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**Photocatalytic process in TiO<sub>2</sub>/graphene hybrid materials. Evidence of charge separation by electron transfer from reduced graphene oxide to TiO<sub>2</sub>**

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1           **Photocatalytic process in TiO<sub>2</sub>/graphene hybrid materials.**  
2           **Evidence of charge separation by electron transfer from**  
3           **Reduced Graphene Oxide to TiO<sub>2</sub>**

4  
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10  
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12  
13           **Abstract**

14           Different amounts of graphene oxide were chemically reduced with hydrazine in the presence  
15 of nanometric TiO<sub>2</sub> and SiO<sub>2</sub>. The photocatalytic performance of the resulting hybrid materials  
16 was compared with pristine supports using phenol and methylene blue (MB) under two different  
17 irradiation conditions (UV-Vis and Vis only light). MB is strongly adsorbed on the hybrid  
18 materials. Significant MB degradation rates were observed on pristine TiO<sub>2</sub> and hybrid TiO<sub>2</sub>-  
19 reduced graphene oxide (rGO) material under both irradiation conditions. In the presence of the  
20 hybrid catalyst, the degradation of MB under Vis is due to the dye-sensitized mechanism, while  
21 under UV-Vis there is an additional semiconductor-based photocatalytic mechanism.  
22 Conversely, the presence of rGO reduces the rate of photocatalytic transformation for the poorly  
23 adsorbed phenol under UV irradiation, and a negligible degradation rate was observed under Vis.

24           The UV-Vis absorption spectra of aqueous suspensions of hybrid materials with different rGO  
25 loading indicate a strong interaction of the two materials and a reduction of the light absorption  
26 due to the presence of rGO. Among many mechanisms reported on the role of rGO, it is inferred  
27 that the working mechanism involves electron transfer from photoexcited states of rGO onto the  
28 titania, and holes migration from titania to rGO, where adsorbed substrates are oxidized. This  
29 oxidation is possible only if the substrate HOMO has higher energy (less positive standard redox  
30 potential) than the empty states of excited rGO, supposedly for MB and not for phenol. Then,  
31 reduced graphene is advantageous when substrates are adsorbed and when the charge separation  
32 is possible (coupled with a proper semiconductor like TiO<sub>2</sub>). Alone, or coupled with low work  
33 function oxides like SiO<sub>2</sub>, rGO could be ineffective.

34  
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36  
37           **Keywords**

38           Reduced Graphene Oxide; TiO<sub>2</sub>-rGO hybrid materials; Visible Sensitization; Charge  
39 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 TiO<sub>2</sub>-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 TiO<sub>2</sub>-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 TiO<sub>2</sub>-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 TiO<sub>2</sub>-rGO composites, the main active oxidation species were inferred from the disappearance kinetics of different substrates in the presence of •OH and hole (h<sub>vb</sub>) 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 TiO<sub>2</sub>-rGO hybrids has not been reached. The operational mechanisms active on TiO<sub>2</sub>-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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 (TiO<sub>2</sub> 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 TiO<sub>2</sub>. 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 TiO<sub>2</sub> 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

89 mechanism. The injected electron located in interfacial states then moves into bulk TiO<sub>2</sub>  
90 dissipating the energy *surplus* due to electron-vibrational interactions. [32]

91 2) Electron transfer from TiO<sub>2</sub> to rGO. A UV-based transaction promotes electrons into the  
92 TiO<sub>2</sub> CB which are rapidly transferred onto the graphene-like sheets. The common reaction  
93 scheme proposed for the interface rGO/TiO<sub>2</sub> allows the delocalization of TiO<sub>2</sub> CB electrons onto  
94 the rGO structure (rGO in this case acts as an electron reservoir). The work function of graphene  
95 is 4.42 eV, while the conduction band (CB) of TiO<sub>2</sub> is located at -4.21 eV with energy gap  
96 amplitude of 3.2 eV (for the most photoactive anatase allotrope). [34,35,36] As a consequence,  
97 the electrons photo-promoted in the CB can be injected into the graphene aromatic structure  
98 avoiding their recombination with the valence band (VB) holes. The decrement of the electron  
99 transfer resistance at the TiO<sub>2</sub>-rGO/electrolyte interface compared to that at the TiO<sub>2</sub>/electrolyte  
100 interface, observed with EIS by Wang et al., suggested a rapid photoinduced charge separation  
101 and a diminished possibility of electron-hole recombination on irradiated TiO<sub>2</sub>-rGO materials.  
102 [31] Wang et al. proposed that not only electrons can be easily transferred from photo-excited  
103 TiO<sub>2</sub> onto rGO sheets, but also valence holes can move toward the rGO phase promoting an  
104 effective degradation of adsorbed phenol molecules. [37]

105  
106 The injection of electrons from excited rGO states toward TiO<sub>2</sub> CB or alternatively from TiO<sub>2</sub>  
107 CB toward delocalized empty rGO states is not a sufficient condition to guarantee the  
108 degradation of the substrate, because the photogenerated empty states (a hole in the VB or an  
109 empty states in the rGO) must be low enough in energy (redox potential sufficiently positive) to  
110 promote the oxidation of the substrate itself (injection of an electron from the substrate to the  
111 photogenerated empty state). It is worth noting the stability of certain organic substrates under  
112 UV irradiated TiO<sub>2</sub> as a consequence of their too low HOMO energetic position (e.g. cyanuric  
113 acid is stable in photocatalytic conditions [38,39]). Consequently, the energetic position of the  
114 HOMO of a substrate is a key point to allow its transformation under irradiated TiO<sub>2</sub>-rGO  
115 hybrids especially in the case of Vis only irradiation which does not activate TiO<sub>2</sub> band to band  
116 transitions which generate very oxidant VB holes.

117  
118 C. In the presence of dyes, other two different visible-activated dye-sensitized pathways  
119 have to be considered: in the case of a pure TiO<sub>2</sub> catalyst the adsorbed dyes can inject  
120 photo-excited electrons onto the titania CB, while in the presence of TiO<sub>2</sub>-rGO  
121 composites this mechanism can couple with an alternative reaction path in which the dye  
122 photo-excited electrons can be delocalized in the electronic diffuse states of rGO. In both  
123 cases the oxidized dye molecules, formed as a consequence of a single or multi-electron  
124 injection from the photo-excited dye to the delocalized empty states of rGO or TiO<sub>2</sub>, can  
125 autonomously evolve toward transients or stable by-products and consequently toward  
126 the substrate degradation. Pastrana-Martínez et al. from an in depth analysis of the  
127 photocatalytic activity of TiO<sub>2</sub>-rGO composites toward the colorless diphenhydramine  
128 and the organic dye methyl orange, emphasized the complexity of the operational  
129 mechanisms concluding that rGO can operate as visible light sensitizer of TiO<sub>2</sub>, but in the  
130 presence of visible-absorbing species the degradation process can be dominated by a  
131 direct self-oxidation of the visible-absorbing species. [30]

132  
133 Herein, we report the two-steps synthesis of TiO<sub>2</sub>-rGO hybrid materials (synthesis of GO by  
134 chemical oxidation of graphite, exfoliation and in situ reduction of GO on the TiO<sub>2</sub> surface) and  
135 the investigation of their photocatalytic behavior. The photocatalytic tests were carried out  
136 comparing two substrates and two illumination sources aiming to give insight on the working  
137 mechanisms and on the relation between the absorbing optical properties of the tested catalyst  
138 and its photocatalytic behavior. This approach allows us to discriminate among the potential

139 operational photocatalytic mechanisms cited above and, hopefully, to clarify some aspects of the  
140 photo-reactivity of TiO<sub>2</sub>-rGO composites.

## 141 **2. Materials and Methods**

### 142 **2.1 Materials**

143 Graphite natural powder (briquetting grade,  $\approx$  100 mesh, 99.9995%) was purchased from Alfa  
144 Aesar, H<sub>3</sub>PO<sub>4</sub> (85%), H<sub>2</sub>SO<sub>4</sub> (96%), KMnO<sub>4</sub> (>99%), HCl (37%), methanol gradient grade from  
145 Carlo Erba and HClO<sub>4</sub> (85%), Methylene Blue (MB) trihydrate (>99%), H<sub>2</sub>O<sub>2</sub> (35%), hydrazine  
146 monohydrate (98%) and phenol (>99%) from Sigma Aldrich. Titanium dioxide (Hombikat  
147 N100: 100% anatase, BET specific surface area 100 m<sup>2</sup>/g, average crystal size 20 nm) was  
148 purchased from Sachtleben Pigments. Fumed silica SiO<sub>2</sub> Aerosil OX 50 (BET specific surface  
149 area 50 m<sup>2</sup> g<sup>-1</sup>) was bought from Evonik. Zero-grade air for Total Organic Carbon (TOC)  
150 analysis was purchased from Sapio (Turin, Italy). All the compounds were used as received  
151 without any further purification step. Water was purified with a MilliQ plus apparatus (in-line  
152 TOC = 2 ppb, conductivity 18.2 M $\Omega$  cm, Merck Millipore).

### 153 **2.2 Synthesis of GO and TiO<sub>2</sub>-rGO hybrid materials**

154 Graphene oxide was produced by chemical oxidation using the modified Hummers and  
155 Staudemaier's method [40] proposed by Huang et al. [41]. Briefly, 500 mg of graphite powder  
156 were dispersed in a solution obtained with 27.3 mL H<sub>2</sub>SO<sub>4</sub>, 3.30 mL H<sub>3</sub>PO<sub>4</sub> and 2.78 g KMnO<sub>4</sub>.  
157 The suspension was magnetically stirred at r.t. for 1, 2 or 3 days, respectively. After 12-15 hours  
158 a viscous brownish gel was obtained. After the desired oxidation time the suspension was  
159 carefully diluted in 120 mL of water and titrated with H<sub>2</sub>O<sub>2</sub> till a bright yellow suspension was  
160 obtained (the violet MnO<sub>4</sub><sup>-</sup> ions are completely reduced to colorless Mn<sup>+2</sup>). The yellow graphite  
161 oxide formed was washed three times with 1 M HCl and the solid separated with centrifugation  
162 (1200 G). During the washing procedure the color changed from bright yellow to brownish. The  
163 solid was then washed 3 times with water. During the washing procedure the graphite oxide  
164 experienced exfoliation. The suspension was then dialyzed toward water (Spectra/Por® Dialysis  
165 Membrane, MW cut off 6-8000 Da) until the pH of the external solution was stable and close to  
166 4. The concentration of carbon in the GO suspensions was evaluated measuring the TOC on  
167 diluted suspensions after dialysis.

168 The TiO<sub>2</sub>-rGO hybrid materials were obtained by chemical reduction with hydrazine solution  
169 (65 %) of different amounts of GO (3 days of oxidation) in the presence of TiO<sub>2</sub> according to a  
170 modification of the method reported in [42]. Stable suspensions of 4 g dm<sup>-3</sup> TiO<sub>2</sub> in water were  
171 obtained by sonication. Different amounts of GO were added to obtain materials with different  
172 carbon loading. The addition of GO quickly destabilized the TiO<sub>2</sub> colloids owing to adsorption  
173 of GO on the titania surface. Then 300  $\mu$ L of hydrazine were added drop wise at r.t. After 12  
174 hours of vigorous stirring the suspensions were filtered on 0.45  $\mu$ m hydrophilic filters  
175 (Whatman, NL 17 membrane filters, polyamide) and washed with water. Finally, the produced  
176 powder was dried at 373 K for 1 hour.

177 By using the same method adopted for the synthesis of TiO<sub>2</sub>-rGO materials, we produced  
178 hybrid SiO<sub>2</sub>-rGO materials with different loading of rGO. GO was adsorbed on fumed silica  
179 SiO<sub>2</sub> Aerosil OX 50 and reduced with hydrazine. The synthesis of these hybrid materials was  
180 aimed to study the photochemical behavior of the rGO adsorbed on an inert support. The low  
181 work function of SiO<sub>2</sub> ( $\chi \approx$  1.2 eV [43]) hinders the injection of electrons from the excited states  
182 of rGO to the inorganic support allowing the study of the photochemical behavior of rGO alone.

### 183 **2.3 Photocatalytic Tests**

184 The photodegradation experiments were carried out using cylindrical Pyrex cells (4.0 cm  
185 diameter and 2.5 cm height, cut-off at 295 nm) on 5 cm<sup>3</sup> of aqueous suspension containing the  
186 desired amount of the photocatalyst powder ( $C_{\text{cat}}$  0.5 g dm<sup>-3</sup>), substrate (1 mM phenol or 4×10<sup>-5</sup>  
187 M MB) and HClO<sub>4</sub> 10<sup>-3</sup> M to execute the test at pH 3±0.2. The slurries containing the  
188 photocatalyst were prepared using sonication. The irradiation was carried out with a set of three  
189 TLK 40W/05 (UV-Vis) or TLK 40W/03 (Vis only) fluorescent lamps (Phillips, Eindhoven,  
190 Nederland). The former has an integrated irradiance of 25.2±1 W m<sup>-2</sup> in the 300-400 nm  
191 wavelength range, with a maximum emission at 365 nm (able to activate the band to band  
192 transition in TiO<sub>2</sub> based materials), and minor emission in the Vis range (10.5±1 W m<sup>-2</sup> in the  
193 400-800 nm range). The latter has an integrated irradiance of 40±1 W m<sup>-2</sup> in the 400-800 nm  
194 wavelength range, with a maximum emission at 423-436 nm, and negligible emission in the UV  
195 range (1.5 W m<sup>-2</sup> in the 300-400 nm range). The emission spectra are reported in Fig.1A of the  
196 Supplementary Materials (hereafter SM).

197 During irradiation the suspension was magnetically stirred and the cell temperature was 30±3  
198 °C. After irradiation the suspension was filtered through 0.45 µm cellulose acetate membrane  
199 filter (Millipore HA) and analysed as required (HPLC-UV for phenol, spectrophotometrically at  
200 665 nm for MB).

201 The photocatalytic transformation of the studied substrates followed pseudo-first order  
202 kinetics. The profiles of concentrations of the phenol and MB were fitted with a pseudo-first  
203 order equation of the form  $C_t / C_0 = \exp(-k t_{\text{irr}})$ , where  $C_t$  is the substrate concentration at the  
204 irradiation time  $t_{\text{irr}}$ ,  $C_0$  the initial concentration, and  $k$  the pseudo-first order degradation rate  
205 constant. The values of  $k$  are reported with their uncertainty (confidence intervals evaluated  
206 through the goodness of the fit, representing intra-series variability at 0.95 level of confidence).  
207

### 208 **2.4 Methods**

209 The extinction spectra of TiO<sub>2</sub>, TiO<sub>2</sub>-rGO, SiO<sub>2</sub> and SiO<sub>2</sub>-rGO suspensions were recorded with  
210 a Varian CARY 100 Scan UV-Vis spectrophotometer, using quartz cuvettes with a path length of  
211 1 cm. The % reflectance spectra were recorded on opaque homogenized powdered samples with  
212 a Varian Cary 5000 UV-VIS-NIR reflectance spectrometer.

213 The UV-Vis lamp irradiances were measured with an Ocean Optics USB2000+UV-VIS  
214 equipped with a 400 µm optical fiber (30 cm length) with a cosine corrector (Ocean Optics, CC-  
215 3-UV-T, optical diffuser in PTFE, wavelength range 200-2500 nm, OD diameter 6.35 mm, Field  
216 of View 180°). The spectrometer was calibrated with an Ocean Optics DH-2000-CAL  
217 Deuterium-Halogen Light Sources for the UV-Vis-NIR calibrated for absolute irradiance  
218 measurements from the vendor (Radiometric Calibration Standard UV-NIR, certificate of  
219 calibration #2162).

220 Phenol degradation kinetic was monitored with HPLC-UV (Hitachi L2200, LaChrom Elite,  
221 Lichrospher R100-CH 18/2 column (250 mm)). The elution was carried out at 1 cm<sup>3</sup> min<sup>-1</sup> with  
222 H<sub>3</sub>PO<sub>4</sub> 4.2 mM: Methanol 85:15 in isocratic mode. The retention time of phenol under this  
223 condition is 9.9 minutes. The injection volume was 60 µL.

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

228 The morphology of the hybrid samples before (TiO<sub>2</sub>-GO) and after the reduction with  
229 hydrazine (TiO<sub>2</sub>-rGO) was investigated by means of a high-resolution transmission electron  
230 microscope (HR-TEM, JEOL JEM 3010), equipped with a LaB<sub>6</sub> source with an accelerating  
231 voltage of 300 kV.

232 The XPS analysis was carried to investigate the nature of the carbon atoms in the TiO<sub>2</sub>-GO and  
233 TiO<sub>2</sub>-rGO samples. The XPS spectra were recorded on pelletized samples with a VSW TA10 Mg  
234 K $\alpha$  X-ray source (1253.6 eV) equipped with a VSW Class 100 Concentric Hemispherical  
235 Analyzer (VSW Scientific Instruments Ltd).  
236

## 237 **3 Results and Discussion**

### 238 **3.1 Material characterization**

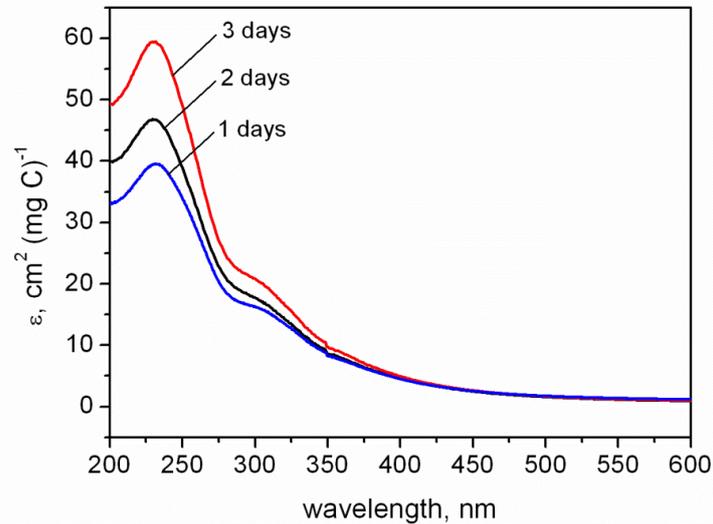
239 The simple oxidation method here adopted allows the preparation of significant amount of GO,  
240 the raw material for the successive synthesis of rGO, contrariwise to the sonochemical methods  
241 adopted for the exfoliation of graphite and one-step production of micro-amount of graphene  
242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

243 Fig. 1 shows the UV-Vis absorption spectra of the suspensions of GO obtained after 1, 2 and 3  
244 days of chemical oxidation, respectively. The spectra are normalized for the TOC concentration  
245 of the analyzed suspensions. The spectra are dominated by the peaks at  $\approx$ 230 nm. These signals  
246 are due to the  $\pi \rightarrow \pi^*$  transition of the C=C bonding. [41,46,47] The accurate position of the  
247 peaks are 231, 229 and 228 nm for the samples oxidized for 1, 2 and 3 days (*1D*, *2Ds*, *3Ds*),  
248 respectively. The lower is the peak position (as wavelength) the lower is the degree of  
249 aromaticity of the graphene-like planar structure. Accordingly, the *3Ds* sample shows the peak at  
250 the shortest wavelength. The main peaks has a shoulder at roughly 300 nm, due to the  $n \rightarrow \pi^*$   
251 transition of the carbonyl groups. [48,49] The larger is the intensity of the 300 nm shoulder, the  
252 larger is the concentration of C=O (carbonyl or carboxyl) groups in the samples and so the  
253 degree of oxidation. The ratio between the absorbance at 230 and 300 nm is also informative.  
254 This ratio is 2.4, 2.6 and 2.8 for the *1D*, *2Ds* and *3Ds* samples, respectively. It increases with the  
255 increment of the oxidation degree because superior is the oxidation of graphene basal planes,  
256 greater it is the amount of isolated aromatic rings which increment the absorbance at 230 nm  
257 [49]. The obtained ratios ( $> 2$ ) are very similar to those reported by Huang et al. [41] for GO  
258 samples with significantly larger lateral size.

259 The size of the GO particles after three days of oxidation in the same condition above  
260 described has been previously measured with dynamic light scattering (DLS) and reported in  
261 [29]. After exfoliation the GO particles have a hydrodynamic radius equal to  $500 \pm 70$  nm. This  
262 value is in agreement with those reported by other authors for GO obtained in very similar  
263 experimental conditions [50].

264 The proposed methods for the reduction of GO to graphene are numerous (thermal annealing,  
265 microwave and photo reduction [29], chemical, photocatalytic and solvothermal reduction) and  
266 affect the final performance of materials. For a full analysis of this topic please refer to the  
267 review by Pei and Cheng [51]. The production of the TiO<sub>2</sub>-rGO was here carried out by chemical  
268 reduction of different amount of GO (*3Ds*) adsorbed on the TiO<sub>2</sub> surface with aqueous hydrazine  
269 solution. Different materials with increasing amount of carbon loading (from 0.5 to 5% w/w)  
270 were successfully synthesized. The chemical reduction in water by hydrazine and its derivatives  
271 results in agglomerated graphene-based nanosheets due to the increase of hydrophobicity. [37]  
272 We carried out the reduction of GO adsorbed on TiO<sub>2</sub> at r.t. and at the boiling point. We  
273 observed that only in the former case is a single solid phase synthesized, while in the latter case  
274 two separated phases are produced. Gao et al. [49] studied systematically the reduction of GO by  
275 hydrazine at r.t. and at high temperature. The hydrazine reduction at r.t. completely reduces the  
276 epoxide and hydroxyl groups located at the interior of the aromatic domains and only partially  
277 the carboxyl moieties at the edge of the aromatic domains. At higher temperature the reduction  
278 of the hydroxyls at the edge of the aromatic domains and of the carboxyl groups occurs. [49] Our  
279 experimental results support the conclusion that heating allows further reduction of the

280 oxygenated groups which links GO to the TiO<sub>2</sub> surface (e.g. the ester groups obtained from the  
 281 reaction between the TiO<sub>2</sub> hydroxyls and the carboxyls of GO). Furthermore, the increment of  
 282 the hydrophobicity of rGO at higher reduction temperature hinders the interaction between rGO  
 283 and the hydrophilic TiO<sub>2</sub> surface causing phase separation. Thus, the materials used for the  
 284 photocatalytic tests are those obtained by reduction at r.t. only.



285  
 286  
 287  
 288

**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.

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

294 The effective reduction with aqueous hydrazine of the GO to rGO was evaluated with XPS-  
 295 ESCA. Fig. 4-SM shows the spectra of the TiO<sub>2</sub>-GO and TiO<sub>2</sub>-rGO (both with a 5% carbon  
 296 loading) in the C(1s) core level peak region. The spectrum of TiO<sub>2</sub>-GO is dominated by three  
 297 main overlapped peaks. The peak centered at ≈ 285 eV is related to carbon atoms in sp<sup>2</sup>  
 298 hybridization typical of graphitic/graphenic structures, while the components at higher binding  
 299 energy (BE at ≈ 287 and 289 eV) can be attributed to carbon species in higher oxidation state.  
 300 [52,53 and references therein]. In the case of the reduced sample one peak dominates the spectra  
 301 (BE at ≈ 285), concurrently with a strong suppression of signals for high C-oxidation state. From  
 302 the comparison of the two spectra (Fig. 4-SM a and b) it is manifest the effective reduction of the  
 303 carbonaceous phase was obtained with hydrazine.

304 Fig. 5-SM shows the diffuse Reflectance spectra of the produced TiO<sub>2</sub>-rGO materials in the  
 305 200-800 nm range, as %R and as Kubelka-Munk (K-M) function (eq. 1, left). The rGO phase  
 306 induces the improved light absorption in the Vis range in line with data previously reported for  
 307 TiO<sub>2</sub>-rGO hybrid materials. [54,55,56] The energy band gap values of the synthesized materials  
 308 were evaluated from the K-M functions by considering the relation which links the ratio between  
 309 the absorption and scattering coefficients and the photon energy for semiconductors with indirect  
 310 band gap, e.g. TiO<sub>2</sub> (eq. 1, right).

311 
$$f(R) = \frac{(1 - R_\infty)^2}{2R_\infty} = A(h\nu - E_g)^2 \quad \text{eq. 1}$$

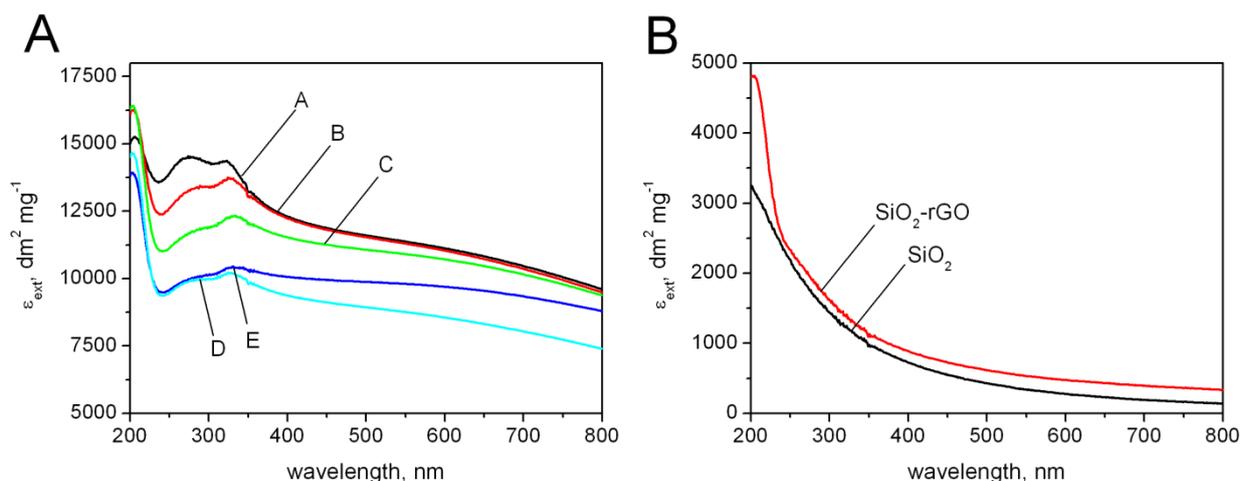
312 where  $f(R)$  is the K-M function,  $R_\infty$  the diffuse reflectance approaching infinite sample thickness,  
 313  $h\nu$  the photon energy,  $E_g$  the energy gap and  $A$  is a constant.

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

321 The extinction spectra of water suspensions of the studied catalysts at different concentration  
 322 (10, 50 and 100  $\text{mg dm}^{-3}$ ) were recorded and the average extinction coefficient  $\epsilon_{\text{ext}}(\lambda)$  (Fig. 2A)  
 323 computed from the plot of absorbance vs concentration, according to the Beer-Lambert law. The  
 324 linear fits have  $r > 0.998$  for all the wavelengths. The analysis of the  $\epsilon_{\text{ext}}(\lambda)$  values (sum of the  
 325 absorption,  $\epsilon_{\text{abs}}$ , and scattering,  $\epsilon_{\text{scat}}$ , coefficients) reveals that the increment of the rGO loading  
 326 decreases the intrinsic ability of catalyst suspensions to absorb the radiation in the whole  
 327 wavelength range, and consequently the overall amount of photons able to activate the UV-based  
 328 photocatalytic mechanism is diminished. In addition the spectrum of hybrid materials suggests  
 329 that there is strong interaction between  $\text{TiO}_2$  and rGO, as the ratio of typical UV absorption  
 330 bands of  $\text{TiO}_2$  is changed (see bands at 273 and 323 nm, respectively). Moreover a large  
 331 extinction (absorption + scattering) is present in the Vis range.

332 Fig. 2B shows the extinction spectra of water suspensions of nanometric silica (average size 40  
 333 nm) and of the composite  $\text{SiO}_2$ -rGO with 1% of carbon loading. The addition of rGO slightly  
 334 increases the extinction. The spectrum of the  $\text{SiO}_2$  colloid, because of the high band gap of silica  
 335 (8.9 eV [59]), is dominated by the contribution of Mie-scattering only. The  $\text{SiO}_2$ -rGO colloid  
 336 retains the scattering profile of silica, overlapped with an almost flat absorption of rGO till 240  
 337 nm. Conversely, the rGO loading on  $\text{TiO}_2$ , which has similar surface hydrophilicity of  $\text{SiO}_2$ ,  
 338 reduces the UV-Vis extinction and totally changes the absorption spectrum, indicating a strong  
 339 interaction between rGO and the semiconductor electronic structure. The absorption peak of rGO  
 340 below 240 nm (Fig. 2B) is also manifest in the spectra of  $\text{TiO}_2$ -rGO colloids at  $\lambda < 240$  nm (Fig.  
 341 2A), where this peak overlaps with the complex profile resulting from the scattering and  
 342 absorption properties of  $\text{TiO}_2$  strongly modified by the interaction with rGO.

343



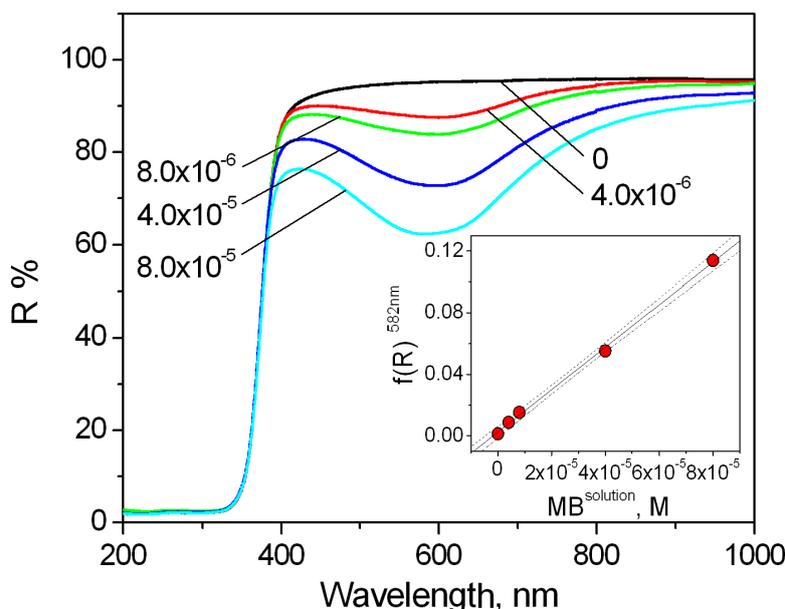
344

345 **Fig. 2** Extinction coefficient ( $\epsilon_{\text{ext}}$ ) of water suspensions of A)  $\text{TiO}_2$ -rGO hybrid materials with different %  
 346 rGO: A= 0 %; B= 0.5 %; C= 1.0 %; D= 2.5 %; E= 5.0 %; B)  $\text{SiO}_2$  and  $\text{SiO}_2$ -rGO (1 % of rGO) The values of  $\epsilon_{\text{ext}}$   
 347 were obtained from the extinction spectra of suspensions with concentrations equal to 10, 50 and 100  
 348  $\text{mg dm}^{-3}$  of the hybrid material.

349 **3.2 Photocatalytic experiments**

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

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



377  
 378 **Fig. 3** % Reflectance spectra of  $\text{TiO}_2$  Hombikat N100 equilibrated in the presence of different amount of  
 379 MB (mol MB / g  $\text{TiO}_2$  from  $0$  to  $8.0 \times 10^{-5}$  mol/g). Inset: K-M function value at 582 nm ( $f(R)^{582\text{nm}}$ ) for the  
 380 samples equilibrated at different concentrations of MB in solution.

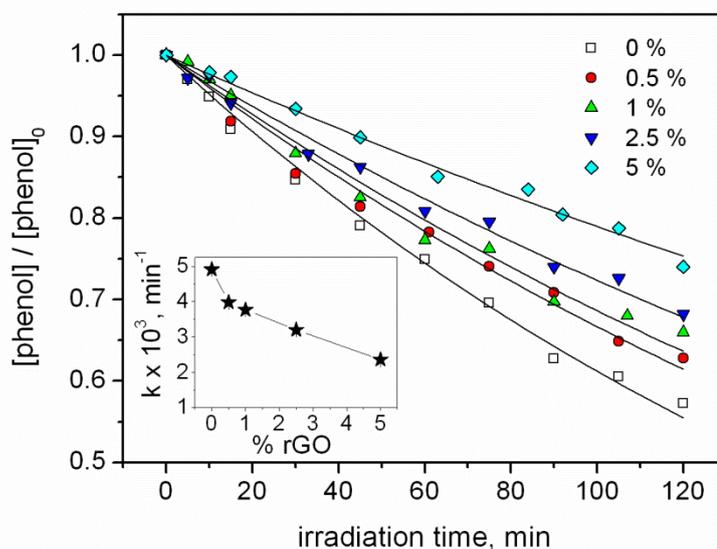
381

### 3.2.1 Phenol

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

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

412



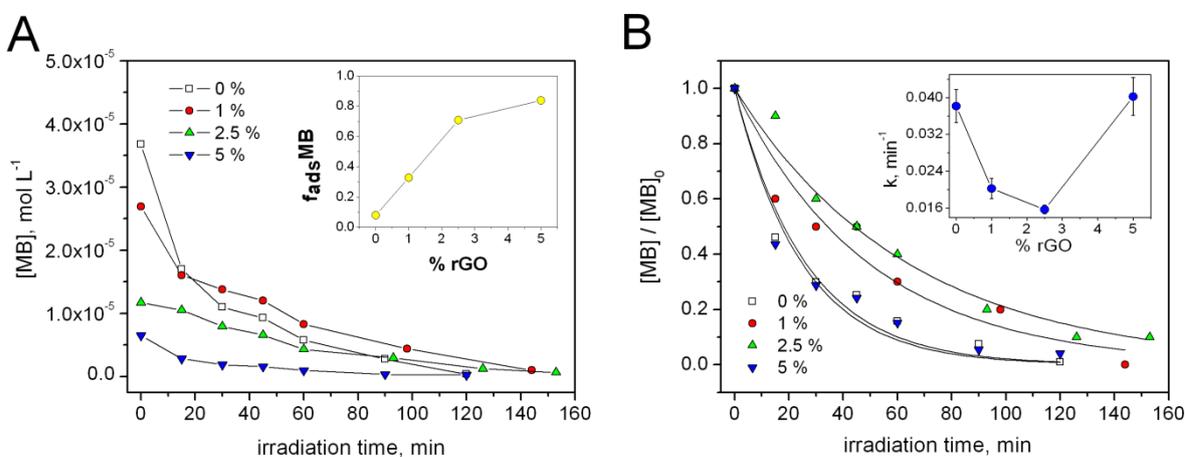
413

414 **Fig. 4** Photocatalytic degradation under UV irradiation (TLK 40W 05) of 1 mM phenol at pH 3 on  $\text{TiO}_2$ -  
 415 rGO hybrid materials with different rGO loading.  $C_{\text{cat}} 0.5 \text{ g dm}^{-3}$ . Inset: pseudo first order kinetic  
 416 constants for the photocatalytic transformation of phenol as a function of the % rGO.

417 Phenol degradation was also carried out under Vis light (TLK 40W 03 lamp). Very low  
 418 degradation rates were observed in the presence of both pristine  $\text{TiO}_2$  and  $\text{TiO}_2$ -rGO materials.  
 419 The kinetic constant observed for  $\text{TiO}_2$ -2.5% rGO was  $(1.9 \pm 0.1) \times 10^{-4} \text{ min}^{-1}$ , 17 times lower than  
 420 the degradation kinetic constant measured under UV irradiation. These results indicate that the  
 421 absorption of the hybrid photocatalyst, and mainly of rGO, as pristine  $\text{TiO}_2$  is not excited in the  
 422 Vis, does not produce photoexcited species able to carry out the reaction with phenol. The  
 423 possible hypotheses are two: 1) the excited rGO is not able to inject electrons in  $\text{TiO}_2$ , and  
 424 photogenerated species recombine in rGO very rapidly compared to their reaction rate with  
 425 phenol; 2) The excited electrons in high energetic rGO states can be delocalized toward  $\text{TiO}_2$   
 426 conduction band (rGO injects electrons into  $\text{TiO}_2$ ), charge separation is attained and  
 427 photogenerated species do not recombine, but HOMO of the substrate to be transformed (here  
 428 phenol) is lower in energy than the energy state of rGO where an electron vacancy has been  
 429 photogenerated. In this case the reaction is thermodynamically impeded. However it is possible  
 430 that with other substrates this thermodynamic impediment is removed. As an example, in the  
 431 case of risperidone, which does not absorb in near UV-Vis, the loading of rGO on  $\text{TiO}_2$  increases  
 432 the photocatalytic rate both under near UV and Vis irradiation.[64]

### 433 3.2.2 Methylene Blue

434 Fig. 5A shows the change in the MB concentration under UV-Vis irradiation. The dye  
 435 concentration in solution before the irradiation is lower than the nominal value in every instance  
 436 in agreement with the adsorption discussed before (see also Fig. 3). The adsorption of MB in the  
 437 adopted conditions is significant and increases with the increment of the rGO loading (e.g.  $\text{TiO}_2$ -  
 438 5%rGO adsorbs more than 85 % of the added MB, see inset of Fig. 5A).  
 439

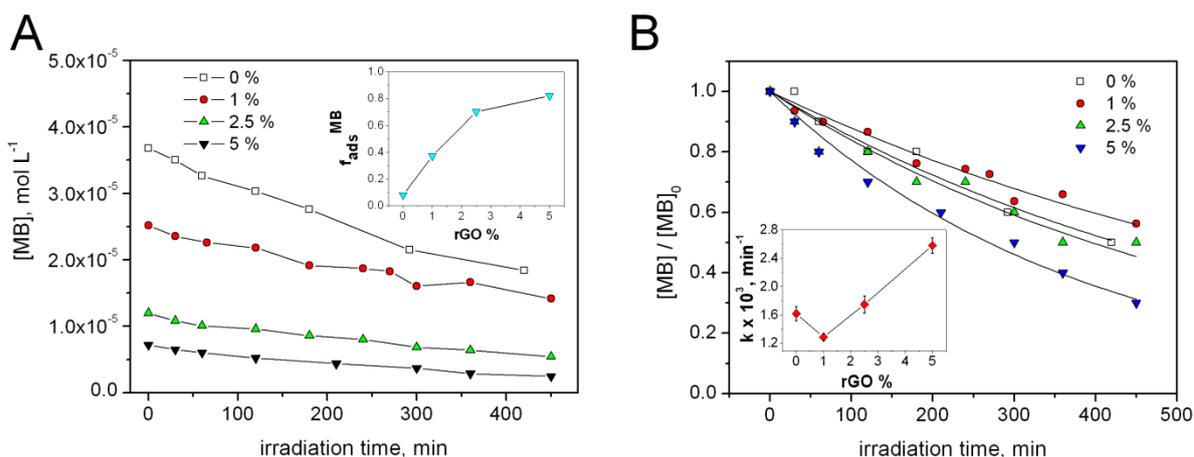


440  
 441 **Fig. 5** Photocatalytic degradation under UV-Vis of  $4 \times 10^{-5} \text{ M}$  of MB at pH 3 in the presence of  $\text{TiO}_2$ -rGO  
 442 with different % rGO.  $C_{\text{cat}} 0.5 \text{ g dm}^{-3}$ . MB concentration (A) and fraction of MB (B) in solution as a  
 443 function of the irradiation time. Insets: (A) fraction of MB adsorbed on the catalyst as a function of the %  
 444 rGO; (B) pseudo first order kinetic constants for the MB transformation as a function of the % rGO.

445 The  $C/C_0$  showed exponential decay (Fig. 5B). The overall observed kinetic constants  $k_{\text{obs}}$  are  
 446 reported as inset in Fig. 5B and in entries 6-9 of Table 1-SM. The observed kinetic constants are  
 447 deduced from the time evolution of  $[\text{MB}]$  in aqueous solution as  $d[\text{MB}_{\text{sol}}]/dt = -k_{\text{obs}} \times [\text{MB}_{\text{sol}}]$ . The  
 448 linear relation of  $[\text{MB}]_{\text{ads}}$  vs  $[\text{MB}]_{\text{sol}}$  evidenced in Fig. 3 suggests that  $[\text{MB}]_{\text{ads}} = \beta \phi C_{\text{cat}} K$   
 449  $[\text{MB}]_{\text{sol}}$ , where  $\beta$  is the moles of sites per catalyst mass,  $\phi$  is the fraction of constituent of the  
 450 hybrid catalyst,  $C_{\text{cat}}$  is the mass  $\text{dm}^{-3}$  of hybrid catalyst, and  $K$  is the equilibrium adsorption  
 451 constant. In the case of linear partition between the aqueous phase and rGO /  $\text{TiO}_2$  phases, it can  
 452 be demonstrated that  $k_{\text{obs}} = k_{\text{tot}}$ , where  $k_{\text{tot}}$  is the first order kinetic constant that would be obtained  
 453 following the time evolution of the total concentration in the system (both adsorbed and free)

454 from  $d[MB_{tot}]/dt = -k_{tot} \times [MB_{tot}]$ . In other cases they are proportional. Then, the trend of observed  
 455 kinetic constants  $k$  are representative of the overall degradation of substrate in the hybrid system.  
 456 The rate equations that can be derived from a kinetic model by taking into account the adsorption  
 457 constants and kinetic constants specific for the two adsorbing phases ( $k_G$  and  $k_T$ , for rGO and  
 458  $TiO_2$ , respectively), are not developed here as they are outside of the scope of the paper.  
 459 However, assuming that the rate at the surface is proportional to the local (adsorbed)  
 460 concentration it can be easily demonstrated that there is no minimum or maximum of  $k_{obs}$  as a  
 461 function of the rGO amount. When  $k_G > k_T$ , the rate increases with graphene content and vice  
 462 versa, irrespective of the value of the adsorption constants. Then the observed effects must be  
 463 explained with factors other than those above cited (adsorption constants and kinetic constants  
 464 specific for the two adsorbing phases).

465 As observed for the UV photocatalytic abatement of phenol, also in this case the presence of  
 466 rGO has an initial negative effect. The kinetic constants show a minimum for 2.5% rGO. This is  
 467 conflicting with the previously reported bell-shaped profile of the rate with the increment of  
 468 %rGO. [31] The discrepancies point out the role of the method of synthesis which can  
 469 significantly affect the properties of the material and consequently its photocatalytic behavior.  
 470 The observed dependence of the rate on the rGO amount can be explained invoking two different  
 471 effects. At low rGO loading the shielding of  $TiO_2$ , as already discussed for phenol, decreases the  
 472 light absorbed by  $TiO_2$ . In addition, assuming that the reactivity is mainly dominated by  $TiO_2$ , a  
 473 stronger adsorption on graphene than on  $TiO_2$  implies that the substrate is scarcely transferred  
 474 during the photocatalytic reaction to the  $TiO_2$  surface. It is apparent that because the substrate is  
 475 adsorbed on graphene, it must react on its surface. Consequently, due to the two cited reasons the  
 476 overall reaction rate will be reduced unless holes on  $TiO_2$  (already decreased by light shielding)  
 477 are transferred to rGO. As a further increase of rGO loading increases both the MB adsorbed on  
 478 rGO and the rate, it must definitely concluded that MB reacts on rGO and transfer of holes from  
 479  $TiO_2$  to rGO is operating. This conclusion agrees with Wang et al. [31] that holes are the main  
 480 oxidant species and that in the hybrid catalyst oxidative species are not changed by introduction  
 481 of graphene-like carbon to  $TiO_2$ . Concurrently with  $TiO_2$  excitation, also rGO absorbs light and  
 482 excited electrons in high energetic rGO states must be delocalized toward  $TiO_2$  conduction band  
 483 (rGO injects electrons into  $TiO_2$ ) to avoid recombination.  
 484



485  
 486 **Fig. 6** Photocatalytic degradation under Vis irradiation of  $4 \times 10^{-5}$  M of MB at pH 3 in the presence of  $TiO_2$ -  
 487 rGO with different % rGO.  $C_{cat}$   $0.5 \text{ g dm}^{-3}$ . MB concentration (A) and fraction of MB (B) in solution as a  
 488 function of the irradiation time. Insets: (A) fraction of MB adsorbed on the catalyst as a function of the %  
 489 rGO; (B) pseudo first order kinetic constants for the MB transformation as a function of the % rGO.

490 Fig. 6A and Fig. 6B show the change in the MB concentration in solution under Vis irradiation  
 491 and the related  $C/C_0$  profiles. The amount of MB adsorbed in this experiment (inset of Fig. 6A)

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

498 The kinetic constants, after a minimum for TiO<sub>2</sub>-1%rGO, increase with the increment of the  
499 %rGO, with a shape similar to that observed under UV-Vis irradiation, but with values lower of  
500 about one order of magnitude. Under Vis irradiation both rGO and MB can absorb, whilst TiO<sub>2</sub>  
501 does (almost) not. The slight decrease of the rate at TiO<sub>2</sub>-1%rGO could be due to the previous  
502 invoked effect of light shielding on TiO<sub>2</sub>, as also with the Vis lamp a small absorption by TiO<sub>2</sub> is  
503 still possible and a minimal contribution of semiconductor mechanism is present. So the  
504 degradation mechanism must involve the light absorption by rGO, or a dye sensitized  
505 mechanism.

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

515 The dye-sensitized mechanism involves the light absorption by MB, charge injection into TiO<sub>2</sub>  
516 or rGO and evolution of the oxidized MB to products. The absorption of light from the MB-TiO<sub>2</sub>  
517 surface species was well studied [21,65,66] and the role of self-induced photosensitization  
518 outlined.[67] The excited electrons, which occupy the LUMO of the adsorbed MB on TiO<sub>2</sub>, can  
519 be injected into titania CB promoting the MB degradation. As MB is adsorbed on TiO<sub>2</sub> (Fig. 3)  
520 but preferentially adsorbed on rGO (insets of Fig. 5A and Fig. 6A), the electron must be injected  
521 from the LUMO of MB to rGO. Then, according to the conclusions drawn from MB irradiation  
522 under UV-Vis lamp, rGO would transfer these electrons to TiO<sub>2</sub>.

523 To confirm these conclusions, experiments of MB photodegradation under Vis irradiation was  
524 carried out in the presence of the SiO<sub>2</sub>-rGO hybrid materials synthesized by using the same  
525 methods adopted for producing TiO<sub>2</sub>-rGO. Under the adopted experimental conditions (0.5 g  
526 dm<sup>-3</sup> of catalyst, initial MB concentration  $4 \times 10^{-5}$  M, pH 3), the silica adsorbs a significant  
527 amount of MB (around 75%) and this value increases with the increment of the % rGO. Both on  
528 pristine SiO<sub>2</sub> and on SiO<sub>2</sub>-rGO hybrid materials, no MB photocatalytic degradation was observed  
529 under the adopted conditions. From an energetic point of view an electron in the LUMO of MB  
530 adsorbed on the catalyst surface (SiO<sub>2</sub> or SiO<sub>2</sub>-rGO) is not able to move toward the CB of SiO<sub>2</sub>.  
531 This conclusion was expected for SiO<sub>2</sub> due to its very high work function [43]. Then on SiO<sub>2</sub>  
532 after light excitation of MB only recombination is possible. In the presence of rGO, as reaction  
533 does not proceed and also electron transfer from rGO to SiO<sub>2</sub> is impeded because of the SiO<sub>2</sub>  
534 high work function, the electron transfer to empty electronic states of rGO must be followed by  
535 recombination with oxidized MB, giving a null cycle.

536 Then the mechanism of MB degradation in the presence of the hybrid TiO<sub>2</sub>-rGO is initially  
537 promoted by a dye-sensitized mechanism. In the presence of rGO, electrons are mostly  
538 transferred to rGO, and then from rGO to TiO<sub>2</sub>. When excited electrons in rGO cannot be  
539 released (for example to TiO<sub>2</sub>, for which rGO acts as sensitizer and also as hole acceptor), rGO  
540 acts a recombination center.

## 541 **4. Conclusions**

542 The analysis of the photocatalytic behavior of TiO<sub>2</sub>-rGO hybrid materials synthesized at  
543 different loading of rGO, underlines its complexity as the working mechanisms depend not only  
544 on the substrate degraded, but also on the kind of irradiation adopted. A careful optical  
545 characterization of the hybrid materials and lamp emission allows disentangling many tricky rate  
546 trends observed changing % rGO in the hybrid catalyst. Phenol is degraded predominantly via  
547 UV-based photocatalysis and the content of rGO decreases the rate by increasing the amount of  
548 scattered light. MB is degraded via UV-based photocatalysis and in the case of visible irradiation  
549 via a dye-sensitized mechanism. Visible sensitization driven by rGO phase seems not to be the  
550 predominant mechanism in the studied experimental conditions and with the studied  
551 photocatalytic materials. However, rGO plays a key role for adsorption and as electron  
552 passageway for dye-sensitized mechanism. Because the adsorption of MB on the TiO<sub>2</sub> surfaces  
553 activates the dye-sensitized process which is not directly related to the real photocatalytic  
554 features of the hybrid material, the studies that use MB alone with hybrid materials and  
555 illumination with not well characterized emission could lead to misleading conclusions on the  
556 role of rGO. It is not possible to generalize the conclusions obtained on the photocatalytic  
557 behavior of the materials we synthesized to the entire set of reported TiO<sub>2</sub>-rGO materials,  
558 because the numerous modifications of the TiO<sub>2</sub>-rGO synthetic strategies can affect abruptly  
559 their photocatalytic performance. In particular the degree of rGO reduction can influence the  
560 energy position of its LUMO allowing/hindering the electron injection from/toward adsorbed  
561 species. Residual oxygenated groups on rGO can also be involved in acid-base equilibria which  
562 can shift the Fermi level position of rGO as a function of pH, changing the relative position of its  
563 electronic states in comparison with those of TiO<sub>2</sub>.

564 Our study strongly suggests that among many mechanisms reported on the role of rGO (and  
565 graphene) the electron transfer process can occur from photoexcited states of rGO onto the  
566 titania, and holes from titania migrate to it, where adsorbed substrates are oxidized only if their  
567 HOMO has higher energy (less positive standard redox potential) than the empty state of excited  
568 rGO. Then, reduced graphene (and possibly also graphene) is advantageous when substrates are  
569 adsorbed and when the charge separation is possible (coupled with a proper semiconductor like  
570 TiO<sub>2</sub>). Alone, or coupled with low work function oxides, rGO could be ineffective.

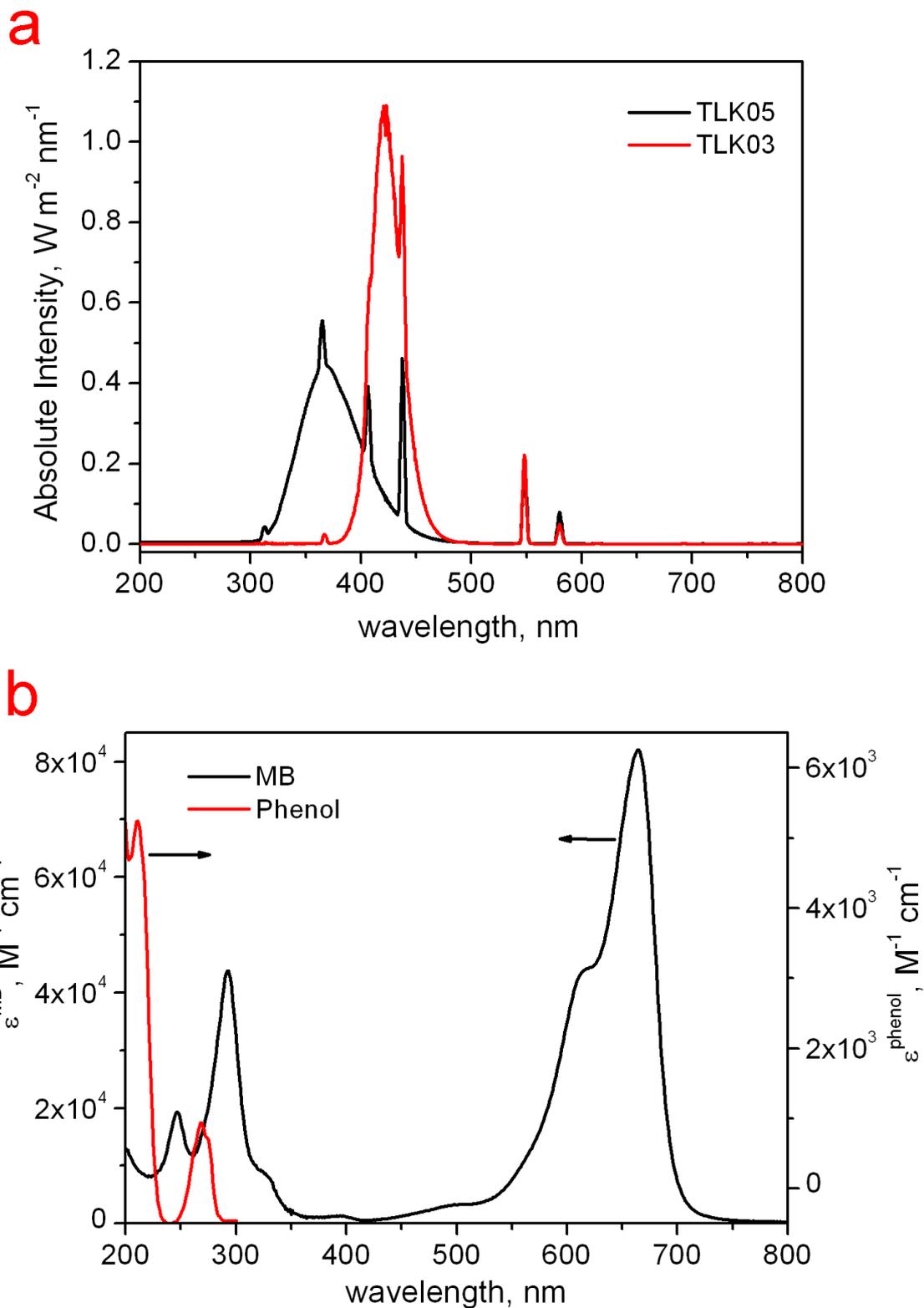
## 571 ***Acknowledgements***

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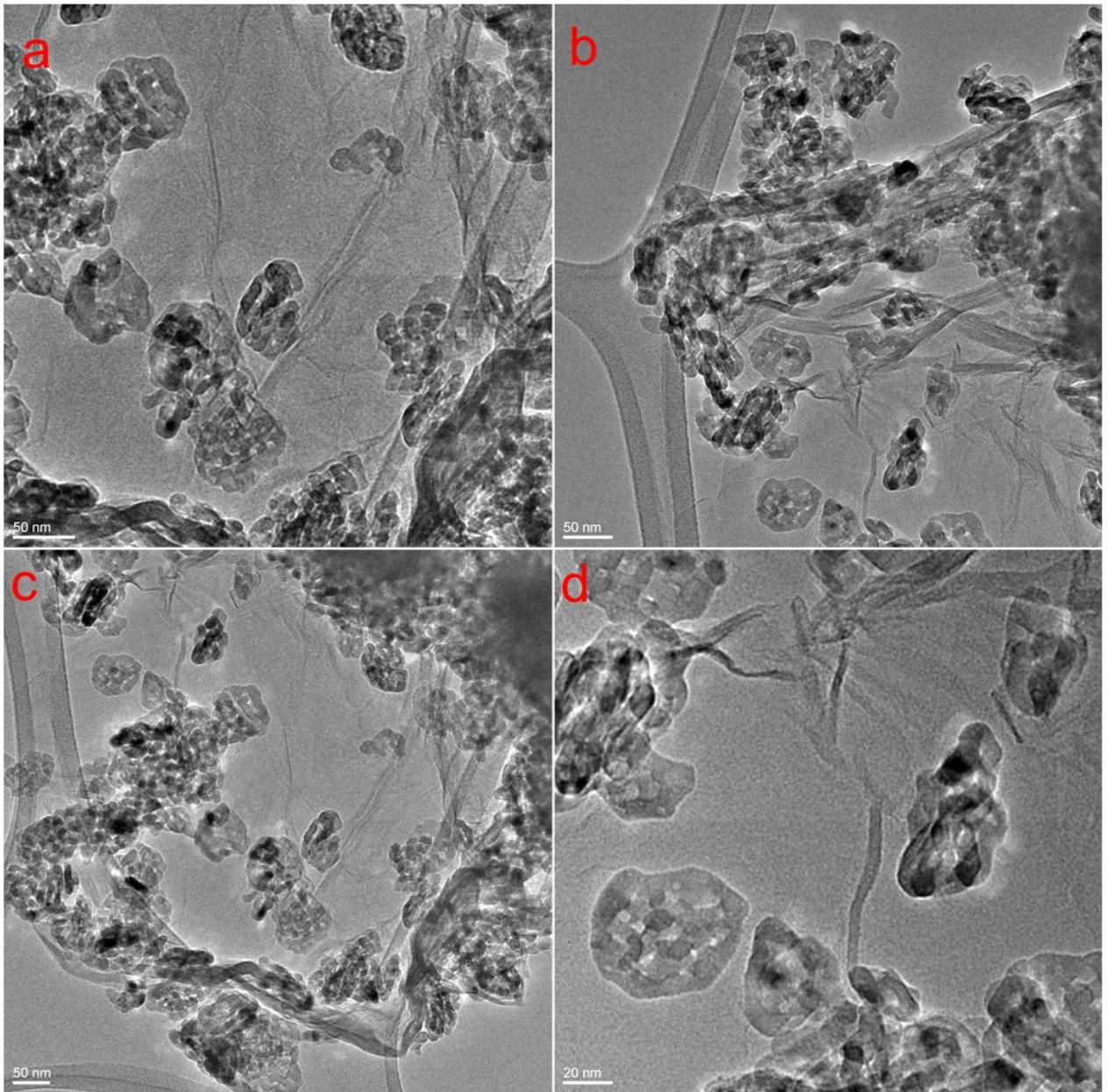
## SUPPLEMENTARY MATERIAL



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**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.

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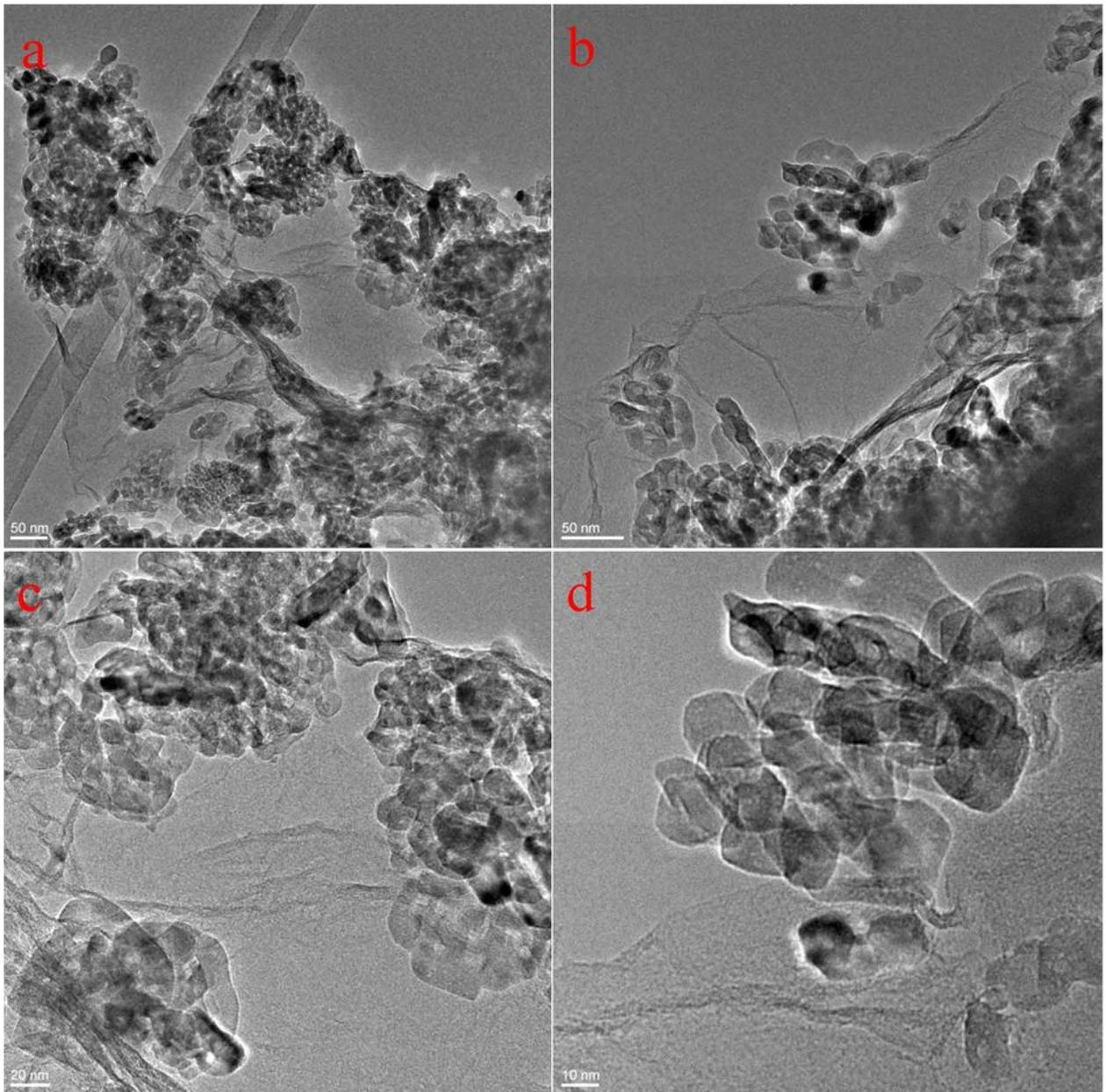


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**Fig. 2-SM** HR-TEM micrographs of the sample TiO<sub>2</sub>-GO before chemical reduction with 5% GO loading. Original magnifications: a) × 50 k, b) × 40 k, c) × 30 k and d) × 100 k.

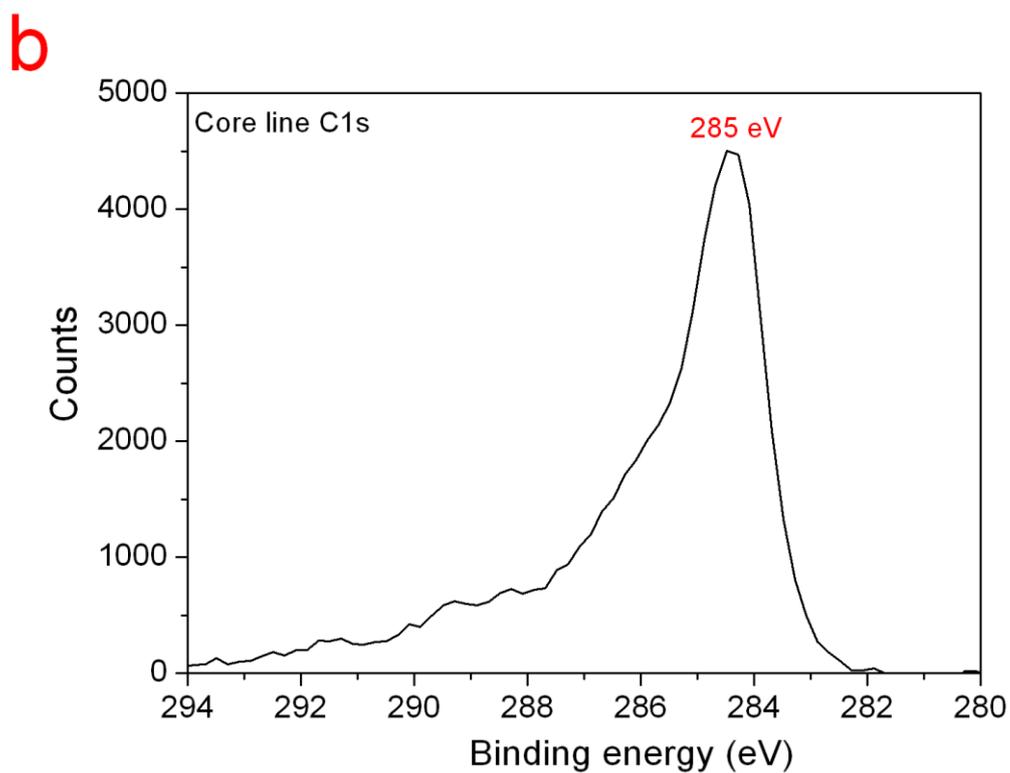
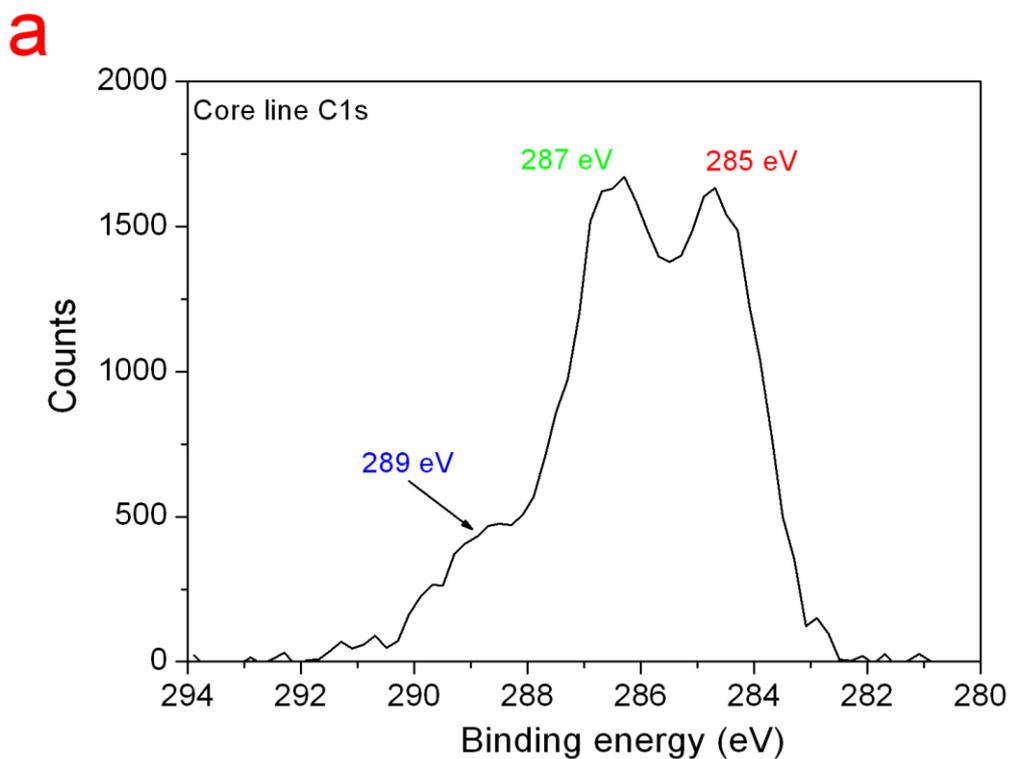
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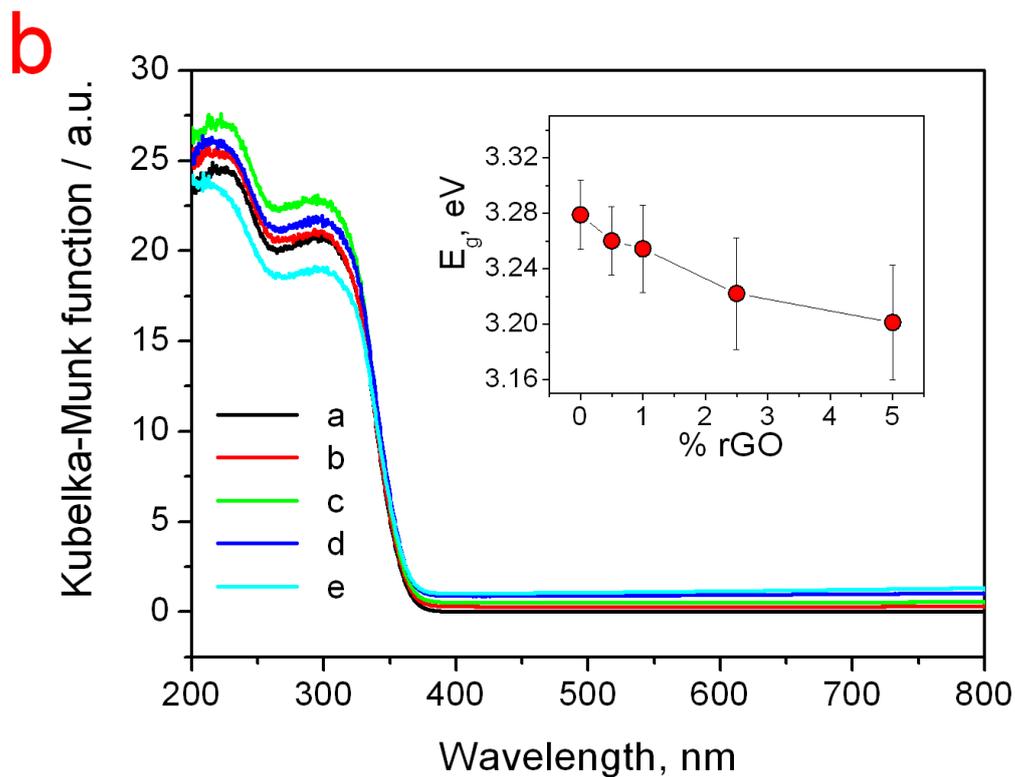
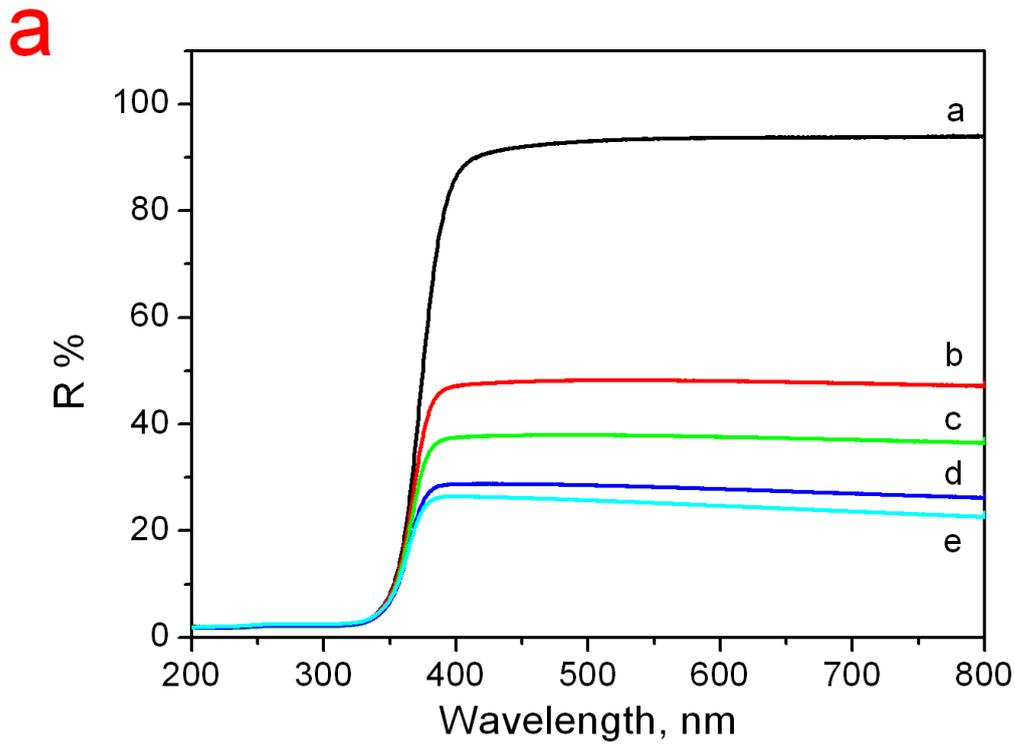
594 **Fig. 3-SM (A)** HR-TEM micrographs of the sample TiO<sub>2</sub>-rGO with 5% rGO loading. Original  
595 magnifications: a) × 30 k, b) × 40 k, c) × 100 k and d) × 200 k.

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**Fig. 4-SM.** XPS-ESCA peak of C(1s) core level of a) TiO<sub>2</sub>- GO, b) TiO<sub>2</sub>-rGO(chem), with a 5% GO/rGO loading.



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604 **Fig. 5-SM** Diffuse reflectance spectra of TiO<sub>2</sub>-rGO hybrid materials at different rGO loadings: a = 0, b =  
605 0.5, c = 1, d = 2.5 and e = 5 %; A) Spectra in % Reflectance; B) Spectra in Kubelka-Munk function (inset:  
606 apparent band gap as a function of the % rGO.

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608 **Table 1-SM** Pseudo first-order kinetic constants with the related error for all the photocatalytic  
 609 transformation of phenol and MB under irradiated (UV-Vis and Vis only)  
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Entry	Substrate	Irradiation	%rGO	k, min <sup>-1</sup>
1	Phenol	UV-Vis	0	$(4.91 \pm 0.09) \times 10^{-3}$
2	Phenol	UV-Vis	0.5	$(4.0 \pm 0.1) \times 10^{-3}$
3	Phenol	UV-Vis	1	$(3.8 \pm 0.1) \times 10^{-3}$
4	Phenol	UV-Vis	2.5	$(3.20 \pm 0.07) \times 10^{-3}$
5	Phenol	UV-Vis	5	$(2.36 \pm 0.06) \times 10^{-3}$
6	MB	UV-Vis	0	$(3.8 \pm 0.4) \times 10^{-2}$
7	MB	UV-Vis	1	$(2.0 \pm 0.2) \times 10^{-2}$
8	MB	UV-Vis	2.5	$(1.6 \pm 0.1) \times 10^{-2}$
9	MB	UV-Vis	5	$(4.0 \pm 0.4) \times 10^{-2}$
10	MB	Vis only	0	$(1.6 \pm 0.1) \times 10^{-3}$
11	MB	Vis only	1	$(1.29 \pm 0.05) \times 10^{-3}$
12	MB	Vis only	2.5	$(1.75 \pm 0.12) \times 10^{-3}$
13	MB	Vis only	5	$(2.6 \pm 0.1) \times 10^{-3}$

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