Differential Effects of Graphene Materials on Metabolism and Function of Human Skin Cells

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Table S1. Total reflection X-Ray fluorescence (TXRF) data for GO and FLG

GO

Element & line		Conc. ± sigma [ppm (mg/L)]	RSD [%]	Peak area ± sigma [counts/sec]	Fit index
Si	K	1039.258 ± 5.317	0.51	468.95 ± 1.16	7.2
P	K	0.406 ± 0.182	44.89	0.51 ± 0.23	5.2
S	K	0.851 ± 0.076	8.90	1.99 ± 0.18	1.5
Cl	K	0.125 ± 0.040	31.75	0.54 ± 0.17	0.4
Ar	K	1.757 ± 0.041	2.32	13.02 ± 0.30	0.6
K	K	1.395 ± 0.028	2.03	15.85 ± 0.31	1.0
Ca	K	0.276 ± 0.013	4.59	4.89 ± 0.22	1.3
Ti	K	3.198 ± 0.025	0.77	110.19 ± 0.69	37.0
Cr	K	0.015 ± 0.003	20.27	0.84 ± 0.17	2.6
Mn	K	1.473 ± 0.012	0.84	102.06 ± 0.73	2.6
Fe	K	0.025 ± 0.004	15.31	2.12 ± 0.32	1.3
Ni	K	0.020 ± 0.002	8.52	2.51 ± 0.21	3.4
Cu	K	0.013 ± 0.002	12.45	1.88 ± 0.23	10.3
Zn	K	0.046 ± 0.002	4.64	7.63 ± 0.35	11.4
Ga	K ref.	2.000 ± 0.009	0.45	368.59 ± 1.65	8.5
As	K	0.042 ± 0.002	4.75	9.04 ± 0.43	0.6
Br	K	0.010 ± 0.001	12.19	2.19 ± 0.27	0.5
Rb	K	< 0.001		0.13 ± 0.28	0.7

FLG

Element	Line	Conc./ mg/l	Sigma/ mg/l	RSD/ %	LLD/ mg/l	Net area	Backgr.	Chi
Si	K12	25.23	0.14	0.6	0.12	40098	4209	3.44
P	K12	0.078	0.031	39.2	0.064	252	4725	0.88
S	K12	2.531	0.027	1.1	0.033	14772	4100	1.48
Cl	K12	0.034	0.011	31.3	0.022	324	4967	0.98
K	K12	0.526	0.007	1.3	0.010	11043	4909	0.81
Ca	K12	2.137	0.011	0.5	0.009	54326	5396	0.75
Ti	K12	16.768	0.023	0.1	0.004	814170	3938	1.57
V (IS)	K12	6.710	0.012	0.2	0.003	410652	3071	0.72
Cr	K12	0.012	0.001	7.6	0.002	922	2002	1.39
Mn	K12	0.005	0.001	13.9	0.001	436	1608	1.14
Fe	K12	0.186	0.001	0.7	0.001	21949	1477	1.43
Ni	K12	0.012	0.000	3.4	0.001	2069	1369	1.13
Cu	K12	0.046	0.001	1.2	0.001	9253	1453	0.76
Zn	K12	0.113	0.001	0.7	0.000	26498	1499	1.11
Ga	K12	Not det.			0.000	95	1599	1.07
As	K12	0.002	0.000	8.9	0.000	666	1403	1.42
Br	K12	0.007	0.000	2.9	0.000	2652	1663	1.38
Sr	K12	Not det.			0.000	1	3234	17.85
Pb	L1	0.019	0.000	1.9	0.000	4349	1290	1.40

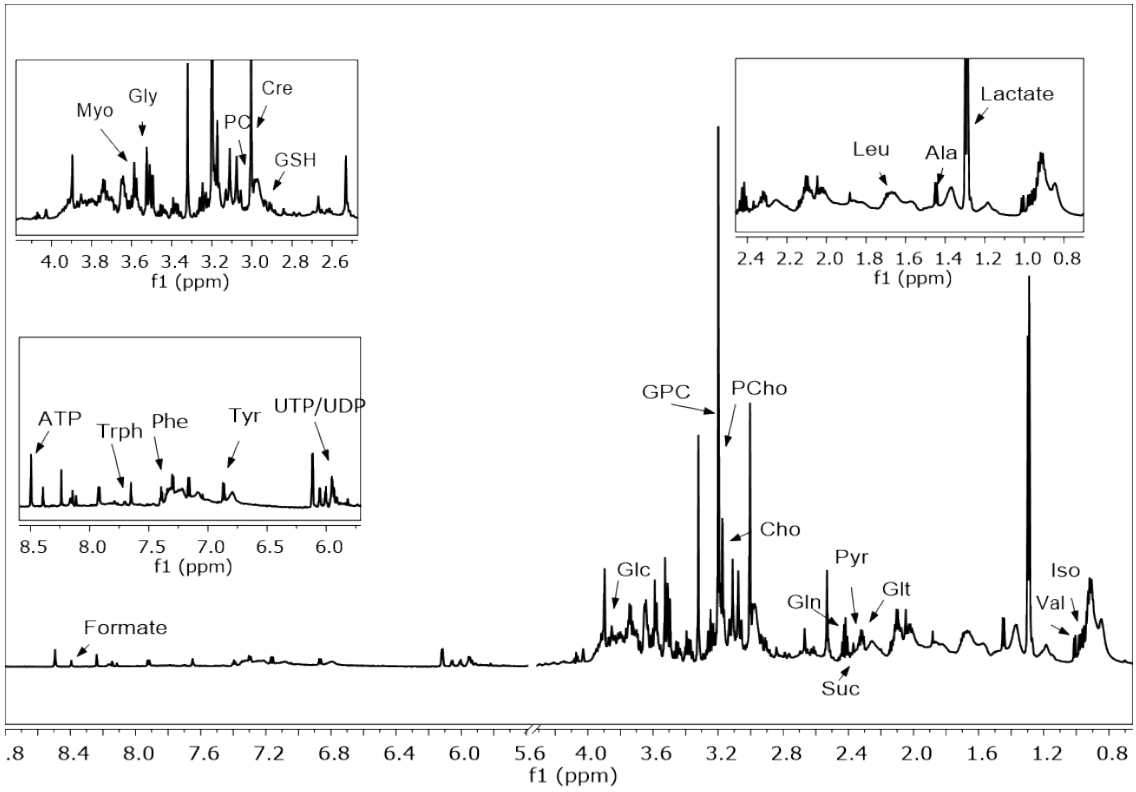

Figure S1. ^{1}H-NMR spectrum of an aqueous extract of untreated HaCaT cells at 800 MHz.. Peak identification was carried out matching spectral data to reference spectra from Birmingham Metabolite Library (BML-NMR) and Human Metabolites Databases (HMDB) and the software Chenomx, by means of 2D homo- and heteronuclear NMR experiments and by addition of standard samples for the identification of certain metabolites.

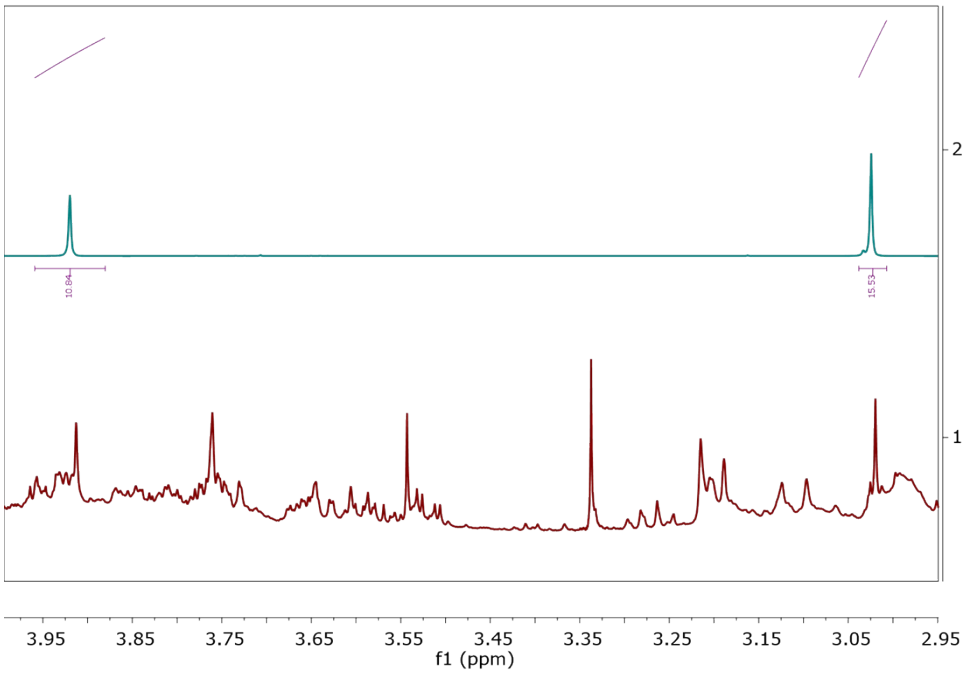

Figure S2: Stacked 1H NMR spectra for the identification of creatine in a control sample. Top: 1H NMR spectrum of creatine from BML-NMR (298K, pH 7.4). Bottom: 1H NMR spectrum of a control sample registered at 500 MHz (298K, pH7.4)

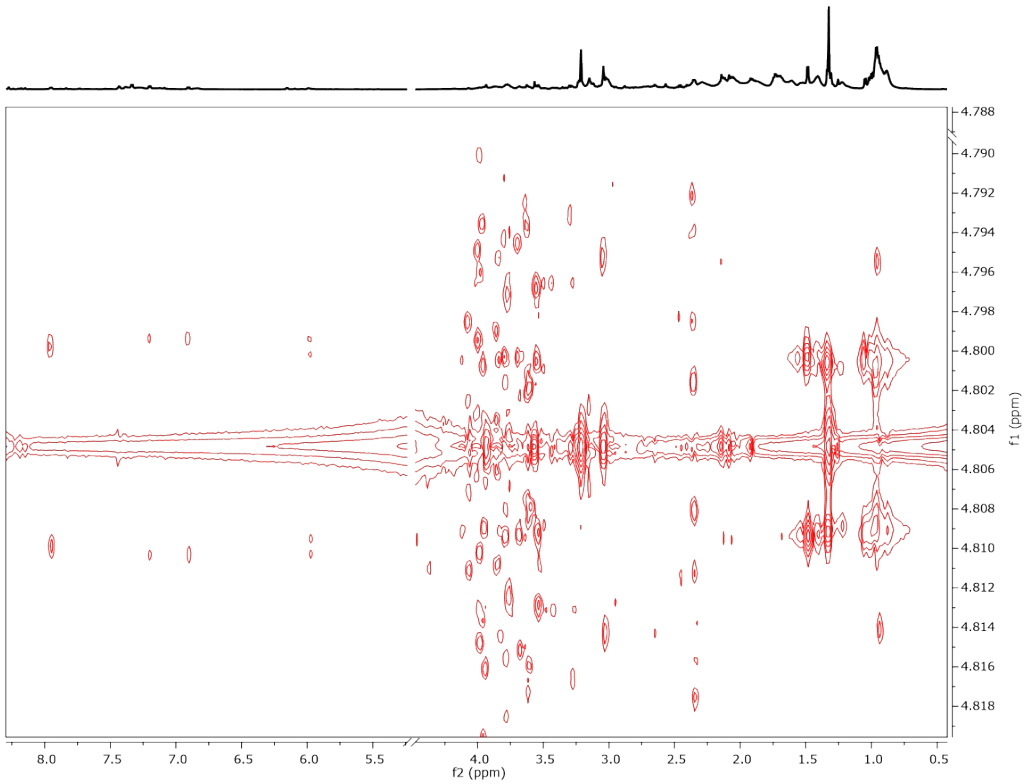

Figure S3: 2D *J*-resolved NMR spectrum of an aqueous extract from untreated HaCaT cells (control sample).

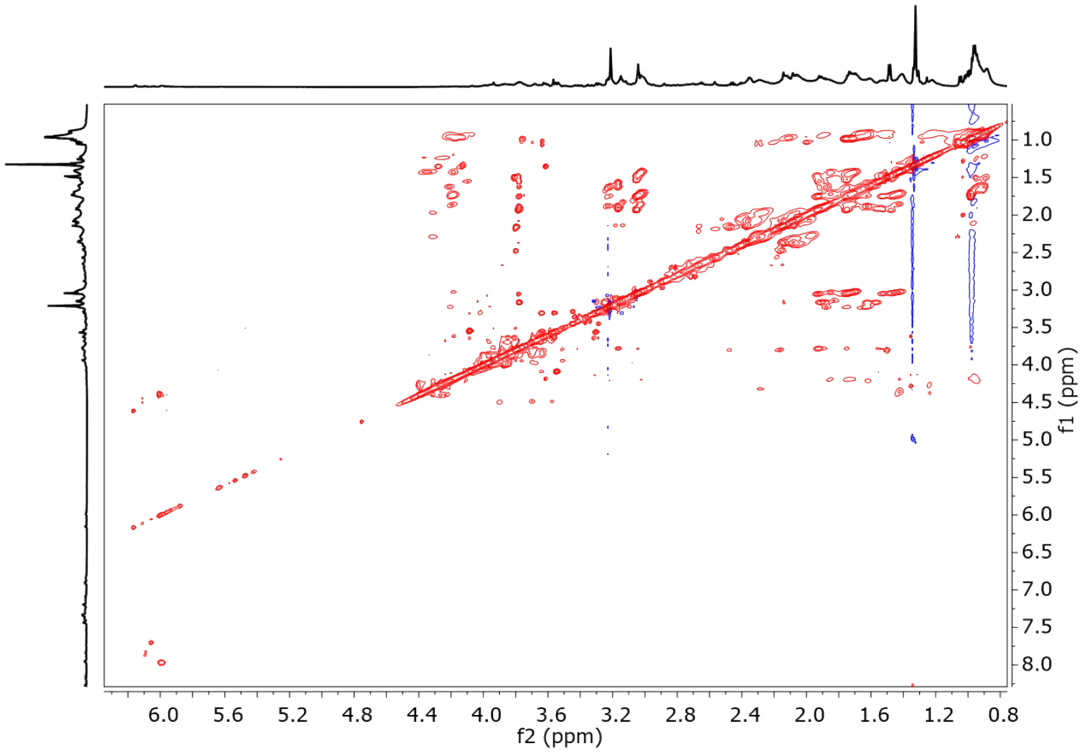

Figure S4: 2D TOCSY NMR spectrum of an aqueous extract from untreated HaCaT cells (control sample).

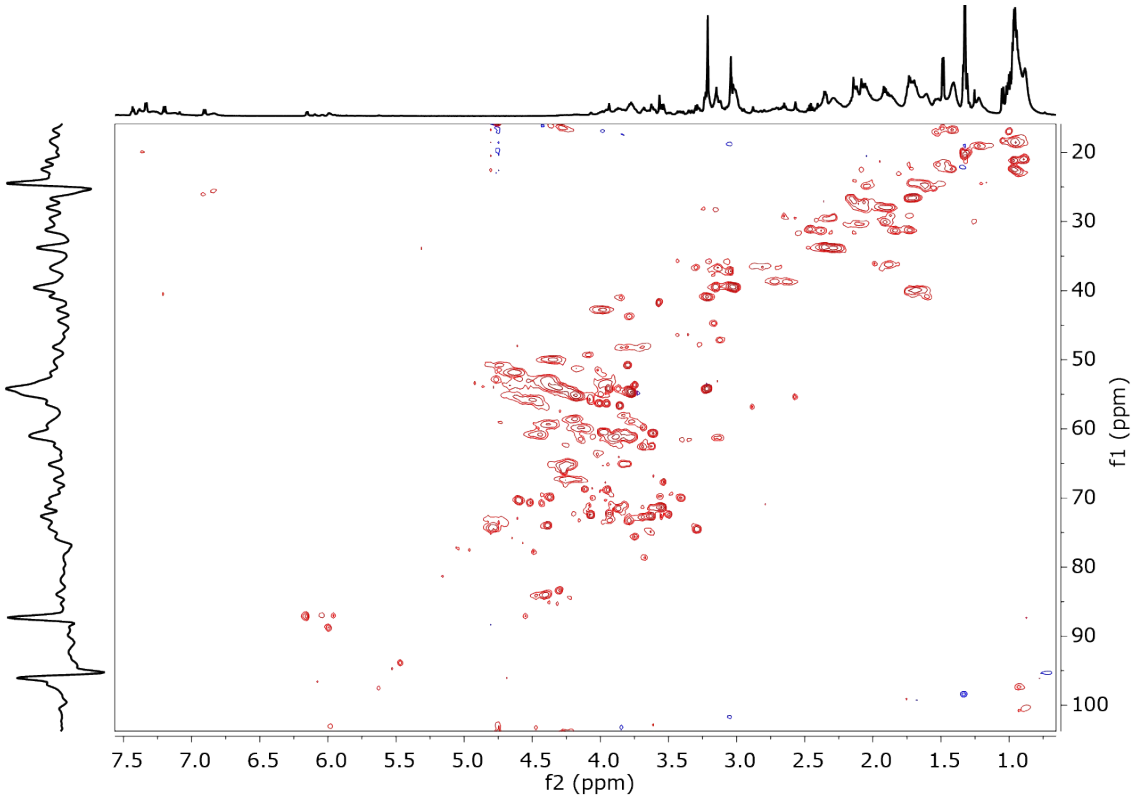

Figure S5: 2D $^{1}H,^{13}C$-HSQC NMR spectrum of an aqueous extract from untreated HaCaT cells (control sample).

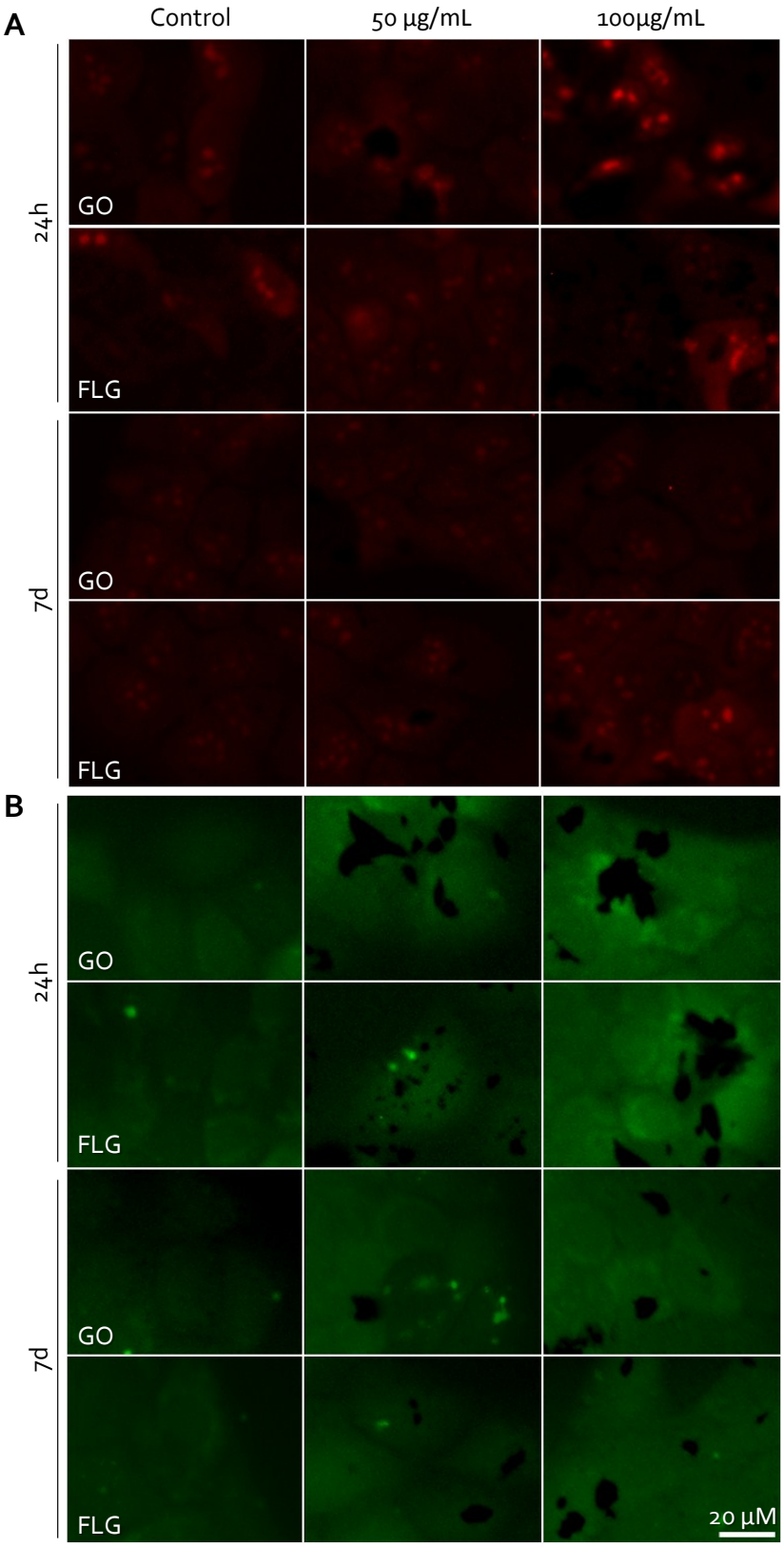

Figure S6. Representative pictures of cells stained with $O_2^{\cdot-}$ and H_2O_2 probes: a) MitoSOX-AM ($O_2^{\cdot-}$), b) H2DCF-DA (H_2O_2) levels in cells treated with GO or FLG during 24h or 7d).

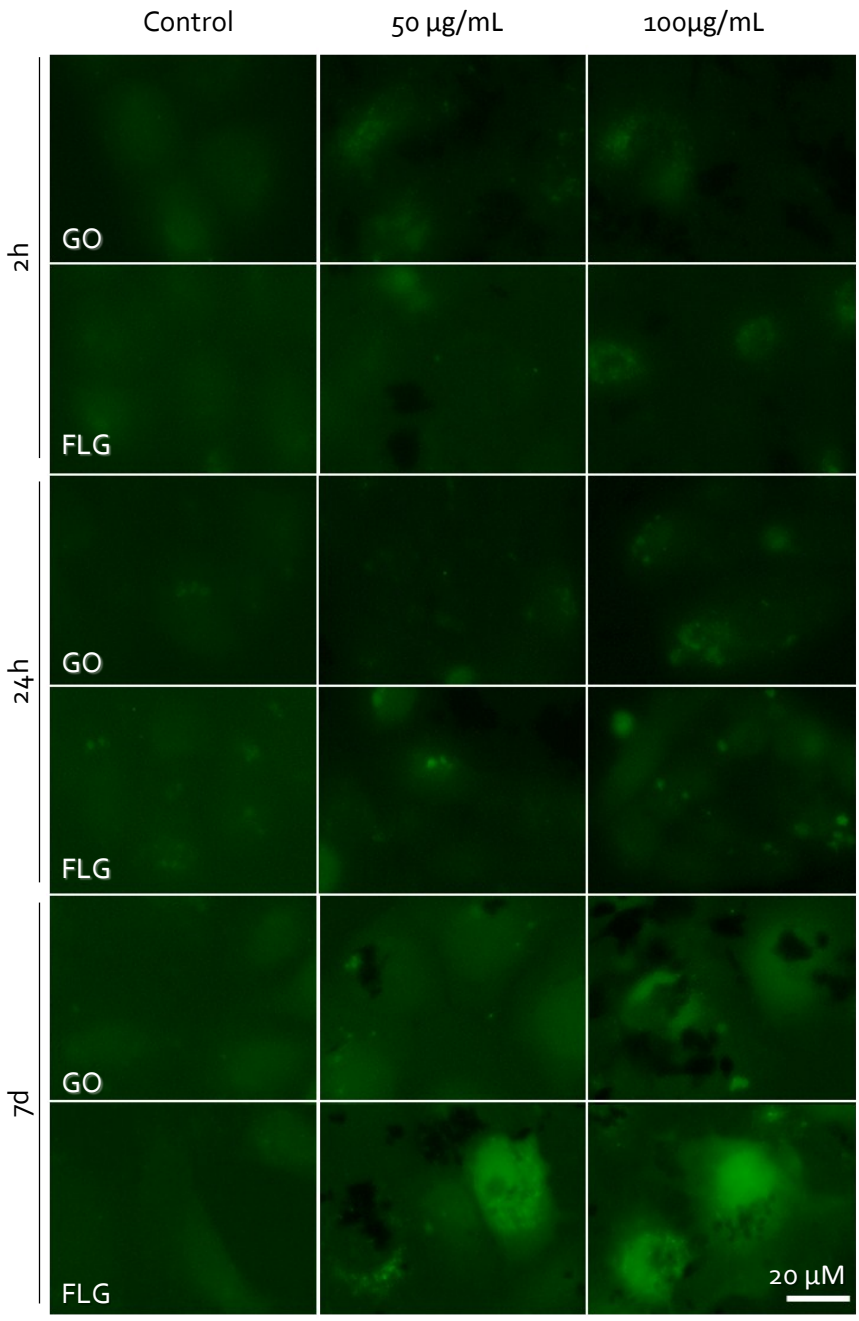

Figure S7. Representative pictures of cells stained with Fluo-4 probe. Free cytosolic calcium levels in cells treated with GO or FLG during 2h, 24h or 7d.

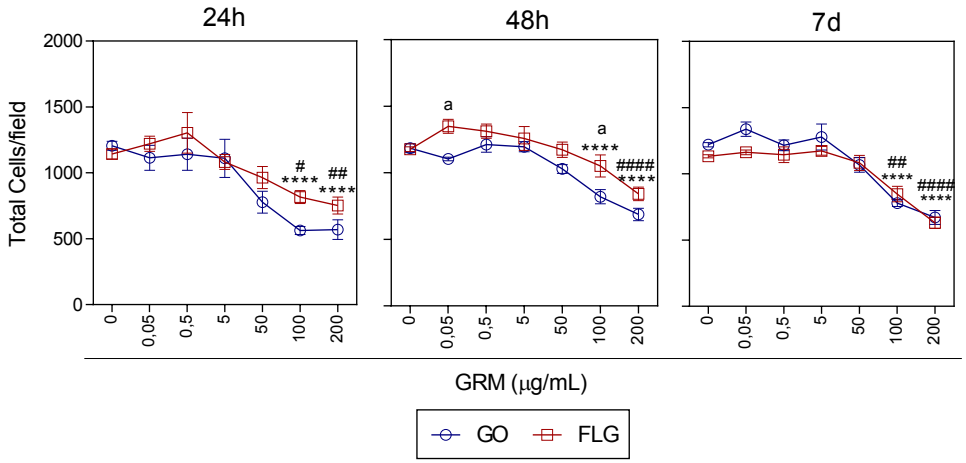

Figure S8. Effect of GO and FLG on HaCaTs cell number. Number of total cells/field in HaCaTs treated with GO (blue) or FLG (red) during 24h, 48h and 7d (n=4).

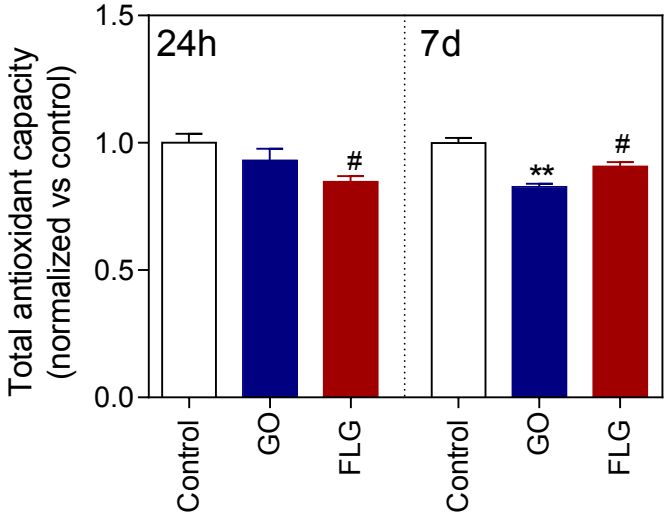

Figure S9. Effect of exogenous GO and FLG total antioxidant capacity. Total antioxidant supernatant in cells treated with 5µg/mL of GO (blue) or FLG (red) during 24h or 7d.