UV and Visible light photodegradation of methylene blue with graphene decorated titanium dioxide

M A Acosta-Esparza, L P Rivera, A Pérez-Centeno, A Zamudio-Ojeda, Daniel Ramírez González, A Chávez-Chávez, M A Santana-Aranda, J Santos-Cruz and J G Quiñones-Galván

1 Unidad Académica de Física, Universidad Autónoma de Zacatecas, Calzada Solidaridad esq. Paseo de la Bufa s/n, Zacatecas, Zacatecas, C P 98060, México
2 Centro Láser, Universidad Politécnica de Madrid, Spain
3 Departamento de Física, Centro Universitario de Ciencias Exactas e Ingeniería, Universidad de Guadalajara, Boulevard Marcelino García Barragán 1421, Guadalajara, Jalisco, C P 44430, México
4 Posgrado en Físico Matemáticas, Centro Universitario de los Valles, Universidad de Guadalajara, Carretera Guadalajara-Ameca, Km 45.5, C.P. 46600, Ameca, Jalisco, México
5 Facultad de Química, Materiales, Universidad Autónoma de Querétaro, Querétaro C P 76010, México

E-mail: jose.quinones@academicos.udg.mx

Keywords: graphene, TiO2, visible photodegradation, composites

Supplementary material for this article is available online

Abstract
Photocatalytic degradation of methylene blue by graphene decorated titanium dioxide (TiO2) powders heated at different temperatures was analyzed. The powders were prepared by mixing TiO2 with graphene prepared by the modified Hummers method. A thermal treatment was applied to mixed and pure TiO2 powders with the aim of analyze their structural dependence on temperature, and consistently their photocatalytic degradation effect on methylene blue solutions exposed to UV and visible radiation. Structural characterization of the powders was carried out by x-ray diffraction and Raman spectroscopy. When irradiated with UV, the mixed powders showed as high as 87% photocatalytic degradation, while the pure TiO2 reached values of 59%. For visible radiation, as it is expected, the pure TiO2 showed no activity, while the mixture presented degradation of 40%.

Introduction
Semiconductor photocatalysis is an emerging field in materials science due to its application in environmental remediation. Among the semiconductors studied for photocatalysis, TiO2 is one of the most attractive materials due to its high photoactivity in the UV range [1]. Furthermore, it is non-toxic, relatively cheap and chemically stable [2, 3]. In the photocatalytic process, the semiconductor is irradiated with photons with energy enough to be absorbed by the semiconductor allowing electrons to be promoted from the valence band to the conduction band, which gives place to the production of high energy electron-hole pairs [4]. This effect can produce reduction or oxidation processes of reactants in contact with the semiconductor surface, and thus, lead to an eventually decomposition of these compounds. However, for the visible range of the spectrum, TiO2 does not have photocatalytic activity due to its wide bandgap (3.2 eV in case of anatase) [5, 6]. In order to activate photodegradation in the visible range, which would make this process cheaper by using solar light, TiO2 can be combined with different materials to produce ternary compounds, doping [1, 6–10], nitriding [11], decorating [2] or composites fabrication [7]. The synergetic activity of the external element or compound and the TiO2 matrix enhances visible light absorption and thus photocatalysis can be produced.

Due to its unique properties, such as good optical transmittance, large specific surface area, and high electron mobility [12], graphene is a great candidate material to couple TiO2 for photocatalysis [7]. The first property that helps degradation is the zero bandgap (this property makes graphene to be considered as a semi-metal); it allows excitation of photons by visible light. The second property, is the high electron mobility that suppresses the
recombination of electron-hole pairs and finally, the third property is a large surface area that offers a scaffold with which to anchor TiO\textsubscript{2} particles and improves the adsorption of many contaminants [7].

**Experimental**

TiO\textsubscript{2} powders were prepared using the following methodology: 10 ml of TiCl\textsubscript{4} were added dropwise to a 100 ml cold deionized water magnetically stirred at 60 rpm, after that, a mix solution of acetic acid and 30\% wt of NH\textsubscript{4}OH were added dropwise until it reached a pH value of 8 in order to induce precipitation. After 72 h resting, the solution was filtered, washed with deionized water and dried at 300 °C during 4 h. On the other hand, graphene was synthesized by the modified Hummer methodology [13]. The materials used were reagent grade graphite flakes, NaNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}MnO\textsubscript{4}, 30\% H\textsubscript{2}O\textsubscript{2} and distilled water. The synthesis was achieved following a graphene oxide (Gox) synthesis with a subsequent reduction to obtain graphene (G). For the synthesis of graphene oxide, we used the method described in [13]. After Gox was dried, sample was heated to 120–150 °C in air, after this process, thermal expansion occurs and brown dark powders, turn into black powders.

TiO\textsubscript{2} powder was mixed with graphene in weight percentage ratio of 93/7 of TiO\textsubscript{2}/graphene. The mixture was manually milled in a ceramic mortar during 1 h in order to homogenize it, then it was divided into three equal parts; one of them was heated to 100 °C and another to 200 °C. Two samples of pure TiO\textsubscript{2} were heated with the same conditions than the mixtures. One sample of the mixture and one of pure TiO\textsubscript{2} without thermal treatment were let as control samples. The thermal treatment processes were carried out in a furnace Barnstead Thermolyne model 1400. The heating rate was set to 50 °C min\textsuperscript{-1}. As prepared and heated samples were characterized by Raman spectroscopy with an excitation line of 473 nm. Scattered light was collected with an Acton SpectraPro 2755i and amplified by a Hamamatsu photomultiplier tube R925. X-ray diffraction measurements were carried out on a Panalytical Empyrean diffractometer system. Transmission electron microscopy (TEM) measurements were performed in a JEM-JEOL-2100 microscope, using an acceleration voltage of 200 kV.

For the degradation experiments, 0.01 g of each powder was poured in 200 ml methylene blue (MB) aqueous solutions with molar concentration of 2.3 × 10\textsuperscript{-3} M. A total of 6 solutions were prepared in order to evaluate the powders thermal treatment effect in the catalytic response of the pure and mixed samples. The solutions were exposed to UV and Visible radiation using commercial lamps. The UV source, was a lights of America brand lamp model F17T8/BLB with 17 W of power and a color temperature of 30000 K, its maximum emission is centered at 360 nm (see the spectrum of the UV lamp in supplementary material figure UV-spectrum). The LED visible source was a lamp from Philips model 3PM5 with 14 W of nominal power and a color temperature of 5000 K (see spectrum in supplementary figure visible-spectrum). No cut-off filters were used for irradiation. The samples were irradiated during 450 min; the degradation analysis was carried out by taking 2 ml aliquots of the corresponding solution at different times to measure the UV–vis absorbance in a Thermo Genesys spectrophotometer at a wavelength of 664 nm, corresponding to the highest absorbance of MB.

In order to evaluate adsorption in the dark of the different powders, experiments were carried out using the same MB concentrations as well as powders quantities than for degradation tests. 2 ml aliquots were taken every certain time to measure absorbance by UV–vis. Adsorption was evaluated for a total time of 200 min, time at which an adsorption equilibrium has been reached for all samples.

Surface morphology of the powders was observed by scanning electron microscopy (SEM) using a Tescan Mira 3 microscope with secondary electrons at a 20 kV as accelerating voltage.

**Results and discussion**

Figure 1 shows the x-ray diffraction patterns of a) TiO\textsubscript{2}, b) TiO\textsubscript{2}/Graphene and c) Graphene samples heated at different temperatures. It can be seen in figure 1(a) that the TiO\textsubscript{2} anatase phase together with a small fraction of brookite phase [14] (peak centered at 30.8° corresponding to (121) plane and marked with a star) were obtained from the HT process; the phases percentages were found to be 94\% anatase and 6\% brookite. Brookite phase percentage was estimated by the methodology used in [15] and [16] by means of the equation $W_b = \frac{k_b A_b}{k_a A_a + k_b A_b}$, where $A_b$ and $A_a$ are the integrated area of the (121) brookite and the (101) anatase signals, respectively. The values of the coefficients $k_a$ and $k_b$ are 0.886 and 2.721, respectively [16]. For calculation, the background was subtracted and the signal smoothed in order to eliminate noise. No significant changes can be observed due to the thermal treatment of the pure TiO\textsubscript{2} powders. For the TiO\textsubscript{2}/Graphene mixed powders, a slight decrease in the FWHM from 1.8 to 1.5° can be observed (figure 1(b)), which would be indicative of crystallite growth because of nucleation and growth of seed crystals. In order to corroborate this effect, the crystallite sizes calculated with the Scherrer equation [17] were: 46, 52, and 55 nm for the non-heated, 100 °C and 200 °C heated samples,
respectively. Notice that this effect was not observed for pure TiO₂. Regarding graphene powders, a decrease in FWHM from 7.4 to 5.4° and an increase in intensity of the (002) band can be observed (figure 1(c)), which means that graphene layers stack together due to the increasing temperature. Figure 1(d) shows a TEM micrograph of a graphene sample. Notice that transparent corrugated layers can be observed which are typical for graphene [18].

Raman spectroscopy measurements were carried out in order to further analyze structural properties of the powders. Figure 2 shows the Raman spectra for the graphene samples; notice that well defined bands centered at 1340 and 1592 cm⁻¹ corresponding to the graphene D and G bands respectively [19, 20], can be observed. Furthermore, the 2D and D + G bands centered at 2673 and 2923 cm⁻¹, respectively [19, 20], can be observed which is indicative of the existence of high quality graphene. No substantial changes are presented for increasing temperature, which is consistent with the data obtained from XRD measurements. Table 1 shows the FWHM for the most intense signals of XRD patterns.

Figure 1. XRD patterns of (a) TiO₂, (b) TiO₂/Graphene, and (c) graphene powders heated at different temperatures. (d) TEM image of a graphene sample.

Figure 2. Raman spectra of non-heated and 100 and 200 °C heated graphene.
Figure 3 shows the Raman spectra of the (a) TiO$_2$ and (b) TiO$_2$/Graphene samples. As it can be seen, the principal signals of anatase TiO$_2$ phase at 152, 400, 526 and 636 cm$^{-1}$ are present in all the spectra [21]. Notice that in the range of 240–350 cm$^{-1}$ low intensity signals can be observed, the small bands centered at 245 and 322 cm$^{-1}$ (marked with * in figure 3) are characteristic of brookite TiO$_2$ [15], which further confirms the mixture of anatase and brookite phases observed by XRD measurements. The thermal treatment temperature does not have visible effects on Raman spectra for both the graphene decorated and pure TiO$_2$ powders. The inset in figure 3 (b) shows the signals associated to graphene, indicating that TiO$_2$ were decorated with graphene.

For the photocatalytic activity evaluation, measurements of the absorbance band maximum of methylene blue centered at 664 nm were performed for different irradiation times. UV–vis spectra in the range of 500–750 nm were recorded from 0 to 450 min of irradiation time. A pure methylene blue without powders was measured at the same conditions in order to observe the photolysis process. Figure 4(a) shows the absorbance as a function of time. The absorbance for TiO$_2$ decreased from 1.25 to 0.5, while the absorbance for the heat-treated powders reduced from 1.3 to approximately 0.7 and 0.9 for 100 and 200 $^\circ$C treatment temperatures respectively. This effect can be attributed to the increase in crystallite size, due to the coalescence of grains during thermal treatments. Crystallite size increase reduces the surface area of the powders and thus, the photoactivity [6]. Percentages of degradation were calculated by taking into account the results from adsorption in the dark measurements, which are lower for the pure TiO$_2$ than for graphene TiO$_2$ decorated samples (see supplementary figure adsorption-in-the-dark). It has been reported in literature that carbon nanostructures decorating TiO$_2$ could have an enhancing effect of both dark adsorption and photocatalytic activity [10, 22].

| Sample   | Thermal treatment temperature $({}^\circ$C) | XRD plane | XRD FWHM (degree) |
|----------|-------------------------------------------|-----------|-------------------|
| G        | —                                         | (002)     | 7.4               |
| G-100    | 100                                       | (002)     | 7.2               |
| G-200    | 200                                       | (002)     | 5.4               |
| TiO$_2$  | —                                         | (101)     | 1.6               |
| TiO$_2$–100 | 100                                      | (101)     | 1.6               |
| TiO$_2$–200 | 200                                      | (101)     | 1.6               |
| TiO$_2$–G | —                                         | (101)     | 1.8               |
| TiO$_2$–G-100 | 100                                      | (101)     | 1.6               |
| TiO$_2$–G-200 | 200                                      | (101)     | 1.5               |
Percentages of degradation for UV irradiation are shown in figure 5. In the graphene-free mixture, the methylene blue reached a maximum value of 59% of degradation under ultraviolet light irradiation for the non-heated samples. Meanwhile, the percentage of degradation for the heated samples were 45.2 and 28.1% for 100 and 200 °C thermal treatment temperatures. This effect could be caused by the reduction of OH groups adsorbed on the TiO₂ surface due to the heat treatment.

On the other hand, graphene decorated samples showed a considerable higher photocatalytic activity. Figure 4(a) shows the MB absorbance as a function of time for UV irradiation. Notice that the absorbance in the non-heated TiO₂/G and the 200 °C heated sample reached the same value of 0.3, while absorbance in the 100 °C sample decreased to approximately 0.1. Percentages of degradation for UV irradiation of the graphene decorated samples are shown in figure 5, were it can be seen that degradation values of 71.8, 86.9 and 74.9% were obtained for non-heated and 100 and 200 °C heated TiO₂/G powders respectively. According to Tang et al, the increase in photocatalytic activity of the graphene decorated samples is a consequence of the capability of graphene to promote separation of electron-hole pairs in TiO₂ due to the high mobility of electrons in graphene [7].
Furthermore, under UV irradiation, the conduction band photo-generated TiO₂ electrons should be transferred to graphene.

Figure 6 shows the MB absorbance of visible light versus time, it can be noticed that MB photolysis is slightly higher for visible light than in the case of UV. For the TiO₂/G sample, it can be observed that heated samples presented less degradation percentages than the non-heated composites. Figure 7 shows degradation percentages for TiO₂/G composite powders. The sample heated to 200 °C shows the lowest degradation percentage (8.7%) meanwhile sample heated to 100 °C degraded 13.1%. On the other hand, non-heated sample presented 40% of degradation, which is a considerable good value for using visible light as irradiation source. Even though with the present data no deep analysis on the degradation mechanism can be conducted, and furthermore, the degradation mechanisms for carbon nanostructures-TiO₂ composites according to the literature, has not been completely understood [23]; a possible explanation for the reduced activity of the heated samples could be that graphene layers stack together affecting its interaction with TiO₂ surface. This stacking could decrease the transfer between photogenerated electrons produced by visible light absorption on graphene and the TiO₂ surface, which is a well accepted mechanism for dye degradation under visible light by carbon nanostructures-TiO₂ composites [23].

A detailed understanding of the degradation mechanism is out of the scope of the present work. Nevertheless, results could be discussed based on the report by Tang et al [7], describing that visible light can be...
absorbed by graphene, and thus generate excited photoelectrons at the Fermi level that will tunnel to the TiO$_2$ conduction band to overcome the Schottky barrier formed by the contact of graphene and TiO$_2$. The presence of these injected electrons will then interact with the dye to induce its degradation.

In order to study the influence of surface morphology in the photocatalytic activity, SEM characterization was carried out; micrographs are shown in figure 8. It can be noticed that TiO$_2$ sample has a granular morphology formed by quasi-spherical particles with diameters less than 50 nm. However, for heated samples, surface morphology is smoother, with less grain boundaries, which is an effect of small particles coalescence producing a decrease in MB degradation as it was observed in figure 5.

Regarding composite samples, notice that surface morphology of un-heated TiO$_2$/G, does not present considerable differences as compared to pure TiO$_2$. However, photocatalytic activity for graphene-containing samples is much higher than pure TiO$_2$, confirming that there is a synergetic effect of graphene and TiO$_2$. When heat is applied to composites, micrographs show no considerable changes; however, as it has been seen in figure 5, degradation increases for UV irradiation and decreases for visible irradiation (figure 7).

**Conclusions**

Degradation of methylene blue (MB) under UV and visible light using graphene decorated titanium dioxide (TiO$_2$/G) as an activator was achieved. Significant differences (>30%) in degradation percentage of the composite samples (TiO$_2$/G) were observed when compared to degradation by pure TiO$_2$ samples. A maximum of 86.9% of MB degradation corresponding to TiO$_2$/G − 100 °C was reached. Regarding visible irradiation, a maximum value of 40% was achieved with the TiO$_2$/G sample. Although, the degradation of MB with TiO$_2$/G composites under visible irradiation was low (≤40%) the possibility to degrade MB with visible light is an important finding due to sun light could be used to activate TiO$_2$. 
The photocatalytic activity improvement was undoubtedly owing to the graphene addition on TiO₂ powders, however, the physical mechanisms involved in the degradation process will give us the key to understand the degradation enhance of TiO₂/G samples. An approach based on the literature, to shed some light on the degradation mechanism, is mentioned along the text for each irradiance source applied to the samples.

Acknowledgments

Authors thank the technical support of Bruno Hernández Flores, Sergio Oliva, Guadalupe Cárdenas and Armando Renteria. MAAE acknowledges UAZ and DELFIN program for financial support. JGQG acknowledges Universidad de Guadalajara for financial support under PRO-SNI program.

ORCID iDs

L P Rivera @ https://orcid.org/0000-0001-6373-654X
A Pérez-Centeno @ https://orcid.org/0000-0003-4309-3465
A Chávez-Chávez @ https://orcid.org/0000-0003-5772-905X
M A Santana-Aranda @ https://orcid.org/0000-0002-6296-4425
J G Quinones-Galván @ https://orcid.org/0000-0001-7931-3955

References

[1] Kim S, Hwang S J and Choi W 2005 Visible light active platinum-ion-doped TiO₂ photocatalyst J. Phys. Chem. B 109 24260–7
[2] Liu Y, Chen L, Hu J, Li J and Richards R 2010 TiO₂ nanoflakes modified with gold nanoparticles as photocatalysts with high activity and durability under near UV irradiation J. Phys. Chem. C 114 1641–5
[3] Adly M S, El-Dafrawy S M and El-Hakam S A 2019 Application of nanostructured graphene oxide/titanium dioxide composites for photocatalytic degradation of rhodamine B and acid green 25 dyes J. Mater. Res. Technol. 8 5610–22
[4] Herrmann J M 2005 Heterogeneous photocatalytic: state of the art and present applications Top. Catal. 34 49–65
[5] Fujishima A, Rao T N and Tryk D A 2000 Titanium dioxide photocatalysis J. Photochem. Photobiol. C: Photochem. Rev. 1 11–21
[6] Fujishima A, Zhang X and Tryk D A 2008 TiO₂ photocatalysis and related surface phenomena Surf. Sci. Rep. 63 515–82
[7] Tang B, Chen H, Peng H, Wang Z and Huang W 2018 Graphene modified TiO₂ composite photocatalysts: Mechanism, progress and perspective Nanomaterials. 8 273–307
[8] Anh N P, Chi H T K, Tri N and Dung H T K 2018 Photoactivity of reducing graphene oxide and titanium dioxide composite for cinnamic acid degradation Mater. Trans. 59 1117–23
[9] Jo W K, Kumar S, Isaac M A, Lee A F and Karthikeyan S 2017 Cobalt promoted TiO₂/GO for the photocatalytic degradation of oxytetracycline and congo red Appl. Catal. B Environ. 201 159–68
[10] Yao L, Dong L, Li X, Xu S, Zhang G and Sun Q 2018 TiO₂-intercalated graphene oxides with highly efficient photocatalytic degradation for methylene blue J. Nanomater. 2018 309170
[11] Camps E, Castrejón-Sánchez V H, Camacho- López M and Basurto R 2015 Influence of the nitriding process on the band-gap of TiO2 thin films with phase mixture Thin Solid Films 581 54–8
[12] Geim A K and Novoselov K S 2007 The rise of graphene Nat. Mater. 6 183–91
[13] Hummers W S and Offeman R E 1958 Preparation of graphitic oxide J. Am. Chem. Soc. 80 3339
[14] Tran H T T, Koslick H, Jih M F, Fischer C, Bentrup U, Vuong T H, Nguyen L Q and Schulz A 2017 Photocatalytic performance of highly active brookite in the degradation of hazardous organic compounds compared to anatase and rutile Appl. Catal. B Environ. 200 647–58
[15] Tran T H T, Bui T N H, Nguyen T L, Man H N and Tran T K C 2019 Phase-pure brookite TiO₂ as a highly active photocatalyst for the degradation of pharmaceutical pollutants J. Electron. Mater. 48 7846–61
[16] Yang M H, Chen P C, Tai M C, Chen T T, Chang I C, Chiu H T and Lee C Y 2014 Anatase and brookite TiO₂ with various morphologies and their proposed building block CrystEngComm. 16 441–7
[17] Quiñones-Galván J G, González-Rivera Y A, Lozada-Morales R, Campos-González E, Jiménez-Sandoval S, Zelaya-Ange O and Rubio-Rosas E 2015 Incorporation of Er³⁺ ions into an amorphous matrix of Cd₃V₂O₇ containing crystalline CdO nanoparticles Mater. Res. Bull. 68 167–79
[18] Hu T, Kim M, Lee E, Lee G, Baeck S H and Shim S E 2017 Bio-degradable polymer-modified graphene/polyaniline electrodes for supercapacitors Synth. Met. 227 61–70
[19] Wang K 2013 Laser based fabrication of graphene Adv. Graphene Sci. ed M Aliolkhazraei 77–95
[20] Peng T, Lv H H, He D, Pan M and Mu S 2013 Direct transformation of amorphous silicon carbide into graphene under low temperature and ambient pressure Sci. Rep. 3 11148
[21] Castrejón-Sánchez V H, López R, Ramón-González M, Enríquez-Pérez A, Camacho- López M and Villa-Sánchez G 2019 Annealing control on the anatase/rutile ratio of nanostructured titanium dioxide obtained by sol-gel Cryst. 9 22
[22] Shaban M, Atrash A M and Abdulkhadi M R 2018 TiO₂ nanoribbons/carbon nanotubes composite with enhanced photocatalytic activity; fabrication, characterization, and application Sci. Rep. 8 7873
[23] Giovannetti R, Rommozzi E, Zanotti M and D’Amato C A 2017 Recent advances in graphene based TiO₂ nanocomposites (GTiO₂Ns) for photocatalytic degradation of synthetic dyes Catalysts. 7 305