Supporting information (SI)

TiO_2-rGO nanocomposite as an efficient catalyst to photodegrade formalin in aquaculture's waters, under solar light

Joana F. Leal [a,b], Sandra M. A. Cruz [c], Bernardo T. A. Almeida [a], Valdemar I. Esteves[a,b], Paula A. A. P. Marques [c], Eduarda B.H. Santos[a,b*]

[a] Department of Chemistry, University of Aveiro, 3810-193 Aveiro Portugal

[b] CESAM – Centre for Environmental and Marine Studies, University of Aveiro, 3810-193 Aveiro, Portugal

[c] TEMA and Department of Mechanical Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

*Corresponding author(s): edsantos@ua.pt

Material and methods

- **Preparation of TiO_2-rGO composites**

Briefly, 15.6 µL (0.25 % GO), 31.3 µL (0.5 % GO), 62.5 µL (1 % GO) and 187.5 µL (3 % GO) of the GO aqueous dispersion (4 mg/mL) were dispersed in a mixture of deionized water (10 mL) and ethanol 96 % (5 mL) and magnetically stirred for 30 minutes, at 500 rpm. Then, 25 mg of TiO_2 P25 were added and the suspension was magnetically stirred (also at 500 rpm), for 30 minutes. At last, 15 mL of this suspension was transferred into a 20-mL Teflon lined autoclave, sealed and kept at 120 ˚C during 3 h. The resultant nanocomposite was washed with deionized water and freeze-dried to avoid the particles agglomeration (Almeida et al., 2016). In parallel, a suspension containing only TiO_2 was subjected to the same treatment previously described for comparison.

- **Photodegradation experiments**

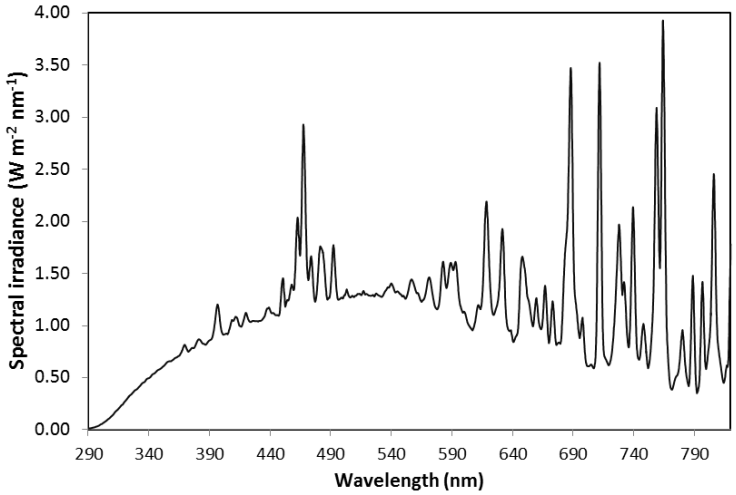


Figure S1 – Spectral irradiance of the 1500 W arc xenon lamp when using an outdoor UV filter, as given by the manufacturer (Solarbox 1500, Co.fo.me.gra, Italy). The spectrum is referred to a total irradiance of 550 Wm^{-2} between 290-800 nm.

- **Formalin quantification using the Nash method**

To quantify FM in the aqueous solutions, the following procedure was applied: 1 mL of irradiated and filtered FM solution (initial concentration of 40 mg/L) was mixed with 2 mL of Nash's reagent and adjusted to the final volume (10 mL) with ultrapure water. Then, samples were heated in a water bath at 50 ºC (Jones et al., 1999), during 30 min. This reaction time was chosen because, after this time, the derivatization reaction attains the equilibrium and the solution absorbance reaches its maximum value (**figure S2**).

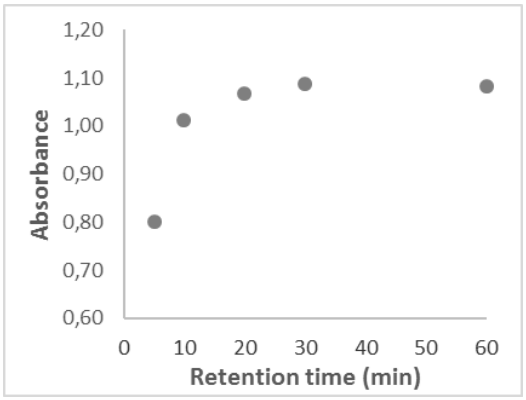
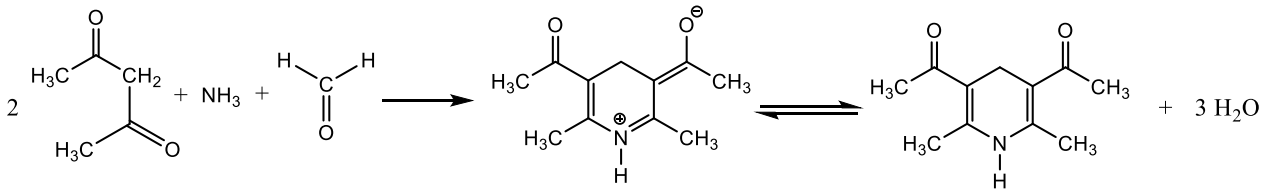


Figure S2 – Derivatization reaction of FM in function of reaction time.

During this process, a condensation reaction of ammonia and acetyl-acetone (2,4-pentanedione) in Nash's reagent with formaldehyde (FM) occurs, originating 3,5-

diacetyl-1,4-dihydrolutidine (DDL) (**Reaction S1**). DDL presents a yellow-green colour and its maximum absorbance occurs at 412 nm (Jones et al., 1999).



Reaction S1 – Reaction between formaldehyde and the constituents of Nash's reagent (ammonia and acetyl-acetone), originating 3,5-diacetyl-1,4-dihydrolutidine (DDL).

To quantify FM, calibration curves were prepared in each day of analysis, using standard solutions of FM, which were subjected to the same derivatization reaction described above.

Results and discussion

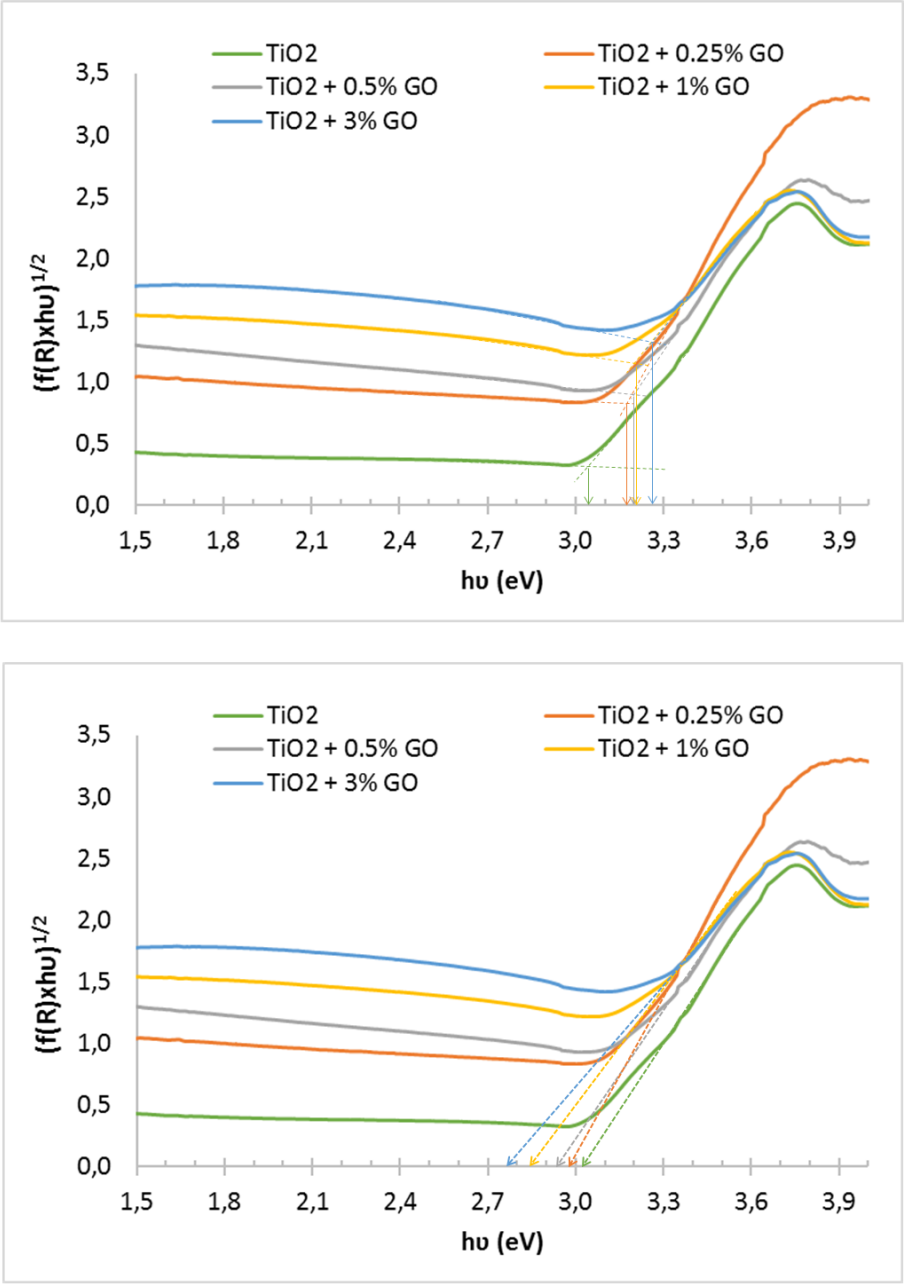


Figure S3 – Tauc plots $(f(R).h\nu)^{1/2}$ versus hν (for indirect allowed transitions) with baseline correction (above) and without baseline correction (below).

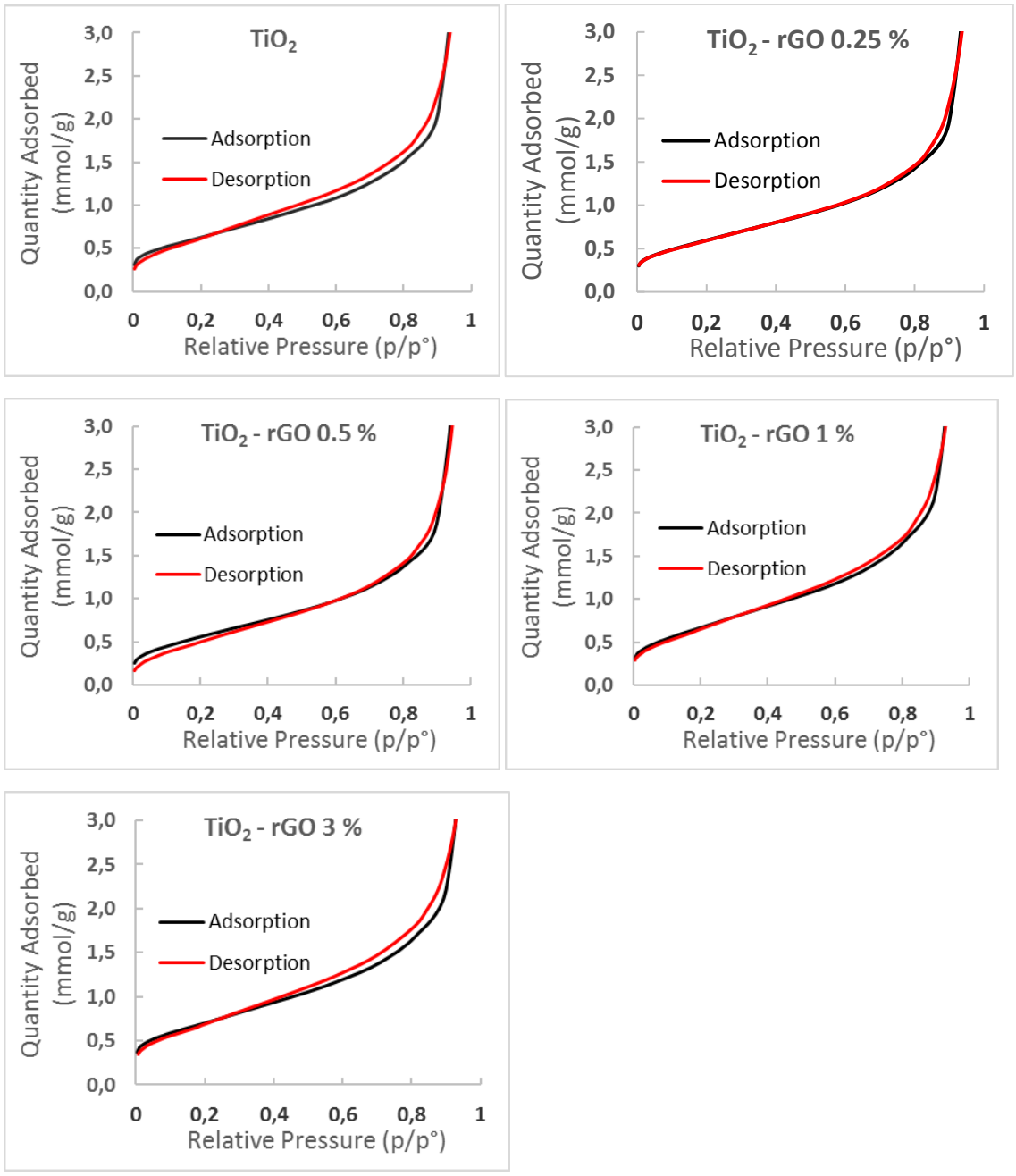


Figure S4 – N_2 adsorption/desorption isotherms of pure TiO_2, TiO_2+GO 0.25%, TiO_2+GO 0.5%, TiO_2+GO 1% and TiO_2+GO 3%.

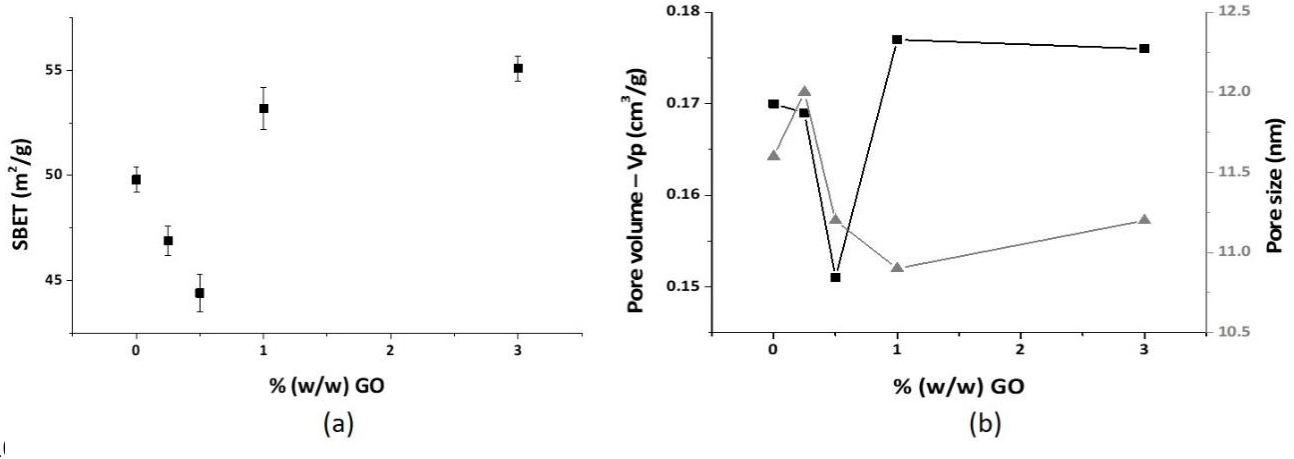


Figure S5 – S_{BET}, pore volume and pore size of nanocomposites of TiO_2-GO with different content of GO.

Almeida, N.A., Martins, P.M., Teixeira, S., Silva, J.A.L.d., Sencadas, V., Kühn, K., Cuniberti, G., Lanceros-Mendez, S., Marques, P.A.A.P., 2016. TiO_2/graphene oxide immobilized in P(VDF-TrFE) electrospun membranes with enhanced visible-light-induced photocatalytic performance. J. Mater. Sci. 51, 6974-6986.

Jones, S.B., Terry, C.M., Lister, T.E., Johnson, D.C., 1999. Determination of Submicromolar Concentrations of Formaldehyde by Liquid Chromatography. Anal. Chem. 71, 4030-4033.