]. The Ag3d region is composed by two main peaks, belonging to the Ag3d_{5/2} and Ag3d_{3/2} doublet. The Ag3d_{5/2} and Ag3d_{3/2} peak positions at 368.8 and 374.8 eV are in good agreement with the values reported in literature for metallic silver [25]. We note that the shape and binding energy values of the Ti2p and Ag3d peaks are very similar for all TiO₂/Ag and TiO₂/GO/Ag nanocomposite films, independently on the ambient oxygen pressure value or the Ag concentration in the composite MAPLE targets.

Fig. 2. Ti2p and Ag3d XPS spectra of TiO₂/GO/Ag nanocomposite thin film obtained by the irradiation of a MAPLE target containing 1 wt.% TiO₂ nanoparticles, 5 wt.% GO flakes and 1 wt.% Ag in 2 Pa O₂ pressure.

In Fig. 3 we present the C1s spectrum of a reference GO drop-cast sample (Fig. 3a) and of the TiO₂/GO/Ag nanocomposite films deposited in 20 (Fig. 3b) and 2 Pa (Fig. 3c) O₂ pressure.

Fig. 3. C1s XPS spectra of drop cast GO reference sample (a) and TiO₂/GO/Ag nanocomposite thin film obtained by the irradiation of a MAPLE target containing 1 wt.% TiO₂ nanoparticles, 5 wt.% GO flakes, and 1 wt.% Ag in (b) 20 and (c) 2 Pa O₂ pressure.

The reference GO drop-cast sample was obtained from a dispersion in distilled water of 5 wt.% GO platelets identical to those used for the preparation of the MAPLE targets. Each C1s spectra was deconvoluted in four lines corresponding to (I) sp^2 C=C bonds centred at 284.8 eV binding energy, and oxygen containing functional groups (II-IV) situated at higher binding energy values [26-28]. The (I) sp^2 C=C bonds correspond to the graphite-like sp^2 C of the conjugated honeycomb lattice. The peaks centred at higher binding energy values are attributed to C-O single bonds (II) of C-O-C epoxy and C-OH hydroxyl groups, as well as C=O double bonds of C=O carbonyl (III) and O-C=O carboxyl groups (IV) [26-28]. The binding energy values of the deconvolution lines of the C1s XPS spectra corresponding to the TiO₂/GO/Au nanocomposite thin films deposited in 20 (Fig. 3b) and 2 Pa O₂ atmosphere (Fig. 3c) are very similar to those of the C1s spectrum of the reference GO sample. However, the intensity of the peaks assigned to C-O single and C=O double bonds of the oxygen functional groups is gradually reduced as compared to the GO sample with the decrease of the ambient oxygen pressure value. This feature indicates a diminishment of the number of the oxygen functional groups under UV laser irradiation, leading to the formation of reduced GO (rGO) structures. The reduction of GO is more effective in low oxygen pressure. The larger number of C-O and C=O bonds in high oxygen pressure can be attributed to possible re-oxidation processes during the transit of the laser ablated material from the target towards the substrate surface.

The initial water contact angles as well as their evolution under UV illumination of pure TiO₂ thin film as well as TiO₂/Ag and TiO₂/Ag/GO nanocomposite films are presented in Fig. 4. The pure TiO₂ surface is highly hydrophobic (Fig. 4a). As can be observed, the contact angle of the TiO₂ thin film decreases progressively under UV illumination. This feature is characteristic for TiO₂ surfaces and was related to the reduction of Ti⁴⁺ to Ti³⁺ under UV light irradiation and creation of oxygen vacancies [5, 29, 30]. Previous results indicate that oxygen vacancy states affect surface adsorption and reactivity of O₂ and H₂O on the TiO₂ surface [5, 29, 30]. It was demonstrated that chemical dissociation of water molecules is energetically favoured on defective TiO₂ surfaces, whereas H₂O molecules are only physically adsorbed on stoichiometric TiO₂ [5]. A direct correlation was found to exist between oxygen vacancies before water exposure and surface hydroxyl groups after exposure [30]. Through the dissociative adsorption of water molecules hydroxyl groups are created, resulting in a hydroxylated surface which enhances polar properties and hydrophilicity [5, 31]. Photoinduced wettability conversion phenomenon of TiO₂ surfaces can be associated also to their photocatalytic activity [13, 32]. It was found that besides the described structural changes, the removal of organic contamination present on air-exposed of TiO₂ surfaces, contributes to the

improvement of surface wettability and hydrophobic to hydrophilic conversion under UV light irradiation [13, 32].

Fig. 4. Water contact angles evolution under UV light irradiation as a function of time for (a) TiO_2 thin film obtained using a MAPLE target containing 1 wt% TiO_2 NPs and nanocomposite thin film obtained using a MAPLE target containing (b) 1 wt% TiO_2 NPs and 5 wt.% GO platelets, (c) 1 wt% TiO_2 NPs, 5 wt.% GO platelets, and 1 wt% Ag, (d) 1 wt% TiO_2 NPs, 5 wt.% GO platelets, and 2 wt% Ag, as well as (e) 1 wt% TiO_2 NPs, 5 wt.% GO platelets, and 5 wt% Ag deposited at 2 Pa O_2 pressure.

The water contact angle of the TiO_2/GO nanocomposite thin films (Fig. 4b) is higher than that of pure TiO_2 (Fig. 4a). The enhanced hydrophobic character can be attributed to the reduction of oxygen containing functional groups of the GO platelets during laser processing and immobilization, as was evidenced by XPS investigations (Fig. 3). The efficiency of the reduction process is directly related to the O_2 pressure inside the irradiation chamber (Fig. 3b, c). Through the diminishment of the O_2 pressure the oxygen containing functional groups are gradually reduced, leading to the formation of hydrophobic graphene-like materials. Indeed, TiO_2/GO layers deposited at high O_2 pressure but under otherwise identical experimental conditions are characterised by much lower, around 50° water contact angle [33]. Similarly to the pure TiO_2 film, the water contact angle of the TiO_2/GO nanocomposite layer decreases upon UV light irradiation. According to recent investigations, reversible wettability transition in graphene from hydrophobic to hydrophilic can be obtained under alternative UV light irradiation and air storage [34, 35], similar as for TiO_2 surfaces. Density functional theory calculations showed that graphene become highly hydrophilic after exposure to UV irradiation due to the dissociative adsorption of ambient H_2O molecules [34].

Conversely, the addition of Ag NPs to the TiO₂/GO composites led to the gradual diminishment of the water contact angle with the increase of the Ag concentration in the targets (Fig. 4c-e). However, the surfaces still preserve their hydrophobic character. Loading of noble metal NPs was found to diminish the water contact angle of metal oxide semiconductor surfaces [36, 37]. The adsorption energy of H₂O molecules on noble metal NPs loaded TiO₂ was reported to be lower than the adsorption energy of H₂O on bare TiO₂ [37].

The electron transfer and reaction mechanisms taking place on the surface of the TiO₂/GO/Ag nanocomposite thin films under UV light illumination are presented schematically in Fig. 5.

Fig. 5. Schematic representation of electron transfer and reaction mechanisms taking place on the surface of the TiO₂/GO/Ag nanocomposite thin films.

Ag NPs in the TiO₂/GO/Ag system prevent electrons-holes pairs recombination acting as electron scavenger and contribute to the generation of O₂⁻ and Ti³⁺:

The photogenerated electrons can be transferred and transported also across the rGO platelets:

The positive holes can oxidize water molecules adsorbed at the films' surface to produce hydroxyl radicals through the dissociative adsorption of H₂O molecules:

Hydroxyl radicals are created also through the reaction of O₂⁻ with H⁺ to form H₂O₂. H₂O₂ is a source of hydroxyl radicals making the surface more hydrophilic through the reaction:

The electrical resistivity of the TiO₂/Ag and TiO₂/GO/Ag nanocomposite thin films are presented in Fig. 6. The TiO₂/Ag thin film obtained from MAPLE targets containing only 1 wt.% Ag NPs is very high, around 0.4 MΩ cm, but around 10³ times lower than the resistivity measured for pure TiO₂ thin films [38]. The resistivity value of the TiO₂/Ag nanocomposites decreases with the increase of the Ag NPs concentration in the targets, until around 250 Ω cm for the highest, 5 wt% Ag NPs concentration. On the other hand, significant decrease of the electrical resistivity takes place upon the addition of GO platelets, until around 9, 7, and 3 Ω cm for Ag NPs concentrations of 1, 2, and 5 wt.% in case of the irradiations performed in 20 Pa O₂ pressure. Further diminishment of the electrical resistivity of the TiO₂/GO/Ag nanocomposite thin films was observed with the decrease of the O₂ pressure to 2 Pa. The low resistivity values can be assigned to decrease in the oxygen content of the GO platelets, and formation of graphene-like structures during laser processing and immobilization, as observed also by XPS investigation (Fig. 3b, c). Our lowest resistivity values are similar to that measured for TiO₂/GO composites reduced by post-deposition treatments of TiO₂/GO films using UV light irradiation [39], and GO films reduced chemically through hydrazine hydrate vapors [40, 41] or by thermal annealing [42]. Our laser based technique is a single-step synthesis and deposition method, without the necessity of post-deposition heat or chemical treatments. The growth process is performed at room temperature and it does not imply the use of harmful chemical substances.

Fig. 6. Electrical resistivity of TiO₂/Ag and TiO₂ /GO/Ag nanocomposite thin films obtained at 20 and 2 Pa ambient O₂ pressure.

Hydrophobic and highly conductive surface coatings are especially valuable for many engineering applications. Through MAPLE technique complex multicomponent materials can be synthesized and deposited on practically any type of substrate material. The functional, wetting and electrical properties of the coatings can be controlled and tailored through the concentration of the base materials in the target solutions and ambient gas pressure.

Conclusions

Highly conductive and hydrophobic TiO₂/GO/Ag nanocomposite coatings were prepared by simple one-step environmentally friendly laser technique. TiO₂ and Ag NPs, as well as GO platelets were used as base materials for the preparation of the MAPLE targets. Our XPS investigations show that GO undergoes partial reduction under the action of the laser pulses. The hydrophobic character of the coatings and their low resistivity values can be assigned to decrease in the oxygen content of the GO platelets during the laser immobilization process. The addition of Ag NPs contributes to the improvement of the coatings electrical conductivity. The synergistic effect, bridging together two

valuable functional properties may be useful in many applications as protection of electrical devices working in high humidity circumstances from short-circuits and corrosion, solar panels, implantable sensor systems for medical applications, fluid transportation, electrodes for fuel cells, nonfouling surfaces.

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