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Photocatalytic process in TiO$_2$/graphene hybrid materials. Evidence of charge separation by electron transfer from Reduced Graphene Oxide to TiO$_2$

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Abstract
Different amounts of graphene oxide were chemically reduced with hydrazine in the presence of nanometric TiO$_2$ and SiO$_2$. The photocatalytic performance of the resulting hybrid materials was compared with pristine supports using phenol and methylene blue (MB) under two different irradiation conditions (UV-Vis and Vis only light). MB is strongly adsorbed on the hybrid materials. Significant MB degradation rates were observed on pristine TiO$_2$ and hybrid TiO$_2$-reduced graphene oxide (rGO) material under both irradiation conditions. In the presence of the hybrid catalyst, the degradation of MB under Vis is due to the dye-sensitized mechanism, while under UV-Vis there is an additional semiconductor-based photocatalytic mechanism. Conversely, the presence of rGO reduces the rate of photocatalytic transformation for the poorly adsorbed phenol under UV irradiation, and a negligible degradation rate was observed under Vis. The UV-Vis absorption spectra of aqueous suspensions of hybrid materials with different rGO loading indicate a strong interaction of the two materials and a reduction of the light absorption due to the presence of rGO. Among many mechanisms reported on the role of rGO, it is inferred that the working mechanism involves electron transfer from photoexcited states of rGO onto the titania, and holes migration from titania to rGO, where adsorbed substrates are oxidized. This oxidation is possible only if the substrate HOMO has higher energy (less positive standard redox potential) than the empty states of excited rGO, supposedly for MB and not for phenol. Then, reduced graphene is advantageous when substrates are adsorbed and when the charge separation is possible (coupled with a proper semiconductor like TiO$_2$). Alone, or coupled with low work function oxides like SiO$_2$, rGO could be ineffective.

Keywords
Reduced Graphene Oxide; TiO$_2$-rGO hybrid materials; Visible Sensitization; Charge separation; Photocatalysis
1. Introduction

The study of the semiconductor/electrolyte and semiconductor/gas interfaces has been driven by their potential multisectorial applications [1,2,3,4,5,6]. The main limits to the application of the related technology are: i) the low photonic efficiency of current photocatalysts; ii) the low absorption in the visible spectrum. Crucial issues are the low efficiency in the photogenerated charge carrier separation and the low rate of interfacial charge transfer reactions. [7] Complex strategies have been proposed to increase the performance of semiconductor photocatalysts [8,9,10,11,12,13,14,15,16,17]. More recently, the enhancement of photocatalytic performances has been obtained with nano-hybrid materials made with semiconductors and carbonaceous structures (fullerenes, carbon nanotubes, carbon nanohorns, and graphene). [18,19,20,21]

The interest in the TiO₂-graphene nano-composites is based on the role that the carbonaceous phase plays in the photocatalytic process. Graphene shows exceptional adsorption ability toward various classes of compounds promoting the adsorption of pollutants on the catalyst surface, prerequisite for their efficient photocatalytic removal if and only if the photogenerated charges move toward graphene.

The methods for the graphene production are numerous [22,23,24,25], but the synthesis of non-functionalized graphene does not allow the production of TiO₂-graphene hybrid materials due to the absence of functional groups able to bond to the semiconductor [26,27]. For these reasons the most useful method for the synthesis of TiO₂-graphene photocatalysts is based on the synthesis of graphite oxide by means of chemical oxidation, its exfoliation in water and subsequent reduction of graphene oxide (GO). The final materials are usually defined as reduced GO (rGO), whatever the reduction strategies are, due to the partial preservation of some oxidized moieties in their structure. [28,29]

In the degradation of organic substrate on TiO₂-rGO composites, the main active oxidation species were inferred from the disappearance kinetics of different substrates in the presence of *OH and hole (h⁴⁺) scavengers. These experiments demonstrated that the main reactive species are not free hydroxyl radicals and that the direct hole transfer is the main mechanism. [30,31]

Till now a complete agreement on the role of rGO during the photocatalytic process on TiO₂-rGO hybrids has not been reached. The operational mechanisms active on TiO₂-rGO composites as emerges from literature can be summarized as follow.

A. In the case of substrates that do not absorb light and are negligibly adsorbed on catalyst the photodegradation could take place mainly via the “classic” UV-based photocatalytic process promoted by UV-activated band to band transition in which no electron transfer between TiO₂ and rGO is operational and rGO acts only as competitive light absorber, because the GO and rGO electronic structure could preclude any injection of electrons from TiO₂ toward the carbonaceous phase or vice-versa. [30]. In addition, the adsorption of carbonaceous phase can generate intraband gap states, located immediately above the VB or below the CB which can extend the absorption of light to the Vis range.

B. When the movement of photogenerated charges from the two phases (TiO₂ and rGO) is not hindered and substrates which do not absorb light are involved, two possible and alternative mechanisms can operate.

1) Electron transfer from rGO to TiO₂. The photocatalytic process is promoted by rGO, which absorbs visible (and UV) photons. Photo-excited electrons in high-energy rGO states are then delocalized (with kinetics in the 0.1-0.2 ps range [32]) onto the TiO₂ structure. Zhang and co-workers demonstrated the role of graphene as a macromolecular photosensitizer instead of an electron reservoir on irradiated rGO-ZnS composites. [33] The time-domain ab initio analysis carried out by Long and co-workers [32] highlighted that electron transfer process can occur from photoexcited states of perfect graphene sheets onto the titania surface with a non adiabatic
mechanism. The injected electron located in interfacial states then moves into bulk TiO$_2$

dissipating the energy *surplus* due to electron-vibrational interactions. [32]

2) Electron transfer from TiO$_2$ to rGO. A UV-based transaction promotes electrons into the

TiO$_2$ CB which are rapidly transferred onto the graphene-like sheets. The common reaction

scheme proposed for the interface rGO/TiO$_2$ allows the delocalization of TiO$_2$ CB electrons onto

the rGO structure (rGO in this case acts as an electron reservoir). The work function of graphene

is 4.42 eV, while the conduction band (CB) of TiO$_2$ is located at $-4.21$ eV with energy gap

amplitude of 3.2 eV (for the most photoactive anatase allotrope). [34,35,36] As a consequence,
the electrons photo-promoted in the CB can be injected into the graphene aromatic structure
avoiding their recombination with the valence band (VB) holes. The decrement of the electron
transfer resistance at the TiO$_2$-rGO/electrolyte interface compared to that at the TiO$_2$/electrolyte
interface, observed with EIS by Wang et al., suggested a rapid photoinduced charge separation
and a diminished possibility of electron–hole recombination on irradiated TiO$_2$-rGO materials.
[31] Wang et al. proposed that not only electrons can be easily transferred from photo-excited
TiO$_2$ onto rGO sheets, but also valence holes can move toward the rGO phase promoting an
effective degradation of adsorbed phenol molecules. [37]

The injection of electrons from excited rGO states toward TiO$_2$ CB or alternatively from TiO$_2$
CB toward delocalized empty rGO states is not a sufficient condition to guarantee the
degradation of the substrate, because the photogenerated empty states (a hole in the VB or an
empty states in the rGO) must be low enough in energy (redox potential sufficiently positive) to
promote the oxidation of the substrate itself (injection of an electron from the substrate to the
photogenerated empty state). It is worth noting the stability of certain organic substrates under
UV irradiated TiO$_2$ as a consequence of their too low HOMO energetic position (e.g. cyanuric
acid is stable in photocatalytic conditions [38,39]). Consequently, the energetic position of the
HOMO of a substrate is a key point to allow its transformation under irradiated TiO$_2$-rGO
hybrids especially in the case of Vis only irradiation which does not activate TiO$_2$ band to band
transitions which generate very oxidant VB holes.

C. In the presence of dyes, other two different visible-activated dye-sensitized pathways
have to be considered: in the case of a pure TiO$_2$ catalyst the adsorbed dyes can inject
photo-excited electrons onto the titania CB, while in the presence of TiO$_2$-rGO
composites this mechanism can couple with an alternative reaction path in which the dye
photo-excited electrons can be delocalized in the electronic diffuse states of rGO. In both
cases the oxidized dye molecules, formed as a consequence of a single or multi-electron
injection from the photo-excited dye to the delocalized empty states of rGO or TiO$_2$, can
autonomously evolve toward transients or stable by-products and consequently toward
the substrate degradation. Pastrana-Martínez et al. from an in depth analysis of the
photocatalytic activity of TiO$_2$-rGO composites toward the colorless diphenhydramine
and the organic dye methyl orange, emphasized the complexity of the operational
mechanisms concluding that rGO can operate as visible light sensitizer of TiO$_2$, but in the
presence of visible-absorbing species the degradation process can be dominated by a
direct self-oxidation of the visible-absorbing species. [30]

Herein, we report the two-steps synthesis of TiO$_2$-rGO hybrid materials (synthesis of GO by
chemical oxidation of graphite, exfoliation and in situ reduction of GO on the TiO$_2$ surface) and
the investigation of their photocatalytic behavior. The photocatalytic tests were carried out
comparing two substrates and two illumination sources aiming to give insight on the working
mechanisms and on the relation between the absorbing optical properties of the tested catalyst
and its photocatalytic behavior. This approach allows us to discriminate among the potential
operational photocatalytic mechanisms cited above and, hopefully, to clarify some aspects of the photo-reactivity of TiO$_2$-rGO composites.

2. Materials and Methods

2.1 Materials

Graphene oxide was produced by chemical oxidation using the modified Hummers and Staudemaier’s method [40] proposed by Huang et al. [41]. Briefly, 500 mg of graphite powder were dispersed in a solution obtained with 27.3 mL H$_2$SO$_4$, 3.30 mL H$_3$PO$_4$ and 2.78 g KMnO$_4$. The suspension was magnetically stirred at r.t. for 1, 2 or 3 days, respectively. After 12-15 hours a viscous brownish gel was obtained. After the desired oxidation time the suspension was carefully diluted in 120 mL of water and titrated with H$_2$O$_2$ till a bright yellow suspension was obtained (the violet MnO$_4^-$ ions are completely reduced to colorless Mn$^{2+}$). The yellow graphite oxide formed was washed three times with 1 M HCl and the solid separated with centrifugation (1200 G). During the washing procedure the color changed from bright yellow to brownish. The solid was then washed 3 times with water. During the washing procedure the graphite oxide experienced exfoliation. The suspension was then dialyzed toward water (Spectra/Port® Dialysis Membrane, MW cut off 6-8000 Da) until the pH of the external solution was stable and close to 4. The concentration of carbon in the GO suspensions was evaluated measuring the TOC on diluted suspensions after dialysis.

The TiO$_2$-rGO hybrid materials were obtained by chemical reduction with hydrazine solution (65 %) of different amounts of GO (3 days of oxidation) in the presence of TiO$_2$ according to a modification of the method reported in [42]. Stable suspensions of 4 g dm$^{-3}$ TiO$_2$ in water were obtained by sonication. Different amounts of GO were added to obtain materials with different carbon loading. The addition of GO quickly destabilized the TiO$_2$ colloids owing to adsorption of GO on the titania surface. Then 300 μL of hydrazine were added drop wise at r.t. After 12 hours of vigorous stirring the suspensions were filtered on 0.45 μm hydrophilic filters (Whatman, NL 17 membrane filters, polyamide) and washed with water. Finally, the produced powder was dried at 373 K for 1 hour.

By using the same method adopted for the synthesis of TiO$_2$-rGO materials, we produced hybrid SiO$_2$-rGO materials with different loading of rGO. GO was adsorbed on fumed silica SiO$_2$ Aerosil OX 50 and reduced with hydrazine. The synthesis of these hybrid materials was aimed to study the photochemical behavior of the rGO adsorbed on an inert support. The low work function of SiO$_2$ ($\chi \approx 1.2$ eV [43]) hinders the injection of electrons from the excited states of rGO to the inorganic support allowing the study of the photochemical behavior of rGO alone.
2.3 Photocatalytic Tests

The photodegradation experiments were carried out using cylindrical Pyrex cells (4.0 cm diameter and 2.5 cm height, cut-off at 295 nm) on 5 cm³ of aqueous suspension containing the desired amount of the photocatalyst powder (C_{cat} 0.5 g dm⁻³), substrate (1 mM phenol or 4x10⁻⁵ M MB) and HClO₄ 10⁻³ M to execute the test at pH 3±0.2. The slurries containing the photocatalyst were prepared using sonication. The irradiation was carried out with a set of three TLK 40W/05 (UV-Vis) or TLK 40W/03 (Vis only) fluorescent lamps (Phillips, Eindhoven, Nederland). The former has an integrated irradiance of 25.2±1 W m⁻² in the 300-400 nm wavelength range, with a maximum emission at 365 nm (able to activate the band to band transition in TiO₂ based materials), and minor emission in the Vis range (10.5±1 W m⁻² in the 400-800 nm range). The latter has an integrated irradiance of 40±1 W m⁻² in the 400-800 nm wavelength range, with a maximum emission at 423-436 nm, and negligible emission in the UV range (1.5 W m⁻² in the 300-400 nm range). The emission spectra are reported in Fig.1A of the Supplementary Materials (hereafter SM).

During irradiation the suspension was magnetically stirred and the cell temperature was 30±3 °C. After irradiation the suspension was filtered through 0.45 μm cellulose acetate membrane filter (Millipore HA) and analysed as required (HPLC-UV for phenol, spectrophotometrically at 665 nm for MB).

The photocatalytic transformation of the studied substrates followed pseudo-first order kinetics. The profiles of concentrations of the phenol and MB were fitted with a pseudo-first order equation of the form \[ C_t / C_0 = \exp(-k t_{irr}) \], where \( C_t \) is the substrate concentration at the irradiation time \( t_{irr} \), \( C_0 \) the initial concentration, and \( k \) the pseudo-first order degradation rate constant. The values of \( k \) are reported with their uncertainty (confidence intervals evaluated through the goodness of the fit, representing intra-series variability at 0.95 level of confidence).

2.4 Methods

The extinction spectra of TiO₂, TiO₂-rGO, SiO₂ and SiO₂-rGO suspensions were recorded with a Varian CARY 100 Scan UV-Vis spectrophotometer, using quartz cuvettes with a path length of 1 cm. The % reflectance spectra were recorded on opaque homogenized powdered samples with a Varian Cary 5000 UV-VIS-NIR reflectance spectrometer.

The UV-Vis lamp irradiiances were measured with an Ocean Optics USB2000+UV-VIS equipped with a 400 μm optical fiber (30 cm length) with a cosine corrector (Ocean Optics, CC-3-UV-T, optical diffuser in PTFE, wavelength range 200-2500 nm, OD diameter 6.35 mm, Field of View 180°). The spectrometer was calibrated with an Ocean Optics DH-2000-CAL Deuterium-Halogen Light Sources for the UV-Vis-NIR calibrated for absolute irradiance measurements from the vendor (Radiometric Calibration Standard UV-NIR, certificate of calibration #2162).

Phenol degradation kinetic was monitored with HPLC-UV (Hitachi L2200, LaChrom Elite, Lichrospher R100-CH 18/2 column (250 mm)). The elution was carried out at 1 cm³ min⁻¹ with H₂PO₄ 4.2 mM: Methanol 85:15 in isocratic mode. The retention time of phenol under this condition is 9.9 minutes. The injection volume was 60 μL.

The measurement of TOC was carried out with a Shimadzu TOC-VCSH Total Organic Carbon Analyzer, equipped with an ASI-V autosampler and fed with zero-grade air. Each suspension of GO, as synthesized, was diluted 200 times with MQ water and analyzed. TOC was obtained from the difference between Total Carbon (TC) and Inorganic Carbon (IC).

The morphology of the hybrid samples before (TiO₂-GO) and after the reduction with hydrazole (TiO₂-rGO) was investigated by means of a high-resolution transmission electron microscope (HR-TEM, JEOL JEM 3010), equipped with a LaB₆ source with an accelerating voltage of 300 kV.
The XPS analysis was carried to investigate the nature of the carbon atoms in the TiO$_2$-GO and TiO$_2$-rGO samples. The XPS spectra were recorded on pelletized samples with a VSW TA10 Mg Kα X-ray source (1253.6 eV) equipped with a VSW Class 100 Concentric Hemispherical Analyzer (VSW Scientific Instruments Ltd).

3 Results and Discussion

3.1 Material characterization

The simple oxidation method here adopted allows the preparation of significant amount of GO, the raw material for the successive synthesis of rGO, contrariwise to the sonochemical methods adopted for the exfoliation of graphene and one-step production of micro-amount of graphene nanosheets. [23,44,45]

Fig. 1 shows the UV-Vis absorption spectra of the suspensions of GO obtained after 1, 2 and 3 days of chemical oxidation, respectively. The spectra are normalized for the TOC concentration of the analyzed suspension. The spectra are dominated by the peaks at ≈230 nm. These signals are due to the π → π* transition of the C=C bonding. [41,46,47] The accurate position of the peaks are 231, 229 and 228 nm for the samples oxidized for 1, 2 and 3 days (1D, 2Ds, 3Ds), respectively. The lower is the peak position (as wavelength) the lower is the degree of aromaticity of the graphene-like planar structure. Accordingly, the 3Ds sample shows the peak at the shortest wavelength. The main peaks has a shoulder at roughly 300 nm, due to the n → π* transition of the carbonyl groups. [48,49] The larger is the intensity of the 300 nm shoulder, the larger is the concentration of C=O (carbonyl or carboxyl) groups in the samples and so the degree of oxidation. The ratio between the absorbance at 230 and 300 nm is also informative. This ratio is 2.4, 2.6 and 2.8 for the 1D, 2Ds and 3Ds samples, respectively. It increases with the increment of the oxidation degree because superior is the oxidation of graphene basal planes, greater it is the amount of isolated aromatic rings which increment the absorbance at 230 nm [49]. The obtained ratios (> 2) are very similar to those reported by Huang et al. [41] for GO samples with significantly larger lateral size.

The size of the GO particles after three days of oxidation in the same condition above described has been previously measured with dynamic light scattering (DLS) and reported in [29]. After exfoliation the GO particles have a hydrodynamic radius equal to 500 ± 70 nm. This value is in agreement with those reported by other authors for GO obtained in very similar experimental conditions [50].

The proposed methods for the reduction of GO to graphene are numerous (thermal annealing, microwave and photo reduction [29], chemical, photocatalytic and solvothermal reduction) and affect the final performance of materials. For a full analysis of this topic please refer to the review by Pei and Cheng [51]. The production of the TiO$_2$-rGO was here carried out by chemical reduction of different amount of GO (3Ds) adsorbed on the TiO$_2$ surface with aqueous hydrazine solution. Different materials with increasing amount of carbon loading (from 0.5 to 5% w/w) were successfully synthesized. The chemical reduction in water by hydrazine and its derivatives results in agglomerated graphene-based nanosheets due to the increase of hydrophobicity. [37]

We carried out the reduction of GO adsorbed on TiO$_2$ at r.t. and at the boiling point. We observed that only in the former case is a single solid phase synthesized, while in the latter case two separated phases are produced. Gao et al. [49] studied systematically the reduction of GO by hydrazine at r.t. and at high temperature. The hydrazine reduction at r.t. completely reduces the epoxide and hydroxyl groups located at the interior of the aromatic domains and only partially the carboxyl moieties at the edge of the aromatic domains. At higher temperature the reduction of the hydroxyls at the edge of the aromatic domains and of the carboxyl groups occurs. [49] Our experimental results support the conclusion that heating allows further reduction of the
oxygenated groups which links GO to the TiO\(_2\) surface (e.g. the ester groups obtained from the reaction between the TiO\(_2\) hydroxyls and the carboxyls of GO). Furthermore, the increment of the hydrophobicity of rGO at higher reduction temperature hinders the interaction between rGO and the hydrophilic TiO\(_2\) surface causing phase separation. Thus, the materials used for the photocatalytic tests are those obtained by reduction at r.t. only.

**Fig. 1** Absorption spectra of graphene oxide colloid (GO) obtained after different oxidation times (1, 2 and 3 days). The measured absorbance is normalized for the total organic concentration (TOC) of each measured solution.

Fig. 2-SM and Fig. 3-SM show the HR-TEM micrographs of TiO\(_2\)-GO and TiO\(_2\)-rGO (both with a 5% carbon loading) at different magnifications. No significant differences were observed before and after the chemical reduction of GO with hydrazine at room temperature. The anatase nanoparticles have an average particle size of \(\approx 20\) nm and are dispersed on the 2D layers of the graphene structure, which in some cases enfold the TiO\(_2\) nanoparticles.

The effective reduction with aqueous hydrazine of the GO to rGO was evaluated with XPS-ESCA. Fig. 4-SM shows the spectra of the TiO\(_2\)-GO and TiO\(_2\)-rGO (both with a 5% carbon loading) in the C(1s) core level peak region. The spectrum of TiO\(_2\)-GO is dominated by three main overlapped peaks. The peak centered at \(\approx 285\) eV is related to carbon atoms in sp\(^2\) hybridization typical of graphitic/graphenic structures, while the components at higher binding energy (BE at \(\approx 287\) and \(289\) eV) can be attributed to carbon species in higher oxidation state. [52,53 and references therein]. In the case of the reduced sample one peak dominates the spectra (BE at \(\approx 285\)), concurrently with a strong suppression of signals for high C-oxidation state. From the comparison of the two spectra (Fig. 4-SM a and b) it is manifest the effective reduction of the carbonaceous phase was obtained with hydrazine.

**Fig. 5** shows the diffuse Reflectance spectra of the produced TiO\(_2\)-rGO materials in the 200-800 nm range, as \%R and as Kubelka-Munk (K-M) function (eq. 1, left). The rGO phase induces the improved light absorption in the Vis range in line with data previously reported for TiO\(_2\)-rGO hybrid materials. [54,55,56] The energy band gap values of the synthesized materials were evaluated from the K-M functions by considering the relation which links the ratio between the absorption and scattering coefficients and the photon energy for semiconductors with indirect band gap, e.g. TiO\(_2\) (eq. 1, right).

\[
f(R) = \frac{(1 - R_e)^2}{2R_e} = A(h\nu - E_g)^2
\]

**eq. 1**
where \( f(R) \) is the K-M function, \( R \) the diffuse reflectance approaching infinite sample thickness, \( h\nu \) the photon energy, \( E_g \) the energy gap and \( A \) is a constant.

A slight decrement of the apparent \( E_g \) values (from 3.28 to 3.20 eV, corresponding to a red shift from 378 to 387 nm, see the inset of Fig. 5B-SM) was observed with the increase of the rGO loading. This can be a consequence of the production of a limited number of localized intraband gap states or simply an apparent band gap due to the superposition of absorption spectra of two different materials. However the slight decrement of the \( E_g \) we observed is negligible if compared to that reported for other TiO\(_2\)-carbon phase (graphene, carbon nanotubes) hybrid materials. [55,57,58]

The extinction spectra of water suspensions of the studied catalysts at different concentration (10, 50 and 100 mg dm\(^{-3}\)) were recorded and the average extinction coefficient \( \varepsilon_{ext}(\lambda) \) (Fig. 2A) computed from the plot of absorbance vs concentration, according to the Beer-Lambert law. The linear fits have \( r > 0.998 \) for all the wavelengths. The analysis of the \( \varepsilon_{ext}(\lambda) \) values (sum of the absorption, \( \varepsilon_{abs} \), and scattering, \( \varepsilon_{scat} \), coefficients) reveals that the increment of the rGO loading decreases the intrinsic ability of catalyst suspensions to absorb the radiation in the whole wavelength range, and consequently the overall amount of photons able to activate the UV-based photocatalytic mechanism is diminished. In addition the spectrum of hybrid materials suggests that there is strong interaction between TiO\(_2\) and rGO, as the ratio of typical UV absorption bands of TiO\(_2\) is changed (see bands at 273 and 323 nm, respectively). Moreover a large extinction (absorption + scattering) is present in the Vis range.

Fig. 2B shows the extinction spectra of water suspensions of nanometric silica (average size 40 nm) and of the composite SiO\(_2\)-rGO with 1% of carbon loading. The addition of rGO slightly increases the extinction. The spectrum of the SiO\(_2\) colloid, because of the high band gap of silica (8.9 eV [59]), is dominated by the contribution of Mie-scattering only. The SiO\(_2\)-rGO colloid retains the scattering profile of silica, overlapped with an almost flat absorption of rGO till 240 nm. Conversely, the rGO loading on TiO\(_2\), which has similar surface hydrophilicity of SiO\(_2\), reduces the UV-Vis extinction and totally changes the absorption spectrum, indicating a strong interaction between rGO and the semiconductor electronic structure. The absorption peak of rGO below 240 nm (Fig. 2B) is also manifest in the spectra of TiO\(_2\)-rGO colloids at \( \lambda < 240 \) nm (Fig. 2A), where this peak overlaps with the complex profile resulting from the scattering and absorption properties of TiO\(_2\) strongly modified by the interaction with rGO.

![Fig. 2 Extinction coefficient (\( \varepsilon_{ext} \)) of water suspensions of A) TiO\(_2\)-rGO hybrid materials with different \% rGO: A= 0 %; B= 0.5 %; C= 1.0 %; D= 2.5 %; E= 5.0 %; B) SiO\(_2\) and SiO\(_2\)-rGO (1 % of rGO) The values of \( \varepsilon_{ext} \) were obtained from the extinction spectra of suspensions with concentrations equal to 10, 50 and 100 mg dm\(^{-3}\) of the hybrid material.](image-url)
3.2 Photocatalytic experiments

The photocatalytic performance of the synthesized photocatalysts was evaluated using two different compounds, phenol and MB, under UV-Vis (TLK 40W 05 lamp) and Vis only irradiation (TLK 40W 03 lamp). The absorption spectra of phenol and MB in water solution are reported in Fig.1B-SM. The comparison of lamp emission spectra and substrate absorption spectra (Fig. 1-SM) shows that phenol does not absorb with both lamps, whilst MB absorbs from both lamps the two emission peaks in the 540-580 nm range and from the TLK03 (Vis spectrum) absorbs in the 420-480 nm range in its peak tail.

The MB spectrum in solution changes when MB is adsorbed. Fig. 3 reports reflectance spectra of MB adsorbed on pristine TiO$_2$ and the MB adsorbed as a function of the solution concentration (KM function, inset of Fig. 3). To measure the spectra, definite amounts of pristine TiO$_2$ were equilibrated in the dark in the presence of increasing amount of MB (0 to 8.0×10$^{-5}$ mol/g TiO$_2$). After equilibration the suspensions were filtered and dried in oven at 373 K for 1 hour. The dried powders were grind and their %R spectra were recorded. As Fig. 3 reports, the quantity adsorbed is linear with MB solution concentration, indicating that at 8.0×10$^{-5}$ mol g$^{-1}$ on pristine TiO$_2$ the surface is far from saturation of the MB adsorbing sites. The same ratio [MB]/C$_{TiO2}$ will be used during the photodegradation experiments. From reflectance spectra of Fig. 3 it is also manifest a blue shift of ≈ 80 nm for the MB absorption maximum. This shift is comparable to that reported in the literature [60,61,62] for the formation of MB dimers. Because the significant adsorption of MB onto the TiO$_2$ surface, the blue shift can be ascribed to adsorption on TiO$_2$ surface. A shift of ≈ 80 nm of the absorption maximum corresponds to a transition between two states separated by 0.24 eV in energy, and an equilibrium adsorption constant of roughly 1.2×10$^4$, slightly larger than the reported values (3–10×10$^3$) for dimerization in solution [60,61,62]. The strong interaction of MB with the catalyst surface is an essential condition for an efficient electron transfer in the case of correct positioning of the energy bands/states. This shift increases the absorption of adsorbed MB in the presence of TLK03 (Vis spectrum), whilst it has only a minor effect on absorption in the case of illumination with the TLK05 (UV spectrum).

![Fig. 3](image-url) % Reflectance spectra of TiO$_2$ Hombikat N100 equilibrated in the presence of different amount of MB (mol MB / g TiO$_2$ from 0 to 8.0×10$^{-5}$ mol/g). Inset: K-M function value at 582 nm (f(R)$_{582nm}$) for the samples equilibrated at different concentrations of MB in solution.
3.2.1 Phenol

Fig. 4 shows the photocatalytic time evolution under UV-Vis light of phenol in the presence of TiO$_2$-rGO, with different rGO loading at total catalyst concentration $C_{\text{cat}} = 0.5$ g dm$^{-3}$. The degradation follow first order kinetics. The degradation kinetic constants are reported in the inset of Fig. 4 and in Table 1-SM (entries 1-5). The phenol degradation rate decreases with the increment of the rGO loading. Opposite to the reported data, where the coexistence of rGO and TiO$_2$ phases induced generally better photocatalytic performances [21,37], in this case the presence of rGO decreases the substrate transformation rate. Under the adopted experimental conditions the amount of phenol adsorbed on TiO$_2$ is negligible compared to the fraction remaining in solution, and in the presence of increasing amount of rGO no increment of the adsorbed fraction of phenol was observed. This evidence is contrasting with data reported by Wang et al. [37] who observed an increment of the adsorbed phenol fraction with the increment of %rGO on TiO$_2$-rGO composites synthesized by a one-step hydrothermal method. The different results could be related to the different synthetic procedure, which could give materials with a significantly different degree of rGO reduction.

As under UV-Vis irradiation only the catalyst absorbs light, the decrease of phenol degradation rate with increasing rGO loading depends on the reduction of extinction spectra as % rGO increases, as already discussed with reference to Fig. 2. Factually, less light is absorbed, leading to a reduced charge carrier production and the decrease of the rate. A competition for UV light between the inorganic and rGO phase was also recently proposed by Xiong et al. [63] to justify the experimental evidences observed with BiOIO$_3$-rGO nanocomposites under Vis and UV irradiation. From spectra in Fig. 2 it is not possible to decouple absorption and scattering processes, although reflectance spectra in Fig. 5-SM suggest that absorption is mainly due to band-gap absorption of TiO$_2$. Then the visible tail observed in Fig. 2 is due only to scattering properties of N100 TiO$_2$. In the presence of rGO, less light is absorbed by TiO$_2$ because of the presence of the adsorbed rGO phase increases the scattering over the entire UV-Vis spectrum. Alternatively, a lowering of the quantum yield due to a larger recombination rate due to an increasing amount of rGO on TiO$_2$ can be invoked. In this case instead of being beneficial, rGO would behave as a recombination center. This would happen independently on the substrate, contrary to many positive effects reported in literature and later in this work. Consequently, this last hypothesis is discarded.

![Photocatalytic degradation under UV irradiation (TLK 40W 05) of 1 mM phenol at pH 3 on TiO$_2$-rGO hybrid materials with different rGO loading. $C_{\text{cat}}$ 0.5 g dm$^{-3}$. Inset: pseudo first order kinetic constants for the photocatalytic transformation of phenol as a function of the % rGO.](image)
Phenol degradation was also carried out under Vis light (TLK 40W 03 lamp). Very low degradation rates were observed in the presence of both pristine TiO$_2$ and TiO$_2$-rGO materials. The kinetic constant observed for TiO$_2$-2.5\% rGO was $(1.9\pm0.1)\times10^{-4}$ min$^{-1}$, 17 times lower than the degradation kinetic constant measured under UV irradiation. These results indicate that the absorption of the hybrid photocatalyst, and mainly of rGO, as pristine TiO$_2$ is not excited in the Vis, does not produce photoexcited species able to carry out the reaction with phenol. The possible hypotheses are two: 1) the excited rGO is not able to inject electrons in TiO$_2$, and photogenerated species recombine in rGO very rapidly compared to their reaction rate with phenol; 2) The excited electrons in high energetic rGO states can be delocalized toward TiO$_2$ conduction band (rGO injects electrons into TiO$_2$), charge separation is attained and photogenerated species do not recombine, but HOMO of the substrate to be transformed (here phenol) is lower in energy than the energy state of rGO where an electron vacancy has been photogenerated. In this case the reaction is thermodynamically impeded. However it is possible that with other substrates this thermodynamic impediment is removed. As an example, in the case of risperidone, which does not absorb in near UV, the loading of rGO on TiO$_2$ increases the photocatalytic rate both under near UV and Vis irradiation.[64]

3.2.2 Methylene Blue

Fig. 5A shows the change in the MB concentration under UV-Vis irradiation. The dye concentration in solution before the irradiation is lower than the nominal value in every instance in agreement with the adsorption discussed before (see also Fig. 3). The adsorption of MB in the adopted conditions is significant and increases with the increment of the rGO loading (e.g. TiO$_2$-5\%rGO adsorbs more than 85\% of the added MB, see inset of Fig. 5A).

![Fig. 5 Photocatalytic degradation under UV-Vis of 4x10$^{-5}$ M of MB at pH 3 in the presence of TiO$_2$-rGO with different \% rGO. C$_{cat}$ 0.5 g dm$^{-3}$. MB concentration (A) and fraction of MB (B) in solution as a function of the irradiation time. Insets: (A) fraction of MB adsorbed on the catalyst as a function of the \% rGO; (B) pseudo first order kinetic constants for the MB transformation as a function of the \% rGO.](image)

The C/C$_0$ showed exponential decay (Fig. 5B). The overall observed kinetic constants $k_{obs}$ are reported as inset in Fig. 5B and in entries 6-9 of Table 1-SM. The observed kinetic constants are deduced from the time evolution of [MB] in aqueous solution as $d[MB]_{sol}/dt=-k_{obs}\times[MB]_{sol}$. The linear relation of $[MB]_{ads}$ vs $[MB]_{sol}$ evidenced in Fig. 3 suggests that $[MB]_{ads} = \beta \phi C_{cat} K [MB]_{sol}$, where $\beta$ is the moles of sites per catalyst mass, $\phi$ is the fraction of constituent of the hybrid catalyst, $C_{cat}$ is the mass dm$^{-3}$ of hybrid catalyst, and $K$ is the equilibrium adsorption constant. In the case of linear partition between the aqueous phase and rGO / TiO$_2$ phases, it can be demonstrated that $k_{obs}=k_{sols}$, where $k_{sols}$ is the first order kinetic constant that would be obtained following the time evolution of the total concentration in the system (both adsorbed and free).
from \( \frac{d[MB_{tot}]}{dt} = -k_{tot} \times [MB_{tot}] \). In other cases they are proportional. Then, the trend of observed kinetic constants \( k \) are representative of the overall degradation of substrate in the hybrid system. The rate equations that can be derived from a kinetic model by taking into account the adsorption constants and kinetic constants specific for the two adsorbing phases (\( k_G \) and \( k_T \), for rGO and TiO\(_2\), respectively), are not developed here as they are outside of the scope of the paper. However, assuming that the rate at the surface is proportional to the local (adsorbed) concentration it can be easily demonstrated that there is no minimum or maximum of \( k_{obs} \) as a function of the rGO amount. When \( k_G > k_T \), the rate increases with graphene content and vice versa, irrespective of the value of the adsorption constants. Then the observed effects must be explained with factors other than those above cited (adsorption constants and kinetic constants specific for the two adsorbing phases).

As observed for the UV photocatalytic abatement of phenol, also in this case the presence of rGO has an initial negative effect. The kinetic constants show a minimum for 2.5% rGO. This is conflicting with the previously reported bell-shaped profile of the rate with the increment of \%rGO. [31] The discrepancies point out the role of the method of synthesis which can significantly affect the properties of the material and consequently its photocatalytic behavior. The observed dependence of the rate on the rGO amount can be explained invoking two different effects. At low rGO loading the shielding of TiO\(_2\), as already discussed for phenol, decreases the light absorbed by TiO\(_2\). In addition, assuming that the reactivity is mainly dominated by TiO\(_2\), a stronger adsorption on graphene than on TiO\(_2\) implies that the substrate is scarcely transferred during the photocatalytic reaction to the TiO\(_2\) surface. It is apparent that because the substrate is adsorbed on graphene, it must react on its surface. Consequently, due to the two cited reasons the overall reaction rate will be reduced unless holes on TiO\(_2\) (already decreased by light shielding) are transferred to rGO. As a further increase of rGO loading increases both the MB adsorbed on rGO and the rate, it must definitely concluded that MB reacts on rGO and transfer of holes from TiO\(_2\) to rGO is operating. This conclusion agrees with Wang et al. [31] that holes are the main oxidant species and that in the hybrid catalyst oxidative species are not changed by introduction of graphene-like carbon to TiO\(_2\). Concurrently with TiO\(_2\) excitation, also rGO absorbs light and excited electrons in high energetic rGO states must be delocalized toward TiO\(_2\) conduction band (rGO injects electrons in to TiO\(_2\)) to avoid recombination.

From Fig. 6A and Fig. 6B show the change in the MB concentration in solution under Vis irradiation and the related \( C/C_0 \) profiles. The amount of MB adsorbed in this experiment (inset of Fig. 6A)
is quite similar to that observed for previous experiments (inset of Fig. 5A), so a strong adsorption of MB with increasing rGO loading is confirmed. Opposite to the case of phenol photocatalytic degradation under Vis irradiation where negligible removal of the substrate was detected, in this case the MB disappearance is significant, although at irradiation times longer than under UV-Vis irradiation. The abatement profiles follow an exponential decay and the overall $k$ kinetic constants are reported in the inset of Fig. 6B (and entries 10-13 of Table 1-SM).

The kinetic constants, after a minimum for TiO$_2$-1%rGO, increase with the increment of the %rGO, with a shape similar to that observed under UV-Vis irradiation, but with values lower of about one order of magnitude. Under Vis irradiation both rGO and MB can absorb, whilst TiO$_2$ does (almost) not. The slight decrease of the rate at TiO$_2$-1%rGO could be due to the previous invoked effect of light shielding on TiO$_2$, as also with the Vis lamp a small absorption by TiO$_2$ is still possible and a minimal contribution of semiconductor mechanism is present. So the degradation mechanism must involve the light absorption by rGO, or a dye sensitized mechanism.

Between the two hypotheses made for justifying the very scarce reactivity of phenol, the first one (fast recombination of photogenerated species in rGO because the excited rGO is not able to inject electrons into TiO$_2$) must be rejected as MB transforms. The second hypothesis (rGO injects electrons into TiO$_2$) could be fine if the HOMO of MB is higher in energy than the energy state of rGO where an electron vacancy has been photogenerated. In this case the reaction is thermodynamically favored and charge separation is attained. However, the increase of rGO content implies that the amount of absorbed light is reduced (see Fig. 2A) and consequently the rate would be diminished, contrary to what is observed (inset of Fig. 6B). Then, the MB degradation must be explained by considering a dye-sensitized mechanism.

The dye-sensitized mechanism involves the light absorption by MB, charge injection into TiO$_2$ or rGO and evolution of the oxidized MB to products. The absorption of light from the MB-TiO$_2$ surface species was well studied [21,65,66] and the role of self-induced photosensitization outlined.[67] The excited electrons, which occupy the LUMO of the adsorbed MB on TiO$_2$, can be injected into titania CB promoting the MB degradation. As MB is adsorbed on TiO$_2$ (Fig. 3) but preferentially adsorbed on rGO (insets of Fig. 5A and Fig. 6A), the electron must be injected from the LUMO of MB to rGO. Then, according to the conclusions drawn from MB irradiation under UV-Vis lamp, rGO would transfer these electrons to TiO$_2$.

To confirm these conclusions, experiments of MB photodegradation under Vis irradiation was carried out in the presence of the SiO$_2$-rGO hybrid materials synthesized by using the same methods adopted for producing TiO$_2$-rGO. Under the adopted experimental conditions (0.5 g dm$^{-3}$ of catalyst, initial MB concentration 4x10$^{-5}$ M, pH 3), the silica adsorbs a significant amount of MB (around 75%) and this value increases with the increment of the %rGO. Both on pristine SiO$_2$ and on SiO$_2$-rGO hybrid materials, no MB photocatalytic degradation was observed under the adopted conditions. From an energetic point of view an electron in the LUMO of MB adsorbed on the catalyst surface (SiO$_2$ or SiO$_2$-rGO) is not able to move toward the CB of SiO$_2$. This conclusion was expected for SiO$_2$ due to its very high work function [43]. Then on SiO$_2$ after light excitation of MB only recombination is possible. In the presence of rGO, as reaction does not proceed and also electron transfer from rGO to SiO$_2$ is impeded because of the SiO$_2$ high work function, the electron transfer to empty electronic states of rGO must be followed by recombination with oxidized MB, giving a null cycle.

Then the mechanism of MB degradation in the presence of the hybrid TiO$_2$-rGO is initially promoted by a dye-sensitized mechanism. In the presence of rGO, electrons are mostly transferred to rGO, and then from rGO to TiO$_2$. When excited electrons in rGO cannot be released (for example to TiO$_2$, for which rGO acts as sensitizer and also as hole acceptor), rGO acts a recombination center.
4. Conclusions

The analysis of the photocatalytic behavior of TiO$_2$-rGO hybrid materials synthesized at different loading of rGO, underlines its complexity as the working mechanisms depend not only on the substrate degraded, but also on the kind of irradiation adopted. A careful optical characterization of the hybrid materials and lamp emission allows disentangling many tricky rate trends observed changing % rGO in the hybrid catalyst. Phenol is degraded predominantly via UV-based photocatalysis and the content of rGO decreases the rate by increasing the amount of scattered light. MB is degraded via UV-based photocatalysis and in the case of visible irradiation via a dye-sensitized mechanism. Visible sensitization driven by rGO phase seems not to be the predominant mechanism in the studied experimental conditions and with the studied photocatalytic materials. However, rGO plays a key role for adsorption and as electron passageway for dye-sensitized mechanism. Because the adsorption of MB on the TiO$_2$ surfaces activates the dye-sensitized process which is not directly related to the real photocatalytic features of the hybrid material, the studies that use MB alone with hybrid materials and illumination with not well characterized emission could lead to misleading conclusions on the role of rGO. It is not possible to generalize the conclusions obtained on the photocatalytic behavior of the materials we synthesized to the entire set of reported TiO$_2$-rGO materials, because the numerous modifications of the TiO$_2$-rGO synthetic strategies can affect abruptly their photocatalytic performance. In particular the degree of rGO reduction can influence the energy position of its LUMO allowing/hindering the electron injection from/toward adsorbed species. Residual oxygenated groups on rGO can also be involved in acid-base equilibria which can shift the Fermi level position of rGO as a function of pH, changing the relative position of its electronic states in comparison with those of TiO$_2$.

Our study strongly suggests that among many mechanisms reported on the role of rGO (and graphene) the electron transfer process can occur from photoexcited states of rGO onto the titania, and holes from titania migrate to it, where adsorbed substrates are oxidized only if their HOMO has higher energy (less positive standard redox potential) than the empty state of excited rGO. Then, reduced graphene (and possibly also graphene) is advantageous when substrates are adsorbed and when the charge separation is possible (coupled with a proper semiconductor like TiO$_2$). Alone, or coupled with low work function oxides, rGO could be ineffective.

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**SUPPLEMENTARY MATERIAL**

**Fig. 1-SM** (A) Emission spectra of the lamps adopted for the irradiation tests in the 200-800 nm range; (B) Absorption spectra of phenol and methylene blue in the 200-800 nm range.
Fig. 2-SM HR-TEM micrographs of the sample TiO$_2$-GO before chemical reduction with 5% GO loading. Original magnifications: a) × 50 k, b) × 40 k, c) × 30 k and d) × 100 k.
Fig. 3-SM (A) HR-TEM micrographs of the sample TiO$_2$-rGO with 5% rGO loading. Original magnifications: a) $\times$ 30 k, b) $\times$ 40 k, c) $\times$ 100 k and d) $\times$ 200 k.
Fig. 4-SM. XPS-ESCA peak of C(1s) core level of a) TiO$_2$-GO, b) TiO$_2$-rGO(chem), with a 5% GO/rGO loading.
Fig. 5-SM Diffuse reflectance spectra of TiO$_2$-rGO hybrid materials at different rGO loadings: a = 0, b = 0.5, c = 1, d = 2.5 and e = 5 %; A) Spectra in % Reflectance; B) Spectra in Kubelka-Munk function (inset: apparent bang gap as a function of the % rGO.)
**Table 1-SM** Pseudo first-order kinetic constants with the related error for all the photocatalytic transformation of phenol and MB under irradiated (UV-Vis and Vis only)

<table>
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<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Irradiation</th>
<th>%rGO</th>
<th>( k, \text{ min}^{-1} )</th>
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<tr>
<td>1</td>
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<tr>
<td>5</td>
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<tr>
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<tr>
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<td>MB</td>
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<tr>
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<td>( (1.6\pm0.1)\times10^{-2} )</td>
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<tr>
<td>9</td>
<td>MB</td>
<td>UV-Vis</td>
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<td>( (4.0\pm0.4)\times10^{-2} )</td>
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<tr>
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<td>MB</td>
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<tr>
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<tr>
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## References


