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MASTER'S THESIS

"3D Laser Lithography with Applications in Photocatalysis"

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<u>Ευχαριστίες</u>

Η πραγματοποίηση της μεταπτυχιακής μου εργασίας έγινε εφικτή με την καθοδήγηση και την βοήθεια κάποιων ανθρώπων, χωρίς την συμπαράσταση των οποίων δεν θα ολοκληρωνόταν αυτή η προσπάθεια και θα ήθελα να τους ευχαριστήσω. Την Δρ. Μαρία Φαρσάρη, ερευνητική διευθύντρια και αργηγός του εργαστηρίου «Μη-Γραμμικής Λιθογραφίας» στο Ινστιτούτο Ηλεκτρονικής Δομής και Laser (ΙΗΔΛ) που είναι τμήμα του Ιδρύματος Τεχνολογίας και Έρευνας (ΙΤΕ). Η Δρ. Μαρία Φαρσάρη μου έδωσε την ευκαρεία να αποκτήσω γνώσεις και να εκπαιδευτώ στο εργαστήριο της από τις προπτυγιακές μου σπουδές. Θέλω να ευγαριστήσω την Δρ. Ελμίνα Καμπουράκη, μεταδιδακτορική ερευνήτρια στο εργαστήριο «Μη-Γραμμικής Λιθογραφίας», που ήταν πάντα δίπλα μου και με συμβούλευε στα περισσότερα βήματα της εργασίας μου. Επίσης, θέλω να ευγαριστήσω τον Δρ. Γεώργιο Κενανάκη, κύριο ερευνητή στο ΙΗΛΔ-ΙΤΕ για την επιστημονική του βοήθεια και την καθοδήγηση του για την ανάπτυξη και τον χαρακτηρισμό των νανοράβδων από TiO2. Ακόμα, θέλω να ευχαριστήσω τον Δρ. Στέλιο Τζωρτζάκη, καθηγητή στο Τμήμα Επιστήμης και Τεχνολογίας Υλικών, για την συνεργασία. Θέλω να ευχαριστήσω την Δρ. Αργυρώ Κλίνη, κύρια ερευνήτρια στο ΙΗΛΔ-ΙΤΕ για την συνεργασία και την υποστήριξη της. Επίσης, θέλω να ευχαριστήσω τον Δρ. Ζαχαρία Βισκαδουράκη, μεταδιδακτορικό ερευνητή στο ΙΗΛΔ-ΙΤΕ για την συνεργασία. Θέλω να εκφράσω ένα θερμό ευχαριστώ στην κα. Αλέκα Μανουσάκη, για την συμπαράσταση, υποστήριξη και την συνεργασία κατά τις ατελείωτες ώρες στο ηλεκτρονικό μικροσκόπιο σάρωσης. Τέλος, θέλω να ευχαριστήσω τον κ. Θανάση Κωστόπουλο για τις μετρήσεις στο προφιλόμετρο.

Abstract

In this work three-dimensional (3D) structures covered by titanium dioxide (TiO_2) nanorods were designed and developed. These devices were designed for photocatalytic applications due to the properties of this material and the increase in active surface through the 3D structuring. Although in past, 3D scaffolds covered by zinc oxide (ZnO) nanorods have been realized, the photocatalytic performance of the new TiO₂ hybrid 3D devices have shown showing promising results. As a consequence, the implementation of the same idea but with different and more efficient photocatalytic material would further enhance the photocatalytic performance.

Five important steps were realized for the accomplishment of this work. First, hybrid 3D structures were fabricated via the MultiPhoton Lithography (MPL) method. Then, the hybrid structures underwent a Post-Thermal Treatment (PTT) in order to be transformed into 3D structures consisting of a ceramic-like material. The next step was the deposition of a seed layer of TiO₂ on the 3D structures by the Pulsed Laser Deposition (PLD) method. Next, the hydrothermal synthesis of TiO₂ nanorods was achieved using an Aqueous Chemical Growth (ACG) technique. Finally, the photocatalytic performance of new 3D devices was characterized via photocatalytic degradation of organic pollutants such as methylene blue (MB) and stearic acid. The photocatalytic performance of TiO₂ nanorods grown on 2D surfaces. Also, the hybrid 3D structures performance was compared with photocatalytic films. The expected increase of photocatalytic efficiency of the new 3D devices has been confirmed showing a dramatic decrease of organic pollutants concentration with a decomposition coefficient of k = 0.059min^{-1} .

<u>Περίληψη</u>

Σε αύτη την εργασία τρισδιάστατων δομές (3D) επικαλυμένες με νανοράβδους από διοξείδιο του τιτανίου (TiO₂) σχεδιάστηκαν και αναπτύχθηκαν. Αυτές οι συσκευές κατασκεύαστηκαν με σκοπό την χρήση τους σε φωτοκαταλυτικές εφαρμογές εξαιτίας των ιδιοτήτων του υλικού και της αύξησης στην ενεργή επιφάνεια μέσα από την 3D κατασκεύη τους. Παρότι στο παρελθόν, υπήρξαν επιστημονικά αποτελέσματα για την κατασκεύη 3D δομών επικαλυμένων από νανοράβδους από οξείδιο του ψευδαργύρου (ZnO), η φωτοκαταλυτική τους απόδοση των νέων 3D υβριδικών συσκεύων από TiO₂ ερεύνηθηκε παρουσιάζωντας υποσχόμενα αποτελέσματα. Κατά συνέπεια, η εφαρμογή της ίδιας ιδέας αλλά με διαφορετικό και πιο αποδοτικό φωτοκαταλυτικό υλικό θα διέυρυνε περαιτέρω την φωτοκαταλυτική τους απόδοση.

Πέντε σημαντικά βήματα έλαβαν χώρα για την ολοκλήρωση αυτής της εργασίας. Αρχικά, υβριδικές 3D δομές κατασκεύστηκαν μέσω της μεθόδου της Πολυφωτονικής λιθογραφίας. Έπειτα, οι υβριδικές δομές υπέστησαν μία θερμική επεξεργασία προκειμένου να μετατραπούν σε 3D δομές από ένα υλικό με κεραμικές ιδιότητες. Το επόμενο βήμα ήταν η εναπόθεση ενός πρόδρομου στρώματος από TiO2 πάνω στις 3D δομές μέσω της μεθόδου της Παλμικής εναπόθεσης λέιζερ. Στο τέλος, επιτεύχθηκε η σύνθεση των νανοράβδων από TiO2 χρησιμοποιώντας μια Υδάτινη χημική τεχνική αναπτυξης. Η φωτοκαταλυτική απόδοση των νέων 3D συσκεύων χαρακτηρίστηκε μέσω της φωτοκαταλυτικής αποδόμησης οργανικών ρύπων όπως του κυανού του μεθυλενίου και του στεαρικού οξέος. Η φωτοκαταλυτική απόδοση των 3D δομών επικαλυμένων με νανοράβδους από TiO2 συγκίθηκε με την απόδοση νανοράβδων από TiO₂ που είχαν αναπτυχθεί σε 2D επιφάνειες. Επίσης, οι αποδόσεις των υβριδικων 3D συσκεύων συγκρίθηκαν με την απόδοση φωτοκαταλυτικών επιφάνειών. Η αναμενόμενη αύξηση της φωτοκαταλυτικής απόδοσης των νέων 3D συσκεύων επιβεβαίωθηκε παρουσίαζωντας μία δραματική μείωση της συγκέντρωσης των οργανικών ρύπων με σταθερά αποδόμησης $k = 0.059 \text{min}^{-1}$.

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1. Introduction

Nowadays there is a plethora of scientific projects in the research field of photocatalysis such as self-cleaning surfaces, air purification, water treatment, water-splitting and photoelectrochemical storage [1]–[5]. This is because photocatalysis promises a solution to the expanding energy demand. It is based on exploitation of solar energy which is a renewable energy source. During this procedure, photons from solar irradiation, are harvested resulting in the desired chemical reactions. This work refers to heterogeneous photocatalysis in which the catalyst, reactants and products occupy different phase. When a semiconductor (SM) is illuminated by photons whose energy is equal to or greater than its band-gap energy, there is absorption of these photons resulted in electron-hole pairs. These pairs dissociate into free electrons and holes in the conduction and valence band respectively. As a result, the immersion of a SM in an organic pollutant solution induces the degradation of the organic pollutant and its conversion into harmless products via redox reactions between solution, free electrons and holes [6].

Currently, the research is rapidly expanding for semiconducting materials in order to enhance the photocatalytic performance as catalysts. The photocatalysts used must have bandgap energies within solar spectrum for efficient photons harvesting [7]. Among semiconducting materials, titanium dioxide (TiO₂) and zinc oxide (ZnO) are widely-researched materials. They are demonstrating impressive properties for example, high electron mobility, large band gaps and reasonably good conductivity [8]. TiO₂ is preferred most for industrial use as it has high stability, it is biocompatible, low-cost and it is abundant in nature. A major drawback is that TiO₂ absorbs ultraviolet light, owing to its large bandgap of (3-3.2) eV. In order to enhance the phenomenon of photocatalysis, the photocatalyst used, have to absorb the solar spectrum possessing a bandgap which corresponds to light in visible region.

In addition, a different way to enhance photocatalysis is to increase the "active" surface of the catalyst. The idea is that, there are more interactions between a semiconductor and its environment by increasing its surface reaction sites. Generally, there are three main requirements for photocatalysis: light irradiation, a pollutant and a photocatalyst. It has been confirmed that by nano-structing the catalyst, there is enhancement in photocatalytic degradation of organic pollutants. Thus, an abundant of TiO₂ nanomaterials-based devices were extensively investigated for environmental and energy applications through photocatalysis [9].

The purpose of this work was to develop 3D structures and to be used as substrates for subsequent growth of TiO₂ nanorods. The concept is that 3D structuring of TiO₂ nanorods can further enhance their photocatalytic performance by increasing the surface-volume ratio. The idea came from a past research on fabrication of 3D structures covered by ZnO nanorods showing promising results [10]. Giakoumaki reported this research in her master thesis combining four different techniques. In this work, TiO₂ nanorods were synthesized instead of ZnO nanorods. In contrast to growth of ZnO nanorods, TiO₂ nanorods require high temperatures and pressures. Thus, one additional step was followed related to Giakoumaki's work.

2. State of the art

Nano-dimensional structures of semiconductors are greatly investigated due to the wide area of potential technological applications [11]. The reason is the extremely large surface-to-volume ratio of nanomaterials that can significantly increase the surface reaction sites improving the catalytic performance. A large variety of nanostructures have been fabricated such as: nanotubes, nanobelts, nanorods, nanowires and nanosheets. The interest is directed to those types of nanostructures which show enhanced properties comparing to the bulk.

First, Iijima reported the formation of carbon nanotubes in 1991 [12]. This turned out to be a milestone in materials science and technology. Growth of TiO₂ nanotubes was first reported by Kasuga et al. in 1998 [13]. The hydrothermal synthesis of TiO₂ nanorods was found by Du et al. in 2001 [14]. Since then, most work reported has included hydrothermal alkali reactions for nanotube-type shape. Nanotubes of RuO₂, ZnO coated by TiO₂, ZnO, SnO₂, were reported as nanostructures with increased photosensitivity [15]–[18]. In the nanometer scale, due to the appearance of the quantum confinement effects, the electronic band structure could be blue shifted. Peng et al. found that the quantum confinement effects of rutile TiO₂ nanorods becomes significant when its diameter is smaller than 2.5nm [19]. The quantum confinement effect says that the size of the absorbent is related to the energy that it absorbs. Consequently, there is ability to engineer the bandgap energy of nanorods by modulating their size in nanometer-scale affecting their photocatalytic performance.

 TiO_2 nanorods are on the top of the research finding use in gas sensors, photocatalysis, photovoltaics, and high efficiency solar cells. Titania nanorods exhibited incredible transport of electrons owing to the fact that the electron lifetime in nanorods was higher. Yanagida et al. also claimed that the electron transport in titania nanotube electrodes was efficiently higher than in electrodes prepared with nanoparticles [20]. This should be attributed to the low dimensionality of the nanotube structures which resulted in the higher diffusion length of charge carriers. The results of parallel photocatalytic experiments in the presence or the absence of air revealed that the nanotube structures can generate more trapped electrons. Therefore, TiO₂ nanorods were introduced as electrodes to batteries, solar cells, and photoelectrochemical cells for effective charge separation and collection.

The light absorption wavelength range can be adjusted from ultraviolet to visible in order to maximize the utilization of solar irradiation like Grätzel-type solar cells [21]. Experimental efforts have been undertaken to alter the band structure of TiO₂ by doping, and the results indicated that doping can significantly enhance the photocatalytic properties of TiO₂. Asahi et al. reported nitrogen doping of TiO₂ [22]. By introducing doping elements into the TiO₂ lattices the charge transport properties and redox reaction rates can be modified. By now, there are scientific reports of TiO₂ nanorods doped with other elements such as: Cu, Fe, Co, Nb in order to shift the bandgap energy of nanorods and improve electron transport [23]–[26].

3. Principles

3.1. MultiPhoton Lithography (MPL)

2.1.1 Fabrication technique for 3D structures

Nowadays, the escalating demand for the fabrication of three-dimensional (3D) structures of smaller and smaller features has increased the efforts to develop various micro/nano-fabrication processes. Manufacturing techniques such as multibeam interference lithography, inkjet printing and UV laser stereolithography (SL) can produce 3D structures but with poor resolution and they require optical masks [27]-[29]. In addition, other techniques such as electron/beam lithography require expensive equipment and produce structures with low speed [30], [31]. In conventional SL, photopolymerization is achieved when an ultraviolet (UV) laser beam illuminates selectively a photosensitive material resulting in its phase transition process [32]. In contrast, multiphoton lithography (MPL) is a microfabrication method exploiting the nonlinear dependency of the polymerization rate on the irradiating light intensity to produce 3D structures with feature sizes beyond the diffraction limit. MPL is a direct laser technique which is based on multiphoton polymerization (MPP) of a photosensitive material. MPP is the result of another process called multiphoton absorption (MPA) [33]. The process of MPA was predicted theoretically by Maria Göppert-Mayer [34] in 1931 and 30 years later experimentally confirmed by Kaiser and Garret [35] in 1961 with the advent of laser technology as high photon intensities required. MPF was reported as lithographic technique in 1965 by Pao and Rentzepis [36]. 3D structures with feature sizes as small as 100 nanometers (nm) can be accomplished [37].

MPA is defined as the simultaneous absorption of two or more photons of identical or different frequencies in order to excite molecule from one state to higher state. High light intensities are required due to the very small cross-section of the multiphoton processes. Thus, MPA is feasible when a laser beam is tightly focused onto a volume of a photosensitive material, the polymerization process can be initiated by nonlinear absorption of light. There is analogy between MPA of n photons and the rate of a concerted chemical reaction involving n molecules, generally the n-photon absorption leads to n-photon polymerization [33]. It comes from the fact that the rate of MPA for n photons is proportional to light intensity (number of photons per volume per time) to nth power.

An example of MPP processes is the two-photon polymerization (TPP) which is based on two-photon absorption (TPA) [38]. The TPP occurs when the laser beam intensity is high enough to overcome the polymerization threshold of the material. The nonlinear intensity dependence of the absorption process allows the excitation to be localized within the focal volume of a laser beam leading to localized TPP. By moving the focal volume of the laser beam through a transparent and photopolymerizable material, 3D structures can be fabricated. There are many applications where MPL method can be employed such as: photonic crystals, sensor devices, metamaterials, microfluidics devices and scaffolds for tissue engineering and photocatalysis [10], [39]–[44].

2.1.2 Two-Photon Absorption (TPA)

As aforementioned in conventional lithography, when a UV laser beam illuminates a photosensitive material a phase transition process takes place, inducing the phenomenon of one-photon polymerization (OPP). The process occurs via one-photon absorption (OPA), which is illustrated in Figure 2.1, following the Beer-Lambert law [45]. As a result, OPP is a process that takes place only on the surface of a sample not enabling us to obtain complex 3D structures. The simplest example of multiphoton absorption is the TPA. In this case, the excitation energy comes from two photons usually in the near red-infrared (NIR) spectral region in order to impact the same amount of energy. There are two ways to achieve TPA, depending on the existence or not of a real intermediate state. If this state is real the TPA process is called sequential, otherwise, it is called simultaneous. The existence of a real state between the initial and the final state implies that the material used absorbs in that spectral region.



Figure 2.1: Illustration of one-photon absorption (a) and two-photon absorption (b). TPA occurs via an intermediate state between the absorptions of first and second photon. In this case, the electron transition is caused by two photons of energy equal to hv/2 rather than one photon with energy hv. As a result, the wavelength of two photons is 2λ where λ is the excitation wavelength in OPA.

In simultaneous TPA, which is illustrated in Figure 2.2, a virtual intermediate state is formed when the first photon arrives and the electron excitation happens only if the time distance of the second photon arrival isn't longer than the lifetime of the virtual state [38]. Virtual state's lifetime can be calculated from the Heisenberg's uncertainty principle. Considering that the state's energy level is around 10^{-1} eV, it is estimated that state's lifetime is of the order of few femtoseconds [45].



Figure 2.2: Sequential TPA (a) and simultaneous TPA (b). In the latter case the intermediate state is virtual unlike the first one. An essential requirement is a laser beam with short pulse duration closely focused onto a volume of transparent, photosensitive material.

Generally, in nonlinear processes including TPA, the energy and momentum are exchanged between the optical fields and molecules through absorption and emission. TPA is a nonlinear optical property related to the imaginary part of the third-order susceptibility in the material polarization. The light-matter energy change per unit time and unit volume is [32]:

$$\frac{\mathrm{dW}}{\mathrm{dt}} = \langle \vec{\mathrm{E}} \cdot \vec{\mathrm{P}} \rangle$$

where: \vec{E} is the electric field vector \vec{P} is the material polarization vector The brackets denote time average.

The value of P is:

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots$$

where: $\chi^{(1)}$ is the linear susceptibility $\chi^{(2)}$ is the second-order susceptibility and so on

For the centrosymmetric molecule systems absorbing two photons with the same frequency, the even tensors $\chi^{(2)}$, $\chi^{(4)}$ do not contribute to the resonant process [46]. Therefore, the nonlinear absorption is described by the imaginary parts of $\chi^{(3)}$, $\chi^{(5)}$, of which typical effects are two-photon and three-photon absorptions, respectively. The imaginary part of nonlinear susceptibility represents the energy transfer from the light field to a medium. The n-order susceptibility, $\chi^{(n)}$ is the sum of the nonlinear refraction, $\text{Re}[\chi^{(n)}]$ and the nonlinear absorption, $\text{Im}[\chi^{(n)}]$. In TPA the energy absorption rate is:

$$\frac{\mathrm{dW}}{\mathrm{dt}} = \frac{8\pi^2\omega}{\mathrm{c}^2\mathrm{n}^2}\mathrm{I}^2\mathrm{Im}\big[\chi^{(3)}\big]$$

where: n is the refractive index ω the incident light optical frequency c the speed of light in vacuum I the intensity of the light Im[$\chi^{(3)}$] is the imaginary part of the third-order susceptibility

The TPA rate depends quadratically on the light intensity, which is an important mechanism to improve the spatial resolution in two-photon fabrication. A high capability of materials to absorb photons via TPA is desired. The measure of material's TPA effectiveness is described by TPA cross-section, δ , defined by:

$$\frac{\mathrm{dn}_{\mathrm{p}}}{\mathrm{dt}} = \delta \mathrm{NF}^2$$

where:

N is the number density of absorbing molecules n_p number of absorbed photons $F = \frac{1}{h_N}$ denotes photon flux

The TPA cross-section is:

$$\delta = \frac{8\pi^2 h v^2}{c^2 n^2 N} I^2 Im[\chi^{(3)}]$$

The cross-section of simultaneous TPA is small due to the virtual state's short lifetime. To achieve TPA, high light intensities (high photon densities per time) are required to increase the possibility of simultaneous TPA. A tightly focused pulsed femtosecond laser beam with a short pulse duration can provide the energy needed. It was recognized that laser-matter interactions for femtosecond pulses were fundamentally different from interactions resulting from longer pulses. First, a femtosecond laser carries much greater peak power, sufficient to induce direct bond breaking. Secondly, the time duration of pulses, from a typical femtosecond laser, is of the order of magnitude of several femtoseconds (fs). Typical time needed for the excited electrons to transfer energy to the lattice is few picoseconds (ps). This means that electron excitation from fs pulses is a heat insulation process. Although, lasers with longer pulse duration can be used but thermal effects are created which are not desired as it is difficult to determine them.

The rate of absorption in a transverse cross-section of a laser beam depends upon the product of the intensity (number of photons per time per area) and the number of molecules in the cross section (which is proportional to the area). Thus, the absorption rate does not depend upon area in OPA. The number of molecules excited by single-photon absorption is constant in any transverse plane of a focused laser beam, and so there is no localization of excitation in the focal region. On the contrary, the rate of MPA processes depend on light intensity as the relation between absorption and light intensity is nonlinear. The phenomenon is depicted in Figure 2.3. Generally, the rate of nth-photon absorption in a transverse cross-section of a laser beam depends on the nthpower of light intensity and the number of molecules in the cross-section. Light intensity is the product of (number of photons x photon energy)/(time x area). In the case of TPA, the rate of absorption in a transverse cross-section of a laser beam is proportional to the intensity squared times to the number of molecules in the crosssection. Therefore, the absorption rate scales inversely with area following a gaussian like distribution. A TPA process is localized as it can only happen inside the focal volume of a laser beam where the light intensity is large enough [33].



Figure 2.3: OPA rate (a) and TPA rate along the optical axe of a focused laser beam (b). In the case of TPA, the density of excited molecules will therefore be in the volume element in which the laser beam is focused most tightly.

A critical parameter is the numerical aperture (NA) of the microscope objective lens. High NA objective lenses are used to focus the laser beam and create the photon density needed for nonlinear absorption. The greatest focus is achieved when the laser beam is adjusted properly so that to overfill the back aperture of the lens as the beam comes through the objective. The NA of an objective is defined as:

$$NA = n \cdot sin(\alpha)$$

where: n is the refractive index

 α is the maximum angle measured from the outer edge of the objective lens with respect to the optical axis

The two-photon process has two major advantages, which are illustrated in Figure 2.4, compared to other lithographic methods. First, there is the ability of deep penetration of light as the most of commercially available materials have negligible absorption of the near infrared (NIR) region (laser emission spectrum). Secondly, there is the quadratic dependence of TPA rate to light intensity enables accurate spatial resolution better than 100nm. Thereby the laser beam can penetrate deeply into materials and directly drive polymerization without contaminating outside of the focal volume [38].



Figure 2.4: Schematic illustration of the polymerization process OPA or sequential TPA (a) and from simultaneous TPA (b) as a laser beam is focused in a photopolymerizable material by an objective lens. In the first case, only processes close to the surface are taking place. In contrast, TPP induced by simultaneous TPA can be initiated only in the volume of a tightly focused laser.

2.1.3 Two-Photon Polymerization (TPP)

Polymerization is a process in which monomer molecules are connected with bonds to form polymer molecules. When light is used as the initiation energy source, the process is called photopolymerization. This can be realized when a laser beam is tightly focused into a photosensitive material resulting in the production of radicals arising from photoinitiator molecules. The radicals produced from the optically cleaved photoinitiator molecule led to the breaking of the monomer's double carbon-carbon bond. Most monomers do not produce an initiating species for polymerization so it is necessary to introduce low molecular weight organic compounds that act as photoinitiators. Photoinitiators absorb light irradiation and initiate the polymerization process giving radicals through their excitation and decomposition. This process includes chain reactions in which there is addition of a monomer molecule to an active chain-end which regenerates the active site at the chain-end. Thus, polymers can be formed by the connection of monomer molecules with bonds along a chain [47]:

$$M \xrightarrow{M} M_2 \xrightarrow{M} M_3 \dots M_{n-1} \xrightarrow{M} M_n \dots$$

where: M is the monomer unit

M_n is the macromolecule with the active site at the chain-end containing n monomer units

Briefly, TPP can be described by the following steps [48]:

• Initiation:
$$I \xrightarrow{hv/2, hv/2} I^* \longrightarrow R^{\cdot}$$

• Propagation: $R^{\cdot}+M \longrightarrow RM^{\cdot} \xrightarrow{M} RMM^{\cdot} \xrightarrow{M} RM_{n}^{\cdot}$
• Termination: $RM_{n}^{\cdot} + RM_{m}^{\cdot} \longrightarrow RM_{n+m}R$

where: I is the photoinitiator

I* is the excited photoinitiator

R[.] is the radical

 RM_n is the macroradical with the active site at the chain-end containing n monomer units $RM_{n+m}R$ is the polymer containing n+m monomer units

In the TPP process, the first essential step for photopolymerization is initiation, where radicals are produced via the photoinitiator excitation and decomposition. The next step is the propagation where a radical reacts with a monomer unit so that these are connected to form a first active monomer radical. An active monomer radical can react with a new monomer unit. Monomers continue to add in the same manner resulting in the formation of macroradicals, which are end-active polymers. The final step called termination, where chain propagation stops when two macroradicals meet each other, so deactivation occurs with their connection. TPP can take place only into the "voxel", the volume element inside material where polymerization occurs, defying the fabrication resolution.

There is a natural limit on how much a light beam can be focused so the fabrication resolution should be determined by this. The highest resolution that can be achieved by a focused laser beam is given by Abbe's diffraction limit [48]:

Diffraction limit =
$$\frac{0.5\lambda}{NA}$$

where: λ is the laser wavelength NA is the numerical aperture of the objective lens

In fact, this is only valid in reversible, noninvasive procedures, such as imaging. When there is a permanent modification of the sample, like in photopolymerization, then there is more than one process involved [49].

To start with, when absorbing light, the photoinitiator becomes excited and produces radicals; these radicals attack monomer molecules to form macroradicals of the polymer. Finally, the radicals are terminated to give the polymer. Radical termination can be also induced by oxygen and other molecules in the system, known as scavengers. Quenching competes with photopolymerization and is usually considered detrimental to the process. By employing a radical quenching mechanism, a spatial resolution beyond the diffraction limit of the light can be obtained. The quenching process is expressed in equations [50]:

 $\begin{array}{l} \mathrm{R}^{\cdot} + \mathrm{Q} \rightarrow \mathrm{R}\mathrm{Q}^{\cdot} \\ \mathrm{R}\mathrm{Q}^{\cdot} \rightarrow \mathrm{R}\mathrm{Q} + \mathrm{heat} \ \mathrm{or} \ \mathrm{hv} \end{array}$

where: R[·] is the radical Q is the quencher RQ[·] is the quenched radical RQ is the deactivated quenched

The radicals combine with radical quenchers instead of monomers to produce quenched radicals. Then, they are deactivated by irradiation or release of heat. Thus, the radical quenchers prevent the reactions of polymerization. The spatial concertation of radicals is proportional to the square of light intensity. Therefore, when the light intensity at the focal point is large enough so that the number of light-produced radicals exceeds the quenchers, polymerization occurs. In our work, there is capability to modify the light intensity at the focal volume in a manner such that the light-produced radicals exceed the quenchers and initiate polymerization only in a region where exposure energy is larger than the threshold. In this case the diffraction limit becomes just a measure of the focal spot size and it does not really determine the voxel size. The energy required for the polymerization process depends on the material and the more the peak power get closer to the threshold power, the smaller the voxel gets. The existence of a polymerization threshold, which is depicted in Figure 2.5, leads to the conclusion that there is the capability to control the fabrication process by knowing and modifying the incident light intensity.



Figure 2.5: A diagram that shows the light intensity profile of a laser beam as it is focused by an objective lens along the position inside a photopolymerizable material. TPP can take place only in volume where the light intensity is higher than the polymerization threshold of a material so the photochemical region is defined.

3.2. Post-Thermal Treatment (PTT) 2.2.1 Technique for pyrolysis

An approach to produce well-defined nanoscale features in 3D microstructures with functional properties is the combination of Direct Laser Writing (DLW) methods with the Post-Thermal Treatment (PTT) technique [51]. PTT is achieved by pyrolysis, which is a chemical transformation induced by thermal energy when a compound is heated at a temperature significantly higher than ambient. The main effect of pyrolysis is typically the decomposition of the initial compound with formation of smaller molecules and elimination of others. In this concept, by applying pyrolysis via PTT on 3D structures, we can remove the organic component of the hybrid material, leaving structures composed mainly of the inorganic component. It is a new pathway to fabricate inorganic 3D structures that are made from materials that possess useful electrical, magnetic, optical, and chemical properties due to a tailored final material composition. Also, PTT can improve the resolution of 3D structures as during thermal treatment the crosslinked resist is partly decomposed and volatile species are removed. Apart from the reduced in size, the resist of 3D structures is made more robust and improving the mechanical stability of the structures [52].

The organic component of the standard hybrid materials is the reason why freeform laser nano-structuring is possible but on the other hand, they have limitations imposed by their organic component. Generally, organic materials have serious limitations regarding stability against harsh environments. Recently, the combination of Two-Photon Lithography (TPP) with PTT on 3D structures made from hybrid organic-inorganic sol-gel resist SZ2080 resulted in conversion into a material with entirely different properties [53]. In this work, pyrolysis is employed to homogeneously shrink structures up to 40% by removing organic SZ2080 constituents opening a route of fabrication mechanically robust glass-ceramic microstructures. The Zr containing hybrid photopolymer, mostly referred to as SZ2080, is especially interesting. It combines all of the best properties offered by these materials, such as low shrinkage, a hard gel form during fabrication, and transparency for visible light, and thus is widely used in creating structures to be employed in various applications in medicine, microoptics and photonics. By pyrolysis, there is ability that 3D structures retain a particular geometry made from TPL and obtain characteristics of ceramic-glassy like materials being more rigid and optically resilient [54]. There is no doubt that ceramics and glassy materials cover an important part of science and industry, due to outstanding thermal, mechanical, chemical properties [55]-[57].

Thermal decomposition of polymers is a subject of considerable interest and PTT is a well-studied technique for pyrolysis of carbon micromechanical systems (C-MEMS) as polymer resins can be transformed into to functional structures [58]. After PTT C-MEMS have significantly enhanced physical properties such as superior chemical resistance, oxidation resistance, thermal stability, high elastic modulus, and biocompatibility. That is why, they find use in production of complex parts for several medical and industrial applications such as water treatment [59]. Preserving the complex 3D geometry at micro/nanometer length, products of hybrid 3D structures after PTT are also used widely as electrode components in electrochemistry such as solid- and liquid-state batteries, flow batteries, and fuel cells. 3D functional components enable control over the distribution of current and potential and can enhance ion and electron transport [60]. Also, their biocompatibility makes them potential components of prosthetic devices [61].

2.2.2 Heat treatment mechanism

The aim is to decompose the functional organic groups in order to benefit from the final hybrid material (Figure 2.6). It is expected that during pyrolysis of polymer resins, removal of the organic part of the structures is achieved. The C-O and O-O bonds are weak and as a result, they are broken first upon heating the hybrid material [62]. The result is 3D functional structures consist of a pure inorganic glassy-ceramic material. In addition, a shrinkage of the actual size of the 3D structures is resulted in after the removal of organic constituents with volume change \sim 20-80% depending the experimental conditions of PTT technique.

During pyrolysis, resins are thermally decomposed in vacuum or inert atmosphere at temperatures in the range of 500°C-3.000°C. The results of the pyrolysis process in air in the presence of atmospheric oxygen are seen more like a vacuum pyrolysis catalyzed by oxygen. According to literature in PTT, with the rise of temperature from room temperature to 300°C would result in no engineering effects on the hybrid material [63]. The elimination of small molecules such as H₂O, HCI is done, while the polymer backbone still remains intact. As the applied temperature is increased at typical pyrolysis temperatures values of 500°C-800°C, the organic constituents of the resists start to decompose, while the inorganic part is well preserved, behaved as backbones to support the whole structure. Until 1200°C, it is seemed that geometrical stability of 3D structures is retained. By temperature increasing further, the structures show signs of melting and deformation. Sharp features become noticeably rounded by surface tension of the molten phase [62].

Depending on the initial composition of the resist, in this work SZ2080 hybrid material, the remaining elements rearrange to form a glassy carbon or zirconium doped silica carbon mixture. A homogeneous reduction in the size of 3D structures is desired keeping a well-defined morphology. Composition control via different portions of organic and inorganic components of the final material can be achieved. Experimental parameters in PTT rule the degree of decomposition. The main reason is that the energy of chemical bonds is different across material depending on the chemical elements, indicating that different components decompose at different applied temperatures. Apart from heating temperature and heating rate, the nature of the environment in which pyrolysis takes place influence the process. Usually, pyrolysis is performed in an inert gas or at reduced pressure to eliminate the reaction with the ambient atmosphere. However, pyrolysis in the presence of a specific reagent such as oxygen or in the presence of a catalyst added intentionally can be practiced [64].

The Si and Zr precursors in this work will lead to the emergence of silica and zirconia crystalline phases in the final sintered ceramic material [65]. Generally, the thermal treatment under oxidative atmosphere opens the possibility for the formation of various crystalline phases with distinctive chemical and physical properties. Also, heating of hybrid materials is attractive not only because of the formation of new crystalline phases but also due to the shrinkage in dimensions of 3D structures expanding the application possibilities.



Figure 2.6: Processing flow of Post-Thermal Treatment (PTT).

3.3. Pulsed Laser Deposition (PLD)

2.3.1 Method for thin film deposition

PLD is a physical vapor deposition method for the growth of thin films, it is based on light and matter interaction under vacuum conditions [66]. This method is achieved when a pulsed laser beam is introduced into a vacuum chamber through an optical window and focused onto a target material. There is light absorption by material and the result of this process was determined by the incident laser power density [energy/ (surface x time)] related to the ablation threshold [67]. Ablation threshold depends on the target material's coefficient, laser pulse wavelength and duration. For values of laser fluence (laser power density) lower than ablation threshold, laser pulse simply heats the target. Laser ablation and material vaporization of target occurs only if laser fluence is large enough to transcend the ablation threshold. In this case, a finite volume of solid target material is converted into vapor phase constituents such as ions and neutrals. In this way, a high-temperature "plasma plume" is created and expanding adiabatically transfer matter from target material to substrate. Finally, recondensation of plasma plume provides the material flux needed for film growth. Changing the deposition parameters allows one to tune the physical properties of deposits according to their use and application. There is ability to obtain well defined nanostructures and surface morphologies by controlling target and substrate materials, target to substrate distance, type of laser, laser wavelength, pulse duration, repetition rate, form and size of the laser irradiation focused spot [68].

The use of a pulsed laser as a directed energy source for evaporative film growth has been explored since the discovery of lasers. In the 1960s when Smith and Turner [69] introduced the PLD method, they showed that this growth technique could efficiently produce various types of thin films. The growth of epitaxial thin films starts by Cheung [70] in 1983 followed by the growth of a high temperature superconductor by Dijkkamp [71] in 1987, these milestones lead to a wide spread interest and practice of producing thin films by PLD. It is now established as one of the simpler, cheaper and more versatile methods for depositing thin films of a very wide range of materials. In PLD technique, it is easy to change the growth parameters to get various properties of doped films. Its controllability and reproducibility to deposit thin films of very different types of materials. PLD also facilitates the generation of atomically abrupt interfaces between different materials, including oxide/semiconductors and oxide/metals [72].

It is useful to outline the most common methods to provide a standard for comparison with the PLD technique. The simplest approach to transport material from a bulk onto a thin film is via thermal evaporation. Deposition techniques based on thermal evaporation are chemical vapor deposition (CVD) [73], metalorganic chemical vapor deposition (MOCVD) [74] and molecular-beam epitaxy (MBE) [75]. CVD and MOCVD dominate in large-scale commercial production of electronic materials due to their high homogeneous growth rates, subsequent modest vacuum requirements and low cost. On the other side, MBE is used for quantum well devices where film growth must be controlled at a sub-nanometer level and high crystal purity is essential.

Thermal growth techniques are unable to accommodate two chemical systems on the same substrate, as the growth conditions needed for one can result in the thermal decomposition of the other. The ability to deposit films under nonthermal conditions may alleviate such difficulties. Ion-beam techniques are nonthermal methods, which make them promising for film deposition [76]. Such techniques are RF-sputtering and RF-magnetron sputtering, in which the energy of the impinging flux can be controlled by an electric field. These techniques have proved to be advantageous for the congruent transfer of multi-elemental materials without the presence of micrometer sized droplets. This is necessary characteristic for semiconductor industrial fields, like solar cells, where smooth and uniform surface is desirable.

Laser ablation for thin-film growth overcomes problems of other thin film growth techniques. In PLD method, a laser is used as energy source, the laser is localized outside of vacuum chamber away from the other system components. Material deposition can be achieved on any solid phase material as a target no matter which is substrate morphology. This is because material transferring on atomic scale, from target to substrate is accomplished due to laser light absorption, plasma plume creation, expansion and recondensation. The most important reason for using PLD in preference to other deposition techniques lies primarily in the ability to reproduce in thin films the same elemental ratios of even highly chemically complex bulk ablation targets due to nature of plasma plume [77].

PLD also has technical and fundamental drawbacks. In particular, angular distribution of plasma plume is often cited as a weakness in PLD in contrast to other techniques, limiting the deposition area typically to a few cm². Also, the thickness distribution is quite nonuniform due to the highly forward-directed nature of the ablation plume making micrometer-sized droplets at target. These disadvantages can be overcome by raster scanning of the ablation beam over the target and/or rotating the substrate. In this way, uniform film coverage over large areas can be produced [78].

2.3.2 Ablation mechanism

The mechanism of the PLD technique apart from 4 stages (Figure 2.7), the laser light absorption, the formation of a plasma plume, the expansion of this plume and finally its recondensation for material deposition on a substrate for film growth [79]. In the first stage, as laser beam irradiates target surface, light is absorbed by material according to Beer-Lambert law:

$$I = I_0 e^{-\mu z}$$

where μ is the absorption coefficient

 I_0 is the incident laser light intensity

 \mathbf{z} is light distance through the medium

I is the laser light intensity at distance z inside the medium.

The absorption coefficient depends on the medium, its temperature, wavelength and pulse duration of incident light irradiation. In general, the laser wavelength and the laser pulse duration are important parameters for the ablation process. Firstly, as decreasing the wavelength so energy increasing, the absorption coefficient is increasing. That is why laser sources, in UV spectral region, are more attractive because their use leads to high value of absorption coefficient. That means small interaction area between laser beam and target surface, so more effective light-material coupling [80].

Light absorption causes the excitation of material through electronic transitions. The energy of excitation is transferred by electrons to material lattice through phonon emissions resulting in irradiated area's heating. During this stage, the temperature around the irradiated area rises up on the order of $\sim 10^4$ K within a few picoseconds (ps). In the case of a femtosecond (fs) laser-pulse, there is no laser-material lattice interaction because the pulse duration is shorter than the time required for plume development. Thereby, there is direct breaking of chemical bonds means that a phase transition is induced from solid to the vapor phase omitting the liquid one avoiding thermal effects. With fs laser pulse, the photon energy is deposited much faster than electrons could transfer it to the lattice through phonon emission as referred, so thermal effects are avoided. A typical laser source for ablation is a KrF excimer laser with pulse duration few tens of nanoseconds (ns) and pulse wavelength in UV spectral region. High laser power output can be accomplished with this laser because it can provide great amounts of energy in short time making it favorable for laser ablation. In this way, breaking of chemical bonds is achieved, resulting in vaporizing of target material.

The second stage consists of target material vaporization and plasma formation. If incident energy per time per area from laser beam (laser fluence) overcomes an ablation threshold, species in the irradiated area are ejected from the target material creating the characteristic plasma plume. Plume apart from ionized matter which consists of ground- and excited-state neutral atoms, electrons that are came from the chemical bonds breaking of the ablated material. During multiphoton ionization of the target surface, these ejected species continually absorb the incident laser light resulting in a strong interaction between the plume and the laser beam as well as the reheating of plume. The amount of evaporated material is localized only to that area defined by the laser focus and ejected atoms, molecules, electrons, ions, clusters and micron-sized particulates flow away from the target surface to the substrate at high mass transport velocity. The kinetic energy of plume species is on the order of few tens of eV. Laser parameters such as laser fluence, wavelength, pulse repetition rate and pulse duration can affect the kinetic energy, flux and ionization degree of ablated species [81].

The third stage involves the plasma plume expansion in vacuum, after the laser pulse. The plume expansion is considered adiabatic because there is no mass or energy transfer to the ablation plume. As plasma expands adiabatically, it cools to temperatures typically on the order of 10^3 K as expected due to volume increasing. Because of temperature decreasing, the kinetic energy of plasma species is decreased too on the order of few eV [82].

The final stage is the film growth of ablation material. Ion-electron recombination of the plasma plume is occurred providing the material flux needed for film growth. During ablation and material transfer by the plasma plume, the deposition of the material to substrate is nonuniform due to the beam-like direction of the plume. Scanning of the ablation beam over a rotating target could lead to more uniform film coverage of the desired material over the substrate. The thickness of the deposited film on the substrate is strongly dependent on the chamber pressure.



Figure 2.7: Processing flow of PLD process. Approximate time scales during laser ablation and plume propagation are shown. A bulk pellet of TiO_2 is used as target material and a 3D structure is employed as substrate.

That is to be expected because higher pressure (lower vacuum) means that there are more atoms and molecules inside the chamber. Those particles collide with the ablated atoms of the target, scatter with them and reduce the total amount of ablated material reaching the sample. The process occurs under vacuum conditions $\sim 10^{-6}$ mbar for this reason. In addition, the distance between target material and substrate plays a dominant role in thickness of thin-film. Film thickness is inversely proportional to distance, so with an appropriate adjustment of distance, not only large areas can be deposited homogeneously, but also it is a way to produce the desired thickness. In addition, pulsed nature of PLD means that film growth rates may be controlled, by repetition rate adjustment, to any desired amount adding a parameter for film thickness. Substrate temperature is another important parameter as it affects the diffusion length of plume species during deposition. When PLD method is performed in the presence of ambient gas in combination with vacuum conditions, two effects are expected. The first one is the reduction of the kinetic energy of the vapor flux. The other one is the production of molecular species in the ablation plume by interaction of ablated species with the background gas effecting the material composition on film growth. Under typical conditions, the deposition rate per laser pulse can range from 0,001 to 1Å per pulse.

3.4. Photocatalysis via titanium dioxide (TiO_2) nanorods 3.4.1. TiO_2

TiO₂ is an n-type, wide-bandgap semiconductor, which has attracted a lot of attention due to its photocatalytic properties and its potential applications in environmental purification and self-cleaning coatings [83]. Also, titania has high optical transmittance in the visible–IR spectral range, high chemical stability and mechanical resistance. The physical properties are significantly dependent on the crystal structure. TiO₂ is known to crystallize in three different crystallographic phases as shown in Figure 2.8, rutile (tetragonal) anatase (tetragonal) and brookite (orthorhombic) with a band-gap energy of 3, 3.2, 3.15eV respectively [84]. The first two phases dominate for TiO₂ at ambient conditions in bulk form. The rutile is extensively studied and widely used as it is the most stable and the most common crystal phase in nature. Anatase is not as thermodynamically stable as rutile and is only synthesized at relatively low temperatures. The phase transformation of anatase to rutile is irreversible and occurs at a wide range of temperatures, 400-1100°C, though normally it takes place at an annealing temperature of about 900°C [85].

As referred above, TiO_2 has attracted much attention in the field of photocatalytic applications for purifying contaminants in air and water [86]. Generally, anatase has more active photoelectrochemical properties than rutile. Fotou et al [87]. however, reported that the photoactivity of anatase TiO_2 mixed with the rutile phase was higher than that of pure anatase for the decomposition reaction of phenol. Degussa P25, a commercial powder material used frequently in photocatalysis studies, contains both the rutile and anatase phases in the approximate proportions of 20/80. The observation of the relatively high photoactivity for this form of TiO_2 was interpreted in terms of the enhancement of the magnitude of the space-charge potential, which is created by contact between the different phases [88]. Achieving high-quality film depositions of such mixed-phase materials, therefore, is of paramount importance. The interface between mixed-phase TiO_2 is responsible for higher photocatalytic reaction. This is due to an electron channel from rutile to anatase where electrons are trapped in lower energy anatase lattice (Ti^{4+}) sites [89].



Figure 2.8: Visual illustration of different crystal structures of TiO_2 . (a) rutile, (b) brookite, (c) anatase.

Extensive studies have been specifically done to understand the fundamental processes of the photocatalytic reactions and enhance their efficiency. The dependence of properties on their nanostructure has motivated the use of nanometer-sized TiO_2 particles and nanostructures to significantly reinforce the photocatalytic properties [90]. It is observed that nanosized titanium dioxide structures exhibit more efficient photocatalytic process as surface area is increased. Consequently, in recent years there is an abundance of scientific research for nanosized titania structures. Also, the bandgap energy of TiO_2 is a disadvantage related to solar spectrum but there is a way to tackle it. TiO_2 nanocrystals are usually doped with organic dyes or metals in order to shift their absorbance to the visible light region. As a result, new hybrid nanocrystals are more effective energy converters [91].

3.4.2. Photocatalysis

The principle of heterogeneous photocatalysis is based on the excitation of a semiconductor (SM) via light absorption. The SM produces highly oxidizing free radicals allowing the destruction of organic compounds adsorbed on its surface. In particular, the SM converts photon energy into chemical energy by oxidation-reduction (redox) reactions leading to molecular degradation of the compounds present. Redox reactions initiated by strong oxidants such as $OH \cdot$ and reductants such as O^- respectively. As a result, a degradation process is occurred by breaking chemical bonds of organic pollutants giving non-toxic mineral species. Figure 2.9 schematize the process of photocatalysis [92]:



Figure 2.9: Schematic illustration of Photocatalysis process leading to degradation of organic pollutants.

When a SM is illuminated with photons whose energy is equal to or greater than SM band-gap energy E_G ($hv \ge E_G$), there is absorption of these photons and creation of electron-hole pairs, which dissociate into free photoelectrons in the conduction band and photoholes in the valence band. Simultaneously, in the presence of a fluid phase (gas or liquid), a spontaneous adsorption occurs and according to the redox potential of each adsorbate, an electron transfer proceeds towards acceptor molecules, whereas positive photoholes are transferred to donor molecules [93]:

$$SM + hv \rightarrow e^{-} + h^{+}$$
$$R + e^{-} \rightarrow R^{-}$$
$$O + h^{+} \rightarrow O^{+}$$

where SM is semiconductor photocatalyst h is the Max Planck constant v is the frequency of incident photons e⁻ is the free-electron in conduction band h⁺is the hole in valence band R is the acceptor molecule for reduction O is the donor molecule for oxidation R⁻ is the product of reduction reactions

0⁺ is the product of oxidation reactions

The photoefficiency can be reduced by the electron-hole recombination, which corresponds to the degradation of the photoelectric energy into heat.

$$e^- + h^+ \rightarrow N + E$$

where N is the neutral center

E is the energy released under the form of light ($hv' \leq hv$) or of heat.

Generally, the kinetics of redox reactions follows the Langmuir–Hinshelwood mechanism with the rate r varying proportionally with the coverage θ as [94]:

$$r = k\theta$$

The photocatalytic process is divided into two steps: adsorption of contaminant species and following redox reactions. As a result, the degradation capacity of the semiconductor is related to several parameters such as the nature of the reaction medium, the amount of SM, the water content for the production of hydroxyl radicals and the nature and concentrations of pollutants. The larger contact area induces higher decomposition rate by reinforcing redox reactions [95]. The main problems of photocatalysis from light absorption to organic degradation are the narrow the band gap for visible light and the recombination of electrons and holes. It is desirable that the band gap of the semiconductor is near that for optimum utilization of solar energy, which would be ~ 1.3 eV. Also, recombination of the photoexcited electron-hole pair needs to be retarded for an efficient charge transfer process to occur on the photocatalyst surface. Charge carrier trapping would suppress recombination and increase the lifetime of the separated electron and hole to above a fraction of a nanosecond. Once excitation occurs across the band gap there is a sufficient lifetime for the created electron-hole pair to undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact [96].

It is expected that the reduction in lattice imperfections or irregularities in the film scan suppress the recombination between the photogenerated electron-hole pairs, thereby increasing the efficiency of the electron-hole separation in the surface region of a semiconductor. The morphology of semiconductor's surface affects the charge recombination. For example, charge carrier traps are used to promote the trapping of electrons and holes at the surface leading to a more efficient charge transfer process [97]. Obviously, electron and hole recombination are detrimental to the efficiency of a semiconductor photocatalyst. Modifications to semiconductor surfaces such as addition of metals, dopants, or combinations with other semiconductors are beneficial in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the photocatalytic process. One of the most important aspects of heterogeneous photocatalysis is that photoelectric effect depends upon the energy of the incident photons but not on their intensity. Thus, even if these are just a few photons of the required energy, they can induce photocatalysis. This means that even ordinary room light may be sufficient to help to purify the air or to keep the walls clean in the indoor environment, because the amounts of pollutants are typically small [89].

The materials used as photocatalysts is in the heart of the photocatalytic process as photocatalysis is based on the excitation of a photocatalyst with irradiation of light energy at least equal to that of its band gap. The best photocatalytic performances with maximum quantum yields are always obtained with TiO₂. There are many other semiconductors represent a large part of the semiconductors used for photocatalytic properties namely: ZnO, ZnS, WO₃, CdS, SnO₂, GaP. TiO₂ is preferred among the list of semiconductors reported in the literature as it is biologically and chemically inert, resistant to chemical corrosion and can work at ambient temperature and pressure, without addition of chemical species. Generally, a large variety of organics could be totally degraded and mineralized into CO₂ and harmless inorganic anions. As a result, photocatalysis has found several applications in the field of environment such as destruction of aqueous pollutants, air purification, metal recovery, and especially more recently, production of materials such as self-cleaning glass surfaces [98].

3.4.3. Aqueous chemical growth (ACG)

Nanostructures of materials exhibit improved properties as compared with their 2D surface due to large ratios of surface area to volume. TiO₂ nanostructures have been prepared by a number of chemical methods such as the thermal oxidation of metal, sol-gel and dip-coating [9]. Aqueous chemical growth (ACG) is a promising method for growing well-aligned TiO₂ that can be employed in solar cell applications and photocatalytic systems. It is a quite simple method for growth of nanostructures of various materials requiring low-cost equipment and reducing the quantity of harmful chemicals used. This procedure is preferred over other techniques for synthesis of nanorods as single- and poly-crystalline can be produced in an autoclave at high pressure and a low temperature (<200°C). Nanorods are more interesting because their size, shape and crystallographic orientation can be more easily tuned to vertical orientations [99]. As a result, nanorods can serve as good channels that enable orderly electron transfer [100].

As referred, a TiO₂ thin film was previously deposited on 3D structures via PLD. It is crucial parameter for growth of TiO₂ nanorods as the thin film is employed as a seed layer to improve the uniform alignment of nanorods on 3D structures. The role of initial titania seed layer is shown in Figure 2.10. TiO₂ works as a precursor providing preferred sites for the further growth of TiO₂ nanorods. Morphological and structural characteristics such as: phase, aspect ratio or shape of TiO₂ nanorods can be controlled by experimental parameters such as: the pH of solution, the growth time of procedure and the material of substrate. There is a plethora of approaches explaining growth mechanisms of TiO₂, which are interesting and beneficial to this research. Following reactions are occurred for synthesizing TiO₂ nanorods [101]:

Hydrolysis:	$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH$
Dehydration:	$Ti(0H)_4 + Ti(0H)_4 \rightarrow 2TiO_2 + 4H_2O$
	$Ti(OH)_4 + Ti(OR)_4 \rightarrow 2TiO_2 + 4ROH$

The entire reaction via the hydrothermal process between precursor and water is:

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4ROH$$

where R is the component of titanium isopropoxide that designates a butyl-group.



Figure 2.10: Schematic illustration of $\text{Ti}O_2$ nanorods grown on flat substrates via ACG. (a) the result of ACG technique without seed layer of $\text{Ti}O_2$, (b) the result of ACG technique with seed layer of $\text{Ti}O_2$ via PLD.

4. Characterization methods

4.1. Scanning Electron Microscopy (SEM)

SEM is a characterization method, which is based on the interaction of a focused electron beam with the surface of a material. Images of the surface can be produced via differences in the interaction in space. Electrons are accelerated and directed into a sample by an electromagnetic field. Their destination is the surface of a sample in order to interact with it under vacuum conditions. The production of images of a sample is feasible by scanning the electron beam into its surface. When the electron beam hits the surface of a sample, it penetrates the sample to a depth of a few microns and interacts with it as it is shown in Figure 3.1. The depth of the penetration depends on the accelerating voltage and the density of the sample. A lot of signals are produced by the interaction of the electron beam and the sample. In SEM only secondary electrons and backscattered electrons are used for formation of the image.

The backscattered electrons are high energy electrons which originate from the electron beam. They are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with atoms of specimen. The secondary electrons are low energy electrons, which are ejected from conduction or valence bands of the atoms of specimen by inelastic scattering interactions with beam electrons. Due to their low energy, the secondary electrons originate from within a few nanometers below the sample surface. The differences in energy of the collected electrons are turned into differences in light intensity by a detector in space. As a result, an image of the surface of a sample is created [102].

4.2. Energy Dispersive Spectroscopy (EDS)

EDS is a characterization technique, which is used for chemical characterization of materials. This system is usually attached to a SEM system as it is shown in Figure 3.1, using of characteristic x-rays after the interaction of electron beam of a sample. When the electron beam penetrates a sample, there are electron excitations through absorption. Characteristic x-rays are produced via the de-stimulation of electrons. The energy levels of the emitted x-rays correlate to individual chemical elements. As a result, the collection of these x-rays by a detector, reveal the chemical element composition of the investigated sample [103].



Figure 3.1: Schematic illustration of the interaction of an electron beam and the surface of a sample in SEM and EDS.

4.3. X-ray Diffraction spectroscopy (XRD)

XRD, as a characterization technique of a material's structure, is based on the interaction between x-ray beams with electrons in a material. When x-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they originally travel and some (scattering).

Apart from scattering, some photons can be absorbed by the material (absorption) or some may not interact with material (transmittance). If the wavelength of scattered x-rays did not lose any energy, the process is called elastic scattering and only momentum has been transferred in the scattering process. These are the x-rays that are measured in diffraction experiments, as the scattered x-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process, x-rays transfer some of their energy to the electrons. As a result, the scattered x-rays will have different wavelength than the incident x-rays [104].

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic way, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Therefore, by measuring the diffraction pattern, the distribution of atoms in a material can be deduced. The peaks in a XRD pattern are directly related to the atomic distances. Consider an incident monochromatic x-ray beam interacting with the atoms arranged in a periodic manner as shown in Figure 3.2. The atoms can be viewed as forming different sets of planes in the crystal. The path difference for x-rays reflected from a given set of lattice planes, with an interaction distance of d, is $2d\sin\theta$, where θ is measured from the plane. Constructive interference of the radiation reflected from successive planes occurs whenever the path difference is an integral number (n) of wavelengths λ of th x-ray. Thus, the condition for constructive reflection of the incident radiation is:

$2dsin\theta = n\lambda$

which is known as the Bragg equation. So, the above relation describes the condition for a diffraction peak.



Figure 3.2: Visualization of the Bragg equation. Maximum scattered is only observed when the phase shifts add to a multiple of the incident wavelength λ .

For this work, the Grazing incidence XRD (GXRD) was utilized. The difference with the standard XRD set-up is that only the detector of scattered x-rays is moving to different angles but the x-ray source remains at a stable angle θ =1,6°. Measurements were made by θ -2 θ scan, where θ is the angle between the incident beam and the surface of the sample and 2 θ is the angle between the incident beam and the reflected beam which arrive at the detector as shown in Figure 3.3. During the measurement the 2 θ is always two times θ .





Figure 3.3: Illustration of GXRD θ -2 θ scan.

5. Experimental

5.1. MPL materials and experimental set-up

The idea is that the combination of two or more materials with different functionalities in the same system has allowed the preparation of new hybrid materials with advanced properties [48]. A way to accomplish that is to produce materials consisting of both organic and inorganic components. The advantage of these hybrid organic-inorganic materials is that they represent good mechanical and chemical stability, great photosensitivity and they are easily processed. Sol-gel technology provides a very powerful tool for the development of hybrid photosensitive materials.

In this work, the materials used to synthesize the hybrid organic-inorganic material for the MPF method are the methacryloxypropyltrimethoxysilane (MAPTMS) as hybrid monomer and zirconium n-propoxide (ZPO) as the inorganic precursor. Also 4,4'-bis(diethylamino) benzophenone (BIS) was used as the photoinitiator. All chemicals were purchased from Sigma-Aldrich and used without further purification. First, MAPTMS (8:2 molar ratio in respect to ZPO) is hydrolyzed in a flask with the addition of HCL at concertation 0,1M. The mixture is then stirred for 15 minutes until becoming homogeneous. Next, ZPO is added to the solution and the mixture is left for stirring for another 15 minutes. In the next step, BIS is added to the mixture at 1% w/w in respect to the monomer and the solution is stirred for another 15 minutes. In the final step, a filtering process is necessary in order to remove contaminants from the solution. Filters with a pore size 0,22 μ m were utilized for this purpose. The hybrid material is then stored at 4°C for future use [105].

The first step of the sol-gel method is hydrolysis, where monomer units (MAPTMS) are mixed with water and the alkyloxy groups of MAPTMS are replaced with hydroxy groups. HCL is employed as a catalyst. Next, adding ZPO to the mixture results in the second step of the sol-gel process, the condensation, where ZPO is condensed with the hydrolyzed MAPTMS monomer to form a Si - 0 - Zr network. Hydrolysis and condensation procedure takes place simultaneously with gelation process. During gelation, alcohol, water, and any other solvents present are released from the system and the unstructured material shrinks. Sample drying can be done by leaving it at low vacuum conditions for a few hours. This procedure results in the formation of a soft glass matrix onto which there are covalently attached organic methacrylate groups. After TPA, the organic groups attached to the inorganic backbone are polymerized using TPP with the aid of the photoinitiator. The combination of the sol-gel condensation and the effect of irradiation produces a non-shrinkable material, consisting of an organic skeleton rigidified by strong mineral bonds [106].

A thin layer of MAPTMS must be deposited on the surface of the glass substrates before casting droplets of the material to prepare samples for MPL. The aim is to promote structure adhesion during laser writing. First, we immerse glass substrates for 1 hour in an ultrasound machine in acetone, isopropanol and ethanol sequentially to clean them. Next, glass substrates are added to a solution of 20mL dichloromethane and 250µL MAPTMS following 4 hours of stirring. Next, casting droplets of the material on glass substrates is followed, then the samples are dried by placing them at vacuum conditions overnight. As described, during photopolymerization radicals are created forcing chemical bonds to break along the network. The hybrid material used is a negative photoresist, in such materials the absorption of light irradiation results in the cross-linking of polymer chains, making the exposed area insoluble to a solvent [50]. Thus, the unpolymerized material is removed by immersing the samples for 10 minutes into a solution of 4methyl-2pentanone and isopropanol at 1:1 volume ratio. The structural formulas of all chemicals used in MPL process are illustrated in Figure 4.1.



Figure 4.1: Structural formulas of the materials making the new hybrid material (MAPTMS, BIS, ZPO) and structural formulas of the solvents used for sample preparation and curing before and after TPP (CH₂Cl₂, C₆H₁₂O).

In this work, the light source is a femtosecond fiber laser (Toptica Photonics) operating at 780nm, which typically produces pulses larger than 130fs. Its repetition rate is 80MHz and its output power is smaller than 1Watt. The laser beam is shared through a beam splitter (7:3) into two optical paths enabling the existence of two setups. As it is shown in Figure 4.2, a series of mirrors are employed in order to direct the laser beam via various optical components to the sample. On the first set-up called "Nano", a fast mechanical shutter is used to allow passing or not the laser beam. On the other set-up called "Galvo", an optoacoustic modulator is used for the same purpose. In addition, for both set-ups an attenuator is employed to modify the light intensity. Moreover, a two-lens system serving as a telescope is employed as beam expander to adjust properly the laser beam size to overfill the back aperture of the objective lenses for better focusing conditions. Real time monitoring of fabrication process is feasible via a dichroic mirror and a charge-coupled device (CCD) camera. The dichroic mirror is located just before the objective lens and reflects the incoming laser beam but allows green light pass through. Therefore, the sample is illuminated by green light from a led, which is located underneath the sample during laser writing. Due to the difference in refractive index between the polymerized and the unpolymerized material, an image is created in realtime via a CCD camera. The camera is mounted behind the dichroic mirror receiving information and sending them to a computer with which is connected.



Figure 4.2: Schematic illustration of experimental set-up which consists of two paths. On the right side of the figure the focusing of the laser beam through an objective lens on the sample is depicted in more detail.

The main difference between the two set-ups is the way that fabrication occurs. In the "Nano" system, the sample is placed on x-y-z piezoelectric stages and the structures are generated by the stages' movement three-dimensionally while the laser beam remains stable. In the "Galvo" system, the sample is placed on linear stages which moves only in z direction. There is capability for structuring layer by layer as x-y galvanometric mirrors manipulate the laser beam while sample remains immobile. One layer is first hardened using the galvanometric mirrors according to the design pattern and then a new layer of the sample is added by moving the sample in the z direction, thus creating the 3D structure in a layer-by-layer manner. The advantage of using galvo scanners lies in there is no need to slice the design, as the stages can move in a high scanning speed that can be used for the fabrication process while the Nano system is used when high precision is required.

There is the capability to define any kind of the 3D design pattern with its dimensions through computer software. The computer aided manufacturing (CAD) is 'sliced' and each slice is exported an. stl (stereolithography) file. Thus, computer is connected with both set-ups in order to control the fabrication process. There is also ability to modify fabrication parameters like: the light intensity of the laser beam, the estimated time of fabrication process and the exposure time by adjusting the velocity of stages or mirrors respectively. The resolution of microstructures fabricated with TPP is dependent on a number of fabrication conditions and system parameters like laser power, exposure time, distance between two voxels (hatching), the NA of the objective lens, the sensitivity of the photoinitiator. At the end of optical paths and just before the samples, objective lenses are used to focus the laser beam. The sample is localized bottom up in order to avoid distortion the laser beam from already photopolymerized material. Structuring starts from the volume of the material according to the CAD pattern and finish with the structure's last features on the substrate. After photopolymerization, the unpolymerized material is removed and the exposed 3D pattern remained on the substrate by immersing the sample into appropriate solvents. The process is depicted in Figure 4.3. Shrinkage is a common disadvantage associated with polymers due to the change in density before and after curing. By minimizing shrinkage, the desired 3D structures stand can be obtained [107].



Figure 4.3: The four-step fabrication process, from sol-gel method and photopolymerization to structuring and development of the fabricated 3D structure.

5.2. PTT experimental process

In the next experimental step, 3D microstructures underwent a heat treatment step. Thermal treatment is a vital step for this work as there is the need for removal of the organic part of the structures in order to achieve the growth of TiO_2 nanorods on 3D microstructures in the next steps. An effect of PTT is the deformation of structures as the lower part of the structures is attached to their substrate. By decreasing the surface of contact between structure-substrate, the influence of the substrate is decreased. As can be noted from Figure, rods are used to support the desired 3D structure. In this way, nearly isotropic shrinkage and minimum effect from the substrate are achieved. The purpose is to find an efficient way to remove the organic part minimizing the distortion of 3D structures which is crucial for their subsequent role of structures as substrates for TiO₂ nanorods.

3D microstructures were located in a furnace (TL 1100-8, Thermolab, Borel) and heated up from room temperature to 600°C with constant rate of 1°C/min in air atmosphere and left for 1hour. After heat processing, 3D structures are cooled down to room temperature at the same constant rate. 3D structures were fabricated onto silicon wafers. Melting point of silicon is high (1.414°C) thus, silicon as substrate can endure the applied temperatures during PTT. By using the above experimental conditions for the PTT technique, thermal decomposition of hybrid 3D structures is achieved in a controlled manner preserving their complex architecture [108].



Figure 4.4: Schematic illustration of PTT experimental set-up.

5.3. PLD set-up and process

The energy source is a KrF excimer laser operating at 248nm and its pulses last 30 nanoseconds (ns). There is the capability to adjust its repetition rate as well as its operating voltage. As it is shown in Figure 4.5, a set of mirrors is used in order to guide the laser beam to a vacuum chamber. A spherical lens (f=+30cm) before the chamber focuses the laser beam into a spot in order to irradiate the target. The laser beam is introduced to vacuum chamber through a quartz glass, which allows only light from the laser beam to pass. The vacuum chamber is comprised of a pumping system, a vacuum gauge, a target holder and a substrate holder. The pumping system consists of a mechanical pump which is employed to create a preliminary low-vacuum on the order of 10^{-2} mbar and a turbo-molecular pump which is activated on this vacuum in order to reach the pressure on the order of 10^{-6} mbar. These vacuum conditions are essential for plume propagation and pure film growth. The vacuum gauge is achieved by a Pirani and a Penning gauge. The Pirani gauge is used to measure the pressure values between (10^3-10^{-3}) mbar and the Penning is employed to measure lower pressure values at the range of $(10^{-3}-10^{-7})$ mbar.

3D structures, which are prepared via MPF and PTT methods, are employed as substrates. Also, Si (100) substrates, which were previously immersed in acetone and methanol for 10 min, are used as substrates in order to investigate deposition on 3D surfaces. The substrate temperature was maintained at 300°C, 400°C and 500°C during PLD in order to investigate this fabrication parameter [109]. The substrates are placed on the substrate holder at a target-to-substrate distance of 4cm. The beam was incident on a rotating target at an angle of 45° with respect to the target normal. The targets used for ablation were TiO₂ rutile pellets made by pressing rutile powder (Sigma Aldrich, particle size less than 5µm) at 4ton/cm² for 10 min, followed by 2h sintering at 900°C [110].

The first step for the preparation of the PLD process is alignment of the beam optical path so as the laser beam irradiates the target. In this way, there is the ability to calculate laser spot size at target by irradiating a photosensitive paper. A powermeter is utilized to measure the laser beam energy just before the chamber. Therefore, as the spot size of the laser beam is measured there is ability to calculate the laser fluence (energy/surface) and adjust it to the desire value. In this work, the laser fluence is regulated at $2/\text{cm}^2$. The desired vacuum conditions are obtained with the use of the pumping system and vacuum gauge. The vacuum deposition chamber is also provided with a gas inlet in order to deposit TiO₂ thin films in an O₂ atmosphere. During laser ablation, oxygen pressure is constant pressure at 5×10^{-3} mbar using the pumping system [111], [112].

The repetition rate is adjusted at 10Hz and a motor is activated in order to rotate the target holder during the PLD process to avoid repeated ablation from the same spot on the target. Each deposit was grown by delivering a total number of 2000 laser pulses on the target. The number of pulses on the target can be adjusted, either by the repetition rate or the total time of the deposition:

total time (s) = $\frac{\text{number of pulses}}{\text{repetition rate (Hz)}}$

After laser ablation and film growth, both pumps are isolated from the chamber and turned off. There are optical windows along the vacuum chamber so the PLD process can be observed.



Figure 4.5: Schematic illustration of PLD experimental set-up, which is used in this work.

5.4. ACG set-up and process

TiO₂ nanorods with rutile structure were grown via ACG on silicon (Si) wafers coated with a thin layer of mixed-phase of TiO₂ via PLD. The seed layer is essential for the growth of the rutile nanorods by providing nucleation for titania molecules on Si (100) substrates [113]. At growth temperature of 175° C, the growth of rutile nanorods was accompanied by the phase transformation of this base layer from mixed-phased anatase/rutile to rutile. Also, 3D structures, which are deposited with TiO₂ thin film via PLD, are used as substrates for growth of TiO₂ nanorods.

Growth solution is prepared by dissolving 10mL hydrochloric acid (HCL, 37wt%, Fluka) in 10mL of deionized water under magnetic stirring. After 10 minutes of stirring, 340µL of titanium isopropoxide (Ti [OCH(CH₃)₂]₄, 97%, Sigma-Aldrich) is added. Hydrothermally TiO₂ nanorods growth is carried out by suspending the 3D structures with an angle and the coated side was kept face down in a Teflon-lined stainless-steel autoclave (50mL) filled with the growth solution (Figure 4.6). The autoclave containing the substrate was sealed and annealed inside an oven at 175°C for 3h. After that, the autoclave was cooled to room temperature under tap water. The substrate was finally washed with deionized water. Then, drying in air is followed for another 15 minutes [114]. In order to compare the characteristics and the performance of the TiO₂ nanorods on 3D structures, TiO₂ nanorods are also grown on flat substrates coated with TiO₂ thin film as referred above.



Figure 4.6: Schematic illustration of ACG experimental set-up.

6. Results and Discussion

6.1. 3D microstructures via MPL

Scanning Electron Microscopy (SEM) images of the 3D microstructures fabricated via the MPL technique are shown in Figure 5.1. Synthesis of hybrid organicinorganic material SZ2080 without methacrylic acid was previously taken place in order to be used in MPL technique. All of the samples were coated with approximately 10nm in thickness of gold (Au) using a sputter coater in order to deposit a conductive thin film on 3D structures. As a result, images of 3D structures were created through the backscattered electrons in SEM. Surface morphology, width and period of the 3D structures were examined using SEM. These measurements were useful as the fabricated 3D structures had to have the ability to retain their morphology in subsequent experimental steps. In addition, the aim was to fabricate 3D structures which gave high surface-to volume ratio as it is expected the active surface area which interact with the environment is increased inducing enhancement of photocatalytic performance in next steps.



Figure 5.1: SEM images of a 3D microstructure called "cylinders" fabricated via the MPL. (a) Top view, (b) Magnification view of the structure, (c) Higher magnification, (d) Even higher magnification.

In this work, 3D structures with different geometry were fabricated as shown in Figure 5.2 and in Figure 5.3. Their common characteristic is that all 3D structures have a spherical or cylindrical symmetry to withstand the next PTT process. As a result, 3D structures supported by rods in order to minimize their distortion due to substate during shrinkage.



Figure 5.2: SEM images of "cylinders" fabricated via the MPL. (a) Perspective view, (b) Magnified top view of the structure, (c) Magnified perspective view, (d) Side view.



Figure 5.3: SEM images of a 3D microstructure called "rings" via the MPL. (a) Top view, (b) Magnification view of the structure, (c) Perspective view, (d) Side view.

The chemical composition of 3D structures was analyzed through an EDS system, which is integrated in SEM. The EDS system used is INCA Energy EDS X-ray Microanalysis System, constructed by Oxford Instruments. The scanning electron microscope used was the JEOL model JSM-6390 LV and was operated at 15 kV. Due to the limited area of 3D microstructures, the EDS spectra (Figure 5.4) was obtained from 10.000x magnified images. EDS analysis revealed that the fabricated 3D structures have a composition of 22at% C, 16at% O, 48at% Si and 14at% Zr/Au. It was not possible to accurately determine content of light elements using EDS because of its low sensitivity. Also, the accuracy of EDS in quantifying the carbon content may not be sufficient because it is sensitive to the carbon-tape, which sticks the substates of 3D structures on SEM substrate. The existence of the gold (Au) is not related with the material but it is necessary for the implementation of SEM as referred above. Also, it can be observed that here is only one peak for both chemical elements of zirconium (Zr) and Au. The reason is that the electronic transitions in Zr and Au is 2.04 and 2.12keV respectively, which are close enough to cannot be distinguished by the experimental set-up. A Si peak is also present from the Si substrate.



Figure 5.4: EDS spectra from a 3D microstructure fabricated via MPL using the hybrid material SZ2080 without methacrylic acid.

6.2. Ceramic structures after PTT

A study was carried out where the results of the thermal treatment were evaluated in order to conclude to the final designs of 3D structures, which should be fabricated. A crucial parameter in PTT process is the applied temperature. All the presented 3D structures in this work underwent pyrolysis with applied temperature of $T = 600^{\circ}C$ for 1h. The 3D microstructures were heated up with a constant rate of 1°C/min from room temperature and after pyrolysis they were cooled down until room temperature with the same rate. In Figure 5.5 and in Figure 5.6, it is clearly illustrated the 3D structures' skinkrage as a result of the removal of organic part. The degree of shrinkage is examined by measuring 3D structures' dimensions. Before PTT, the characteristic size of 3D structures was $\sim (850 \times 850) \mu m^2$ and after PTT the size was \sim (550 × 550)µm². By calculating it was found that the final structure is about 62-66% of the initial size preserving their original geometry. From literature [53], [62], an increase in applied temperature will result in more effective thermal degradation and larger skinkrage. A 3D structure is $(550 \times 550)\mu m^2$ in x-y dimensions after PTT. A lattice of 3D structures is (5×5) mm², which is the minimum size that can be measured for photocatalytic efficiency in next steps. A lattice of 3D structures is depicted in Figure 5.7.



Figure 5.5: SEM images of "cylinders" after post-thermal treatment at T=600°C for 1 hour. (a) Top view, (b) Magnified top view of the structure, (c) Magnified perspective view, (d) Side view.



Figure 5.6: SEM images of "rings" after post-thermal treatment at T=600°C for 1 hour. (a) Top view, (b) Magnification view of the structure, (c) Higher magnification, (d) Side view.



Figure 5.7: SEM images of "rings" in lattice after post-thermal treatment at 600°C for 1 hour. (a) Top view, (b) Magnification view of the lattice, (c) One 3D microstructure, (d) Higher magnification view.

EDS analysis revealed that the fabricated nanolattices had a composition of 2 at% C, 10 at% O, 64 at% Si and 24 at% Zr/Au (Figure 5.8). In addition, in order to confirm the degree of chemical transformation of the samples, the weight percentage of chemical elements was compared before and after pyrolysis using EDS (Figure 5.9). Thermal degradation resulted in the content of C-O to degrease and the content of all other chemical element to increase. This is because the sum of ratio of all elements is constant in the material.



Figure 5.8: EDS spectra from a 3D microstructure fabricated via MPL and treated at T=600°C for 1hour.



Figure 5.9: EDS spectra from a 3D microstructure fabricated before and after post-thermal treatment at $T=600^{\circ}C$ for 1hour.

6.3. TiO₂ thin film after PLD

Grazing incidence X-ray Diffraction (GXRD) measurements were obtained from TiO₂ thin films, which were deposited via PLD. The purpose is to examine the crystallinity of thin films. The film growth was taken place on ceramic-like 3D structures and on Si (100) wafers as substrates. Typical film thickness was (40 ± 5) nm as measured by a profilometer (Veeko Dektak 150). The layer thickness depends on the experimental conditions in PLD. The influence of deposition parameters on the crystallinity of the deposits was studied by a X-ray diffractometer (Bruker D8 ADVANCE) using Cu Ka ($\lambda = 1.5406$ Å) radiation in the $\theta/2\theta$ configuration. Figure 5.10 presents the $\theta/2\theta$ XRD pattern of a TiO₂ bulk pellet, which is used as target material in PLD.



Figure 5.10: XRD pattern of TiO_2 pellet, which is used as target material in PLD technique.

GXRD patterns obtained from TiO_2 thin films at different applied temperature during PLD were analyzed in order to examine this deposition parameter. Figure 5.11, Figure 5.12 and Figure 5.13 present TiO_2 thin films at T=300°C, 400°C and 500°C respectively. All thin films consist of both rutile and anatase crystalline phases as shown in Figures. The intensity of the XRD peaks depend on the layer thickness of thin films. As the applied temperature is increased, during PLD, the layer thickness of thin films is increased.



Figure 5.11: XRD pattern of Ti O_2 thin film deposited at T=300°C.

The difference between the thin film grown at T=300°C and T=500°C is ~5nm. As a result, the intensity of the GXRD peaks is a little sharper as the applied temperature, during PLD, is increased. The background in GXRD patterns confirms a substantial amount of amorphous material. As the layer thickness is increased, the peaks are increasing showing dominance of the crystalline phase [72]. The peaks of intensity in GXRD patterns were ascribed to the anatase phase according to JCPDS card (No: 21-1272) and to the rutile phase according to JCPDS card (No: 21-1276).



Figure 5.12: XRD pattern of Ti O_2 thin film deposited at T=400°C.



Figure 5.13: XRD pattern of Ti O_2 thin film deposited at T=500°C.

6.4. TiO_2 nanorods after ACG

GXRD pattern was obtained from TiO_2 nanorods. Figure 5.14 shows the phase transformation of TiO_2 nanorods from mixed-phase rutile/anatase to rutile.



Figure 5.14: XRD pattern of Ti O_2 nanorods grown on 2D substrate. Ti O_2 thin film was previously deposited at T=400°C.

The TiO₂ nanorods crystallized in rutile phase as it is expected according to literature [114]. However, TiO₂ nanorods were grown on the mixed-phase rutile/anatase thin film deposited at T=400°C. Figure 5.15 shows the GXRD pattern from TiO₂ nanorods were grown on the mixed-phase rutile/anatase thin film deposited at T=500°C. The results are the same, as expected because the experimental process, in ACG, is the same. The only difference is the absence of the intensity peak which corresponds to rutile (110).



Figure 5.15: XRD pattern of Ti O_2 nanorods grown on 2D substrate. Ti O_2 thin film was previously deposited at T=500°C.

Compositional analysis of TiO_2 nanorods is occurred using EDS analysis (Figure 5.16). EDS revealed the chemical composition of 5at% C, 35at% Ti and 60at% O, which is very close to a 1:2 atomic ratio of Ti to O characteristic of titanium dioxide considering the limited accuracy of EDS.



Figure 5.16: EDS spectrum from a 3D microstructure covered by TiO_2 nanorods.

The morphology and structure of the TiO_2 nanorods were characterized by using SEM. In particular, Figure 5.17 and Figure 5.18 shows SEM images of TiO_2 nanorods. The analysis of these images reveals that the nanorods have an average length of around 2 μ m and diameter of around 100nm.



Figure 5.17: SEM images of TiO_2 nanorods synthesized at 175°C on 2D substrate. (a) Top view, (b) Magnification view of the titania nanorods, (c) Higher magnification, (d) Side view.



Figure 5.18: SEM images of TiO_2 nanorods synthesized at 175°C on 2D substrate. (a) Top view, (b) Magnification view of the titania nanorods, (c) Higher magnification, (d) Perspective view.

6.5. 3D structures covered by TiO_2 nanorods

SEM images of the 3D structures covered by TiO_2 nanorods are shown in Figure 5.19 and in Figure 2.20. ACG process was taken place in order to synthesize TiO_2 nanorods. In order synthesize nanorods directed perpendicular to their substrate and achieve uniform growth of nanorods, the existence of a seed layer of TiO_2 is crucial. Moreover, in Figure 5.21 and in Figure 5.22 the effect of multiple use of TiO_2 target in PLD is depicted. A flower-like growth of TiO_2 nanorods is induced by the multiple use of the target as the deposition of TiO_2 is not uniform.



Figure 5.19: SEM images of a 3D structures covered by TiO_2 nanorods. (a) Perspective view, (b) Magnification view of the titania nanorods, (c) Higher magnification, (d) Even higher magnification.



Figure 5.20: SEM images of a 3D structure covered by TiO_2 nanorods. (a) Perspective view, (b) Magnified perspective view (c) Different perspective view, (d) Magnified top view.



Figure 5.21: SEM images of a 3D structure covered by TiO_2 nanorods. (a) Perspective view, (b) Magnified perspective view, (c) Higher magnified perspective view, (d) Even higher magnified perspective view.



Figure 5.22: SEM images of a 3D structure covered by TiO_2 nanorods. (a) Top view near the 3D structure, (b) Top view, (c) Magnified perspective view, (d) Higher magnified top view.

Figure 5.23 present XRD pattern obtained by 3D structures covered by TiO_2 nanorods revealed again the rutile phase of nanorods. 3D structures were immersed in solution as described at ACG experimental process. The most important step is the deposition if seed layer of TiO_2 thin film via PLD at T=400°C.



Figure 5.23: XRD pattern of Ti O_2 nanorods grown on 3D structure. Ti O_2 thin film was previously deposited at T=400°C.

6.6. Photocatalytic performance

The photocatalytic performance of the TiO₂ nanorods grown on 3D structures was studied by recording the degradation of Methylene Blue (MB) - (C₁₆H₁₈ClN₃S) contaminant under UV irradiation. This is a typical potent cationic dye widely used as model organic probe to test the performance of photocatalysts [115]. The decrease of MB concentration was recorded for 3D structures in lattice of $5 \times 5 \text{ mm}^2$ overall area covered by TiO₂ nanorods, possessing the complex geometry presented in Figure 5.19 As well as, the decrease of MB concentration was recorded on TiO₂ nanorods deposited on flat substrates of the same area (Figure 5.17). Also, the photocatalytic performance was compared with TiO₂ sol-gel films of a proposed method for maximum efficiency [116].

The time evolution of the MB concentration under the UV irradiation is shown in Figure 5.24 for all tested samples. The photolysis curve (black curve in Figure 5.24), recorded in the absence of the TiO₂ photocatalyst, is also displayed for comparison. No change in the concentration of the dye solution was observed, confirming the high resistance of methylene blue to direct photodegradation. This result also confirms that the MB photodegradation occurs onto the TiO₂ nano-structured material surface and is attributed to the reaction of MB with highly oxidative radicals generated on the TiO₂ surfaces under UV irradiation. As clearly seen, the largest decrease occurs in the case of 3D structures covered by TiO₂ nanorods (red curve in Figure 5.24) compared to TiO₂ nanorods grown on 2D surface (blue curve in Figure 5.24). The green curve in Figure 5.24 depicts the photocatalytic degradation of MB on a sol-gel TiO₂ film, which is synthesized according to Mills research [116]. In particular, 3D TiO₂ nanorods induced the degradation of ~91% of the MB, after 30min irradiation, while the TiO₂ nanorods, which are grown on flat substrate provided only ~75% decolorization, after a period of 30min. Respectively, the sol-gel films induced the degradation of ~81%.

In order to quantify the photocatalytic degradation of MB concentration, the apparent rate constant (k) of the reaction has been estimated, according to the equation [111]:

$$\ln\left(\frac{C_{t}}{C_{o}}\right) = -kt$$

where C_o is the initial MB concentration C_t is the concentration after a time interval t k is the decomposition coefficient

The good linear fit of the experimental data to above equation, confirms that the photodegradation of MB on TiO₂ nanostructures follow first-order kinetics. The TiO₂ nanorods grown on 3D structures and TiO₂ nanorods grown on 2D substrates provided apparent rate constants k of 0.059 min⁻¹, 0.027 min⁻¹ respectively, while the value corresponds to sol-gel films is 0.054 min⁻¹. This is in agreement with previous results reported in literature and can be justified on the basis of an optimum surface-to-volume ratio that yields a higher total surface available for interaction with MB. Also, the morphology of 3D structures has larger specific surface area due to its rough morphology, which leads to a strong adsorption ability enhancing the rate of the reaction. Moreover, the lower response of the flat samples can be attributed to the high jamming of the nanorods that in effect reduces the available absorption sites of MB on TiO₂ surface.



Figure 5.24: Methylene blue photodegradation over time under UV light irradiation of TiO_2 nanorods. Blue line refers to TiO_2 nanorods grown on 2D substrate, green line refers to TiO_2 thin film synthesized via a sol-gel method and red line refers to TiO_2 nanorods grown on 3D microstructure.

In addition, the photocatalytic degradation of stearic acid, in above substrates, is shown in Figure 5.25. Stearic acid ($C_{18}H_{36}O_2$) is a widely-used pollutant in industry, which is in bulk phase in contrast to MB which is in liquid phase. Stearic acid has better adhesion on TiO₂ nanorods compared to MB due to the fact that they are in difference phases. Therefore, stearic acid demonstrated higher photocatalytic degradation compared to MB. In particular, the TiO₂ nanorods grown on 3D microstructures induced the degradation of ~93% of the stearic acid, after 15min irradiation, while the TiO₂ nanorods grown on flat substrate provided only ~80% degradation, after a period of 15min. Respectively, the sol-gel films induced the degradation of ~86%.



Figure 5.25: Stearic acid photodegradation over time under UV light irradiation of TiO_2 nanorods. Blue line refers to TiO_2 nanorods grown on 2D substrate, green line refers to TiO_2 thin film synthesized via sol-gel method and red line refers to TiO_2 nanorods grown on 3D microstructure.

7. Conclusions

To summarize, the fabrication and the characterization of 3D structures covered by TiO₂ nanorods is achieved by combining a series of crucial steps. First, hybrid 3D structures were fabricated via the MultiPhoton Lithography (MPL) method. Then, the hybrid structures underwent a Post-Thermal Treatment (PTT) in order to be transformed into 3D structures consisting of a ceramic-like material. The next step was the deposition of a seed layer of TiO₂ on 3D structures by the Pulsed Laser Deposition (PLD) method. Finally, the hydrothermal synthesis of TiO₂ nanorods was achieved using an Aqueous Chemical Growth (ACG) technique. The characterization techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction spectroscopy (XRD) gave important information during fabrication. Finally, the photocatalytic performance of new 3D devices was characterized via photocatalytic degradation of organic pollutants such as methylene blue (MB) and stearic acid. The photocatalytic performance of the 3D structures covered by TiO₂ nanorods was compared with the performance of TiO₂ nanorods grown on 2D surfaces. Also, the performances were compared with TiO₂ sol-gel films of a proposed method for maximum efficiency. The expected increase of photocatalytic efficiency of new 3D devices has been confirmed showing a dramatic decrease of organic pollutants concentration with a decomposition coefficient of $k = 0.059 \text{min}^{-1}$.

8. References

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