α-Ga$_2$O$_3$ as a Photocatalyst in the Degradation of Malachite Green

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α-Ga$_2$O$_3$ is a wide-bandgap semiconductor material which was prepared by a novel synthesis method from metallic gallium. It is characterized by X-ray diffraction, infrared spectroscopy, ultraviolet spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy. This oxide was also evaluated as a photocatalyst toward the decomposition of malachite green (MG). X-ray photoelectron spectroscopy was used with the purpose of analyzing the changes on the surface of the material before and after the photocatalytic reaction. The results found by X-ray diffraction shows that alfa phase did not transform to another crystalline phase during the reaction. However, a slight change on the relative intensities of the planes (104) and (110), may explain the variation of the morphology of the oxide, associated to a preferential particle erosion. High resolution XPS analyses revealed a shift toward lower binding energies of the O 1s level after the photocatalytic reaction, suggesting the presence of oxygen bound to carbonyls or alcohols. Organic nitrogenous residues associated to MG were also detected by the presence of the N 1s band observed at 396.7 eV.

The methods of synthesis of gallium oxides are a challenge that provide information about the vacancies in the crystal structure. Among semiconductor metal oxides, gallium oxides exhibit a wide band gap energy between 4.2 and 4.9 eV. These oxides have five crystalline phases: α, β, γ, δ and ε, from which the most stable are the α and β phases. Even though the α phase is stable, it has been little explored in photocatalytic reactions in aqueous media, being the β phase the most studied for this purpose. This was one of the main reasons of this investigation, focused in the degradation of the malachite green by means of nanostructured α-Ga$_2$O$_3$. About the photocatalytic properties of other Ga$_2$O$_3$ phases, Jin et al. reported photocatalytic activity of the γ phase in rhodamine-590 degradation.

The methods of synthesis of gallium oxides are a challenge that must be solved to make way for applications. The synthesis methods reported in the literature for these oxides are sol-gel, hydrolysis, sonochemical processes, heat-assisted microwave, biominalization and precipitation, as well as post-synthesis hydrothermal treatments. Applications found for gallium oxides are in different areas like sensors, photo electronics, adsorption, optical or fluorescent materials, in electrochemistry, solar cells, blue light emitters and photocatalysis, among others.

On the other hand, the photocatalysis is greatly determined by the morphology and size of the materials; for example, Fut et al. studied three polymorphic structures of gallium oxide (α, β and γ) of which the alpha phase showed greater photocatalytic activity. Their results also showed that the morphology of the precursor (GaOOH) and its subsequent calcination controlled the formation of α-Ga$_2$O$_3$. Further photocatalytic experiments performed with two different morphologies demonstrated the key role of the morphology on the degradation of acid orange and Cr(VI). Therefore, controlling the morphology and surface area are of interest because the oxides are affected in their physicochemical properties by crystalline defects, such as oxygen vacancies.

Malachite green (MG) is an organic dye containing three aromatic rings linked by covalent bonds, which confer great stability to the molecule. The latter gives to MG characteristics of light absorption in the visible region, which are attributed to the conjugated system of bonds corresponding to its structure of benzene rings. The triphenylmethane dyes, when presenting these conjugated bonds in their aromatic groups, are quite stable and together with a low solubility they become highly persistent compounds in the environment. Besides, they are not easily degradable by common chemical or physical means.

This work proposes the study of the α-Ga$_2$O$_3$ phase as a photocatalyst in the degradation of MG in aqueous media. α-Ga$_2$O$_3$ was produced from metallic gallium through the following sequence of reactions:

\[ \text{Ga}^+ + 6 \text{HNO}_3 \rightarrow \text{Ga}^{3+} (\text{NO}_3)_2 + 3 \text{H}_2\text{O} + 3 \text{NO}_2 \]  

\[ \text{Ga}^{3+} + 3 \text{OH}^- \rightarrow \text{Ga(OH)}_3 \]  

\[ \text{Ga(OH)}_3 \rightarrow \text{GaOOH} + \text{H}_2\text{O} \]  

\[ 2 \text{GaOOH} \rightarrow \text{Ga}_2\text{O}_3 + \text{H}_2\text{O} \]  

The synthesized material was characterized by infrared spectroscopy, ultraviolet spectroscopy, X-ray powder diffraction and scanning electron microscopy. After the photocatalytic degradation of MG, a study concerning the surface characteristics of the catalyst was done using X-ray photoelectron spectroscopy (XPS). For the case of gallium oxides, XPS can be a handy tool to know if there are changes in the oxidation state of gallium and oxygen ions. Moreover, XPS can provide information about the vacancies in the crystal structure.
Figure 1. XRD patterns of: (a) gallium oxyhydroxide used as a precursor and (b) $\alpha$-Ga$_2$O$_3$ and its crystalline planes before and after photocatalysis.

Figure 2. (a) GaOOH particles obtained from metallic gallium, (b) $\alpha$-Ga$_2$O$_3$ synthetized through the dehydration of the precursor GaOOH, (c) $\alpha$-Ga$_2$O$_3$ after being used in the photocatalytic degradation of MG.

Figure 3. Aspect ratio results obtained from: (a) GaOOH synthesized by precipitation, (b) $\alpha$-Ga$_2$O$_3$ as a calcined product and (c) gallium oxide removed after MG degradation.
Material characterization.—X-ray diffraction (XRD) patterns were collected with an Empyrean (PanaAnalytical) diffractometer, having a copper anode excited at 45 kV and 30 mA. The wavelength of the Cu Kα radiation is 1.5406 nm. The diffraction pattern was collected using a step of 0.02° and the acquisition time was 20 s at each step. The analysis by infrared spectroscopy (IR) was done with the attenuated total reflectance (ATR) mode with a Thermo Scientific instrument, model Nicolet iS5-iDS-ATR. For each sample, spectra ranging from 500 to 4000 cm⁻¹ were averaged with a resolution of 4 cm⁻¹. For this purpose, 2 mg of gallium oxide was suspended in 6 ml of distilled water and stirred with ultrason for 15 min. Afterwards, the sample was left to rest for 3 minutes and the supernatant was transferred to a quartz cuvette for spectrum reading using a Thermo Scientific Genesys 10S UV–vis spectrophotometer, collecting the spectra with a resolution of 1.8 nm. Determination of the bandgap energy was carried out through mathematical treatment of the UV–vis spectra. The spectra were treated with the Tauc equation, which is given by the relationship $E_g = \frac{(hv)^{1/2}}{\alpha}$, where $E_g$ is the bandgap energy (eV), $h$ is Planck's constant, $v$ is frequency (1/2) and $\alpha$ is absorption coefficient. The $E_g$ value is obtained from the intersection of the linear part after plotting $(\alpha h v)^{1/2}$ versus hv. A scanning electron microscope (Tescan, Mira) was used to analyze the morphology of the samples. The powder samples were placed on a double-sided carbon tape. The images were obtained with a potential of 20 kV and were used to determine the aspect ratio of particles using the ImageJ software. The XPS analyses were performed with a SPECX system with Phoibos 150 analyzer. It has a Mg/Al X-ray source operating at a potential of 10–14 kV.

Results and Discussion

Figure 1a shows the XRD pattern of a sample obtained by precipitation using ammonium hydroxide, where the most intense reflections are observed for 2θ = 21.4, 33.7 and 37.4°. The search of this pattern in the International Crystallography Diffraction Database (ICDD) indicates that it matches with gallium oxyhydroxide (GaOOH), with file number 054-0910. The above reflections correspond to the crystallographic planes (110), (130) and (111), respectively.

Figure 1b shows the pattern of the product obtained after calcination, in this case, intense reflections were observed in the 2θ = 33.7 and 36°. The profile matched with that of α-Ga2O3 reported in the ICDD with number 006-0503, and the more intense diffraction lines correspond to the planes (104) and (110). This result indicates that calcination at 600°C produced single phase α-Ga2O3. The lack of literature about this material is associated to its low stability in applications such as a catalyst. In previous studies, it has been observed that aqueous solutions of organic compounds can transform the alpha phase. However, in the conditions of degradation of MG of this work this did not occur, because the XRD profile of the powder retrieved after the photocatalytic degradation is similar to that of the powder before the reaction. A slight change is observed in the relative intensities of the planes (104) and (110), suggesting a variation on the population of these planes, a fact that may be due to a preferential erosion of the crystallites, where the plane (104) was preferably affected.

By scanning electron microscopy, the morphology of gallium oxyhydroxide obtained at pH = 7 corresponds to ellipsoids, as shown in Figure 2a. This shape is preserved after its thermal decomposition producing α-Ga2O3 (Figure 2b). It can be observed in Figure 2c that gallium oxide removed from the MG degradation reaction maintains its morphology, which indicates that this compound is stable. However, the suspicion of a slight degradation observed in the XRD profile was verified when the particles were measured, and the length to width aspect ratio was measured. Figure 3 shows the histograms of the aspect ratios obtained from the corresponding SEM micrographs.

Of particular interest is the change in the aspect ratio of gallium oxide after the photocatalytic degradation of MG. It can be noted that the average aspect ratio was 2.5; however, after the reaction, there is a dispersion of values in such way that the population of particles with greater aspect ratio increased, given by an increase of length or a decrease of width. The latter is consistent with the result of XRD.
suggesting preferential erosion; therefore, the grain edges oriented to the plane (104) could be associated to the degradation reaction.

Infrared spectroscopy patterns (Figure 4) display the expected bands of GaOOH, where the symmetric stretching of O-H groups appears at around 3450 cm\(^{-1}\), whereas the Ga-O-H bending mode is located at 750 cm\(^{-1}\) and the Ga-O stretching and Ga-O-Ga torsion are found at approximately 600 and 550 cm\(^{-1}\), respectively.\(^{21–25}\) The spectrum of \(\alpha\)-Ga\(_2\)O\(_3\) is composed by bands of Ga-O-Ga torsion movements at around 600 and 500 cm\(^{-1}\).\(^{24–26}\)

Figure 5 shows the infrared spectrum of \(\alpha\)-Ga\(_2\)O\(_3\) retrieved after MG degradation. Here there are additional bands corresponding to organic residues adsorbed from the reaction medium. One of these signals appears at around 3450 cm\(^{-1}\), which can be attributed to O-H, indicating the formation hydroxyl radicals that have been previously reported for gallium oxide.\(^{27}\) On the other hand, the formation of GaOOH, which can be an alternative way to explain the photocatalytic properties of \(\alpha\)-Ga\(_2\)O\(_3\), should be detected in the corresponding XRD pattern, because the population of OH\(^{-}\) groups is high enough according to the IR spectrum. Therefore, since the presence of GaOOH was not observed by XRD, the results suggest that the pathway for the decomposition of MG was by an oxidation reaction. Another evidence of the latter is that the advance of oxidation would produce carbonyl groups (C=O) and this formation is consistent with the presence of the band at 1600 cm\(^{-1}\), shown in Figure 5.\(^{28}\) Furthermore, the generation of carboxylates associated to a pair of bands at 1550 and 1300 cm\(^{-1}\) may confirm the proposed pathway.\(^{27,28}\) Moreover, gallium oxide signals continue to be present at 600 cm\(^{-1}\), associated to the Ga-O-Ga torsion mode.\(^{27,28}\) Based on this evidence, the degradation of MG catalyzed by gallium oxide follows a gradual oxidation route.

According to the literature, the bandgap energy of gallium oxyhydroxide, determined by UV-vis spectroscopy, is between 4.75 and 5.06 eV; whereas for gallium oxide spans from 4.8 to 4.9 eV.\(^{29–33}\) In this work, the bandgap energy value obtained for GaOOH and \(\alpha\)-Ga\(_2\)O\(_3\) was the same for both compounds (5 eV) and is consistent with the literature (Figure 6). A gallium oxide sample taken after the degradation of malachite green was analyzed, and a slight reduction of the bandgap energy to 4.5 eV was measured (Figure 6c). This change may be influenced by the preferential erosion of \(\alpha\)-Ga\(_2\)O\(_3\) particles detected by XRD. The latter should involve the formation of crystalline defects, where oxygen vacancies may be present. A possible phenomenon of surface functionalization may also took place, which is witnessed through the by-products generated during the MG degradation and detected by IR spectroscopy, such as oxidized species.\(^{34–37}\)

To understand what occurred on the surface of \(\alpha\)-Ga\(_2\)O\(_3\), XPS was performed before and after the photocatalytic degradation of malachite green. The wide survey scans of these samples are shown in Figure 7. The main peaks of these spectra are associated with the gallium and oxygen electronic levels, as well as those corresponding to nitrogen. The latter appear mainly on the sample retrieved after photocatalysis, which can be attributed to by-products containing nitrogen. The main peaks of gallium are located at 1119.87 eV for Ga 2p\(_{3/2}\), 1146.54 eV for Ga 2p\(_{1/2}\) and 20.4 eV for Ga 3d, whereas for O 1s level it can be observed at 530.97 eV. In the case of nitrogen, the N 1s level can be identified by a peak centered at 397.12 eV. It is worth to note that all these results agree with those reported in the literature.

Before the photocatalysis, the spectrum obtained for the gallium at level 2p\(_{3/2}\) consists of two components at 1145.4 and 1147.3 eV (Figure 8a). After photocatalysis, only one component is observed at 1145 eV (Figure 8c), so it can be said that the gallium species that generates the component at 1147.3 eV were transformed during
photocatalysis. It is known that for polymers, XPS spectra are shifted to higher energies when oxidized.\textsuperscript{38,39} In this case, the gallium species that generated the 1147.3 eV peak may have participated in the reaction and were reduced to form only the 1145.4 eV signal. This gallium reduction may have generated the MG oxidation detected by IR spectroscopy. For the Ga 3d level, a similar trend can be noticed; before the photocatalysis there are 3 signals (Figure 8b), and the peak corresponding to a larger bond energy disappeared after the photocatalysis. Since the energy values reported here are congruent with those already published for gallium hydroxide, our results indicate that gallium species were reduced during the photocatalysis, forming Ga-OH species.\textsuperscript{40}

The spectrum of the N 1s level was also analyzed and a signal corresponding to NO\textsubscript{x} residues formed during the synthesis process was detected (Figure 9b).\textsuperscript{41} Through the deconvolution of this curve, three main components were found (398.0, 395.9 and 393.3 eV) all of them associated to NO\textsubscript{x} species. After photocatalysis, α-Ga\textsubscript{2}O\textsubscript{3} continues presenting the N 1s signal, with two components still present (394.7 and 392.7 eV), that are very close to those found before the photocatalysis (Figure 9d). However, the component with the largest intensity of this spectrum is located at 396.4 eV, which is consistent with the presence of organic nitrogen residues.\textsuperscript{42,43} The disappearance of the component in 398.0 eV may suggest that nitrogen species were also involved in the oxidation degradation process of MG.\textsuperscript{44}

The O1s spectrum of α-Ga\textsubscript{2}O\textsubscript{3} before the photocatalytic process was represented by two curves centered at 531.9 and 530.9 eV (Figures 9a).\textsuperscript{41,45} Since gallium and nitrogen are present in the pristine sample, the component at 531.9 eV can be associated to oxygen in gallium oxide, whereas the signal at 529.6 eV corresponds to oxygen contained in the NO\textsubscript{x} compounds. After photocatalysis, the spectrum shifted to lower energies and the deconvolution revealed the presence of two peaks corresponding to energies of 530.6 and 529.6 eV. These values are congruent with the presence of gallium oxides or hydroxides (530.6 eV).\textsuperscript{45} The peak centered at 529.6 eV agrees with the reported energy value of oxygen bonded to carbon (carbonyls or alcohols). This result suggests that MG degradation occurs through an oxidation process, as detected by IR spectroscopy, where the oxidizing agents are gallium oxides and nitrogen oxides.\textsuperscript{46}

The experiments for the photocatalytic degradation under UV radiation of MG were performed using 10 and 30 mg of α-Ga\textsubscript{2}O\textsubscript{3}; Figures 10a and 10b show the corresponding UV-vis spectra. From these results it is possible to observe a decrease on the intensity of the absorbance with exposure time. The degradation percentage was calculated from the main band of MG centered at approximately 617 nm. Figure 10d shows that after 360 min of exposure to UV the degradation was 45.8%, when 30 mg of α-Ga\textsubscript{2}O\textsubscript{3} were used, whereas with 10 mg a degradation of 40% was measured. Then, is possible to conclude that the concentration of gallium oxide increased the degradation rate of the dye. On the other hand, the UV-vis spectra obtained from a MG solution irradiated with UV, without α-Ga\textsubscript{2}O\textsubscript{3}, is shown in Figure 10c. The latter revealed that the exposure to UV contributes to the decomposition of MG, but when it is combined with α-Ga\textsubscript{2}O\textsubscript{3} as photocatalyst an increase on the oxide-reduction process can be achieved, as shown in Figures 10a and 10b.
Figure 9. High-resolution XPS spectra corresponding to: a) O 1s and b) N 1s before the photocatalytic process; c) O 1s and d) N 1s after photocatalysis.

Figure 10. UV-vis spectra showing the photocatalytic degradation of MG when (a) 10 mg and (b) 30 mg of $\alpha$-Ga$_2$O$_3$ were used; (c) effect of UV radiation on the decomposition of MG and (d) calculated degradation percentages.
Conclusions

The synthesis of gallium oxyhydroxide was performed from metallic gallium and after calcination at 600°C single phase $\alpha$-Ga$_2$O$_3$ was obtained. The mechanism of degradation of malachite green proposed in this work involves the oxidation of the dye. The intermediates generated during the photocatalysis show different degrees of oxidation (OH$^-$, C=O and COO$^-$) and were absorbed on the surface of the catalyst. The identification of them was performed through different analytical techniques. It was found that the oxidation process was consistent with the information obtained by XPS, where the loss of oxygen species from the catalyst could contribute to the redox process. Moreover, the oxygen vacancies formed in $\alpha$-Ga$_2$O$_3$ could be involved in the decrease on the bandgap energy measured on samples obtained after the photocatalysis.

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