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Controlling the surface chemistry of graphene oxide: Key towards efficient ZnO-GO photocatalysts

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Abstract

Graphene oxide (GO) and related materials are widely reported to enhance the photocatalytic activity of zinc oxide. However, the origin of the observed performance improvements remains elusive and studies contributing to a deeper understanding of this critical issue are largely missing. In this work, we have prepared a set of benchmark ZnO-GO hybrid materials in order to systematically put under closer scrutiny the influence of the surface chemistry of GO on the photocatalytic degradation of methylene blue. The set of ZnO-GO hybrids has been synthesized in an ultrasonication process involving ZnO nanoparticles obtained in a microwave synthesis process and GO with three distinct oxidation degrees, employed in three different loading fractions. Structural and physical-chemical characterization by XRD, FTIR, Raman, UV-Vis, photoluminescence and spectroscopy and XPS, consistently demonstrate the importance of the surface chemistry of GO for establishing photo-induced charge-transfer interface interactions with ZnO, facilitating the enhancement of the catalytic activity of the ZnO-

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GO catalyst. Optimized interface interactions thus enabled the design of a ZnO-GO catalyst exhibiting a conversion rate of 80% obtained in a time of 70 minutes and at a catalyst concentration of only 0.045 mg/mL.

Keywords

graphene oxide; zinc oxide; ZnO-GO hybrid; photocatalysis; surface chemistry

1. Introduction

Graphene oxide (GO) has become the object of many research studies in the last years for its multifunctional character based on its large surface area, amphiphilicity, and tunable electronic properties by surface modification [1, 2]. GO is obtained by oxidation and exfoliation of graphite [3, 4] and consists of a single graphenic sheet with π -conjugated sp^2 domains together with regions of sp^3 character, which contain oxygen functional groups (oFGs) covalently attached to the carbon atoms, both in the basal plane and on the edges. It can be described as a wide band-gap semiconducting material with a highly complex non-stoichiometric chemical structure [5-7]. Exhibiting additionally a much higher hydrophilic character than graphene, further facilitates its processing in aqueous media and, therefore, its use in a wide variety of technological applications [8, 9]. Moreover, the chemically active surface of GO enables the attachment of different organic molecules or metal oxides that modify its electronic properties. This surface-tuning flexibility is of particular interest in photocatalysis, since GO can form hybrids in combination with photocatalytically active semiconducting metal oxides, improving their photocatalytic response [10, 11]. One of the most studied metal oxides has been zinc oxide (ZnO) since it exhibits several advantages including low production cost, chemical stability, non-toxicity, high photosensitivity and wide band gap (3.37 eV) [12-14]. Its nanostructuration, moreover, opens new possibilities in

photocatalysis as it enables higher efficiency and facilitates the ulterior recovery of the photocatalyst [15, 16]. Additionally, its combination with GO results in remarkable photocatalytic performance [16-20] since GO has an active role in photocatalysis by decreasing the aggregation of ZnO particles and acting as electron-acceptor material, hindering the electron-hole recombination [17, 21-23]. Furthermore, graphene has been proven to enhance adsorption of organic pollutants on the hybrid surface probably due to the π - π interaction between the aromatic pollutants and the sp^2 region of graphene, which eventually improves the photocatalytic efficiency [24]. Also, GO induces the formation of oxygen vacancies in ZnO improving its photoresponse [25]. Likewise, increased loading fractions of GO are reported to significantly enhance the photocatalytic performance up to certain threshold values. [22].

A vast majority of literature studies claims that GO should be transformed to rGO in ZnO-GO composites to achieve photocatalytic enhancement effects. Hereto processes either involving the direct mixing of (functionalized) rGO with ZnO or thermal post-reduction of a ZnO-GO composites are reported [26-30]. Consequently, the superior conducting properties of rGO, combined with its high surface area are made responsible for the improvement of the photocatalytic activity. While this usually is explained in a rather general way, the deeper reasons are not fully understood.

On the other hand, our former studies revealed that even non-reduced GO is able to improve the photocatalytic activity in TiO_2 -GO composites [31, 32]. Here it was shown that the enhancement effect strongly depends on the applied synthesis method and the fact to achieve a perfect coverage of TiO_2 nanoparticles by GO. It was demonstrated that the oxygen functional groups mediate the efficient and uniform assembly of the TiO_2 nanoparticles on the GO sheets, leading to highly efficient photocatalysts both under near-UV/Vis and visible light, when an optimum amount of GO was employed.

On the contrary, using synthesis conditions not resulting in the formation of TiO₂ nanoparticles perfectly covered by GO, i.e. comprised of TiO₂ nanoparticles not well connected to GO sheets, improvement of the photocatalytic properties only can be obtained through the use of rGO.

These findings clearly underline that the conductivity of GO, i.e. the presence of rGO, does not constitute a fundamental intrinsic requirement for obtaining improved photocatalytic activity and that certain critical issues, not looked-up yet, need to be scrutinized in more detail

In this article, we focus on the impact of the oxygen functional groups of GO for achieving enhanced photocatalytic activity in ZnO-GO hybrid materials. By using GO with three distinct degrees of oxygen groups we systematically study the influence of the surface chemistry of GO on the photocatalytic activity of ZnO-GO hybrids for the degradation of methylene blue under UV-light irradiation. Thorough analyses by various physicochemical techniques provide evidence on the establishment of specific interface interactions between ZnO and GO, and how this influences the final photocatalytic behavior. Moreover, we demonstrate that by solely controlling the oxidation degree of GO and by optimizing the loading fraction highly efficient ZnO-GO catalysts can be prepared, without any further need to apply tedious reduction steps. The performance is tested in photocatalytic degradation reactions of methylene blue and diphenhydramine (up-scaling and recyclability), as well as in the photoelectrocatalytic oxidation of water.

2. Experimental

2.1. Materials

Graphite flakes, zinc acetate dihydrate ($\text{ZnAc} \cdot 2\text{H}_2\text{O}$), Titanium (IV) oxide (TiO_2 P25), sodium nitrate (NaNO_3), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), potassium chloride (KCl), sodium sulfate (anhydrous), methanol, methylene blue (MB) and diphenhydramine (DP) were purchased from Aldrich and used as received.

2.2. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by a sol-gel procedure based on microwave irradiation of a solution of zinc acetate dehydrated (ZnAc) in ethylene glycol (EG), using a CEMTM S-class Microwave Synthesis System. Briefly, 0.025 mol of ZnAc solved in 0.5 ml of deionized water were added to 250 ml EG, and the obtained solution was microwave heated under stirring at 160 °C for 5 min, using 300 W of power. The ZnO precipitate was collected by centrifugation, washed repeatedly with deionized water and dried in an oven at 100 °C.

2.3. Synthesis of graphene oxide with different oxidation degrees (GOX)

First, graphite oxide was prepared using a modified Hummers method as reported elsewhere [3, 33]. Specifically, 5 g of graphite flakes were put into a mixture of 170 ml H_2SO_4 and 3.75 g NaNO_3 , and the mixture was cooled in an ice bath and stirred for 30 minutes. Thereafter, 25 g of KMnO_4 were slowly added and stirred for another 30 minutes. Then, the ice bath was removed and the mixture warmed to 35-40 °C and stirred for different times (2 h, 4h and overnight), yielding graphite oxide with increasing oxidation degree. The reaction was terminated by slowly adding 250 ml of deionized water and then 20 ml H_2O_2 (30 %) solution. The resulting dispersion was filtered and the obtained powder material was repeatedly washed with 400 ml of HCl : H_2O (1:10 v/v) to remove metal ions followed by deionized water until neutral pH. Finally, the graphite oxide obtained was dried at room temperature.

Graphene oxide was obtained by bath sonication (45kHz) of an aqueous graphite oxide dispersion (2 mg/ml) for 2 hours, followed by centrifugation at 4500 rpm during 60 minutes, obtaining a brown-colored dispersion of exfoliated GOX (X= 1, 2 or 3, for the oxidation during 2h, 4 h, and overnight, labeled as the lowest, medium and highest oxidation degree, respectively) with a final concentration of 1 mg/ml.

2.4. Preparation of ZnO-GOX catalysts

Catalysts were prepared in solution by a novel method based on ultrasonic mixing and subsequent freeze-drying. ZnO powder was added to a 0.5 mg/ml aqueous dispersion of graphene oxide (GO1, GO2 or GO3) in the convenient amount to obtain the required ZnO to GOX ratio (3:1, 10:1 or 20:1 w/w). The resulting dispersion was bath sonicated for 20 minutes, frozen and freeze-dried for 24 hours to obtain the ZnO-GOX catalysts in the form of a fine powder.

2.5. Characterization

The surface morphology of the synthesized materials was investigated by scanning electronic microscopy (SEM) using a Hitachi S-3400N microscope and transmission electron microscopy (TEM) employing a JEOL-2000 FXII. Elemental analysis of the GOX materials was performed in a Thermo Flash 1112 analyzer. The sample in Ag capsules was pyrolyzed at 1070 °C under He flow. The produced gases flow through a reducing bed of carbon black that transforms all CO_x into CO. Subsequently, the gases flow through a polar chromatographic column that separates CH₄ from CO and the latter is detected and quantified using a thermal conductivity detector calibrated with sulphanilamide.

Powder X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8

Advance diffractometer provided with a Cu K α as X-ray irradiation source ($\lambda_{\text{Cu K}\alpha}$ =

1.541 Å) through the 2θ range from 20° to 80°. The software EVA and the Powder Diffraction File (PDF) database were utilized for the semi-quantitative estimate of the phase composition. The size of crystal domains was calculated by the Scherrer equation with a shape factor of 0.89. Crystallite sizes were not calculated for phase contents of less than 5%, as the error was very high. Fourier-transform infrared (FTIR) spectra in KBr powder-pressed pellets were recorded in a Bruker Vertex 70 spectrometer. Raman spectroscopy was performed using a Horiba Jobin Yvon spectrometer (model HR 800 UV) working with a green laser (excitation $\lambda = 532$ nm). X-ray photoelectron spectroscopy (XPS) of the powder materials was performed in an ESCAPlus Omicron spectrometer provided with an Mg anode (1253.6 eV) working at 225 W (15 mA, 15 kV) and the peaks were calibrated with C1s peak (284.5 eV). The XPS peaks were fitted to a GL(70) Voigt lineshape (a combination of 70% Gaussian and 30 % Lorentzian character), performing a Shirley background subtraction. Asymmetry for the sp^2 peak of the C1s spectra was defined as a function LA (α , β , m), where $\alpha=0.4$ and $\beta=0.38$ describe the spread of the tail on each side of the Lorentzian component and the parameter $m=70$ specifies the width of the Gaussian used to convolute the Lorentzian curve.

The optical properties of the materials were characterized by a UV-Vis spectrometer (Shimadzu UV-3600) from 190 to 900 nm. Photoluminescence emission spectra (PL) were recorded at 350 nm of excitation in a Horiba Jobin Yvon Fluoromax-P, slits of excitation and emission at 1 mm. All the spectra were recorded at room temperature using 10 mm path-length quartz cuvette.

2.6. Photocatalytic Experiments

The photocatalytic activity of the synthesized materials was evaluated based on the degradation of methylene blue (MB) in aqueous solution under UV light irradiation. Photocatalytic activity of a commercial TiO₂ photocatalyst (P25) was also measured and used as reference. An UV lamp (Philips TL8W (Hg)) was utilized as a radiation source. The lamp emitted a minute fraction of the total radiation at 324 and 325 nm and the rest between 342 and 400 nm with a maximum irradiance peak at 365 nm (3.4 eV). In a typical experiment, 3.3 ml of MB aqueous solution (0.015 mg/ml) and the corresponding photocatalyst (0.045 mg/ml) were mixed and magnetically stirred in a quartz cuvette during 30 min in dark conditions before switching on the lamp, in order to achieve the adsorption–desorption equilibrium condition. The cuvette, placed 5 cm away from light source, was irradiated under UV light without a filter. Degradation of methylene blue was analyzed by recording the absorbance of the solutions at the maximum absorption band ($\lambda = 663.5$ nm) of MB, using a UV-vis spectrometer at given time intervals.

The degradation efficiency of the photocatalyst was calculated using the following equation:

$$\text{Degradation (\%)} = (A_0 - A_t / A_0) \times 100\% \quad (1)$$

Where A_0 is the absorbance values of MB at initial stage and A_t is the absorbance of MB at the different time intervals measured. The photodegradation of MB follows pseudo-first-order kinetics, which can be expressed as follows:

$$\ln (A_t / A_0) = - kt \quad (2)$$

Where k (min^{-1}) is the degradation rate constant [34].

2.7. Photoelectrochemical measurements.

Fluorinated tin oxide (FTO) substrates of 2.5x1 cm (Solems SA, France) were sonicated in isopropanol for 5 minutes before spraying. ZnO films were prepared by spraying a ZnO (or ZnO-GO) suspension in ethanol (0.5 mg/ml) onto the FTO substrates using an automatized spray coater (Nadetech ND-SP, Spain), covering an area of 0.7 cm². All the photoelectrochemical measurements were performed using N₂-purged 0.1 M Na₂SO₄ as supporting electrolyte, a Ag/AgCl (3 M NaCl) as reference electrode and a graphite rod as counter electrode, the scan rate was 20 mV/s for all cyclic voltammetry (CV) experiments. The ZnO-GO electrodes were electrochemically reduced by cycling from 0.4 to -1.0 V until a constant voltammogram is attained (eight cycles) in order to obtain the electrochemically reduced ZnO-ECrGO electrodes. Potentiostatic chronoamperograms were recorded at 0.4 V.

2.8. Proof of concept: up-scaling and recyclability of ZnO-GO hybrid catalysts

The photodegradation of diphenhydramine (DP) was carried out at room temperature (25 °C) in a homemade batch reactor, using 7.5 mL of reaction medium in each experiment. A magnetic stirrer was placed inside to homogenize the sample and the reactor was housed within a cooling system, all of it located at 5 cm of the UV light source (~50 mW/cm²). A flow of oxygen was continuously supplied to the reactor, and aliquots were sampled at specific times. The catalyst was separated by filtration at each sampled aliquot. The concentration of DP was fixed in all experiments at 100 mg/L, and the concentration of catalyst was 1 g/L. The reaction mixture (with the suspended hybrid catalyst) was kept in the dark under stirring (30 min), turning on the light source afterwards, and sampling 1 mL aliquots at each desired time. The detection of DP was carried out with an HPLC equipment (Hitachi Elite La Chromsystem), provided with a Hydrosphere C18 column (250 mm × 4,6 mm, 5 µm particle size). The analyses are based on an isocratic method, with a 1 mL/min flow rate of the eluent (A:B, 30:70 v/v

of 20 mM NaH₂PO₄ acidified with H₃PO₄ at pH = 2.80 (A), and acetonitrile (B)), providing a linear response over the whole experimental range.

3. Results and discussion

3.1. Influence of the GO oxidation degree on the catalytic activity of the ZnO-GOX catalysts.

Graphene oxide with three different oxidation degrees (GOX) was prepared from their graphite oxide counterparts by modifying the oxidation time from two hours (GO1) to four hours (GO2) and overnight (GO3). Elemental analysis (Table 1) of the GOX materials reveals a progressive increase of the oxygen content from 39 wt.% in GO1 to 46 wt.% in GO3, confirming the different oxidation degree of the obtained GOX materials. Next, ZnO-GOX hybrid materials based on GO1, GO2 or GO3, and ZnO with 3:1 w/w of ZnO:GOX ratio were prepared and characterized.

Table 1. Elemental Analysis of the different graphene oxide materials. N and S impurities come from the harsh oxidation procedure applied to graphite. Please, note that elemental analysis results do not consider the physisorbed water contribution.

Graphene Oxide	O (wt.%)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)
GO1	38.8	47.2	2.8	0.1	1.1
GO2	42.6	41.5	3.3	0.0	1.0
GO3	46.0	40.8	3.1	0.0	1.4

Electronic microscopy analysis (Fig. S1) confirms the deposition of ZnO nanoparticles ranging from 10 to 30 nm on the surface of graphene oxide. However, no strong morphological differences are observed for the different types of hybrids.

Fig. 1 shows the XRD patterns of the ZnO nanoparticles and the three ZnO-GOX hybrids with equal GOX content (ZnO:GOX ratio equal to 3:1). All the diffraction peaks of the pure ZnO material can be well indexed to the hexagonal wurtzite phase of ZnO, confirming that only the nanocrystalline ZnO phase was detected. No other

crystalline phases were observed. The sharp diffraction peaks evidence the good crystallinity of the prepared particles. The crystalline lattice parameters for the ZnO were $a = 3.251 \text{ \AA}$ and $c = 5.208 \text{ \AA}$, being $c/a=1.601$, close to an ideal hexagonal structure ($c/a= 1.633$) [35]. The crystallite size of the ZnO nanoparticles calculated by the X-ray line broadening method using the Debye-Scherrer's equation is 10 nm.

XRD patterns of the ZnO-GOX materials (Fig. 1) are similar to the XRD pattern of the pristine ZnO, confirming that the wurtzite structure of the ZnO nanoparticles is maintained. However, no evidence on the presence of GOX diffraction peaks (Fig. S2) is found in the XRD diffractograms, indicating that the GOX materials are well exfoliated, and their contribution is masked by the strong scatter of ZnO, which has much more electron density. Also, no shift was observed in the position of ZnO diffraction peaks compared to pristine ZnO, evidencing that the native crystalline structure of ZnO is maintained after preparation of the hybrid material. Interestingly, the relative intensity ratios of the three main diffraction peaks, (100), (002) and (101) vary when GOX with different oxidation degree is used, suggesting the establishment of interfacial interactions between ZnO and GOX. To see this more clearly, Table 2 shows the calculated I_i/I_0 relative intensity ratios for the three main diffraction peaks, i.e. the intensity of a particular diffraction peak (I_i) relative to the intensity of the most intense diffraction peak (I_0), the (101). A significant increase of the (002) relative intensities, especially in the case of the ZnO-GO3, supports a preferential interaction through the (002) plane of the ZnO. The crystalline lattice parameters of the ZnO-GOX materials were similar to the ZnO parameters ($a= 3.251 \text{ \AA}$ and $c= 5.208 \text{ \AA}$) and only the ZnO-GO3 has a slightly different c/a ratio (1.603). The calculated crystallite size of ZnO within the hybrids was 16.6, 22.64 and 21 nm for the ZnO-GO1, ZnO-GO2 and ZnO-

GO3, respectively. Thus, the values for ZnO-GOX hybrids are significantly larger than the ones calculated for the bare ZnO nanoparticles.

Fig. 1. XRD pattern of a) ZnO, and b) ZnO-GO1 (1:3 w/w), c) ZnO-GO2 (1:3 w/w), d) ZnO-GO3 (1:3 w/w)

Table 2. Relative intensity (I_i/I_0) of the three main diffraction peaks (100), (002) and (101) with respect to the most intense (101) for the ZnO and ZnO-GO (3:1 w/w) materials.

Miller index (h, k, l)	2θ (degree)	I_i/I_0			
		ZnO	ZnO-GO1	ZnO-GO2	ZnO-GO3
(100)	31.8	0.65	0.65	0.67	0.67
(002)	34.5	0.55	0.58	0.51	0.66
(101)	36.3	1	1	1	1

Raman spectroscopy evidences the presence of graphene oxide in the hybrids. The Raman spectra of the GOX materials (Fig. 2) show the characteristic D (1358 cm^{-1}) and

G (1592 cm^{-1}) bands of the graphenic materials. The D band is attributed to vibrations of the carbons with sp^3 character and, hence, indicative of structural imperfections, possibly due to the attachment of oFGs on the carbon basal plane and other induced defects during harsh oxidation. The G band is extremely sensitive to sp^2 carbon in-plane vibrations. The spectra of ZnO-GOX show a shift for both D and G bands located at 1347 and 1598 cm^{-1} , respectively. This shift suggests an interaction between ZnO and GO. Importantly, an additional Raman mode emerges at around 1100 cm^{-1} in the spectra of the ZnO-GOX hybrids. This mode, not visible in pure ZnO (Fig. S4), seems to belong to GOX since a very low intensity shoulder is here observable (Fig. 2). However, it is in the Raman of the Zn-GO hybrids where the signal at 1100 cm^{-1} is more evident, especially when less oxidized GOX (GO1 or GO2) is used. The increase of the peak intensity also suggests that an interfacial interaction between ZnO and GO is established. The intensity of the D band with respect to the G band is typically used to characterize the level of disorder in graphene materials [36]. The calculated I_D/I_G ratio is 0.65, 0.67 and 0.62 for GO1, GO2 and GO3, respectively. And the I_D/I_G ratio increases in the hybrids, being 0.95, 0.81, and 0.80 for Zn-GO1, Zn-GO2, and Zn-GO3, respectively. This higher I_D/I_G ratio evidences a higher level of disorder, most likely denoting an advantageous integration of GO with ZnO [36].

Fig 2. Raman spectra of GOX and ZnO-GOX (3:1 w/w) materials

FTIR spectra of the GOX materials (Fig. 3, Fig. S5) confirm their high hydrophilic character, as they show an intense broad band in the 3000-3600 cm^{-1} region due to the stretching vibrations of O-H groups coming from alcohols, carboxylic acids and water. This band increases with the oxidation degree of GOX. Water scissor mode (deformation vibration) is evidenced in the 1600-1700 cm^{-1} region, where it overlaps with the asymmetric stretch of sp^2 C=C vibration modes that should appear at 1500-1600 cm^{-1} and are hidden by the strong water contribution [6]. C=O stretching mode band is observed at 1734 cm^{-1} , compatible with ester/lactone groups. The characteristic

C-O peaks appear in the 900-1500 cm^{-1} region where the presence of overlapped modes from several distinct species impedes an unequivocal assignment. Here signals at 1223 and 1060 cm^{-1} are assigned to alcohol (C-OH) and epoxy (C-O-C) groups, respectively. Increasing the oxidation degree of GOX leads to the increase of the OH band at 3415 cm^{-1} and to a more intense water scissor mode at 1631 cm^{-1} together with the increase of the C-O bands. No modification of the C=O signal is observed, which has interesting implications in the resulting ZnO-GOX hybrids as will show below.

FTIR spectra of the ZnO-GOX materials show the main features of GOX spectra with the clear emergence of the intense band at 457 cm^{-1} characteristic of the stretching vibrations of Zn-O [37]. The most significant difference with respect to the GOX is the disappearance of the C=O band at 1734 cm^{-1} , evidencing an interaction between ZnO and GOX through the C=O groups of GOX.

Fig 3. FTIR spectra of GO2, ZnO and ZnO-GO2 (3:1 w/w).

UV-Vis absorption spectra of the GOX materials (Fig. 4) show the characteristic absorption peak at 230 nm due to the π - π^* transition of C=C bonds and a broad shoulder at around 310 nm, corresponding to n- π^* transition of C=O [8]. ZnO nanoparticles exhibit

the typical absorption edge at 374 nm, indicating the existence of highly crystalline ZnO nanostructure. The π - π^* transition characteristic of GOX is hardly observable in the UV-vis of the ZnO-GOX composites (Fig. 4). Interestingly, an absorption at 250 nm is now visible, suggesting a partial reduction of the GOX in the hybrid [8]. This is accompanied by a blue-shift of the ZnO absorption edge to 366 nm evidencing an interaction with GO. Corresponding shifts are indicated in Fig. 4b, c by dashed lines.

The photoluminescence spectra of ZnO and ZnO-GO materials are shown in Fig 5. A quenching of the emission of ZnO photoluminescence is clearly observed for the hybrid materials. Moreover, when GO is added, the strong emission at 382 nm of the ZnO blueshifts to 375 nm and decreases in intensity with respect to the other emission features. The quenching is ascribed to the electron transfer from the conduction band of ZnO (good electron donor) to the valence band of GO (electron acceptor). This charge transfer, sensitive to suitable interactions at the interface between ZnO and GO, thus reduces the recombination of photogenerated electron-hole pairs. Consequently, the availability of additional charge carriers in ZnO-GO hybrids is expected to enhance photocatalytic performance of ZnO.

Fig 4. UV-vis spectra of (a) pristine GOX and ZnO materials, (b) ZnO, ZnO-GOX (3:1 w/w) hybrids; (c) ZnO and ZnO-GO2 hybrids.

Fig 5. Photoluminescence spectra of the pristine ZnO and ZnO-GO hybrid materials

Next, the photocatalytic activity of the synthesized catalysts (ZnO and the ZnO-GOX) was analyzed by measuring the intensity of the UV-Vis absorption of the maximum absorption band of MB (663.5 nm) during its degradation. During the equilibration period, prior to the photocatalysis experiments, no adsorption of MB in the catalyst was observed due to the small amount of catalyst used and due to the very low surface area of the prepared catalytic materials ($6 \text{ m}^2/\text{g}$ for ZnO and 30 to $38 \text{ m}^2/\text{g}$ for the hybrid materials). Photolysis experiments performed under UV light (without catalyst) and

experiments under dark conditions (with catalyst) did not show any apparent degradation of MB. The use of GOX under light as catalyst did not show any evidence for MB degradation either. ZnO-GOX hybrids show significant enhancement in the photodegradation of MB compared to bare ZnO, being ZnO-GO1 and ZnO-GO2 the most effective catalysts (Fig. 6a). Here, it is important to note that we have always used the same amount of catalyst. Thus, the effective amount of photoactive ZnO is even smaller when ZnO-GO is used. The degradation efficiency at 70 minutes of irradiation is 48.6% for ZnO, 65% for ZnO-GO1, 67% for ZnO-GO2, and 56.3% for ZnO-GO3. The ZnO-GO3 catalyst, synthesized with GO of high oxidation degree, shows less efficiency than the others. This underlines the existence of a certain threshold value beyond which higher oxidation degrees of GO are detrimental for the photocatalytic activity of ZnO-GO hybrids. This observation thus provides another proof of the critical role that GO surface chemistry plays in the catalytic activity of ZnO-GOX hybrids.

The photocatalytic degradation of MB by ZnO, and ZnO-GOX materials fitted well to a first-order linear kinetics up to 40 minutes of irradiation (Fig. S6). After this time, the activity of the catalysts declines. The apparent rate constant (k , min^{-1}), calculated for the 40 first minutes from the slope of the $\ln(A/A_0)$ vs time curve, increased for the ZnO-GO1 and ZnO-GO2 with respect to ZnO, evidencing the improvement of the catalyst efficiency for the degradation of MB when graphene oxide is used.

Analyzing the differences between the ZnO-GO3 catalyst and the catalysts obtained with GO1 and GO2, it is clear that the degree of oxidation has a major influence on the final structural characteristics of the hybrid material. Looking back to the structural characterization of the hybrids, we observe that ZnO-GO3 catalyst showed the largest increase of the (002) XRD diffraction peak intensity. On the other side, it exhibits the smallest Raman peak at 1100 cm^{-1} . While the higher concentration of oxygen functional

groups in GO3 allows a higher level of interfacial interactions with ZnO, resulting in a more compact structure (Fig. S1), concomitantly it obstructs the access to the catalytic centers of ZnO. Consequently, a higher level of interactions, which could be beneficial in other applications, here limits the efficiency of the catalyst, since these apparently affect the active part of the ZnO catalyst. Thus, it seems clear that graphene oxide has an important role in the improvement of the ZnO catalysis efficiency and controlling the degree of oxidation is crucial to establish the adequate level of interfacial GO-ZnO interactions for designing efficient catalysts.

Fig. 6. Photocatalytic degradation of methylene blue (MB) with time under UV light irradiation by a) ZnO and ZnO-GOX catalysts with 3:1 of ZnO:GO w:w ratio. b) ZnO and ZnO-GO2 catalyst with different ZnO:GO w:w ratios

3.2. Influence of the GO loading on the catalytic activity of the ZnO-GO catalysts

One important issue, which notably contributes to improve the activity of the ZnO-GO catalysts, is the GO loading. This must be adequately chosen to reach optimal catalytic performance [38]. With this aim, three different ZnO:GO ratios (3:1, 10:1 or 20:1 w/w) for the synthesis of the new set of catalysts were assayed. Here GO2 was chosen as graphene oxide material since the ZnO-GO2 catalyst showed the best performance for the degradation of MB.

No differences were observed in the XRD patterns of the Zn-GO2 materials with different GO2 loadings (Fig. S3). However, like in the previous section, the relative intensity ratio of the three main diffraction peaks varies when different GO2 loadings are used (Table 3). The I_i/I_0 intensity ratio corresponding to the (100) diffraction peak hardly changes with respect to the ZnO material, but the corresponding (002) diffraction peak decreases for the hybrids with higher GO2 content, and increases for the catalyst with the lowest GO2 content (20:1 w/w), denoting, once more, that the established interfacial interactions are taking place preferentially through the (002) diffraction plane.

Table 3. Diffraction angles of ZnO-GO2 hybrids with different ratios and relative intensity of the peaks.

Miller index (h, k, l)	Angle 2θ	ZnO	ZnO-GO2 (20:1)	ZnO-GO2 (10:1)	ZnO-GO2 (3:1)
		I_i/I_0 (%)	I_i/I_0 (%)	I_i/I_0 (%)	I_i/I_0 (%)
(100)	31.8	0.65	0.64	0.66	0.67
(002)	34.5	0.55	0.59	0.50	0.51
(101)	36.3	1	1	1	1

Fig. 7 shows the Raman spectra of ZnO-GO2 materials with different GO2 content compared to GO2 and bare ZnO. Like in Fig. 2, the spectra of ZnO-GO2 hybrids exhibit the G- (1598 cm^{-1}) and D- (1347 cm^{-1}) bands characteristic of GO2, as well as the

enhancement of the Raman mode at around 1100 cm^{-1} , indicating the establishment of interactions between ZnO and GO. Investigating the low frequency region, we observe prominent bands at 332 , 438 , 580 and 665 cm^{-1} . Among this group, the maximum intensity arises at 438 cm^{-1} . This prominent frequency corresponds to the nonpolar E_2 (high) mode, which involves mostly the oxygen atoms of the ZnO lattice and is characteristic of the wurtzite hexagonal structure of ZnO [39, 40]. The relatively higher intensity and sharp E_2 (high) mode compared to the other observed peaks demonstrates that the synthesized ZnO material exhibits good crystallinity [41, 42]. The intensity of this peak significantly decreases when GO2 is added to the catalyst, probably indicating that the new hybrid material has lower crystal quality, and this decrease of crystallinity might be a consequence of the establishment of interactions between ZnO and graphene. The peak at 580 cm^{-1} is assigned to the $E_1(\text{LO})$ mode, which is associated with the structural defects in ZnO and is very sensitive to the inclusion of “oxygen imperfections” in the ZnO structure [40, 43, 44]. This mode is present in all the materials and it is particularly intense in ZnO-GO2 (10:1), evidencing a stronger interaction between ZnO and oFGs of GO2 in this catalyst. The peaks at 332 and 662 cm^{-1} are due to multiple-phonon scattering processes [45, 46].

Fig. 7. RAMAN spectra of a) ZnO; b, f) ZnO-GO2 (20:1 w/w); c, g) ZnO-GO2 (10:1 w/w); d, h) ZnO-GO2 (3:1 w/w); e) GO2

FTIR of the ZnO-GO2 hybrids with different loadings (Fig. S5) shows an increase of the 3430 cm^{-1} O-H stretching vibration with the GO2 content and no signal corresponding to the C=O stretching mode at 1734 cm^{-1} of the GO2 is observable.

X-ray photoelectron spectroscopy (XPS) analysis was carried out to investigate the surface composition of the prepared catalysts. The C1s spectrum of GO2 (Fig. 8a) was deconvoluted in 5 components at binding energies (BE) of 284.5 eV (I, C=C bonds), 285.2 eV (II, C-C bonds), 286.6 eV (III, C-O groups), 287.7 eV (IV, C=O groups), 289 eV (V, COOH groups). The C1s spectrum widens for the Zn-GO2 hybrids. Thus, two additional peaks have been added on both sides of the spectrum to get a good fitting (grey peaks in Fig 8b,c). The new peak at the lowest BE (283 eV) has been assigned to

a carbon interaction with Zn [47, 48]. And the new peak at the highest BE (291 eV) has been assigned to the π - π^* shake-up satellite band typical for sp^2 hybridized carbon, indicating a partial reduction of GO during preparation of ZnO-GO materials, which might involve a charge transfer between ZnO and GO. Also, this peak might have some contribution of the interaction between oFGs of GO and ZnO. The intensity of the peaks in the carbon bonded to oxygen region (peaks III, IV, V) increases for all the ZnO-GO₂ hybrids, denoting the presence of the oxygen atoms from ZnO in the crystalline network of GO, and together with the new peak at 283 eV evidencing the establishment of interactions between ZnO and graphene oxide through the C=O group of graphene oxide, as observed in FTIR, i.e. C-O-Zn interactions. The Zn 2p core-level spectra of ZnO (Fig. 8d) shows the characteristic doublet at BE 1022.3 and 1046.4 eV, assigned as Zn2p_{3/2} and Zn2p_{1/2} bands, respectively. The BE separation between both bands is 23 eV, in concordance with the standard reference value for ZnO [47]. The binding energy of these peaks, their BE separation and the small full width at half maximum (FWHM) values (2.1 eV) indicate that Zn ions are in +2 oxidation state and, thus, the chemical Zn-O bonds are dominant in the ZnO catalyst. In the ZnO-GO₂ hybrid, wider FWHM values are observed, 2.6 eV for ZnO-GO₂ (3:1 w/w) and 2.5 eV for ZnO-GO₂ (10:1 w/w), indicating the appearance of a Zn-O-C interaction, as it has been seen in the C1s spectra.

Fig. 8. C_{1s} XPS spectra of a) GO2, b) ZnO-GO2 (3:1 w/w), and c) ZnO-GO2 (10:1 w/w). d) Zn 2p core level XPS spectra of ZnO, ZnO-GO2 (3:1 and 10:1 w/w) catalysts

The XPS observations on the ZnO-GO2 materials thus are in agreement with the results from optical characterization, whereby the UV-Vis spectra (see Fig. 4) reveal a blueshift of the ZnO edge and the photoluminescence spectra evidence significant quenching (see

Fig. 5) indicating the establishment of interface interactions facilitating photo-induced charge transfer between ZnO and GO.

Next, the three catalysts synthesized with different GO₂ loadings were tested in the photocatalytic degradation of methylene blue under UV light irradiation. For comparison, we also examined the photocatalytic activity of the standard reference P25 TiO₂ catalyst under the same catalytic conditions (Fig. 6b). After fitting to first-order kinetics, ZnO-GO₂ (10:1 w/w) catalyst showed the highest degradation rate (0.03 min^{-1}), which is 1.7 times higher than that of the ZnO catalyst (Fig S7). Final conversion of 80% in 70 minutes is obtained with the ZnO-GO₂ (10:1 w/w) catalyst, thus exhibiting a much higher performance than the P25 TiO₂ catalyst at these conditions.

3.3. Photostability, photoelectrochemical performance and photocatalysis mechanism

In order to test the potential up-scalability and stability of our photocatalysts, we carried out photocatalytic degradation experiments in a larger scale. We chose diphenhydramine (DP) as model reaction [43-46] to demonstrate the applicability of our catalyst for the degradation of other organic water pollutants, and we undertook the photodegradation process in a larger container to facilitate the recovery and reuse of the photocatalysts. The conversion outcomes at 60 min of reaction time and 1 g/L catalyst concentration are displayed in Figure 9. It is visible how the results are perfectly consistent with those obtained in by our previous benchmark experiments. Analogous to the case of MB, here the ZnO-GO₂ catalyst also reveals the best performance for the photodegradation of DP. The recyclability experiments could be easily carried out in contrast to the previous catalyst screening experiments, in which the experimental configuration and smaller amount of catalyst employed, impeded us to efficiently recover it for further reuse. The ZnO-GO₂ (10:1) catalyst was chosen for this study,

since it exhibited the best DP conversion (equally as the ZnO-GO2 (3:1) catalyst) and the best performance for MB degradation (Fig. 9). Upon the second photocatalytic cycle, the hybrid catalyst experiences a decay in performance, which is indeed a common feature in similar systems. However, the conversion drop is only of about 25% of the initial value, and afterwards, it seems to become stable, showing nearly the same performance in a third photocatalytic cycle.

Fig. 9. Photocatalytic performance of ZnO, ZnO-GOX(3:1), ZnO-GO2(10:1) and ZnO-GO2 (20:1) materials for the degradation of diphenhydramine and 3 cycles degradation for the ZnO-GO2 (10:1) catalyst.

Finally, aiming to evaluate the photocatalytic properties of the ZnO-GO2 (10:1 w/w) material in other applications, we tested the photoelectrochemical performance of several prepared films (bare ZnO, ZnO-GO2, P25 TiO₂) for the photoelectrocatalytic oxidation of water. Photocurrents (difference between currents in the dark and under illumination) measured by CV in the 0.1 M Na₂SO₄ electrolyte (Fig. 10a, also see Fig. S8 for original voltammograms) show that the highest activity corresponds to the electrochemically reduced ZnO-ECrGO2 hybrid. Additionally, potentiostatic

photocurrent measurements performed at 0.4 V (Fig. 10b) reveal that the photocurrent values for ZnO-ECrGO₂ are 2.25 times higher than for the bare ZnO, and 4 times higher than for the reference catalyst P25 TiO₂. For this application, electrochemical reduction of the ZnO-GO₂ hybrid results in a material with higher photocatalytic performance. Please, take into account that we have explored two different reactions: electrochemical water oxidation and photochemical MB degradation. Consequently, the involved processes are different. The original ability of ZnO material to transfer holes to the solution and/or subsequently, electrons to the FTO electrode decreases with the presence of GO (electrical insulator), yielding a lower current. Upon reduction of GO, the current increases due to the improvement of the conductivity properties of the electrochemical reduced GO. However, independent of the electrochemical reduction step required for the probed system, these findings are in full agreement with the previous results on MB degradation, whereby ZnO-GO₂ leads to improved photocatalytic behavior with respect to pristine ZnO and the reference standard P25 TiO₂. Moreover, they clearly reveal that the photocatalytic enhancement by ZnO-GO₂ is not limited to MB or DP degradation, but of even more general character, is applicable to other types of reactions such as water oxidation.

Fig. 10. a) Difference between currents recorded under illumination and in the dark for the different samples in Na_2SO_4 and b) potentiostatic on-off samples for water oxidation.

Our experimental findings on the enhancement of photocatalytic and photoelectrochemical activity can be explained at hand of the scheme of energy levels of ZnO, GO and ZnO-GO shown in Fig. 11. Their values are entirely based on the values obtained from UV-Vis and photoluminescence spectra mentioned in the respective section. In case of the hybrid material it can be seen that trough the establishment of interactions of oxygen functional groups of GO with those of ZnO located at its 002 plane, the resulting alignment of energy levels at the ZnO-GO interface then facilitates the transfer of photo-excited electrons from ZnO to GO states

of lower energy upon irradiation with UV-light. This reduces the recombination rate of the photo-generated electron-hole pair and promotes oxidation reactions with the analyte or/and its medium via the remaining positive charges (holes) in the valence band of ZnO. In this way, GO contributes to the enhancement of the photocatalytic activity of ZnO. Please note that GO in itself is not photoactive due to the large energetic separation of the relevant energy levels from its ground-state, a fact which is confirmed as well by the absence of photoactivity in our corresponding blank experiments. However, this not necessarily assigns GO a purely passive role. On the contrary, the transfer of photo-excited electrons to GO most likely opens additional pathways of more or less complex nature contributing to further improvement of photocatalytic activity of the ZnO-GO hybrid material. However, this problematic yet goes beyond the scope of the present study.

Fig. 11: Schematic diagram of energy levels of (a) ZnO, (b) GO and (c) ZnO – GO displaying valence band (VB), conduction band (CB), absorption edge, $n-\pi^*$ and $\pi-\pi^*$ levels.¹ The proposed alignment of the energy levels in ZnO – GO² indicates the possibility of photo-induced energy transfer from ZnO to GO states of lower energy upon irradiation with UV-light,³ thus reducing the e^-h^+ recombination rate and enhancing the photoactivity of ZnO.⁴

¹ Energy values taken from UV-Vis absorption and photoluminescence spectroscopy. The lowering of the $\pi-\pi^*$ energy level of the GO component in the ZnO – GO by 0.4 eV suggests a (partial) reduction of GO

enabled by effective interface interactions between oxygen functional groups of GO and ZnO at its (002) plane.

² The alignment of the energy levels of GO with respect to ZnO in ZnO-GO may vary as a factor of oxygen functional groups of GO and its density of states, as well as the degree of interactions established with the (002) plane of ZnO. Its exact position requires specific measurements beyond the scope of this study.

³ Excitation energy taken from UV-lamp datasheet.

⁴ GO itself is not photoactive.

With respect to the need for using rGO instead of GO, as claimed in many studies, we would like to point out the following:

As long as favorable interface interactions between ZnO and GO are established via the respective oxygen functional groups, catalytic enhancement is achieved through photo-induced charge-transfer processes, as explained above. There is no need for further reduction processes. In fact, the creation of proper interface interactions leads to a significant lowering of the π - π^* transition by 0.4 eV, typically for shifts observed upon reduction of GO to rGO, indicative of an enhancement of density of states favoring improved conductivity and mobility.

The accompanying band-alignment taking place at the ZnO-GO interface adjusts the GO levels, as a function of the GO oxygen degree, in such a way that electron-transfer from ZnO to GO is enabled, most likely to the rather dense states of oxygen functional groups laying underneath the conduction band of GO formed by its π^* states. Please note that electron-transfer to the conduction band of GO itself is highly unlikely, as suggested by our photoelectrochemical experiments (see below).

Moreover, the fact that our posterior thermal reduction processes of the ZnO-GO hybrids did not contribute to further improvement of the photocatalytic activity (on the contrary, lower activities were observed), underlines that in our ZnO-GO hybrids the photocatalytic process is governed by the established interface interactions. Upon

thermal processes, reduction from GO to more conductive rGO may be achieved, however, we speculate that this is on cost of the established GO-ZnO interface.

In addition, the direct use of rGO to obtain ZnO-GO hybrids is not fruitful through the low dispersibility of rGO in water. This did not result in the formation of homogeneous hybrid materials with photocatalytic properties.

Finally, in what concerns the photoelectrochemical experiment: Photoelectrochemistry relies on the availability of conductive electrode materials. The observation that only by applying an electrochemical reduction step to the ZnO-GO material a photoelectrochemical active material with superior properties is achieved, suggests that photo-generated electrons are not transferred to the GO conduction band, but rather to the underlying dense states formed by the oxygen functional groups. The irreversible electrochemical reduction step, then transforms these states into rather continuous network of states allowing for the required conductivity. (Please note that if the photo-generated electron would be transferred to the conduction band of GO, no further reduction process would be required to obtain a conductive electrode material).

At this point it is important to underline that all this applies to ZnO-GO materials in which effective interface interactions are established via the functional oxygen groups of GO. However, in ZnO-GO materials where this is not achieved (e.g. due to different synthesis conditions, or non-appropriate oxidation degrees of GO), the presence of more conductive rGO may open additional pathways of direct interactions with the analyte/medium thus enhancing the overall photocatalytic activity in these types of hybrid materials. These observations are also in agreement with our former studies on TiO₂-GO hybrid materials [31, 32]. We therefore believe that establishing appropriate interface interactions through adequate synthesis routes and oxidation degrees of GO is

key to achieve enhanced photocatalytic performance without the need for applying additional reduction steps.

4. Conclusions

Using graphene oxide with distinct and well-defined oxidation degree for the preparation of ZnO-GO hybrid materials, we demonstrated that the surface chemistry of graphene oxide is key for establishing interface interactions with zinc oxide, which favorably contribute to improve its photocatalytic and photoelectrochemical activity. We showed that the interactions are established between C=O groups of GO and the (002) crystalline plane of ZnO. The resulting alignment of energy levels at the ZnO-GO interface then facilitates the transfer of photo-excited electrons from ZnO to GO. The remaining positive charges (holes) located at the valence band of ZnO then easily can promote oxidation reactions with the analyte or/and the medium in which it is dissolved. photo-induced charge transfer interactions. In this way GO reduces the recombination rate of the photogenerated electron-hole pair and thus contributes to the enhancement of the photocatalytic activity of ZnO. Most favorable conditions are achieved for an intermediate oxidation degree of GO, while the GO loading fraction needs to be adjusted to ensure the availability of sufficient number of catalytically active ZnO sites. Based on these findings, an optimized ZnO-GO hybrid catalyst was prepared and employed in the catalytic degradation reaction of methylene blue revealing conversion rates of 80 % within a time of 70 minutes obtained at a catalyst concentration of only 0.045 mg/mL.

Moreover, the ZnO-GO catalyst demonstrated high performance and recyclability for the degradation of diphenhydramine and good performance for the

photoelectrochemical oxidation of water. These results are of general character and extendable to other reactions or semiconducting metal oxides used in photocatalytic or photoelectrochemical applications.

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