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This is the author's manuscript
Original Citation:
Availability:
This version is available http://hdl.handle.net/2318/1670733 since 2018-08-07T12:44:08Z
Published version:
DOI:10.1016/j.cattod.2018.03.026
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The complex interplay between adsorption and photoactivity in hybrids rGO/TiO₂

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11 The kinetic of photocatalytic degradation of 2,4-DCP and 1-Naphthol on hybrids 12 TiO_2 /reduced-Graphene Oxide (TiO_2 /rGO) obtained with two commercial TiO_2 specimens 13 and different % rGO loadings was investigated under different irradiation conditions (UV 14 only, UV + Vis and Vis only). 2,4-DCP adsorbs strongly on the rGO phase. With the 15 increment of the rGO loading no increment on the overall reaction rate under UV and UV + 16 Vis irradiation is observed, while a very low but not null photoactivity that increases with the 17 increment of %rGO is observed under Vis only irradiation.

18 It is here proposed for the first time a quantitative kinetic model able to predict the 19 photocatalytic rate of hybrid photocatalysts composed of two phases (whatever the nature of 20 the phases is) with different light absorption and intrinsic reactivity, diverse ability to adsorb 21 the substrate and to partition charge carriers depending on their band alignment. The model is 22 able to decouple the adsorption effect from the kinetic ones.

From the analysis of the adsorption and kinetic data at different rGO loadings emerges that: 2,4-DCP partitions preferentially on the rGO phase; the operational photocatalytic mechanism is based on the band-to-band transition promoted by the UV absorption of the semiconductor; rGO shows a negligible but not null visible photoactivity toward 2,4-DCP; the photo-promoted TiO_2 conduction band electrons are not injected into rGO where 2,4-DCP is mainly adsorbed. In this light some hypothesis are proposed to justify the negative effect of rGO on the overall oxidative photoactivity.

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31 Keywords

Photocatalysis, graphene oxide, titanium dioxide, adsorption, hybrid material, 2,4 dichlorophenol

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35 **1** Introduction

36 The investigation of the photocatalytic process under irradiated semiconductors has been 37 mainly finalized to i) the discovery of new materials able to activate the photocatalytic 38 process with high quantum yield and *ii*) the modification of the original materials with the 39 aim to increase the utilization of light. Among the strategies directed to increase the overall 40 photocatalytic performance, the synthesis of hybrid materials is one of the most explored 41 fields, as recently highlighted.[1] A hybrid material is composed by two or more strongly 42 interacting phases. Its features are not the sum of the properties of the single phases, but 43 derive from their synergistic interaction and are strongly related to the properties of the 44 interface between the materials. In this light not only the relative positioning of the electronic 45 bands of materials, but also their structural matching (and the consequent presence of 46 crystallographic defects) play a crucial role on the kinetic of separation of photogenerated 47 charge carriers and on recombination phenomena. Therefore, also the spectroscopic features 48 of a hybrid material are not generally the sum of the spectroscopic properties of the two 49 materials although weighted for their relative amount in the hybrid, but derive from more 50 complex interactions.

The increase of substrate adsorption can be an effective way to increase the performance when the photogenerated reactive charges (holes or electrons) are able to migrate and react on the adsorption phase.[2] The increment of the adsorption ability cannot be considered an *a priori* beneficial feature, because the partitioning of a substrate on a non-reactive phase can depress the efficiency of the process.

56 Among the different carbon based materials, TiO_2 /graphene or TiO_2 /graphene-like 57 materials play a dominant role (to deepen the knowledge of this topic please refer to [3,4,5]). 58 Recently, experiments with hybrids composed by functionalized graphene nanoparticles 59 (GNPs) and TiO₂ exposing predominantly $\{101\}$ facets showed that the proximity between 60 the {101} facets and the carboxylated GNPs led to a more efficient injection of 61 photoelectrons, decreased the kinetic of recombination, and improved the degradation of 62 phenol.[6] Huang et al. compared photoluminescence (PL) of pristine TiO₂, mechanical 63 mixture TiO₂/rGO and chemically bonded composite and reported that only in the presence of 64 a chemical link between the organic and inorganic phases a significant decrement in the PL emission was observed. The decrement was correlated with a better charge carriers transfer 65 66 and separation as a consequence of the electron transfer promoted by the presence of pure 67 graphene.[7]

68 From the photocatalytic point of view, the role of rGO in TiO₂/rGO hybrids has not yet 69 totally elucidated. The role of rGO as conductive "bridge" was proposed by Lang et al. [8] 70 which concluded that in hybrid systems, in which Ag nanocubes and thin TiO₂ nanocrystals 71 with preferentially exposed (001) facets were co-deposited on the surface of rGO nanosheets, 72 rGO transports electrons from Ag to TiO₂. Recently, rGO nanosheets in MoS_X-rGO/TiO₂ 73 have been proposed to transfer photogenerated electrons from the conduction band of TiO₂ to MoS_X where the reduction of H⁺ to H₂ occurred.[9,10] Hamandi et al. reported that rGO can 74 75 act as final electron acceptor in ternary hybrids composed by anatase, rutile and rGO.[11] 76 Yang et al. reported that TiO₂/Ag₃PO₄/graphene composites showed not only the commonly 77 reported visible activity toward the decomposition of organic dyes, but also a strong ability to 78 inactivate bacteria.[12] The same increment in the photo-assisted decomposition of organic

dyes (e.g. Methyl Orange) has been recently reported on electrospun rGO/TiO₂ compositenanofibers.[13]

81 The role of electron acceptor for rGO in TiO₂-rGO composites has been correlated by 82 Morawski et al. [14] to the presence of oxygen sites of rGO that are able to accept 83 photoinduced electrons during the photocatalytic degradation of acetic acid under visible 84 light. The stability of rGO alone [15] or coupled with TiO₂ [16] was also investigated, demonstrating the vulnerability of rGO (till its mineralization) in photocatalytic conditions. 85 86 This raised concerns regarding its use in many applications where strong oxidants ([•]OH 87 and/or h_{vb}^+) are likely to be formed. Regarding the nature of the photo-formed oxidative species in TiO₂/rGO, a central role of the h^+_{vb} than [•]OH radicals was proposed even for the 88 89 oxidation of dyes, [17] in agreement with the general downsizing of the importance of free 90 •OH in solution even under pristine TiO₂.[18]

91 A critical review of the problems related to the interpretation of basic phenomena 92 occurring in the hybrids TiO₂-rGO indicated several controversies on the sensitization by 93 visible light and the role of graphene.[19] An in-depth study of the photocatalytic properties 94 of TiO₂-rGO hybrids through a systematic investigation of the photocatalytic transformation 95 of both phenol and methylene blue (MB) was carried out. The conclusions were that the 96 former is mainly transformed via UV-based photocatalysis and that rGO decreases the phenol 97 transformation rate because it depresses the amount of light reaching the semiconducting 98 phase through the increase of the UV scattering ability. MB is transformed both via UV-based 99 photocatalysis and in the case of visible irradiation via a dye-sensitized mechanism, while an 100 effective Visible sensitization seems not to be the main mechanism. This study supported that 101 electron transfer can occur from photoexcited states of rGO onto the TiO2 and hole transfer 102 from TiO₂ to rGO where adsorbed substrates can be oxidized only if thermodynamic requirements are satisfied (HOMO higher in energy than the empty states (h^+_{rGO}) of excited 103 104 rGO).[19]

105 The aim of this work was the study of the photocatalytic properties of TiO₂/rGO hybrid 106 materials synthetized with a reported hydrothermal treatment, through a detailed investigation 107 of their photocatalytic activity toward 2,4-dichlorophenol, a substrate able to react not only 108 through the oxidative pathway (promoted by photo-produced holes), but also through 109 reductive pathway. To give insights into the mechanism and to investigate the role of the rGO 110 phase, the degradation of 2,4-DCP was carried out on materials with different rGO loadings, 111 at different substrate concentrations and under different irradiation sources. The role of the 112 type of TiO₂ used was considered using hybrid materials synthesized with two different 113 commercial TiO₂ powders. The TiO₂-rGO hybrids reactivity was also tested using 1-naphthol, 114 which cannot be transformed through reductive pathways, and with hybrid materials 115 synthesized through an alternative synthetic way (chemical reduction of GO).

116 **2 Materials and Methods**

117 **2.1 Materials**

118 All the compounds were used as received without any further purification step. The water 119 solutions were prepared with water of MilliQ grade (TOC = 2 ppb, conductivity 18.2 M Ω 120 cm).

Acetonitrile (gradient grade), H₃PO₄ (85%), HNO₃ (≥65%), H₂O₂ (35%), 2,4-121 122 dichlorophenol (2,4-DCP, 99%), 1-naphthol (99%) and hydrazine monohydrate (N₂H₄ 64-65 %, reagent grade 98%) were purchased from Sigma-Aldrich; H₂SO₄ (96%), KMnO₄ (>99%) 123 124 from Carlo Erba Reagenti (Italy); graphite natural powder (briquetting grade, ≈ 100 mesh, 125 99.9995%) from Alfa Aesar and zero-grade air for TOC analysis from Sapio (Turin, Italy). The commercial TiO₂ used for the synthesis of the hybrid TiO₂-rGO materials were *i*) TiO₂ 126 Hombikat N100 (100% anatase, BET specific surface area 100 m² g⁻¹, average crystal size 20 127 nm) and *ii*) P25 (Evonik-Degussa, 70% anatase -30% rutile, 50 m² g⁻¹, plate-like particles 128 129 with mean size ca. 40 nm).

130 **2.2** GO and TiO₂-rGO synthesis

131 The graphene oxide was produced through the modified Hummers and Staudemaier's method [20] proposed by Huang et al. [21] and described in detail elsewhere [22]. The 132 133 absorption spectra of the GO suspension properly diluted (see Fig. 1A-SM of the 134 Supplementary Material, here after SM) were recorded through a UV/Vis Varian Cary 100 spectrophotometer in the 200-800 nm range. The spectrum showed the classic absorption 135 136 profile of GO [15,21,23] characterized by a peak at 230 nm ($\pi \rightarrow \pi^*$ transition of the C=C 137 double bonds) with a shoulder at $\lambda \approx 300$ nm (n $\rightarrow \pi^*$ transition of carbonyl groups).[23,24] The concentration of the suspension in term of mass of carbon per mass of solution was evaluated 138 139 measuring Total Organic Carbon (TOC) concentration of diluted solutions of the GO. The 140 TOC analyzer adopted was a Shimadzu TOC-VCSH Total Organic Carbon Analyzer, 141 equipped with an ASI-V autosampler and fed with zero-grade air.

142 The hybrids TiO_2 -rGO were produced following literature procedures [25,26,27] through reduction of different amount of GO onto the TiO₂ nanoparticles. In the hydrothermal 143 144 treatment the autogenous pressure inside a sealed autoclave induced an effective reduction of 145 the oxidized moieties of GO to give rGO. We added drop by drop different volumes of the GO suspension to 4 g dm⁻³ suspensions of TiO₂ (N100 or P25) under constant and vigorous 146 magnetic stirring. The addition of GO to the suspension destabilized the colloid as a 147 148 consequence of the strong interaction between the organic and inorganic phase that promoted 149 the coagulation of the particles. The as obtained suspension was transferred in a 1 dm^3 Teflon 150 vessel and hydrothermally treated in a Berghof DAB 3 autoclave according to the temperature 151 ramp profile reported in Fig. 2-SM. At the end of the hydrothermal treatment a grey to darkgrey suspension was obtained as a function of the rGO loading. The suspension was filtered 152 153 on 0.45 µm hydrophilic filters (Whatman, NL 17 membrane filters, polyamide), washed with 154 water and dried at 373 K in oven. Materials with %rGO loadings equal to 0.5, 1, 2, 4, 6, 10 and 20% were produced with N100, while hybrids with %rGO loading equal to 4, 6 and 10% 155 156 with P25. The rGO loading was computed considering a complete conversion of all the 157 carbon of the GO in rGO without any loss of carbon during the hydrothermal reduction.

The chemical reduction of GO to rGO was carried out using hydrazine according to the proposed method.[19] An in-depth characterization of the catalysts here investigated from a physico-chemical point of view has been previously reported.[19,22]

161 In this work n%rGO(X)-Y identifies univocally the catalysts, where n is the rGO loading in 162 %, X is the type of process carried out to reduce the GO to rGO (*HTR* = HydroThermal 163 Reduction, *CR* = Chemical Reduction) and Y is the type of titanium dioxide employed (*N100* 164 = TiO₂ Hombikat N100, *P25* = TiO₂ Evonik P25).

165 **2.3** *Photocatalytic conditions and analytical determinations*

166 The photocatalytic experiments were carried out in cylindrical Pyrex glass cells (dimensions: 4.0 cm diameter and 2.5 cm height; cut-off at 295 nm) on 5 cm³ of suspension 167 168 with the desired amount of the organic substrate to be degraded (e.g. 2,4-DCP), 0.5 g dm⁻³ 169 catalyst suspension at pH 3 for HNO₃. The suspensions were prepared and left in dark for at 170 least 2 hours, measuring the concentration in solution until the adsorption equilibrium was attained. During the irradiation the cells were magnetically stirred. The temperature of the 171 172 cells was kept constant at 30±3 °C. At defined irradiation times the suspension was filtered on 173 0.45 µm cellulose acetate membrane filter (Millipore HA) and HPLC-UV analyzed.

174 The concentration of 2,4-DCP and 1-naphthol was measured through a YL HPLC system 9300 with a YL9330 Column Compartment and a YL9150 autosampler. The column was a 175 176 RP C18 LiChroCART® - LiChrosphere® with 5 µm particles. The detection was carried out at 210 nm and 220 nm for 2,4-DCP and 1-naphthol, respectively. The elution was carried out 177 in isocratic mode at 1 cm³ min⁻¹ with H₃PO₄ 4.2 mM/acetonitrile 55:45 or 65:35 for 2,4-DCP 178 179 and 1-naphthol, respectively. The retention time of 2,4-DCP under the adopted conditions was 5.5 minutes and for 1-napthol 8.9 min. The injection volume was 60 μ L for both substrates. In 180 181 all the photocatalytic degradation experiments an exponential decay of the concentration was observed. From the fitting the pseudo-first order kinetic constants (k_{obs}) for the photocatalytic 182 183 process was obtained.



184

185 **Fig. 1.** Emission spectra normalized to the maximum intensity peak for the lamps used during the photocatalytic degradation experiments of (A) 2,4-DCP and (B) 1-naphthol.

187 The emission spectra of used irradiation sources were recorded through an Ocean Optics 188 USB2000+UV-VIS equipped with a 400 µm optical fiber (30 cm length) with a cosine 189 corrector (Ocean Optics, CC-3-UV-T, optical diffuser in PTFE, wavelength range 200-2500 190 nm, OD diameter 6.35 mm, Field of View 180°). Three different irradiation conditions were 191 adopted: i) a set of three Philips TL-D 18 W BLB fluorescence lamp for UV only irradiation; 192 *ii*) a sun simulator (SOLARBOX, CO.FO.ME.GRA., Italy) with $\lambda \leq 340$ nm cut-off filter for UV+Vis irradiation and *iii*) the same sun simulator, but with a $\lambda \leq 420$ nm cut-off filter for Vis 193 194 only irradiation. The emission spectra of the irradiation sources are reported in Fig. 1A. The 195 additional experiments with 1-naphthol were carried out with three different irradiation 196 sources: i) Philips TL-D 18 W BLB fluorescence lamps (the same used for 2,4-DCP) for UV-197 only; ii) Philips TLK 03 fluorescence lamps for UV+Vis and iii) Philips TL-D 18 W yellow 198 for Vis-only. Fig. 1B shows the emission spectra of the lamps used for the additional 199 experiments with 1-naphthol. The measured light irradiance on the cell from 295-400 nm was

200 22 W m⁻², 28 W m⁻² and 1.5 W m⁻² for the Philips TL-D 18 W BLB fluorescence lamp, the 201 SOLARBOX sun simulator, and the Philips TLK 03, respectively. For the Vis we are unable 202 to measure the irradiance.

203 **3 Results and Discussion**

204 3.1 Photocatalytic transformation of 2,4-DCP

The transformation under UV irradiated TiO_2 of chlorophenols has been reported to produce more oxidized species (such as chlorobenzendiols, chloroquinones...)[28] and less chlorinated or condensation species through reductive pathways activated by the electron transfer of e_{cb} to the substrate and subsequent release of chloride ion in solution.[29] 2,4-DCP represents in this light an ideal substrates to test the photocatalytic properties of the TiO₂-rGO.

The photocatalytic degradations of 2,4-DCP at different initial concentration (C₀ from 211 5×10^{-5} to 1×10^{-3} M) were carried out on both 0.5 and 10%rGO(*HTR*)-N100 under UV only 212 irradiation (Philips 18W BLB lamp). The time profiles in dark (adsorption) and under 213 214 irradiation (photocatalytic degradation) are reported in Fig. 3-SM and Fig.4-SM. At the end of 215 the equilibration time in dark (at least 2 hours) the concentration of 2,4-DCP in solution was 216 stable. From the difference between the nominal concentration and the concentration in dark 217 at the equilibrium the adsorption isotherm of 2,4-DCP on the two catalysts (Fig. 2A) is 218 obtained. From the comparison between the two adsorption profiles at low and high rGO 219 loading it is manifest that i) 2,4-DCP is mainly partitioned on the rGO phase being the 220 amount of 2,4-DCP adsorbed on 10%rGO catalyst more than 3 times that adsorbed on the 221 0.5%rGO one (at the same concentration of free 2,4-DCP); *ii*) in both cases the empirical 222 Freundlich isotherm $C_{bound} = K_{ads} \times C_{free}^n$ well describes the data. This isotherm is usually 223 observed in the case of a marked heterogeneity of the adsorbing surface sites, in line with the 224 hybrid nature of the investigated catalysts. From the fitting of the experimental profiles, 225 $n=0.83\pm0.06$ and $n=0.45\pm0.02$ were obtained for the catalyst with 0.5% and 10% of rGO, 226 respectively, in agreement with the more complex nature of the adsorption sites in the catalyst 227 with the highest rGO loading.





Fig. 2. (A) Adsorption isotherm of 2,4-DCP on 0.5% and 10%rGO(*HTR*)-N100; (B) Photocatalytic degradation rate of 2,4-DCP on 0.5% and 10%rGO(*HTR*)-N100 (pH 3, $C_{cat} = 500 \text{ mg dm}^{-3}$, UV only irradiation source) as a function of the initial concentration (C_0). The continuous lines in Fig. B show the fit according to a square root dependence of the rate from C_0 (reaction order =0.5).

234 The Fig. 2B shows the initial degradation rates measured as a function of the initial 2,4-235 DCP concentration. The transformation rate at low C_0 followed the 0.5 order of reaction often 236 observed [18,30,31]. At larger C_0 the order n=0 was observed for 0.5% rGO. This agrees with 237 the standard kinetic model. [30,32] The bell-shaped profile observed at 10% rGO loading can 238 be interpreted in the light of the increment of the kinetic of recombination at high C₀ as a 239 consequence of the increased concentration of 2,4-DCP at the surface of the catalyst, which 240 can favor recombination processes mediated by adsorbed species (back reactions).[33] Presumably, 2,4-DCP can be oxidized by h_{vb}^+ and later reduced by e_{cb}^- acting as an efficient 241 242 recombination center. A similar behavior was previously reported for glycerol under similar 243 photocatalytic conditions.[34,35] The different behavior between the two loading conditions 244 can be interpreted in the light of their different ability to adsorb 2,4-DCP. The 10%rGO 245 catalyst is a better adsorbent for the substrate and consequently it adsorbs an amount of 2,4-DCP larger than that on the 0.5%rGO. This can promote the recombination process mediated 246 247 by the adsorbed substrate. The lower rate observed with the largest loading of rGO suggests 248 also that rGO could favor the recombination of charge carriers (both h_{vb}^+ and e_{cb}) photo-249 produced in one of the two phases or in both, in addition to the shielding of the TiO_2 phase.

To minimize the recombination reaction mediated by the substrate, we fixed 2,4-DCP 2×10^{-4} M, for which the reaction order is still n≈0.5 (see Fig. 2B), as observed in experiments with pristine TiO₂.[32]

253 **3.1.1 Different irradiation sources**

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The degradation of 2,4-DCP 2×10^{-4} M on TiO₂-rGO hybrids with increasing loading of rGO (from 0 to 20%) under UV-only irradiation was investigated. For the overall profiles of adsorption (in the dark) and subsequent photocatalytic degradation refer to Fig. 5SM. The first order kinetic constants for the photocatalytic degradation are reported in Fig. 3 (black bars). Alongside the increment of the rGO loading a decrease of the transformation rate was observed. The decrease is less marked at large rGO loadings ($\geq 4\%$) in the case of N100 (Fig.3A).



262Fig. 3. Photocatalytic degradation of 2,4-DCP on (A) N100- and (B) P25-hybrids with different rGO263loadings under UV only, UV + Vis ($\lambda \ge 340$ nm) and Vis only ($\lambda \ge 420$ nm). Conditions: pH 3, C_{cat} = 500264mg dm⁻³, C₀ = 2×10⁻⁴ M.

However, the amount of 2,4-DCP adsorbed increases with the overall amount of rGO. Fig.4 reports the fraction of adsorbed 2,4-DCP, C_{bound}/C_0 , where C_0 is the total 2,4-DCP

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267 concentration added to the system. At rGO% loading higher than 2% a monotonic increment

of the 2,4-DCP bound at the catalyst surface as a function of the overall amount of carbonaceous phase was observed.



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Fig. 4. Fraction of 2,4-DCP adsorbed on N100-hybrids as a function of the %rGO loading (conditions: C_0 = 2×10⁻⁴ M, pH 3, C_{cat} = 500 mg dm⁻³, C_{bound} = $C_0 - C_{free}$).

273 The decrease of the kinetic constants with %rGO can be partially interpreted in the light of 274 a shielding effect of the carbonaceous phase for the UV photons able to activate the 275 photocatalytic process on TiO₂. However, an increment of back reactions at higher rGO 276 loading cannot be excluded (see above). Even in this case the trend for the photocatalytic rate 277 with a plateau at $rGO \ge 4\%$ cannot be totally interpreted in this light, because the amount of 278 bound 2,4-DCP is linearly correlated with the rGO loading. To partially compensate both the 279 shielding effect and the increment of the recombination rate (mediated by the adsorbed 2,4-280 DCP), a different reason that would favor the 2,4-DCP transformation at high rGO% has to be 281 invoked. At this stage it is only possible to suppose either a partial activity of rGO itself under 282 UV-only irradiation or an increment of the photogenerated charge separation.[36,37,38]

283 A possible photocatalytic mechanism involving rGO absorption was checked with broad 284 band irradiation. The 2,4-DCP transformation on catalysts with different rGO% loading 285 (*n*%rGO(*HTR*)-N100 with n = 0, 1, 4, 10%) was studied under UV+Vis irradiation obtained through a sun simulator with a cut off filter able to block $\lambda \leq 340$ nm. The related kinetic 286 287 constants are reported in Fig. 3A (red bars). Even in this case a decrement of the overall 288 transformation rate was observed with the increase of the rGO loading, but it is lower than in 289 the case of UV-only irradiation. It emerges that, although rGO does not have a positive effect 290 on the overall photocatalytic, rGO activates some minor processes able to compensate partially for its shielding effect of TiO₂. 291

The first order kinetic constants on the same catalysts (n%rGO(HTR)-N100 with n = 0, 1, 4, 10%) under Vis-only irradiation ($\lambda \ge 420$ nm, with a cutoff filter on SOLARBOX) are reported in Fig. 3A (blue bars). For Vis irradiation the rate is dramatically lower than under UV, but not null. A slight increment of the 2,4-DCP degradation rate was observed with the increment of the rGO%. A small Vis activity of rGO, that implies also a small UV activity, could be one of the reasons previously invoked that are able to compensate the decrement in the photocatalytic rate observed under UV-Vis irradiation.

299 **3.1.2** Activity of hybrids with different TiO₂

With the aim to clarify if the nature of the TiO₂ affects the photocatalytic mechanism, rGO-TiO₂ hybrids with P25 were synthesized (*n*%rGO(*HTR*)-P25 with n = 0, 1, 4, 10%). The photocatalytic activity of these catalysts was compared toward 2,4-DCP degradation in the same conditions adopted in the previous experiments (C₀ = 2×10⁻⁴ M, pH 3, C_{cat} = 500 mg dm⁻³) under the same irradiation sources (UV-only, UV+Vis and Vis-only).

Fig. 5 shows all the experiments carried out with n%rGO(*HTR*)-P25: the columns report the different irradiation systems (UV-only, Vis-only and UV+Vis, respectively) and the rows the different rGO loading (from 0 to 10 %). Fig. 3B reports the related kinetic constants.

308





310Fig. 5. Adsorption (dark) and photocatalytic degradation (light) of 2,4-DCP on P25 hybrids with different311%rGO loadings: (A) 0%, (B) 4%, (C) 6% and (D) 10% and under different irradiation conditions: (I) UV-312only, (II) Vis only ($\lambda \ge 420$ nm) and (III) UV + Vis ($\lambda \ge 340$ nm). Conditions: C₀ = 2×10⁻⁴ M, pH 3, C_{cat}313= 500 mg dm⁻³.

The analysis of all these data and the comparison with the kinetic data measured with N100, suggest:

316 i) In the presence of UV irradiation (UV-only or UV-Vis) the photocatalytic 317 transformation of 2,4-DCP is faster on the pristine P25 than on N100. The ratio between the

318 two kinetic constants on the bare catalysts and under UV-only is $\frac{k_{obs}^{P25}}{k_{obs}^{N100}} = 6.9 \pm 0.8$. A marked

319 dependence of the rate for different substrates from the nature of TiO_2 was previously 320 reported, and a marked selectivity toward specific substrates or classes of substrates 321 emphasized.[39]

ii) The effect of the rGO on the kinetics of transformation of 2,4-DCP is the same both for the N100-based and TiO₂-P25-based catalysts. With the increment of rGO the photoactivity of the catalysts decreases, and the relative decrement is lower under UV+Vis irradiation than under UV-only source. A limited Vis activity was also observed and, as previously observed, this activity increases shlightly with the increment of the rGO loading.

327 The depressing role of rGO on the photocatalytic activity under UV-only is more iii) 328 marked in the P25-based catalysts with respect to N100. Note that the ratio between the 329 kinetic constants observed under Vis-only on 10%rGO(HTR)-P25 and 10%rGO(HTR)-TiO₂ 330 100 is 3.9 ± 0.4 , significantly lower than the ratio reported at point i) for the pristine catalysts. 331 The negative effect due to the rGO phase on the overall photocatalytic activity under UV 332 irradiation is strongly related not only to the nature of the carbonaceous phase synthesized, 333 but also to the type of TiO_2 employed. This outlines the importance of the size of TiO_2 334 particles, for scattering effects, and of the surface texture, that in the synthetic process 335 produces a different coupling between the two phases.

336 **3.2** Adsorption evaluation

337 In the composite catalyst there are two distinct phases (rGO and TiO_2) that concurrently 338 adsorb the analyte. Let fix rGO phase as phase #1, and TiO₂ as phase #2. The adsorption constant for each phase can be expressed as $K_i^{ads} = [A_{b,i}]/([S_i][A_w])$, corresponding to the 339 reaction $a_w + s_i = a_{b,i}$, where $[A_{b,i}]$ is the concentration of analyte bound to the adsorber i, $[S_i]$ 340 341 the concentration of free adsorbing sites s_i , and $[A_w]$ the concentration of the analyte in the 342 water solution. Considering that adsorption on the two different phases is not competitive, for each phase the number balance of sites, $C_{s,i} = [S_i] + [A_{b,i}]$, is worth. Then $[A_{b,i}] = C_{s,i}$ 343 $K_i^{ads}[A_w]/(1+K_i^{ads}[A_w])$. In the approximation of low surface coverage, this can be linearized 344 as $[A_{b,i}] = C_{s,i} K_i^{ads} [A_w]$, and then considering two phases the total amount of adsorbed analyte 345 $[A_b] = [A_w](C_{s,1} K_1^{ads} + C_{s,2} K_2^{ads}).$ 346

For experiments in which the concentration of the hybrid catalyst $C_{cat} = M_{cat}/V$ [g L⁻¹] is constant, the adsorbing sites concentration $[C_{s,i}]$ is easily expressed as $[C_{s,i}] = \varphi_i C_{cat} \sigma_i$, where φ_i is the mass fraction of phase *i* on the composite catalyst and σ_i is the density of adsorbing sites $[n_{sites} g^{-1}]$ of phase *i*. Considering that the fraction adsorbed onto the hybrid catalyst is $f_{ads} = [A_b]/[A_{tot}]$, it can be easily shown that $[A_b]/[A_w] = f_{ads}/(1 - f_{ads})$.

352 For a hybrid catalyst with two adsorbing phases, one obtains:

353
$$\frac{\int ads}{1 - f_{ods}} = K_2 + (K_1 - K_2)\varphi$$
 (eq. 1)

where the adimensional constant $K_i = C_{cat} \sigma_i K_i^{ads}$ at constant C_{cat} and σ_i is proportional to K_i^{ads} [M⁻¹], and where φ refers to the fraction of rGO in the composite catalyst, subscripts (1) and (2) to rGO and TiO₂, respectively. As $f_{ads} = 1 - C/C_o$ is experimentally known from the experimental concentration C in the aqueous phase after adsorption, the above linear

f

- relationship between $f_{ads}/(1-f_{ads})$ versus φ allows to estimate K_1 and K_2 , and then to assess where the substrate is preferentially adsorbed.
- Fig. 6 shows the plot according to eq.(1) of all adsorption data collected at different %rGO for N100 and P25 based hybrids. The values of K_1 and K_2 obtained under different irradiation
- 362 conditions are reported in Table 1 (see later for a discussion).



363 364

Fig. 6. Fit according to eq. 1 of the adsorption experimental data for N100- and P25-hybrids.

365 3.3 Kinetic model to decouple the photocatalytic activity of the two 366 phases

367 Here we develop for the first time a two-phase kinetic model for a hybrid photocatalyst, 368 which is applicable when both phases or only one absorbs light. Here we follow the same 369 treatment already developed for kinetic in photocatalytic systems, [32] as the model was 370 validated several times [30,31]. Each material is considered separately for light absorption, 371 the recombination reaction and reactivity with the oxidant (O_2) and the analyte, and their 372 contribution to the overall rate is proportional to their mass fraction in the catalyst, as done above for the analysis of adsorption. However, as the produced charge carrier after light 373 374 absorption in each material are supposed to exchange between the two phases of the hybrid 375 catalyst, to approach this issue we consider the total amount of formed holes (or total excited 376 electrons), and assume that a fast equilibrium is reached between the two phases regulated by 377 an equilibrium constant $K_h = [h_{eq,l}]/[h_{eq,2}]$ and $K_e = [e_{eq,l}]/[e_{eq,2}]$, respectively for holes and 378 electrons. For example, holes produced on TiO₂ VB can migrate to rGO, adding to that 379 possibly formed on rGO itself after light absorption, the electrons can migrate from rGO to 380 TiO₂, adding to that formed on TiO₂, or the reverse, or any combination of them. Then 381 $[h_{eq,l}] = \beta_h[h_{tot}], [h_{eq,2}] = (1-\beta_h) [h_{tot}], \text{ and } [e_{eq,l}] = \beta_e[e_{tot}], [e_{eq,2}] = (1-\beta_e) [e_{tot}] \text{ where the fraction}$ 382 $\beta_i = K_i/(1 + K_i)$ and $[h_{tot}]$ and $[e_{tot}]$ are the sum of holes and excited electrons, respectively, 383 produced by the independent absorption of the two materials in the hybrid catalyst. Then the 384 actual concentration of reacting species produced by light absorption of the hybrid catalyst ψ_h and equilibrated between the two phases is $[h_{eq,l}] = \beta_h \psi_h$ and $[h_{eq,2}] = (1 - \beta_h) \psi_h$. The same is 385 worth for electrons in the upper energy level. Only in the case that the two materials have not 386 387 a strong electronic coupling, the absorption $\psi_h = (\psi_1 + \psi_2)$, where ψ_i is the absorbed photon flux 388 by each material *i*. Because the amount of absorbed light is proportional to ε_i , the extinction coefficient of the pure phase *i*, and ψ_o , the incident light intensity, then $\psi_i = b \varepsilon_i \psi_o \varphi_i C_{cat}$, 389 where ε_i is the absorption coefficient [g⁻¹] and b the slurry thickness used in the experiments. 390

391 For practical convenience, $(\psi_1 + \psi_2) = [\omega_1 \varphi + \omega_2 (1 - \varphi)]$, where $\omega_i = b \varepsilon_i \psi_o C_{cat}$ are constant if 392 ψ_o and C_{cat} are constant for the set of experimental data.

393 With the above assumptions a steady state approximation is applied to the rate equations for $d[e_{tot}]/dt$ and $d[h_{tot}]/dt$ considering the generation rate $(\psi_1 + \psi_2)$, and in each material the 394 395 recombination of charge carriers, the reaction of excited electrons with oxygen and that of 396 holes with the adsorbed substrate. The solution for the quantum yield $(QY=rate/\psi_h)$ is here 397 developed only for the oxidative side (oxidation by holes) of the photocatalytic process, for 398 sake of simplicity. The solution is identical to that already reported [30], i.e. QY = -y + y $\sqrt{y(y+2)}$), but with a different expression for the master variable y (here omitted). Under 399 the approximation that y<<1, that is a QY<0.20 and definitely at low C₀, $QY = \sqrt{2y}$, and 400 401 then the rate is

402
$$rate = \sqrt{k_{cat}[A_{tot}]} = \sqrt{k_1[A_{b,1}] + k_2[A_{b,2}]} \sqrt{\psi_h}$$
 (eq. 2)

403 The square root dependence on $[A_{tot}]=C_o$ is already evident in Fig. 2B, provided that C_0 is 404 small as in the experiments here analyzed. Using the relationships derived above in the 405 analysis of adsorption for $[A_{b,i}]$ and for ψ_h (under the linear combination hypothesis), the rate 406 constant k_{cat} in the hybrid catalyst is

407

$$k_{cat} = \frac{[k_1 K_1 \varphi + k_2 K_2 (1-\varphi)][\omega_1 \varphi + \omega_2 (1-\varphi)]}{1 + K_1 \varphi + K_2 (1-\varphi)}$$
(eq. 3)

409

410 where $k_I = k_{red,T} [O_2] \beta_h k_{ox,I}$, $k_2 = k_{red,T} [O_2] (1-\beta_h) k_{ox,2}$, $k_{red,T}$ is the composite rate constant of 411 reaction of excited electrons with O_2 equal to $k_{red,T} = (\beta_e k_{red,I} + (1-\beta_e) k_{red,2})/(\beta_e \beta_h k_{R,I} + (1-\beta_e) (1-\beta_h) k_{R,2})$, in which $k_{R,i}$ are the recombination rate constants of charge carriers, and $k_{ox,i}$ 413 and $k_{red,i}$ are the reaction rate constants for oxidation of the substrate by holes and reduction of 414 O_2 in the two phases, respectively. The significance of K_I and K_2 ($K_i = C_{cat} \sigma_i K_i^{ads}$) and $\omega_i = b$ 415 $\varepsilon_i \psi_o C_{cat}$ have been above reported.

416 This is the main result for the two-phase photocatalytic model, where the 417 adsorption/desorption rate is regulated by the adsorption equilibrium constants $K_{i=1,2}$ on the 418 two phases, the fraction φ of rGO and the fraction $(1-\varphi)$ of TiO₂ in the composite catalyst, 419 which is used in the experiments at constant and fixed concentration C_{cat} . The kinetic 420 composite constants k_1 and k_2 are constants at fixed [O₂] as done in the experiments. The dependence of k_{cat} on k_1 , k_2 , K_1 , K_2 , ω_1 and ω_2 is then quite complex and justifies the paper 421 422 title about the complex interplay between adsorption and photoactivity in hybrids rGO/TiO₂. The equation shows that the *rate*= $k_{obs} C_o^{\frac{1}{2}}$ (see Fig. 2B) for low C₀ depends basically from the 423 convolution of the square root of 3 terms: 1) the rate constants weighted with adsorption 424 425 constants and relative mass fraction of each hybrid material constituent; 2) the optical 426 properties of the two materials and used irradiation spectra; 3) the adsorption constants 427 weighted with mass fraction of each hybrid material constituent. The model has a general 428 application to whatever material the hybrid is formed of.

The kinetic model, although approximated for low quantum yields and linear adsorption, is able to foresee, in the case of this paper, if addition of rGO to TiO₂ is beneficial or not, and to decouple the effects of adsorption from intrinsic kinetic factors. Given that K_1 and K_2 can be independently measured (see eq. 1), the partition of charge carriers β_i , included in k_1 and k_2 ,

can be estimated although weighted by the actual true kinetic constants $k_{ox,i}$ (see the definition 433 434 of these constants below eq. 3). As the ratio $k_1/k_2 = \beta_h k_{ox,1}/((1-\beta_h) k_{ox,2})$, and remembering that $\beta_h = K_h/(l + K_h)$, the ratio $k_l/k_2 = K_h k_{ox,l}/k_{ox,2}$ gives a direct information on the partition of 435 436 holes and their reactivity in the two phases. The kinetic constants $k_{ox,i}$ reflect the probability of 437 holes to react with the substrate, and their values depend on the position of energy levels, on 438 which they are located, relative to the substrate redox potential. For example, if holes moves 439 to graphene K_h would be large, but if the energy level where they move is more negative than the redox potential for oxidation of the substrate, $k_{ox,1}$ will be negligible, resulting in a 440 441 negligible value of the ratio k_1/k_2 .

442 In this kinetic model the effect of wavelength of illumination is also contemplated. In UV 443 both TiO₂ and rGO can absorb. However under VIS irradiation, ω_2 is null. The assumption 444 that absorption $\psi_h = (\psi_{1+}\psi_{2})$ is quite approximated, as it does not include possible synergic 445 effects, including strong electron coupling between the materials and their mutual shading, 446 which have been invoked before, and also already reported by our research group [19]. In the 447 quoted paper it was shown that 5% rGO is able to decrease the extinction of the TiO_2 by 20% 448 at 350 nm, probably reducing more the scattering than the absorption. However, the 449 assumption has the merit to show the many dependences of light absorption from material's 450 type and hybrid composition.

451 As the denominator in eq. 3 can be directly calculated from the experiment (see Fig. 6), eq.452 3 can be transformed into:

453
$$\frac{k_{obs}^2}{1 - f_{ads}} = [k_1 K_1 \varphi + k_2 K_2 (1 - \varphi)] [\omega_1 \varphi + \omega_2 (1 - \varphi)]$$
(eq. 4)

454

Eq. 4 forecasts that the experimental LHS term has a parabolic dependence on φ . The parabolic fit on experimental data $k_{obs}^2/(1-f_{ads}) = A \varphi^2 + B \varphi + C$ is reported for N100 and P25 in Fig. 7(inset). The fit is quite good. However, the constant terms *A*,*B*,*C* depend on 6 parameters of which 4 are unknown (actually k_1 , k_2 , ω_1 , ω_2), and then it is not possible to get a value for them. The sole valuable value is the intercept, that corresponds to $k_2 \times K_2 \times \omega_2$ As K_2 is known from adsorption analysis, $k_2 \times \omega_2$ is evaluated and reported in Table 1.



461

462 **Fig. 7.** Experimental k_{obs} as a function of the fraction φ of rGO on N100 (A) and P25 (B) hybrid catalyst. 463 Insets: experimental $k_{obs}^2/(1-f_{ads})$ vs. φ . The solid lines are the quadratic fits according to eq. 4.

464 Alternatively, at low φ the experimental data can be approximated by a straight line. This 465 follows from eq. 4 assuming that under UV irradiation, or UV+VIS irradiation, only TiO₂ 466 absorbs light. This assumption is supported by the low reported extinction of rGO on SiO_2 [19] from which is apparent that the net extinction due to rGO is low at all wavelengths. Eq.4 467 is the convolution of two straight lines $z_1 = k_2 K_2 + (k_1 K_1 - k_2 K_2)\varphi$, and $z_2 = \omega_2 + (\omega_1 - \omega_2)\varphi$. 468 469 Accordingly, z_2 must have a negative slope. The increase of $k^2_{obs}/(1-f_{ads})$ at large rGO 470 fractions can be claimed as a synergic effect of rGO. As the convolution of the two straight lines must increase at large φ , z_1 must have a positive slope. To obtain that at least at $\varphi=1$ the 471 472 function value is equal to that at $\varphi=0$, the following condition must be satisfied: 473 $k_1K_1/k_2K_2 > \omega_2/\omega_1 = \varepsilon_2/\varepsilon_1$. Then from Table 1 $k_1/k_2 > 9.3 \times 10^{-3} \varepsilon_2/\varepsilon_1$ and $k_1/k_2 > 1.7 \times 10^{-2} \varepsilon_2/\varepsilon_1$ for N100 and P25 hybrids, respectively. If these conditions are satisfied, the increase of $k_{abs}^2/(1-k_{abs}^2/k_{a$ 474 475 f_{ads}) at large rGO fractions is possible. As the reported extinction of rGO on SiO₂ (see Fig.2 in [19]) at 360 nm is about 200, then $\varepsilon_2/\varepsilon_1 \approx 12000/200=60$ for N100. It follows for N100 that 476 $k_1/k_2 > 0.56$. A similar condition is worth for P25 [40], for which the extinction coefficient at 477 365 nm $\varepsilon_2 = 2.5 \times 10^4 \text{ cm}^2 \text{g}^{-1}$, i.e $\varepsilon_2 / \varepsilon_1 \approx 25000 / 200 = 120$. Then $k_1 / k_2 > 2.0$ for P25. 478 479 From the limit values $k_1/k_2 > 0.56$ and $k_1/k_2 > 2.0$ for N100 and P25, respectively, the rGO is

beneficial only if the microscopic reactivity on rGO, $k_1 = k_{red,T} [O_2] \beta_h k_{ox,I}$, is almost equal to that of TiO₂, $k_2 = k_{red,T} [O_2] (1-\beta_h) k_{ox,2}$. As $k_1/k_2 = K_h k_{ox,I}/k_{ox,2}$, to obtain the reported ratios $K_h k_{ox,I} \approx k_{ox,2}$. Two limiting hypotheses are possible: 1) if on rGO the substrate oxidation is very efficient, a limited partition of holes on rGO can be compatible; 2) if the holes are quantitatively injected from TiO₂ to rGO, a limited catalytic role of rGO can be tolerated. All other cases are intermediates between the above.

486 As k_2 for P25 is larger than k_2 for N100 (about 3.6 times), the effect of rGO can be seen on 487 P25 only at larger %rGO than those needed for N100 (compare Fig.7A with 7B). This 488 conclusion is relevant as the beneficial effect of rGO in hybrid catalysts is evident only if the 489 semiconductor is not particularly efficient.

490

491 Table 1. Adsorption and degradation constants obtained from the fitting of the degradation kinetic and
 492 adsorption data in the presence of the catalysts with different %rGO loading (left column: N100 hybrids;
 493 right column: P25 hybrids).

N100 hybrids		P25 hybrids		
Adsorption		Adsorption		
κ1	$\textbf{2.79}\pm\textbf{0.12}$	K ₁	3.61 ± 0.32	
<i>K</i> ₂	0.026 ± 0.008	К2	0.060 ± 0.019	
K ₂ /K ₁	(9.3±0.5)×10 ⁻³	K ₂ /K ₁	(1.7±0.5)×10 ⁻²	
Photocatalytic degradation		Photoc	atalytic degradation	
$k_2\omega_2$ (UV only)	(5.5 ±1.9) × 10 ⁻³	$k_2\omega_2$ (UV only)	0.14 ±0.04	
$k_2\omega_2$ (UV+Vis)	$(3.7 \pm 1.3) \times 10^{-3}$	$k_2\omega_2$ (UV+Vis)	(4.6 ±1.4) × 10 ⁻²	

494

The results obtained from the adsorption model and the reduced kinetic model (eq. 1 and 5) are summarized in Table 1 for N100- and P25-based catalysts (left and right column, respectively). The data include the type of irradiation source, except for Vis only. From the comparison between the adsorption and photocatalytic degradation constants obtained in the different experimental conditions, some further conclusions can be drawn: i) The adsorption on P25 phase is roughly double with respect to that of the pristine
N100. This justifies the larger activity of naked P25 with respect to naked N100 already
discussed under paragraph 3.1.2 (see also Fig.4). In all hybrids the 2,4-DCP adsorption is
completely unbalanced toward the rGO phase, with adsorption constant from 60 to 110 times
higher for the rGO phase with respect to TiO₂.

505 ii) Under Vis-only irradiation a very low but not null activity is observed (see Fig.7). As
506 the Vis activity is almost independent of the rGO fraction, this can be mostly attributed to the
507 sensitization of interfacial states created by the coupling with rGO.

508 iii) The degradation kinetic constants related to the inorganic phase are significant higher 509 for TiO_2 -P25 than for N100, particularly under UV-only irradiation, but the decrement is 510 significantly higher for P25-based materials than for N100-based catalysts. This implies a 511 different electron coupling with rGO.

512 **3.4** *Photocatalytic transformation of 1-Naphthol*

A different substrate was also checked to assess if previous conclusions are substratedependent. The substrate chosen was 1-naphthol because *i*) it is strongly adsorbed at the surface of the hybrid catalyst and *ii*) it cannot be degraded through a reductive pathway, as 2,4-DCP does.[29] The catalysts were obtained through the chemical reduction of GO as in [19] with the aim to test if the reductive procedure affects significantly the photoactivity of the catalyst. The results obtained on catalysts synthesized through the hydrothermal and chemical routes did not show significantly differences.

The photocatalytic transformation of 1-naphthol on 2%rGO(CR)-N100 at different 520 substrate concentrations (from 2.5×10^{-5} to 5×10^{-4} M) were carried out under UV-only 521 irradiation. From the raw experimental profiles in the dark and under irradiation (see Fig. 522 523 6SM) the adsorption isotherm (Fig. 8) and the photocatalytic degradation constants as a 524 function of the initial concentration C_0 (inset of Fig. 8) were obtained. As for 2,4-DCP, the adsorption isotherm for 1-naphthol is well described by a Freundlich isotherm with n =525 526 0.33 ± 0.08 . From the photocatalytic kinetic constants measured, the photocatalytic 527 transformation rates were computed and reported as a function of C_0 in Fig. 6SM-(f). As for the 2,4-DCP, a bell-shaped behavior was observed suggesting a surface recombination 528 529 process mediated by the adsorbed substrate.[32] With 1-naphthol the back reactions were 530 kinetically important even at relatively low rGO loading because of the higher adsorption of 531 1-naphthol than 2,4-DCP on the catalyst surface.



532

533 **Fig. 8.** Adsorption isotherm of 1-naphthol on N100 with 2%rGO(*CR*). Inset: 1-naphthol photocatalytic 534 degradation constant k_{obs} (pH 3, $C_{cat} = 500 \text{ mg dm}^{-3}$, UV only) on 2%rGO(*CR*)-N100 at different initial 535 concentration C_0 .

536 The 1-naphthol photocatalytic degradation was explored under UV+Vis irradiation (see 537 Fig. 1B) on catalysts with different rGO loading (n%rGO(CR)-N100 with n = 0, 2, 6 and 10 538 %). The raw profiles are reported in Fig. 7SM and the related kinetic constants summarized in 539 Fig. 9. It is manifest that even in this case the rGO has a detrimental effect on the overall 540 photocatalytic activity. The 1-naphthol photo-catalyzed transformation was tested also under Vis-only irradiation (yellow lamp, see Fig. 1B) on the same catalysts. The raw profiles are 541 542 reported in Fig. 10, and the photocatalytic rate constants are also reported in Fig. 9. The Vis-543 only activity is quite low and the kinetic constants slightly increased with the rGO loading.

544 Interestingly, the analysis of the raw profiles in the dark shows that the adsorption of 1-545 naphthol on the TiO₂-rGO catalyst surface, especially at high rGO loading, is quite complex and apparently follows a double kinetic process in which 1-naphthol is fast adsorbed, 546 probably on a family of adsorption sites easily reachable, and then the adsorption proceeds 547 548 with lower rate, presumably on a family of less reachable sites (i.e. micro-porosity). This adds 549 further difficulties for the interpretation of the data, because it is quite difficult to split the 550 contribution of an effective degradation process from a progressive and slow adsorption. This 551 could be a common drawback of the analysis of the transformation data obtained on highly heterogeneous adsorbing systems. This is not only the case of 1-naphthol (here reported), but 552 553 also the case of the most used dyes employed to test the performance of innovative 554 photocatalysts. In these cases the collection of robust experimental data useful to extract 555 reliable conclusions on the photocatalytic activity is difficult and sometimes impossible. 556 Additionally, data can be biased by large Vis irradiation intensity and improper UV cutoff that 557 increase the modest activity of hybrid catalysts.



558

559 **Fig.9.** Degradation rate constants k_{obs} for 1-Naphthol on n%rGO(*CR*)-N100 (with n% equal to 0, 2, 6 and 560 10%) under UV+Vis and Vis only irradiation sources. Conditions: $C_0 = 1 \times 10^{-4}$ M, pH 3, $C_{cat} = 500$ mg 561 dm⁻³.



562

563 **Fig. 10.** Adsorption (dark) and photocatalytic degradation (Vis only irradiation) of 1-naphthol on N100-564 hybrids with different rGO loadings (%rGO(*CR*) = 0, 2, 6 and 10%). Conditions: $C_0 = 1 \times 10^{-4}$ M, pH 3, 565 $C_{cat} = 500$ mg dm⁻³.

566

567 4 Conclusions

The acquired set of experimental data (different C_0 , %rGO, type of TiO₂ and irradiation spectra) allowed a quantitative analysis of adsorption and kinetic parameters for the hybrid catalyst. The investigated substrates are adsorbed preferentially on the rGO and this gives an unbalanced phase partitioning of the organic substrate.

572 Significant degradation rates were observed only in the presence of UV irradiation. This 573 suggests that the only photocatalytic mechanism operational is that based on the band-to-band 574 transition promoted by the absorption of a UV photon from the semiconductor. The 575 photogenerated carriers in the semiconductor hardly moves to the rGO phase where the 576 substrate is mainly partitioned. Being the reductive pathway active during the 2,4-DCP 577 photocatalytic transformation under pristine TiO_2 , we can conclude that the photo-promoted 578 electrons in the TiO_2 conduction band are difficulty injected in the rGO where the substrate is

- 579 mainly adsorbed. This is in agreement with our previous conclusion that the electron transfer
- 580 process can occur from photoexcited states of rGO onto the titania, and holes can migrate
- 581 from titania to rGO.[19]
- 582 The rGO phase did not give the hoped increment in the transformation rate of both 2,4-DCP 583 and 1-naphtol, even if the inhibition effect caused by the presence of rGO was lower
- 584 under UV-Vis because a not null visible activated degradation mechanism is operational.
- 585 The nature of the TiO_2 employed (N100 vs P25) does not influences significantly the overall 586 photoactivity of the catalysts.
- 587 According to the discussion at paragraph 3.3, if the holes are quantitatively injected from 588 TiO₂ to rGO, a limited catalytic role of rGO can be tolerated. However, since also in UV the 589 rate is depressed, the holes in the rGO phase are not sufficiently oxidizing to promote the 590 transfer of an electron from the HOMO of the adsorbed substrate (both 2,4-DCP and 1-591 naphthol) to the empty state of rGO. In other terms, the redox potential of the hole in the rGO 592 (h^+_{rGO}) is not sufficiently high (low in energy) to promote the electron transfer from the HOMO of the adsorbed substrate to the empty state of rGO. Alternatively, if the 593 594 photogenerated holes are efficiently transferred to the rGO phase, this acts as a recombination 595 center. Furthermore, at high concentration the adsorbed substrate (both 2,4-DCP and 1-596 naphthol) can promote substrate mediated recombination processes.

597 The kinetic model here developed permits enucleation of some key factors influencing the 598 photocatalytic rate. The model has a general validity and can be applied to binary 599 photocatalysts whatever the nature of the phases is (e.g. inorganic/inorganic hybrids, carbon 600 doped semiconductors). However, a more refined model on the dependence of light 601 absorption by hybrid catalyst is desirable.

602

603 4.1 Acknowledgements

The authors are kindly grateful for the financial support to Università di Torino – (Ricerca
Locale). MM acknowledges financial support from Marie Skłodowska-Curie Action – 765860
AQUALITY – H2020-MSCA-ITN-2017.

607

Captions to Figures and Tables

007	
610 611	Fig.1. Emission spectra normalized to the maximum intensity peak for the lamps used during the photocatalytic degradation experiments of (A) 2,4-DCP and (B) 1-naphthol.
612 613 614 615 616 617	Fig. 2. (A) Adsorption isotherm of 2,4-DCP on 0.5% and 10%rGO(<i>HTR</i>)-N100; (B) Photocatalytic degradation rate of 2,4-DCP on 0.5% and 10%rGO(<i>HTR</i>)-N100 (pH 3, $C_{cat} = 500 \text{ mg dm}^{-3}$, UV only irradiation source) as a function of the initial concentration (C_0); (C) 2,4-DCP bound as a function of the %rGO loading. The continuous lines in Fig. B show the fit according to a square root dependence of the rate from C_0 (reaction order =0.5).
618 619 620	Fig. 3. Photocatalytic degradation of 2,4-DCP on (A) N100- and (B) P25-hybrids with different rGO loadings under UV only, UV + Vis ($\lambda \ge 340$ nm) and Vis only ($\lambda \ge 420$ nm). Conditions: pH 3, C _{cat} = 500 mg dm ⁻³ , C ₀ = 2×10 ⁻⁴ M.
621 622	Fig. 4. Fraction of 2,4-DCP adsorbed on N100-hybrids as a function of the %rGO loading (conditions: $C_0 = 2 \times 10^{-4}$ M, pH 3, $C_{cat} = 500$ mg dm ⁻³ , $C_{bound} = C_0 - C_{free}$).
623 624 625 626	Fig. 5. Adsorption (dark) and photocatalytic degradation (light) of 2,4-DCP on P25 hybrids with different %rGO loadings: (A) 0%, (B) 4%, (C) 6% and (D) 10% and under different irradiation conditions: (I) UV-only, (II) Vis only ($\lambda \ge 420$ nm) and (III) UV + Vis ($\lambda \ge 340$ nm). Conditions: C ₀ = 2×10 ⁻⁴ M, pH 3, C _{cat} = 500 mg dm ⁻³ .
627	Fig. 6. Fit according to eq. 1 of the adsorption experimental data for N100- and P25-hybrids.
628 629 630	Fig. 7. Experimental k_{obs} as a function of the fraction φ of rGO on N100 (A) and P25 (B) hybrid catalyst. Insets: experimental $k_{obs}^2/(1-f_{ads})$ vs. φ . The solid lines are the quadratic fits according to eq. 4.
631 632 633	Fig. 8. Adsorption isotherm of 1-naphthol on N100 with 2%rGO(<i>CR</i>). Inset: 1-naphthol photocatalytic degradation constant k_{obs} (pH 3, $C_{cat} = 500 \text{ mg dm}^{-3}$, UV only) on 2%rGO(<i>CR</i>)-N100 at different initial concentration C_0 .
634 635 636	Fig.9. Degradation rate constants k_{obs} for 1-Naphthol on $n\%$ rGO(<i>CR</i>)-N100 (with $n\%$ equal to 0, 2, 6 and 10%) under UV+Vis and Vis only irradiation sources. Conditions: $C_0 = 1 \times 10^{-4}$ M, pH 3, $C_{cat} = 500$ mg dm ⁻³ .
637 638 639	Fig. 10. Adsorption (dark) and photocatalytic degradation (Vis only irradiation) of 1-naphthol on N100-hybrids with different rGO loadings (%rGO(<i>CR</i>) = 0, 2, 6 and 10%). Conditions: $C_0 = 1 \times 10^{-4}$ M, pH 3, $C_{cat} = 500$ mg dm ⁻³ .
640 641 642 643	Table 1. Adsorption and degradation constants obtained from the fitting of the degradation kinetic and adsorption data in the presence of the catalysts with different %rGO loading (left column: N100 hybrids; right column: P25 hybrids).
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The complex interplay between adsorption and photoactivity in hybrids rGO/TiO_2

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SUPPLEMENTARY MATERIAL



Fig. 1SM. Absorption spectrum of a GO suspension synthesized according to the method described in the main body of the text under paragraph 2.2.[1]



Fig. 2SM. Ramp profile adopted to carry out the hydrothermal reductive treatment in autoclave on suspension of TiO_2 -GO at different loading. The hydrothermal condition allows the partial reduction of the GO oxidized moieties to give the desired TiO_2 -rGO hybrids.



Fig. 3SM Adsorption (dark) and photocatalytic degradation (light) of 2,4-DCP on 0.5%rGO(HTR)-TiO₂ N100, at different initial concentration: (a) 5×10^{-5} M, (b) 1×10^{-4} M, (c) 2×10^{-4} M, (d) 5×10^{-4} M, (e) 1×10^{-3} M. Conditions: pH 3, [cat] = 500 mg/L, UV irradiation source (Philips 18W BLB lamp).



Fig. 4SM Adsorption (dark) and photocatalytic degradation (light) of 2,4-DCP on 10%rGO(HTR)-TiO₂ N100 at different initial concentration: (a) 5×10^{-5} M, (b) 1×10^{-4} M, (c) 2×10^{-4} M, (d) 5×10^{-4} M, (e) 1×10^{-3} M. Conditions: pH 3, [cat] = 500 mg/L, UV irradiation source (Philips 18W BLB lamp).



Fig. 5SM. Adsorption (dark) and photocatalytic degradation (light) of 2,4-DCP ($C_0 = 2 \times 10^{-4}$ M) in on (a) TiO₂ N100, (b) 0.5%rGO(HTR)–TiO₂ N100, (c) 1%rGO(HTR)–TiO₂ N100, (d) 2%rGO(HTR)–TiO₂ N100, (e) 4%rGO(HTR)–TiO₂ N100, (f) 6%rGO(HTR)–TiO₂ N100, (g) 10%rGO(HTR)–TiO₂ N100 and (h) 20%rGO(HTR)–TiO₂ N100. Conditions: pH 3, [cat] = 500 mg/L, UV only irradiation source (Philips 18W BLB lamp).



Fig. 6SM. Adsorption (dark) and photocatalytic degradation (light) of 1-naphthol at different initial concentration: (a) 2.5×10^{-5} M, (b) 5×10^{-5} M, (c) 1×10^{-4} M, (d) 2×10^{-4} M, (e) 5×10^{-4} M. Conditions: pH 3, [cat] = 500 mg/L, 2%rGO(CR)-TiO₂ N100, UV only irradiation source (Philips 18W BLB lamp).



Fig. 7SM. Adsorption (dark) and photocatalytic degradation (light) of naphthol ($C_0 = 1 \times 10^{-4}$ M, pH 3, [cat] = 500 mg/L) on (A) TiO₂ N100, (B) 2%rGO(CR)-TiO₂ N100, (C) 6%rGO(CR)-TiO₂ N100 and (D) 10%rGO(CR)-TiO₂ N100. Irradiation source Philips TLK 03 (mainly visible, minor fraction UV).

1 References

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