SUPPLEMENTARY MATERIALS FOR:
CARBOXYLATED GRAPHENE-TiO$_2$ HYBRIDS AS MULTIFUNCTIONAL MATERIALS: FROM PHOTOCATALYSIS TO PEROXIDASE ALTERNATIVES.

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1. Graphene functionalization

Briefly, we used 4-aminophenylacetic acid to produce diazonium cations at acidic pH in presence of NaNO$_2$. The diazonium cations can be reduced by graphene to obtain radicals that react with GNP surface and which lead to surface functionalization, as schematized in Fig.S1.[20]

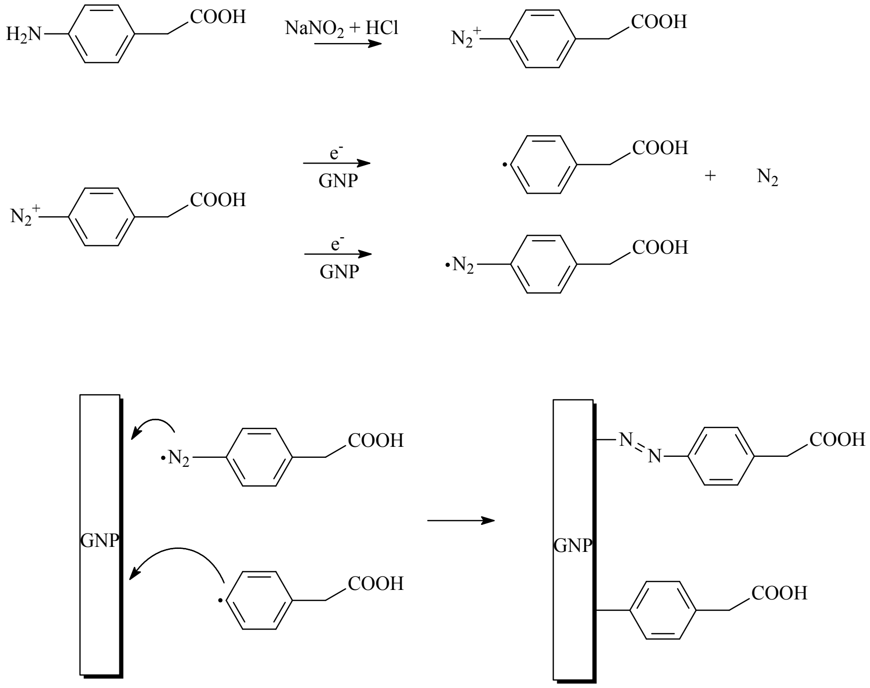

Figure S1: Mechanism of functionalization of the GNP samples

We estimated the content on C, O, N and Ti *via* XPS technique and the results are collected in Tab. S1.

Sample	C at%	O at%	N at%
GNP	99.1 ± 0.2	0.9 ± 0.2	n.d.
GNP-COOH	91.5 ± 0.5	7.5 ± 0.3	1.0 ± 0.2

Table S1: Carbon, oxygen and nitrogen content in the samples prepared in the present work determined by XPS. Uncertainty has been estimated as twice the standard deviation.

COOH–GNP sample shows an increase in O at % due to the formation of carboxylate groups, while the presence of N has to be ascribed to azo-groups.

C 1s high resolution spectra (Fig. 2) show (i) a component at 284.4 eV, due to C–C bonds; (ii) one at 290.0 eV, due to the π–π* transition; and (iii) three components generated by groups containing O (and/or N, in NH_2–GNP): C–O or C–N at 285.5–285.7 eV, C=O at 286.7–286.9 eV. O 1s spectra show two components at 531.3–531.5 eV (C=O, COOH and CONH) and 532.8–533.0 eV (C–O) (Fig.2). A larger fraction of COOH and CONH groups are measured on the functionalized sample than on GNP.

The N 1s high resolution spectrum (Fig.S2) shows only one component centered at 400.1 eV on COOH–GNP, which can be assigned to azo groups, introduced during functionalization. These results agree with our previous work in which this strategy for surface functionalization was followed and confirm that the functionalization happened.[20]

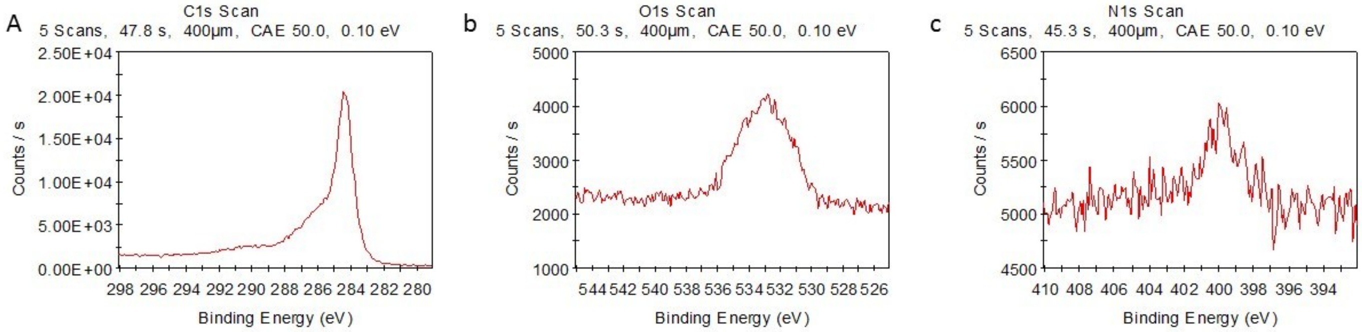

Figure S2: High resolution XPS spectra for GNP-COOH sample

Raman spectra show the presence of D peak (1350 cm^{-1}), characteristic of graphite, graphene multilayers and single layers, and G peak (1580 cm^{-1}), due to the presence of defects on graphene structure, for both samples (Fig. 3). The functionalization of GNP lead to a decrease of the D : G peak intensity ratio because of an increase of the disorder inside the GNP layers.

Both peaks are blue shifted for the chemical doping due to the functionalization. Also in this case the results are in agreement with the previous experience: in fact, the variation of D:G ratio and the blue shift are usually used for the determination of the functionalization of graphene sheets.[20]

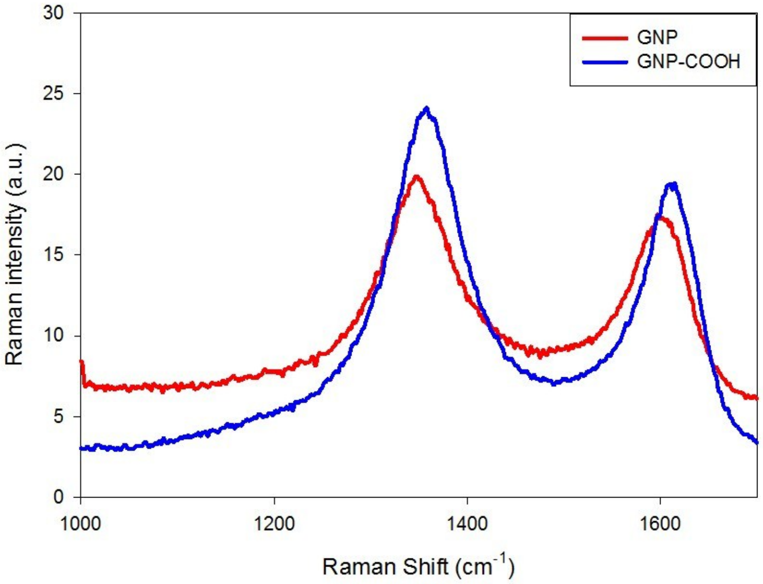

Figure S3: Raman spectra of bare GNP and COOH functionalized GNPs in the 1000–1700 cm^{-1} range.

ATR spectrum of GNP-COOH is shown in Figure S4. The spectra were obtained supporting GNP-COOH sample on a wafer of silicon, whose spectrum is reported in the figure as reference. ATR spectrum show a slight increase around 1300 cm^{-1} and in 1500-1600 cm^{-1} zone, attributable to the carboxylic groups on the GNP surface.

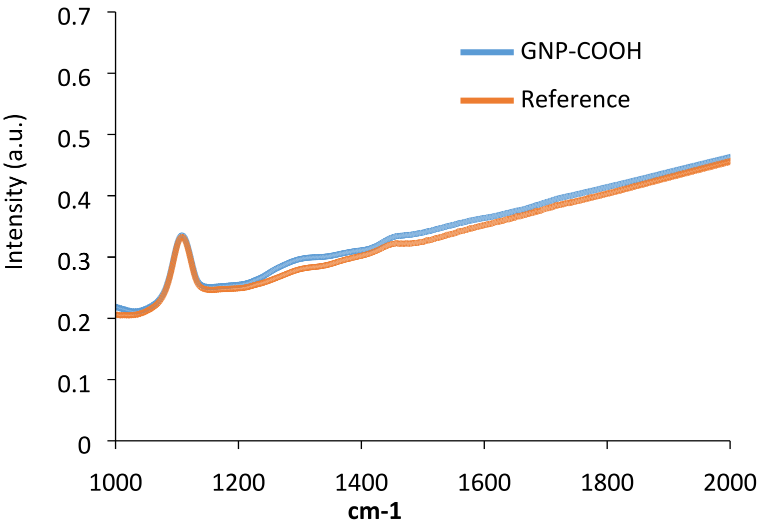

Figure S4. ATR spectrum of GNP-COOH in the 1000–2000 cm^{-1} range.

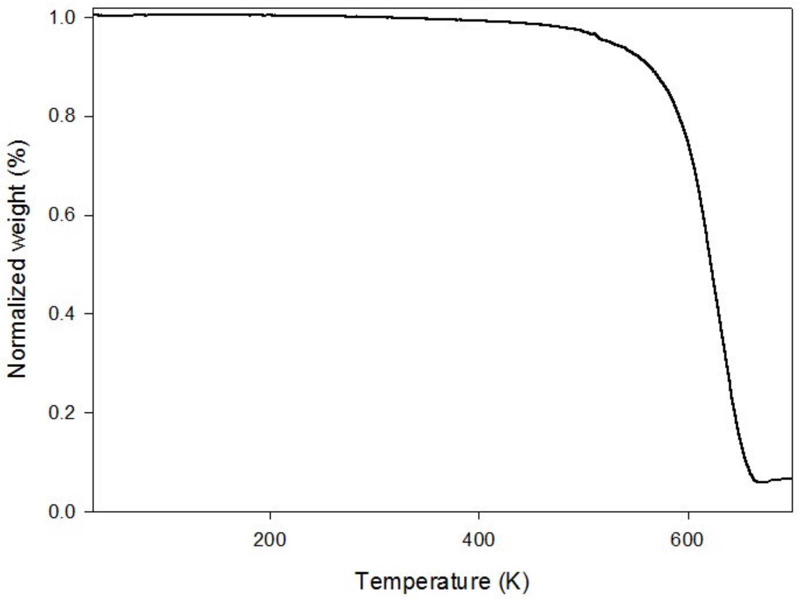

Figure S5: Normalized weight (%) as a function of the temperature for graphene (GNP)

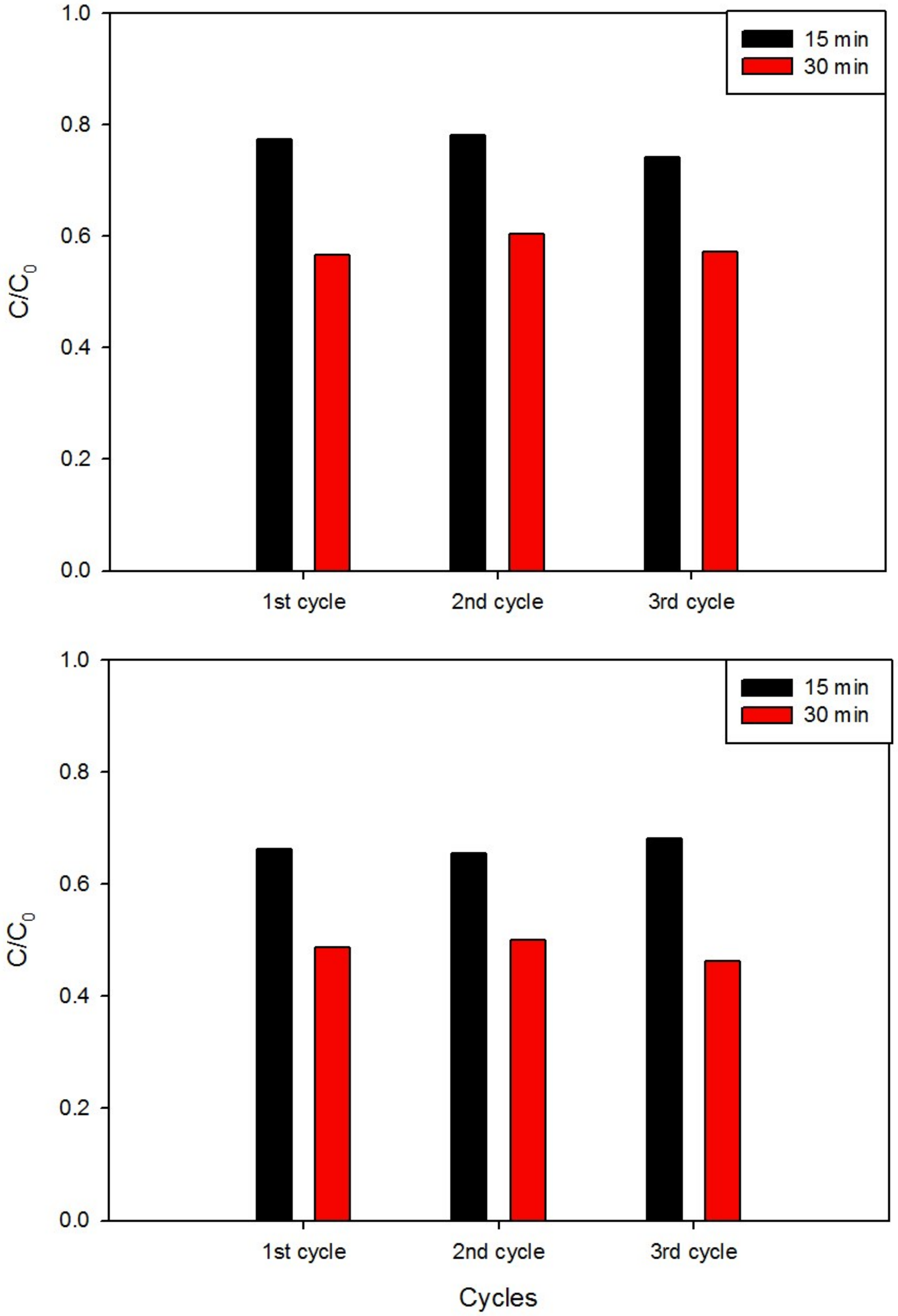

Figure S6. Photoactivity of GNP-TiO_2 (top) and GNP-COOH-TiO_2 (bottom) over different cycles.