Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Stimuli-Responsive Graphene-based Hydrogel Driven by Disruption of Triazine Hydrophobic Interactions

Jorge Leganés,[a,b] Ana Sánchez-Migallón,[a,b] Sonia Merino,*[a,b] and Ester Vázquez*[a,b]

[a]Instituto Regional de Investigación Científica Aplicada (IRICA), 13071 Ciudad Real, Spain

[b]Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha (UCLM), 13071 Ciudad Real, Spain E-mail:ester.vazquez@uclm.es

Experimental section

Preparation of few-layer graphene (FLG) powders

The mechanochemical exfoliation of graphite was performed by following a ball-milling procedure.[1,2] A 30 mg mixture of graphite/melamine (1:3) was ball-milled at 100 rpm for 30 min. The solid was then dispersed and sonicated in 20 ml of ultrapure water; the dispersion was placed in dialysis tubing (Spectrum labs, 6–8 kDa MWCO) and dialyzed against hot water (70 ºC), with the aqueous medium replaced every 2 hours until melamine was no longer detected. The dispersion was then left to stabilize for five days and the aggregated graphite was removed from the dispersion. The graphene aqueous suspension was freeze-dried at -80 ºC and 0.05 mbar and the resulting few-layer graphene powders were collected and characterized.

Characterization of graphene powders

TGA measurements were carried out on a Q50 system from TA instruments at 10 ºC/min under an N_2 atmosphere. The Raman spectra were obtained on an InVia Renishaw microspectrophotometer with a 532 nm point-based laser. The samples were prepared by dropping graphene aqueous dispersions onto silicon oxide surfaces (WRS materials). The resulting spectra were collected by probing different random locations on the sample and applying baseline corrections, noise filtering and normalization. In order to determine the band parameters (widths, normalized intensities and positions) the spectra were fitted with Lorentzian-based bands. Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM) were carried out on a Jeol 2100 HRTEM system. The nickel grid was immersed (LC200-Ni Lacey Carbon Grid from Electron Microscopy Sciences) into the graphene aqueous dispersions.

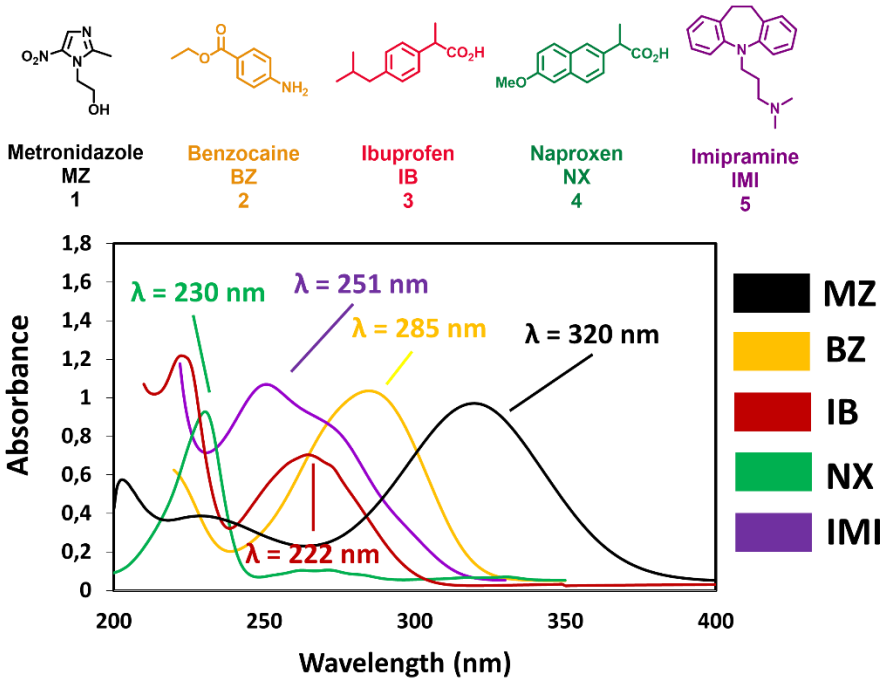


Figure S1. UV/VIS spectra of drug solutions in PBS media

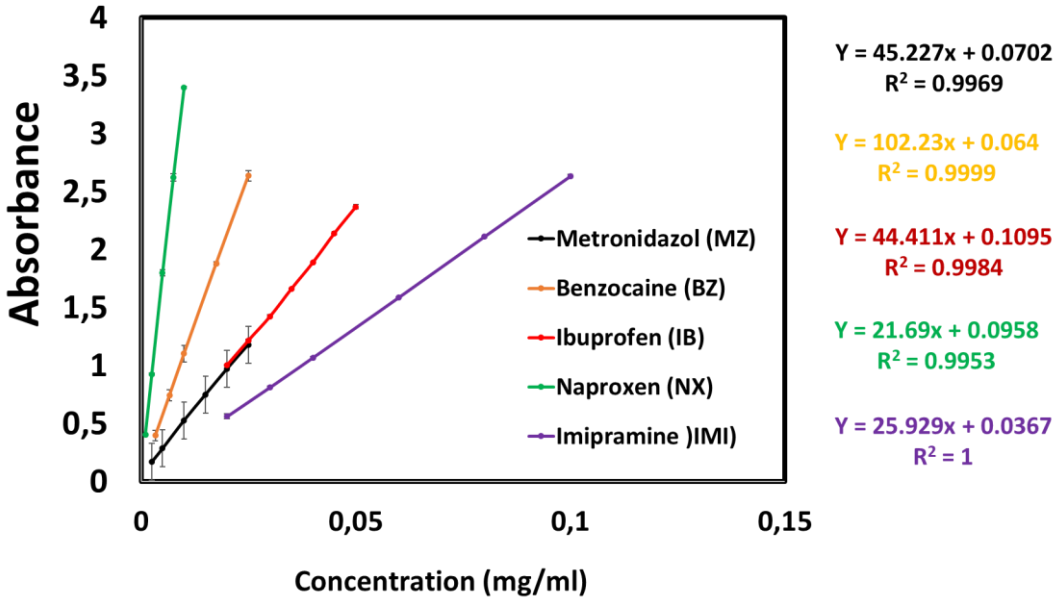
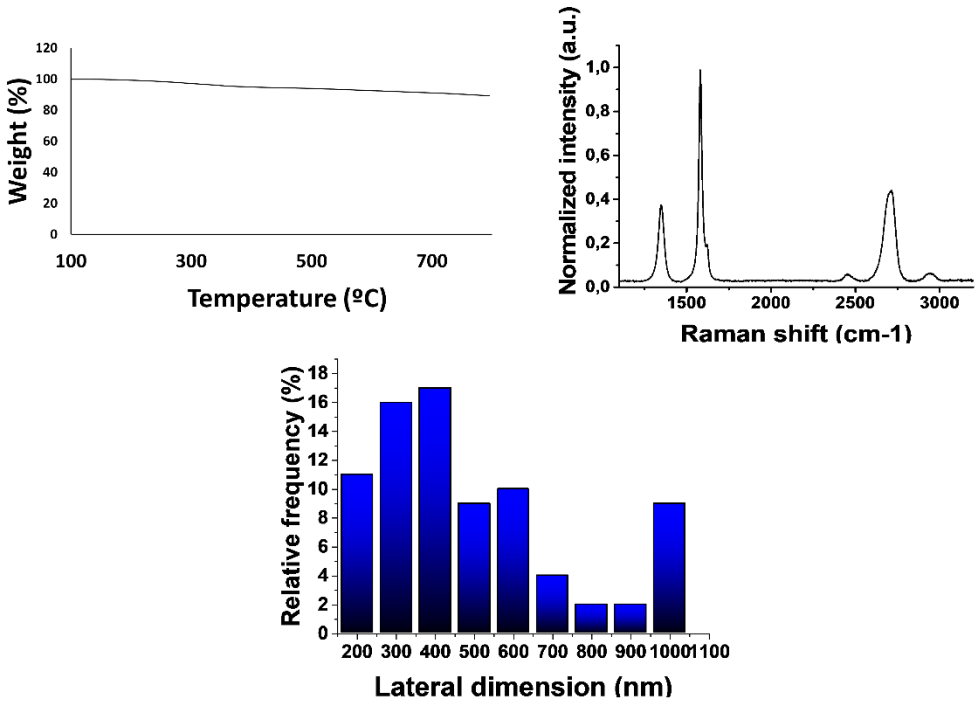
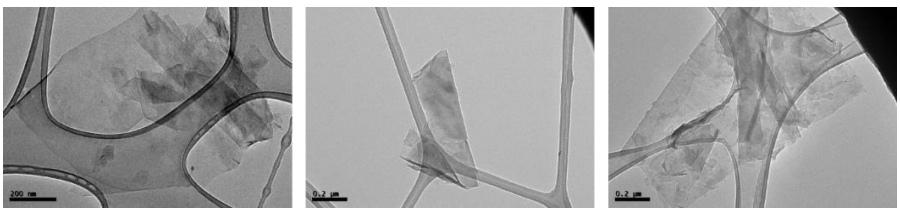


Figure S2. Calibration curves for drug solutions in PBS media

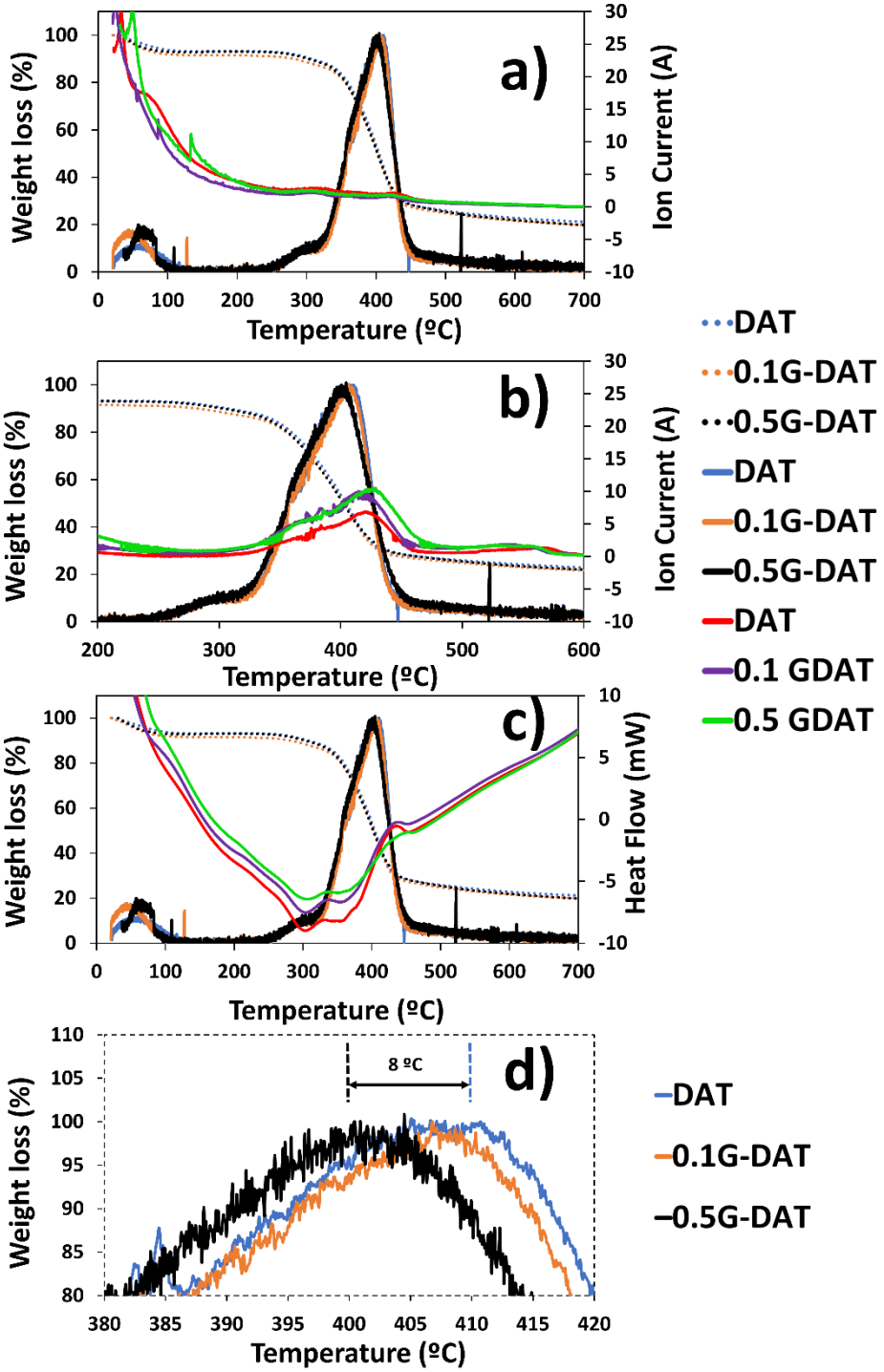




Elemental analysis:

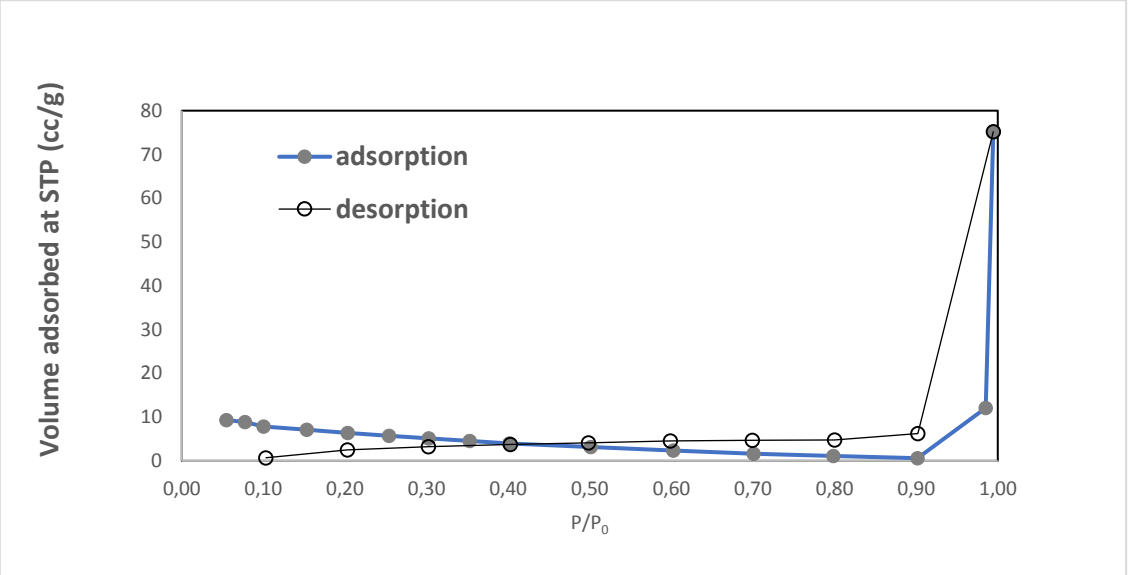
- 95.66±0.04 Wt%C
- 0.51 ± 0 Wt%H
- 0.56 ± 0.02 Wt%N
- 0.16± 0.04 Wt%S

Figure S3. Characterization of graphene: Thermogravimetric Analysis, average Raman spectrum, TEM and lateral flake size images and elemental analysis.



		TGA SDT Q600	
	DAT	**0.1G-DAT**	**0.5G-DAT**
1	407.5567	407.8978	399.8625
2	409.5468	407.4854	401.4568
3	408.4483	407.8898	400.8273
Average	408.517267	407.7576667	400.715533
Desv	0.99684091	0.235823776	0.80300496
Difference	**7.801733333**		

Figure S4. TGA/DSC-MS of DAT-based hydrogels: TGA curves (dotted lines, blue, orange, black), derivatives (solid lines, blue, orange, black). Evolved mass gas analysis of a) water (red, purple, green) and b) carbon dioxide (red, purple, green). c) DSC (red, purple, green) and d) inset of TGA derivatives at their maxima and the numerical values of the temperatures.



Surface Area (m^2/g)	Pore volume (cc/g)	Pore radius (nm)
14.97	0.1167	1.82104

Figure S5. BET N_2 adsorption/desorption isotherm and data of DAT hydrogels

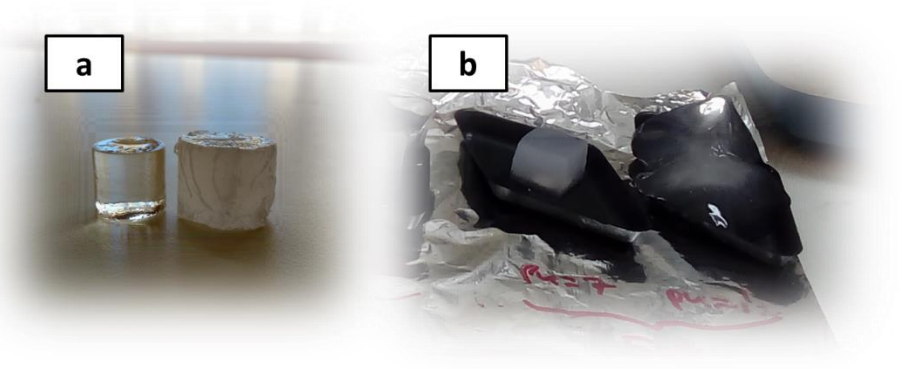


Figure S6. a) DAT hydrogel in the presence (left) and absence (right) of OEGMA and b) AM-free DAT hydrogel swollen in water (left) and SGF media (right)

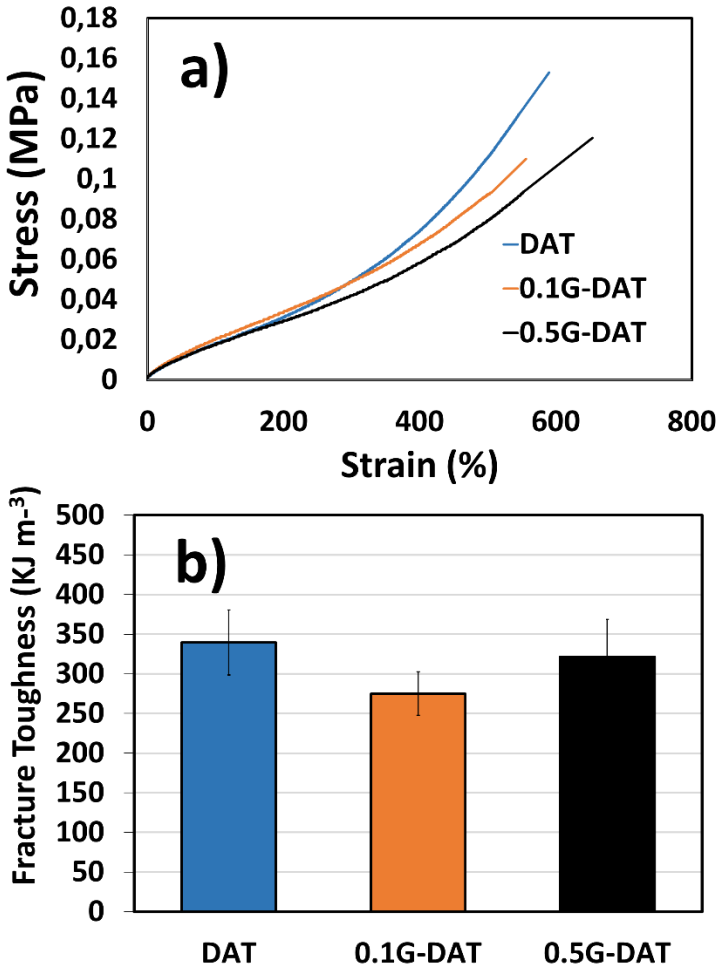


Figure S7. Tensile studies on (G)-DAT hydrogels: a) Stress-strain curve, b) Fracture toughness

	Tensile strength			Compressive strength		
Hydrogel	UTS (MPa)	Enlongation at break (%)	Fracture Toughness (KJ m^{-3})	Compressive strain (%)	Young´s Modulus (KPa)	Fatigue loss (%)
DAT	0.153 ± 0.02	590,3 ± 48,2	339,5 ± 40,8	67,2 ± 0.5	43,8 ± 3,4	26,4 ± 9,9
0.1G-DAT	0.11 ± 0.1	556,3 ± 38,8	275 ± 27,6	71 ± 0,7	40,4 ± 0,7	20,6 ± 2,4
0.5G-DAT	0.112 ± 0.02	654 ± 99,3	321,3 ± 47,1	66 ± 1,1	59 ± 2,4	14,7 ± 3,2

Table S1. Mechanical data for DAT-based hydrogels

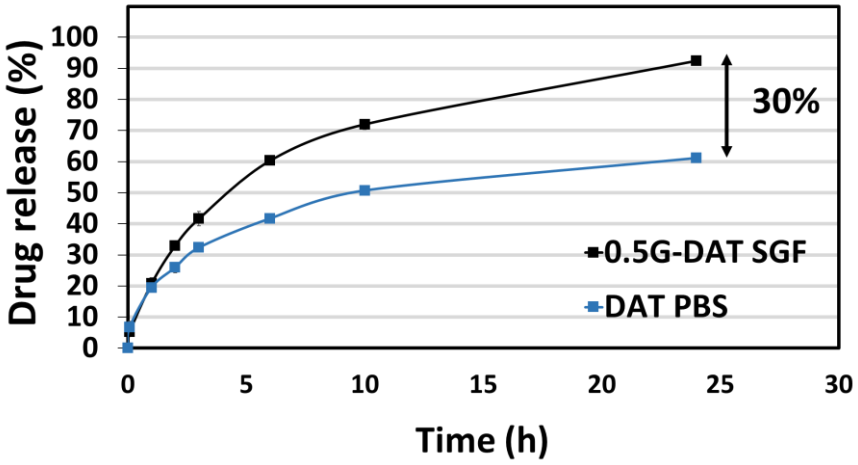


Figure S8. Synergistic effect of graphene and SGF media on the in vitro drug release of model drug IMI

1 V. León, J. M. González-Domínguez, J. L. G. Fierro, M. Prato and E. Vázquez, *Nanoscale*, 2016, **8**, 14548–14555.

2 J. M. González-Domínguez, V. León, M. I. Lucío, M. Prato and E. Vázquez, *Nat. Protoc.*, 2018, **13**, 495–506.