

Supporting Information

Enhancement of graphene–TiO₂ hybrids efficiency in pollutants abatement by employing shape controllers.

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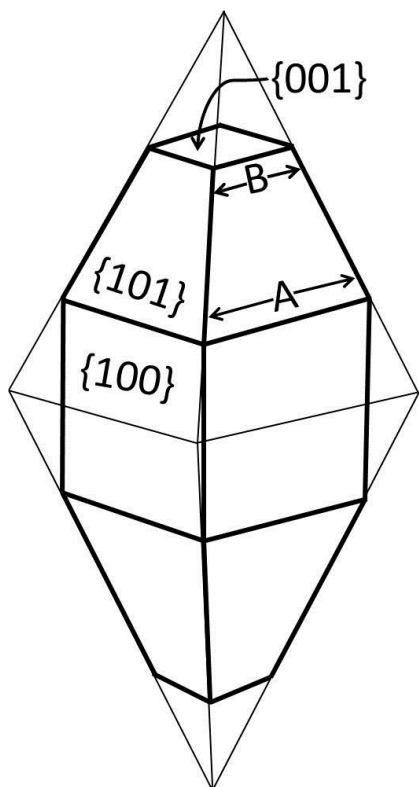
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This document contains details of synthetic procedure followed to achieve graphene functionalization, TEM micrographs (not shown in the first work) of COOH-GNP-TiO₂ and NH₂-GNP-TiO₂, the estimates of the specific surface area of the samples based TEM information, the results of the adsorption experiments carried out in the dark, pictures of the samples before and after irradiation (to show the color change), the effect of the catalyst concentration on the phenol degradation and the Raman spectra of NH₂-GNP-TiO₂-EDA and NH₂-GNP-TiO₂-OA samples and a schematic representation of anatase exposed facets.

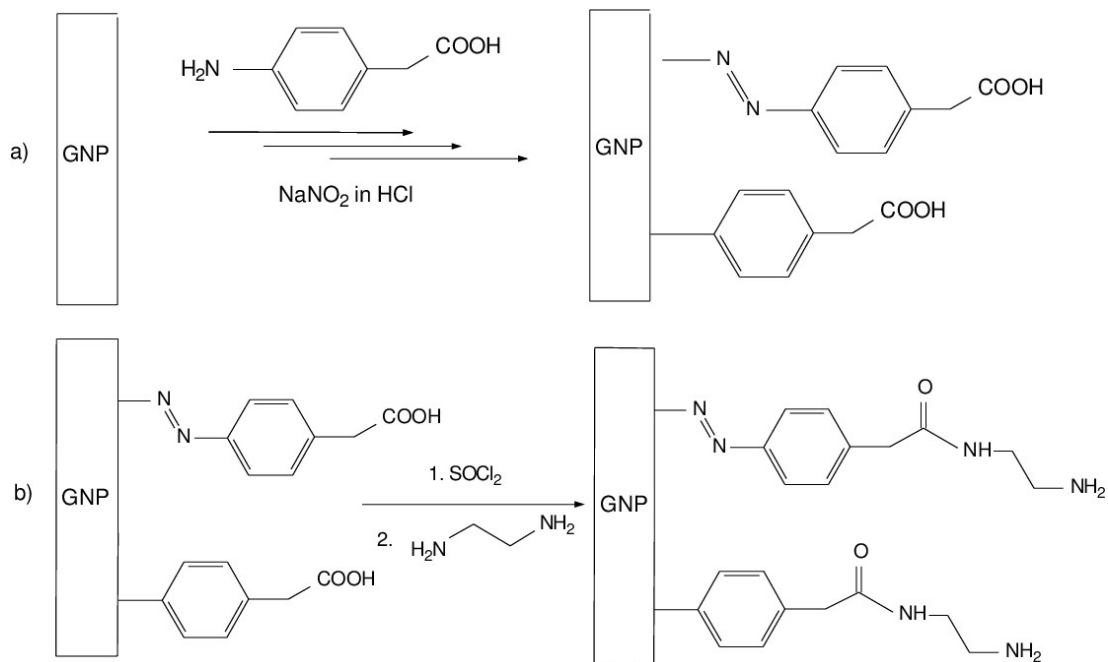
Graphene surface modification

1.1 Carboxylic groups. COOH-GNP samples were prepared using diazonium chemistry. Briefly, we placed 10 mg of GNP in a 150 ml beaker with 10 ml of 0.5 M hydrochloric acid and 0.5 mmol of 4-aminophenylacetic acid, then sonicated for 10 min to obtain a homogeneous GNP suspension, and then added 0.5 mmol of sodium nitrite. We carried out the reaction for 10 min under magnetic stirring. At the end of the reaction, we allowed the solution to cool, then filtered it using a 3.0 μm pore cellulose membrane, washed several times with water and isopropyl alcohol and finally dried it overnight at room temperature.

1.2 Amino groups. We synthesized NH₂-GNP samples via chlorination and amidation of COOH-GNP. Briefly, we refluxed COOH-GNP for 12 hours under SOCl₂ at 70°C. After evaporating any excess SOCl₂, we introduced EDA in the reaction medium and refluxed for 24 hours at 116°C. This method is similar to that proposed by Huang Ke-Jing and coworkers³³. After cooling to room temperature, we filtered the solution using a 3.0 μm pore cellulose membrane, washed with deionized water and isopropyl alcohol several times and allowed it to dry overnight.



Scheme S1: anatase tetragonal belted bipyramid with eight equivalent $\{101\}$ facets, four equivalent $\{100\}$ facets and, when truncated, two equivalent $\{001\}$ surfaces. The degree of truncation is defined as BA^{-1} with $0 < B < A$.



Scheme S2: Surface modification with carboxylic groups (a) or amino groups (b)

Table S1: Estimated specific surface areas for the GNP-TiO₂ hybrids studied

Sample	SSA (m ² g ⁻¹)	
	Mean	St dev
GNP-TiO ₂	40	3
COOH-GNP-TiO ₂	47	7
COOH-GNP-TiO ₂ -EDA	36	8
COOH-GNP-TiO ₂ -OA	59	16
NH ₂ -GNP-TiO ₂	66	5
NH ₂ -GNP-TiO ₂ -EDA	61	2
NH ₂ -GNP-TiO ₂ -OA	50	4

To estimate the surface area (SSA) of each sample we have included: 1) the known SSA of the GNP used (510 m² g⁻¹, as declared by the manufacturer); and 2) the SSA of the TiO₂ NPs used for each sample, estimated based on the particle size measured with TEM. We considered that 97% of the weight was due to TiO₂ NPs and 3% to the GNP, and we provided an estimate based on the hypothesis that TiO₂ NPs and GNP did not aggregate to such an extent to hinder N₂ adsorption. We then estimated the volume and the exposed surface of at least ten nanoparticles for each sample from the TEM micrographs, and, knowing TiO₂ anatase density (3.9 kg L⁻¹), and averaging the results for the different NPs considered, we obtained the results listed on Table S1.

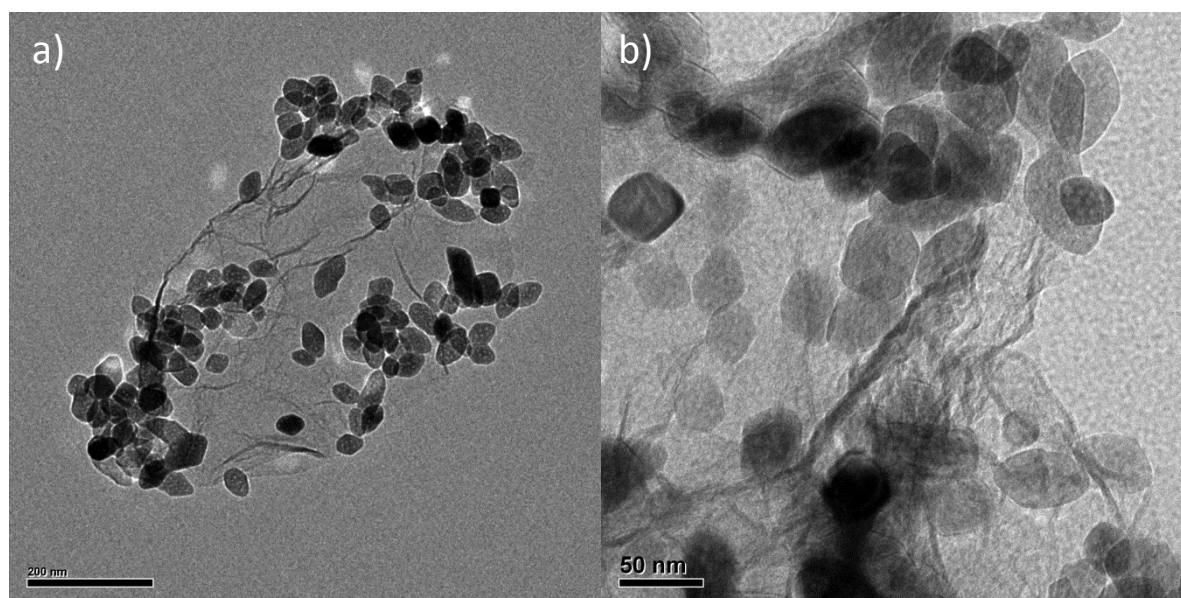


Figure S1: TEM micrograph of COOH-GNP-TiO₂ (a) and NH₂-GNP-TiO₂ (b)

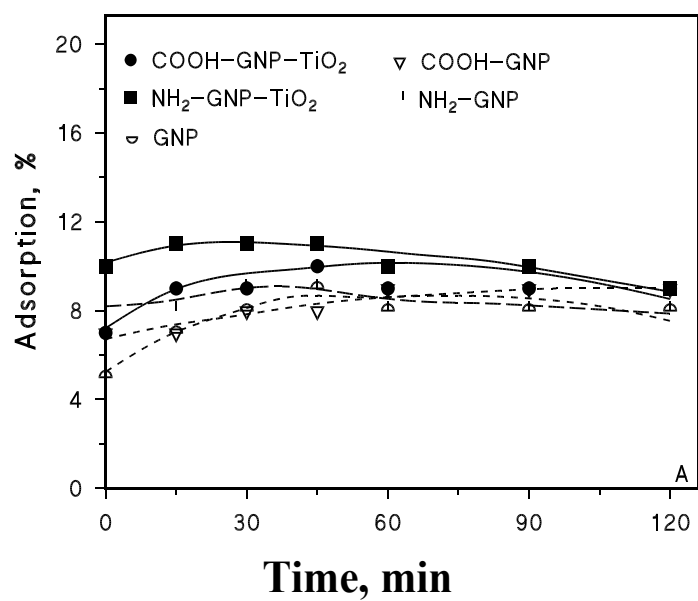


Figure S2: Adsorption experiments on the dark performed on the different materials.



Figure S3: Digital pictures of the sample COOH-GNP-TiO₂ and NH₂-GNP-TiO₂ before (0 min) and after (15 min) irradiation.

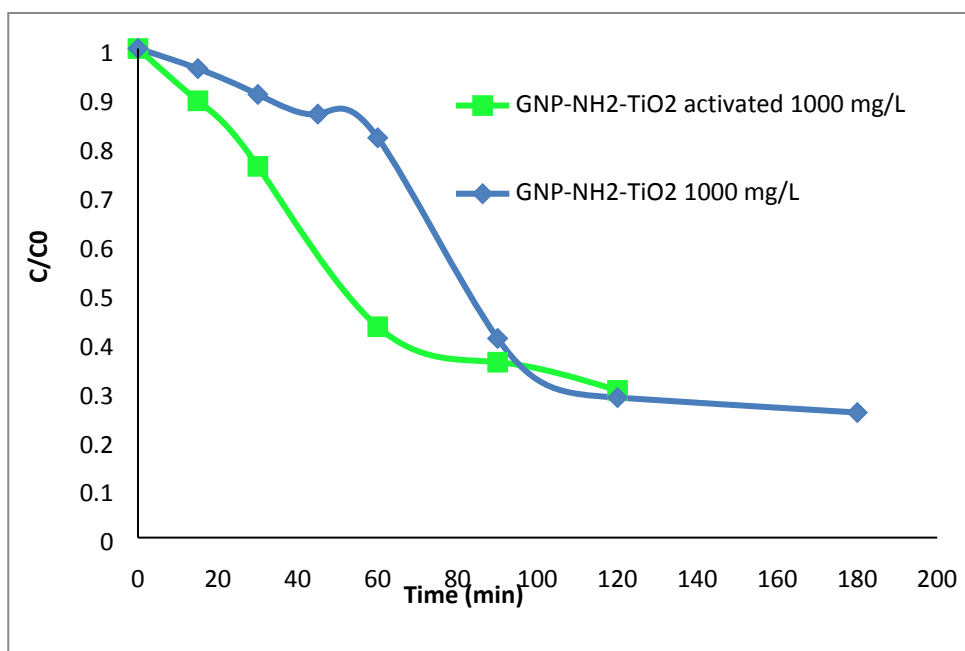


Figure S4: Phenol (P) disappearance as a function of irradiation time. The conditions in all experiments are the following: P 10 mg L⁻¹ NH₂-GNP-TiO₂ (1 g L⁻¹). In activated sample, P was added after 30 min of NH₂-GNP-TiO₂ (1 g L⁻¹) UV-A pre-irradiation (without P).

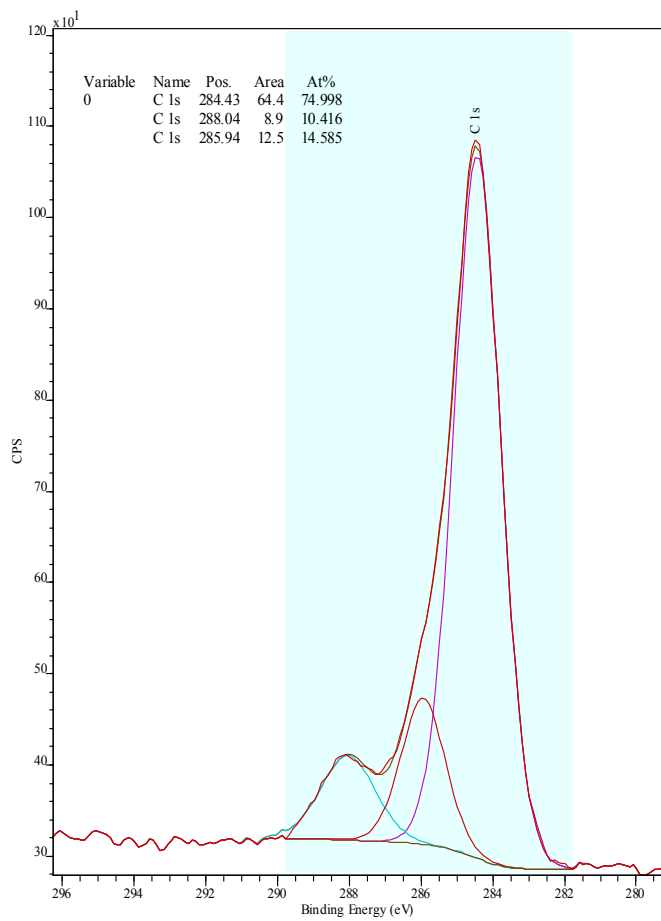
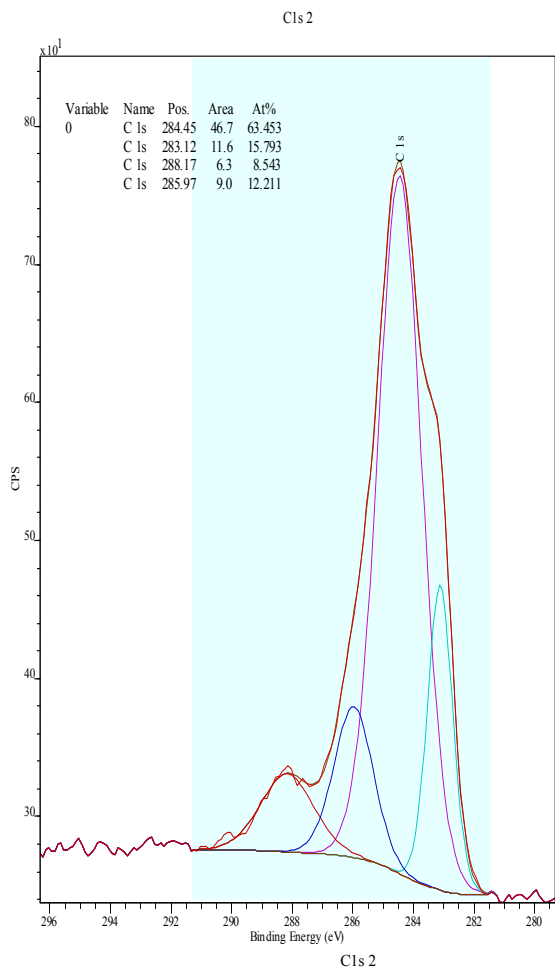


Figure S5: XPS measure performed on

COOH-GNP-TiO₂ before (0 min, left side) and after (15 min, right side) irradiation.

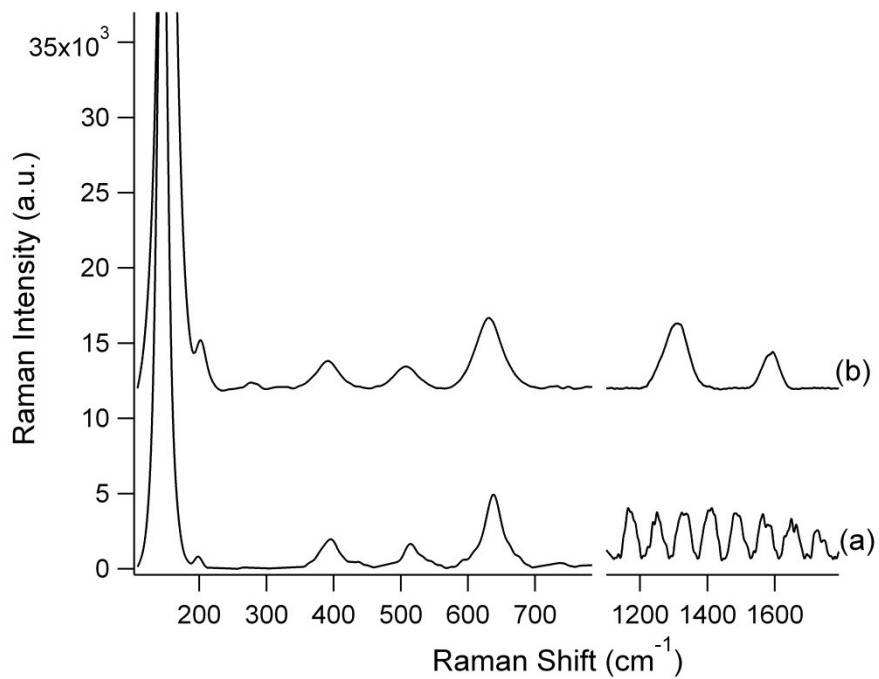


Figure S6: Raman spectra of NH₂-GNP-TiO₂-EDA (a) and NH₂-GNP-TiO₂-OA (b)

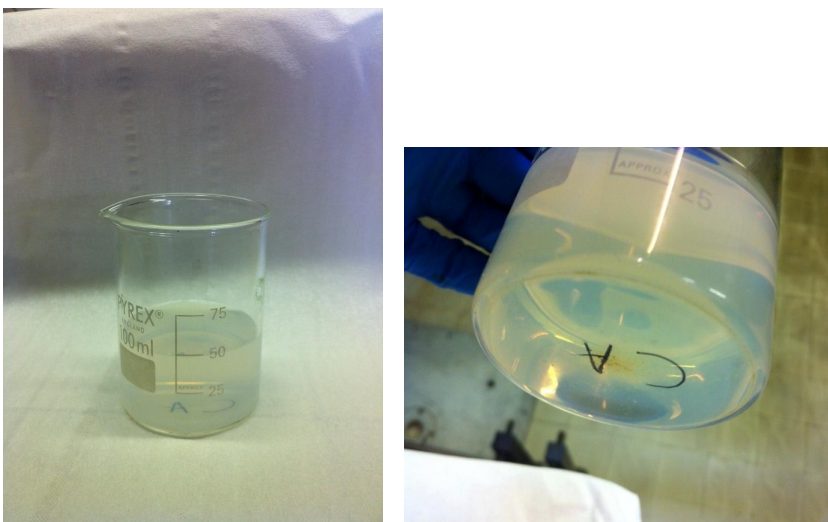


Figure S7: Appearance of the sample TiO₂ before and after the addition of ethylenediamine