Laser induced synthesis and photocatalytic properties of hybrid organic-inorganic composite layers

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Abstract

A laser based method was developed for the synthesis and simultaneous deposition of multicomponent hybrid thin layers consisting of nanoentities, graphene oxide (GO) platelets, transition metal oxide nanoparticles, urea, and graphitic carbon nitride (g-C₃N₄) for environmental applications. The photocatalytic properties of the layers were tested through the degradation of methyl orange organic dye probing molecule. It was further demonstrated that the synthesized hybrid compounds are suitable for the photodegradation of chloramphenicol, a widely used broad-spectrum antibiotic, active against Gram-positive and Gram-negative bacteria. However, released in aquatic media represents a serious environmental hazard, especially owing to the formation of antibiotic-resistant bacteria. The obtained results revealed that organic, urea molecules can become an alternative to noble metals co-catalysts, promoting the separation and transfer of photo-induced charge carriers in catalytic composite systems. Laser radiation promotes the reduction of GO platelets and formation of graphene-like material. During the same synthesis process, g-C₃N₄ was produced, by laser pyrolysis of urea molecules,

without any additional heat treatment. The layers exhibit high photocatalytic activity, being a promising material for photodegradation of organic pollutants in wastewater.

Keywords: laser irradiation; hybrid nanomaterials; noble metal free photocatalysts

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1. Introduction

Following the ground-breaking work of Fujishima and Honda [1], transition metal oxide semiconductor photocatalysts are extensively investigated for environmental remediation, wastewater treatment and air purification [2]. Studies are centered on photocatalytic degradation or mineralization of a wide range of organic contaminants and also pathogens as bacteria and viruses [2-5]. Among organic contaminants, pharmaceuticals, classified as so-called emerging contaminants, attracted the attention of the scientific community. Their release in aquatic environment leads to hazardous mixtures inducing abnormal physiological processes in living organisms [6]. Especially, antibiotic pollution, originating from human and animal medical treatments, represents a severe environmental threat owing to the formation of antibiotic-resistant bacteria, a serious concern both to aquatic and terrestrial ecosystems [6, 7]. Its continuous release into the aquatic system, and the current limitations of the conventional wastewater treatment plants makes antibiotics removal one of the most crucial environmental issue.

Among semiconductor materials, titanium dioxide (TiO_2) is considered the best photocatalyst because of the high oxidation power of its valence band holes and ability to produce reactive oxidizing species (ROS) in water media under UV light irradiation as hydroxyl ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$) [8]. Moreover, TiO_2 is non-toxic and has chemical and photochemical stability [8]. However, UV radiation represents only a small part, about 4-8 % of the total solar emission. For this reason, significant research effort is dedicated equally to synthesize materials which are active in the visible spectral region or to increase the photocatalytic efficiency under UV light irradiation.

Another drawback of semiconductor photocatalysts is the fast recombination of the photogenerated electron-hole pairs which induce the production of ROS necessary for the decomposition of the organic pollutant molecules [8-10]. Photogenerated charge carriers' recombination time is of the order of 10^{-9} s, while the chemical reactions between TiO_2 and adsorbed organic pollutants is in the 10^{-8} - 10^{-3} s range [8]. Thus, the prevention of charge recombination is certainly one of the most important research objectives in photocatalysis implying semiconductor materials. Noble metal nanoparticles have been

reported to act as efficient scavengers for the photogenerated electrons [9-11]. Besides, carbon-based nanomaterials as carbon nanotubes, graphene, or graphene-like reduced graphene oxide (rGO) were found to be good electron conductors contributing to the transport of photo-generated electrons, suppressing their recombination, enhancing the photocatalytic performances of mixed catalysts [12-15]. It is also well-known that carbon-based nanomaterials have exceptional adsorption properties, increasing significantly the concentration of organic pollutant molecules on the catalysts' surface [16]. The higher organic molecules concentration on the catalyst surface leads to the enhancement of the photocatalytic activity of the composite material as compared to bare metal oxide.

In the present study photoactive hybrid organic-inorganic thin films were synthesised through a new laser technique. Photocatalyst layers grown on solid support surfaces are a more feasible alternative as compared to suspensions containing powder-like photocatalysts. The scaled-up in industrial processes of catalysis in form of suspensions is more difficult because of the complex and time consuming particle-recovery processes leading also to additional costs [17]. A laser based materials processing technique, called reactive matrix assisted pulsed laser evaporation (reactive MAPLE) was developed, which allows for simultaneous chemical transformation and deposition of nanomaterials in form of thin films.

During previous investigations MAPLE was found to be a suitable method for the growth of multicomponent thin films, starting from dispersions containing nano-entities as transition metal oxide and noble metal nanoparticles (NPs), as well as graphene oxide (GO) platelets [13-15]. The novelty of the present work consists in the addition of a nitrogen-rich chemical precursor, urea, to the target dispersions consisting of nano-entities. Urea is currently used for the synthesis of g-C₃N₄ by conventional thermal annealing for photocatalytic applications [18, 19]. As compared to TiO₂, g-C₃N₄ has a slightly lower band gap, around 2.7 eV [19], resulting in the extension of the absorption range towards the visible spectral region. Nevertheless, similarly to other semiconductors, the high recombination rate of the photogenerated electrons and holes limits its photocatalytic efficiency. To overcome this drawback, g-C₃N₄ must be mixed with other materials, acting as electron scavengers. Urea was reported to substitute noble metal co-

catalysts which promote the transfer of photoinduced charge carriers, without loss of organic products reduction reactions rates [20]. Acceleration of photoreduction reactions was observed when urea was added to dye sensitized TiO_2 , urea molecules acting as proton transfer mediators [20]. The present investigations revealed that TiO_2 -GO-urea layers containing g- C_3N_4 synthesized from urea during the laser irradiation process is a more efficient catalytic material as compared to TiO_2 -GO or TiO_2 -urea binary compounds. Moreover, the obtained results demonstrate that significant part of urea molecules can be transferred from the target to the substrate surface without any chemical alterations. Methyl orange (MO) organic dye was used as probing molecule for testing the photodegradation efficiency of the synthesized layers. It was further demonstrated that TiO_2 -GO-urea is suitable for the photodegradation of chloramphenicol, a widely used broad-spectrum antibiotic, exhibiting activity against both Gram-positive and Gram-negative bacteria [21, 22]. However, chloramphenicol is also carcinogenic, causing also other physiological reactions as bone marrow depression leading to blood disorders and anemia [22], its removal from aquatic media being of primary importance.

2. Experimental

The experimental workstation used for the synthesis and deposition of the composite layers consists of a stainless steel irradiation chamber and a pulsed UV Nd:YAG ($\lambda = 266$ nm, $\tau_{\text{FWHM}} = 3$ ns, $\nu = 10$ Hz) (Brilliant B, Quantel, France) laser source. Anatase phase TiO_2 NPs with an average diameter of around 20 nm (Sigma Aldrich, 99.5%), GO platelets (NanoInnova Technologies, Spain), and urea powder (Sigma Aldrich, 99.5%) were used as starting materials. Dispersions consisting of 5 wt.% TiO_2 NPs and 2 M urea, 5 wt. % TiO_2 and 5 wt.% GO platelets, as well as 5 wt.% TiO_2 NPs, 5 wt. % GO platelets and 2 M urea in distilled water were prepared and cooled down until solidification in liquid N_2 after thorough sonication. The obtained solid targets were fixed in a double wall target holder and were maintained frozen during the irradiations by circulating liquid N_2 inside the holder walls. The laser fluence at the target surface was fixed at 0.4 J/cm^2 . The laser beam scanned the target surface to avoid irradiation of the same surface location. 10^4 subsequent laser pulses at a repetition rate of 10 Hz were applied for the deposition

of each layer. (001) SiO₂ quartz plates were used as substrates, with 1 x 1 cm² surface area and were positioned parallel to the target surface. The target-substrate separation distance was fixed at 4 cm. The irradiation chamber was evacuated down to a residual pressure of 10⁻³ Pa and then filled with Ar at a pressure value of 20 Pa.

The layers were investigated by field emission scanning electron microscopy (FE-SEM) with the aid of a QUANTA FEI 200 FEG-ESEM system in both secondary electron (SE) and backscattered electron (BSE) emission configurations. The morphology of the laser transferred material and its chemical composition were further studied by transmission electron microscopy (TEM), high resolution TEM (HRTEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDX) using a FEI Tecnai G2 F20 microscope. The crystalline structure of the layers was investigated by fast Fourier transform (FFT) processing of HRTEM images.

The chemical bonds between the elements were investigated by synchrotron FTIR (S-FTIR) microspectroscopy at MIRAS beamline of ALBA synchrotron light source (Barcelona, Spain) [23]. S-FTIR measurements (reflection mode) were performed using the Hyperion 3000 microscope coupled to Vertex 70 spectrometer (Bruker, Germany). This microscope is equipped with a liquid N₂ cooled HgCdTe 50 µm MCT-A detector. The microscope used a 36X Schwarzschild objective (NA=0.65) and a matching 36x condenser. The spectra were obtained using a masking aperture size of 10 µm x 10 µm. Single spectra (9 per sample) were collected in the 4000-700 cm⁻¹ mid-infrared range at 4 cm⁻¹ spectral resolution with 256 co-added scans per spectrum. The chemical bonds were further investigated by X-ray photoelectron spectroscopy (XPS) with the aid of a SPECS XPS spectrometer (SPECS Surface Nano Analysis GmbH, Germany), based on Phoibos 150 electron energy analyser, operated in constant energy mode. The work function of the spectrometer was calibrated to a binding energy of 84 eV for the Au 4f^{7/2} line of metallic gold. A monochromatic X-ray source (Al Kα line of 1486.74 eV) was used for excitation. The measurements were performed in ultrahigh vacuum at around 10⁻⁷ Pa residual pressure. The obtained data were analysed with the aid of the SDP XPS software (version 7.0; XPS International, Mountain View, CA).

The photocatalytic activity of the composite layers was studied by photodegradation tests of model MO organic pollutant molecule and chloramphenicol. The samples were immersed in 2 mL MO or chloramphenicol solutions with 1.25×10^{-5} M (4 ppm) initial concentration (C_0) in quartz vials. The solutions were submitted to continuous stirring during the photodegradation experiments. The concentration changes in time of both organic molecules in aqueous solution was measured by registration of UV-visible absorbance spectra at regular time intervals using a Shimadzu UV-2600 spectrophotometer. The peak absorbance values at 464 and 276 nm of MO and chloramphenicol, respectively, were correlated with the concentration of the solutions. The photocatalytic efficiency (η) of the samples was then calculated at regular time intervals, using the formula $\eta [\%] = (C_0 - C) \times 100 / C_0$, where C_0 is the initial MO or chloramphenicol concentration in the aqueous solutions and C is the concentration measured during the degradation experiments. The photodegradation tests were performed under UV light irradiation, with the aid of a LZC-ICH2 photoreactor, from Luzchem Research Inc, Canada. 16 x 8 W lamps with emission wavelengths centered at 360 nm (300-400 nm emission range, LZC-UVA, Hitachi lamp) were used for irradiations.

3. Results and discussion

3.1. Morphological and nanostructural characterization

FE-SEM images of the TiO₂-urea thin layer are presented in Fig. 1. Both the SE surface topography (a) and BSE (b) images corresponding to the same sample locations are shown. The surface morphology of transition metal oxide layers deposited by MAPLE is characterized by spherical particulates with dimensions ranging from a few tens to hundreds of nm [13, 24, 25]. In contrast to the usual morphology, besides the spherical particulates, lamellar features can be clearly distinguished in case of the TiO₂-urea composite layers (marked areas in Fig. 1a). These regions are not visible in the BSE image of the same surface area (Fig. 1b) suggesting that they are composed by lower atomic number elements, the most probably C and N originating from urea molecules. As known, BSE images are able to provide information on the chemical composition of the surface

since BSE emission coefficient depends on the atomic number of the surface elements, regions with higher atomic number elements appearing brighter [26]. Conversely, the spherical particles can be clearly distinguished in the BSE image, due to the higher atomic number Ti, consisting of Ti oxide.

Fig. 1. FE-SEM (a) SE image and (b) corresponding BSE image of TiO₂-urea thin film. The magnification is the same for both images.

The TiO₂-urea layer was further investigated by TEM, HRTEM, STEM, and EDX and the results are presented in Figs. 2-4. The general TEM image of the sample reveals the existence of different structures, nanocubes and nanosheets with sharp edges shown in more details in Fig. 3a, layered material, and spherical particles with dimensions ranging up to a few tens of nm (Fig. 2a). For part of the spherical particles the TEM image shows a clear contrast between their outer edge and center (Fig. 2a) indicating that they have a hollow structure. Both HRTEM (Fig. 2b) and STEM investigations (Fig. 2c) revealed that the spherical particles are surrounded by a foam-like layered material. EDX investigations were performed in order to obtain information concerning the chemical composition of the spherical particle, zone 1, and surrounding material, zone 2 (Fig. 2c). The EDX spectra (Fig. 2d) are composed by lines assigned to Ti, O, C and N. The small Cu contribution is coming from the TEM microscope grid. However, the relative intensities of the lines are different for the two zones, C and N contributions being much higher in the surrounding material as compared to the spherical particle. As a consequence, it can be concluded that the spherical particles are composed by titanium oxide, covered by an organic material composed by C and N atoms. On the other hand, the surrounding layered material is

mostly organic, with embedded titanium oxide nanoparticles. Further HRTEM investigations confirmed this assumption (Fig. 4).

Fig. 2. (a) TEM, (b) HRTEM, and (c) STEM images of TiO_2 -urea thin film, (d) EDX spectra corresponding to the zones marked in the STEM image (c).

Until some extent similar carbon domains, graphene-like layers formed during the synthesis of MoS_2 nanosheets / TiO_2 nanoparticles system by catalytic acetylene oligomerization [27]. The development of the aromatic domains anchored to the surface of the $\text{MoS}_2/\text{TiO}_2$ photoactive system was found to be promoted by Ti and Mo catalytic sites [23], with special interest for applications in the field of catalysis for advanced green chemistry, H_2 production, or organic pollutants photodegradation.

The HRTEM image of nanocubes and nanosheets is presented in Fig. 3c. The well resolved, lattice fringes with an estimated atomic interlayer distance of 0.352 nm

corresponds to the (101) plane of the anatase phase TiO_2 (tetragonal, space group $I41/amd$, JCPDS 00-021-1272). The angle between the planes is consistent with the theoretical angle between the (101) and (001) crystal planes of tetragonal anatase TiO_2 [28] (Fig. 3c).

Fig. 3. (a) TEM and (b) EDX spectrum corresponding to TEM image (a); (c) HRTEM image and (d) FFT pattern of the zone marked in the HRTEM image (c) of TiO_2 -urea thin film.

The FFT image consisting of bright spots indicate that the TiO_2 nanocrystals are single-crystalline (Fig. 3d). The angle between the planes angles between the planes (101) and (103), (101) and (004), as well as (101) and (114) in Fig. 3d agree well with the theoretically calculated values [28]. Crossed lattice fringes can be also observed, at the superposition of neighboring anatase phase TiO_2 nanosheets (marked areas in Fig. 3c).

On the other hand, the presence of C and N lines in the EDX spectrum (Fig. 3b) indicates that anatase phase TiO_2 nanocrystals are mixed with organic material, the most probably similar to that surrounding the spherical particles.

The HRTEM images of the organic layered structures observed during FE-SEM (Fig. 1) and TEM (Fig. 2) investigations are presented in Figs. 4a, b. The images indicate the formation of an amorphous matrix, supporting nano-sized crystalline domains.

Fig. 4. HRTEM images of (a, b) layered material and (c) spherical particle; FFT images of (d) the marked zone and (e) of whole image as well as (f) line profile along the white line on the particle edge presented in image (c) of TiO_2 -urea thin film.

The measured interplanar distances of 0.352, 0.240 or 0.410 nm can be assigned to the (101) crystallographic plane of anatase phase TiO_2 and (110) as well as (100) lattice

planes of g-C₃N₄ (JCPDS 00-087-1526), respectively. The HRTEM (Fig. 4c) and FFT images (Fig. 4 d,e) of a large, spherical particle similar to those visible in Fig. 2a confirm their anatase TiO₂ composition. The well-defined lattice fringes at the edge of the particle with lattice spacing of 0.352 nm (Fig 4f) and bright spots of the FFT pattern are assigned to the (101) plane of anatase TiO₂ (Fig. 4d). The less intense diffraction spots can be indexed as (114), (004), and (103) crystal planes of anatase TiO₂. In the FFT of the whole surface area of the particle shown in Fig. 4c additional diffraction spots appear around the primary spots (Fig. 4e), due to superposition of crystalline domains, overlapping regions causing double reflection of the electron beam [29].

The TEM and HRTEM images of TiO₂-GO-urea thin film are shown in Fig. 5.

Fig. 5. (a, b) TEM and (c, d) HRTEM images of TiO₂-GO-urea thin film. The FFT pattern in image (c) corresponds to the marked area.

The laser transferred GO platelets are transparent with a wrinkled structure (Fig. 5a). The parallel graphene layers constituting the GO platelets can be clearly distinguished in the HRTEM image presented in Fig. 5b. The surface of the platelets is covered with nanometer sized particles (Fig. 5b). The diffraction spots in their FFT pattern (Fig. 5c) can be assigned to the (101) and (103) lattice planes of anatase phase TiO_2 . Assemblies of TiO_2 nanocrystals, and organic layered material, similar to those observed in case of TiO_2 -urea thin films (Figs. 2-4) can also be clearly identified in Fig. 5a. The atomic interlayer distance of the nanocrystals was estimated to be 0.352 nm, assigned to the (101) plane of the anatase phase of TiO_2 . The Moiré fringes marked by an arrow in Fig. 5d could be attributed to superposition of TiO_2 nanosheets or structural imperfections in some of the TiO_2 nanocrystals, adjacent layers being shifted while stacking.

3.2. Investigation of chemical composition and chemical bonding states

The chemical composition and bonding states between the constituent elements of the hybrid layers was investigated by S-FTIR and XPS. Conventional FTIR microspectroscopy implying global light source offers the possibility to study surface composition with micrometer-sized resolution. However, the signal-to-noise ratio of the FTIR spectra was found to be very low in the spectra of the synthesized samples, the most probably due to the high reduction degree of the laser transferred GO platelets and due to the low quantity of urea. In contrast to conventional FTIR, S-FTIR microspectroscopy due to the ultrahigh brightness of synchrotron IR source, 100 - 1000 times brighter than conventional global sources, can provide FTIR spectra with much higher signal-to-noise ratio, for micrometer-sized sample areas [23, 30]. The baseline corrected S-FTIR spectra of urea reference sample obtained by drop-casting as well as TiO_2 -urea and TiO_2 -GO-urea thin films obtained by MAPLE are presented in Fig. 6 I. The marked region between 1100 and 180 cm^{-1} wavenumbers is presented in more detail in Fig. 6 II. The spectrum of drop-cast sample is constituted by the characteristic bands of urea molecules. The 3428 cm^{-1} band can be assigned to $\nu(\text{N-H})$ asymmetric, out-of-phase stretching vibrations, while the bands at 3332 and 3256 cm^{-1} are present due to the $\nu(\text{N-H})$ in-phase, symmetric stretching vibrations [24, 25].

Fig. 6. S-FTIR micro-spectra of (a) TiO_2 -urea and (b) TiO_2 -GO-urea thin films: (I) general spectra and (II) detailed view of the peaks corresponding to the region marked in (I). The S-FTIR spectrum of urea powder material used for the preparation of the MAPLE targets is also presented.

The highest frequency band in the $1550\text{--}1700\text{ cm}^{-1}$ region, at 1676 cm^{-1} was assigned to both $\nu(\text{C}=\text{O})$ stretching and NH_2 bending vibrations [26]. In other studies, this band was attributed to solely to $\nu(\text{C}=\text{O})$ stretching vibrations [24, 25]. The lower frequency bands at 1619 and 1587 cm^{-1} can be assigned to NH_2 , symmetric $\delta(\text{H-N-H})$ bending vibrations [24, 25]. It was also suggested that the later, 1587 cm^{-1} frequency could be a combination between $\nu(\text{C}=\text{O})$ stretching and NH_2 bending vibrations [29]. The band at 1459 cm^{-1} can be assigned to the $\nu(\text{C-N})$ stretching and asymmetric $\nu_{\text{as}}(\text{N-C-N})$ vibrations [31–34]. The band at 1148 cm^{-1} can be assigned to the H-N-H rocking vibrations [31, 32].

All characteristic bands of urea are present in the spectrum of the TiO_2 -urea thin films (Fig. 6a). However, their relative intensities changed suggesting that part of urea molecules were decomposed and new compounds were formed during the laser irradiation, identified as $\text{g-C}_3\text{N}_4$ during HRTEM investigations (Fig. 4a, b). The bands situated at 1676 cm^{-1} and 1587 cm^{-1} were broadened and slightly shifted toward higher wavenumbers. Moreover, new bands appear at 1624 cm^{-1} and less intense band at 1235 cm^{-1} which can be assigned to $\text{C}=\text{N}$ and C-N stretching vibrations typical for triazine and heptazine ring systems of $\text{g-C}_3\text{N}_4$ [35–37]. Similarly, the broadening and shift of the peaks in the $1400\text{--}1700\text{ cm}^{-1}$ spectral region can be also ascribed to the superposition of urea bands with the stretching and rotation vibration of C-N and $\text{C}=\text{N}$ in CN heterocycles [37–

39]. The Ti-O stretching and Ti-O-Ti bridging modes of titanium oxides are situated at 500-700 cm^{-1} [40]. However, the specific configuration of S-FTIR system do not permitted to register reliable spectra at wavenumbers lower than 700 cm^{-1} . The FTIR spectrum of the TiO_2 -GO-urea thin film (Fig. 6b) is constituted by the same bands observed for TiO_2 -urea sample (Fig. 6a). However, the relative intensity of the peak situated at 1624 cm^{-1} increased as compared to the TiO_2 -urea sample which can be assigned to the superposition of C=C stretching vibration of GO [41, 42] with the C=N vibration of carbon nitride molecules. No additional bands were observed related to oxygen functional groups of GO, the most probably due to the high reduction level of the GO platelets after laser processing.

The C1s XPS spectrum of the TiO_2 -GO composite layer is shown in Fig. 7a.

Fig. 7. C1s XPS spectra of (a) TiO_2 -GO, (b) TiO_2 -GO-urea, and (c) TiO_2 -urea thin films; (d) Ti2p spectrum of TiO_2 -GO-urea thin film.

The spectrum was deconvoluted in four lines. The line C1 situated at the lowest, 284.6 eV binding energy can be attributed to C=C double bonds of the graphite-like sp^2

hybridized C atoms of the conjugated honeycomb lattice of GO platelets. The lower intensity lines, C2-C4 are associated to chemical bonds between C and O atoms of the oxygen containing functional groups of GO platelets [43, 44]. Line C2 centered at 285.5 eV binding energy can be assigned to C-OH hydroxyl groups and the C3 line situated at 286.6 eV to C-O-C epoxide groups of GO platelets [43, 44]. The C4 line centered at 289.1 eV could include contributions from both carbonyl $>C=O$ and $O=C-OH$ carboxyl groups of GO [43, 44]. However, their low intensity and peak areas suggest that commercial GO platelets were highly reduced during laser irradiation. These features are comparable to previous results [13-15].

The C1s spectrum of the TiO_2 -GO-urea layer reveals a higher reduction degree of GO platelets during laser irradiation in the presence of urea molecules (Fig. 7b). Both the intensity and the areas of C2 and C3 lines are diminished, as compared to the C1s spectrum of the TiO_2 -GO layer (Fig. 7a).

As reported, during conventional thermal treatment, at 600 °C urea molecules decompose generating volatile reducing species which promote the removal of oxygen containing groups of GO sheets [45], a green route to produce graphene-like materials. A similar process takes place the most probably during the laser irradiation of urea containing composite targets. Moreover, in the C1s spectrum of TiO_2 -GO-urea layer an additional peak, noted C5 in Fig. 7b can be observed at 290.0 eV, and could be attributed to $O=C-N$ bonds [46] of urea molecules. Additionally, the intensity of the C4 line is significantly higher as compared to the spectrum of the TiO_2 -GO composite layer which could be assigned to the contribution of sp^2 bonded C, $N=C-(N)_2$ bonds, usually observed in the C1s spectra of carbon nitrides and aromatic skeleton rings of $g-C_3N_4$ [34, 37, 38, 47]. Indeed, the C4 and C5 lines are present also in the C1s spectrum of TiO_2 -urea layer (Fig. 7c), which confirm the previous assumptions. The intense C2 line of the spectrum was attributed to binding of hydroxyl groups to C atoms of the aromatic ring of $g-C_3N_4$ or H atoms bonded to the edges of the $g-C_3N_4$ in the form of $C-NH_2$ and $C-NH$ bonds, frequently observed in $g-C_3N_4$ obtained by urea pyrolysis and attributed to the incomplete polymerization of precursor urea molecules [34, 48]. As a consequence, these bonds could contribute also to the C2 and C3 lines of the C1s spectrum of the TiO_2 -GO-urea layer (Fig. 7b).

The Ti2p XPS spectra of the TiO₂-urea, TiO₂-GO and TiO₂-GO-urea composite thin films are very similar. The Ti2p_{3/2} line of the Ti2p doublet in all spectra is situated at 459.3 eV, coinciding with the value assigned to Ti⁴⁺ oxidation state of stoichiometric TiO₂ (Fig. 7d) [49, 50]. Besides, the lines are highly symmetric, without detectable shoulder peaks, which indicate the absence of titanium sub-oxides, or other, Ti-N or Ti-C bonds confirming the HRTEM results.

The intensity of the N1s XPS peak registered for the TiO₂-GO layer is very low (Fig. 8a) and corresponds to molecularly chemisorbed nitrogen.

Fig. 8. N1s XPS spectra of (a) TiO₂-GO and (b) TiO₂-GO-urea thin films.

The N1s spectrum of the TiO₂-GO urea layer can be deconvoluted in two lines denoted N1 and N2, centered at 400.2 and 401.0 eV, respectively. The N1 line can be assigned to

C=N double bonds, C=N-C in which each N atom is bonded to two C atoms from the aromatic rings of g-C₃N₄ located at the edges of the graphite planes, while the high energy peak, N2 corresponds to N-C single bonds N-(C)₃ of g-C₃N₄, as well as O=C-N and C-NH₂ groups of urea molecules [34, 37, 38, 47].

3.3. Evaluation of photocatalytic properties

The results of MO photodegradation tests under UV light irradiation are presented in Fig. 9(I). The self-degradation of MO under UV light in the absence of catalytic material is also shown, (a) in Fig. 9(I)). The highest photodegradation efficiency was measured for the TiO₂-GO-urea composite layer, reaching 60 % of the initial dye concentration, after 450 min of irradiation time (d). On the other hand, the binary compound layer TiO₂-urea has a photocatalytic efficiency of 37 % (b), while TiO₂-GO around 45 % after 450 min irradiation time (c).

Fig. 9. (I) (a) Self-degradation efficiency of MO under UV light irradiation and photocatalytic degradation efficiency of MO in the presence of (b) TiO₂-GO, (c) TiO₂-urea, and (d) TiO₂-GO-urea thin films, measured at regular time intervals; (II) successive degradation cycles of MO in the presence of TiO₂-GO-urea layer under UV light irradiation.

As reported, urea molecules added to TiO₂ catalysts accelerate photoreduction reactions acting as efficient proton transfer agent [20]. Thus, urea molecules could substitute noble-metal co-catalysis required for the separation and transfer of photoinduced charge

carriers. Moreover, g-C₃N₄ molecules contribute to the reduction of charge recombination rate. The conduction band (CB) and valence band (VB) edge potentials of g-C₃N₄ are situated at around -1.39 and 1.54 eV, respectively, while the CB and VB edge potentials of TiO₂ are at around -0.35 and 2.85 eV, respectively [47, 48].

Under UV light illumination, both g-C₃N₄ and TiO₂ can contribute to the formation of electron-hole pairs and thus, generation of reactive species responsible for the degradation of organic molecules (Fig. 10). The photogenerated electrons can be transferred from the CB of g-C₃N₄ to the CB of TiO₂ by interfacial interactions, reducing the electron-hole recombination rate [51, 52]. The electrons from the CB edge of TiO₂ can directly reduce O₂ to form the reactive superoxide radical ions •O₂⁻ (-0.33 eV for O₂/•O₂⁻). In the same time, the TiO₂ VB holes can directly oxidize H₂O into •OH radicals (2.37 eV for H₂O/•OH) [50, 51].

On the other hand, the reduced GO platelets in the TiO₂-GO and TiO₂-GO-urea samples act as photogenerated charge separators and transporters, highly reduced GO being good electron conductor [53-55]. The electron-sink function of GO was reported to be responsible for the higher photocatalytic activity of the TiO₂-GO sample as compared to pure TiO₂ [13, 14, 54, 55]. Moreover, as reported, reduced GO alone can be used also as a photocatalyst under UV or visible light irradiation, depending on its reduction level [50], thus contributing to the generation of electron-hole pairs in the TiO₂-GO and TiO₂-GO-urea composite layers.

The reusability of the composite layers was tested by repeated degradation cycles (Fig. 9 II). The samples were rinsed in distilled water and air-dried after each degradation run. The TiO₂-GO-urea sample retained a photodegradation efficiency of about 50 % after the second and about 35 % after the third degradation cycle (Fig. 9 II). This decrease could be attributed to various factors, as adsorbed organic molecules [55-57], changes of the chemical composition of the catalysts as the gradual transformation of oxides to hydroxides [14], as well as to the gradual dissolution of water soluble urea during the degradation process.

In Fig. 10 I both the photolysis of chloramphenicol in the absence of catalytic material (a) under UV light illumination and the photocatalytic decomposition efficiency in the presence of TiO₂-GO-urea ternary compound layer (b) are presented.

Fig. 10. (I) (a) Photolysis of chloramphenicol under UV light irradiation and (b) photocatalytic degradation efficiency of chloramphenicol in the presence of TiO₂-GO-urea thin film, measured at regular time intervals; UV-visible spectra of chloramphenicol measured at regular time intervals under UV light irradiation (II) without catalyst and (III) in the presence of TiO₂-GO-urea thin film.

The photolysis of chloramphenicol under UV light illumination was widely investigated and was found to be strongly influenced by both the wavelength and the intensity of the UV lamps [58]. In the present experiments, after 450 min of UV light illumination the removal of chloramphenicol by photolysis was about 33 % of the initial concentration. The characteristic absorption of chloramphenicol at 276 nm wavelength can be observed in the UV-vis absorption spectrum before photolysis (Fig. 10 II, the spectrum registered at 0 min). However, this absorption maximum is shifted at 283 nm after 30 min of UV irradiation. Moreover, during photolysis new absorption band appear in the UV-visible spectra of chloramphenicol solution at 311 nm, after only 15 min irradiation time (Fig. 10 II). The peaks at 283 and 311 nm were associated to the formation of by-products, carboxamide and 4-nitrophenol by-products, respectively during UV light irradiation [59]. Subsequent degradation of by-products leads to the decrease of absorbance bands with the increase of the irradiation time.

Similarly, as during photolysis, by-products formation starts after the first 15 min of UV irradiation time also in the presence of TiO₂-GO-urea catalyst layer (Fig. 10 III).

However, the absorption peaks corresponding to the by-products diminished considerably after 120 min irradiation. In the presence of TiO₂-GO-urea catalyst layer the degradation rate of chloramphenicol from the aqueous solution was doubled, around 60 % of the initial concentration as compared to photolysis, for the same, 450 min irradiation time, proving the photodegradation efficiency of the synthesized hybrid layer.

Conclusion

A simple, one-step laser based method was developed for the synthesis and deposition of multicomponent organic-inorganic photoactive layers. Aqueous dispersions of semiconductor inorganic nanoparticles, commercial graphene oxide platelets, and organic, urea molecules starting materials were submitted to laser irradiation. The technique allowed for the formation of g-C₃N₄ from urea without any additional thermal processing, in contrast to the reported synthesis techniques implying high calcination temperatures. The layers composed by TiO₂ semiconductor nanoparticles, graphene oxide reduced during laser processing, g-C₃N₄, and urea exhibited high photocatalytic activity in degradation of organic dye molecules. Furthermore, these layers efficiently reduce antibiotic, chloramphenicol molecules with a degradation rate doubled as compared to UV light induced photolysis. The versatility of the technique open new pathway for light induced synthesis of materials and new compounds starting from organic molecules. The main advantage of the technique is that synthesis and deposition processes take place during the same technological step. It is also believed that laser light induced photochemistry could become a fast and energy efficient alternative to conventional materials synthesis methods, avoiding the use of additional chemical substances or high temperature annealing processes. Possible difficulties related to the water-dispersibility of the base materials during the MAPLE target preparation could be overcome by surface functionalization with more hydrophilic ligands.

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