

Electronic supplementary information

Super-wetting Properties of Functionalized Fluorinated Graphene and its Application in Oil-Water and Emulsion Separation

Iniya Prasanthi^a Kalyan Raidongia^b and K. K. R. Datta^{a*}

^a *Functional Nanomaterials Laboratory, Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur – 603203, Tamil Nadu, India.*

^b *Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India.*

Email: kumarard@srmist.edu.in
kkrdatta@gmail.com

Number of pages: 18
Number of figures: 16
Number of tables: 2

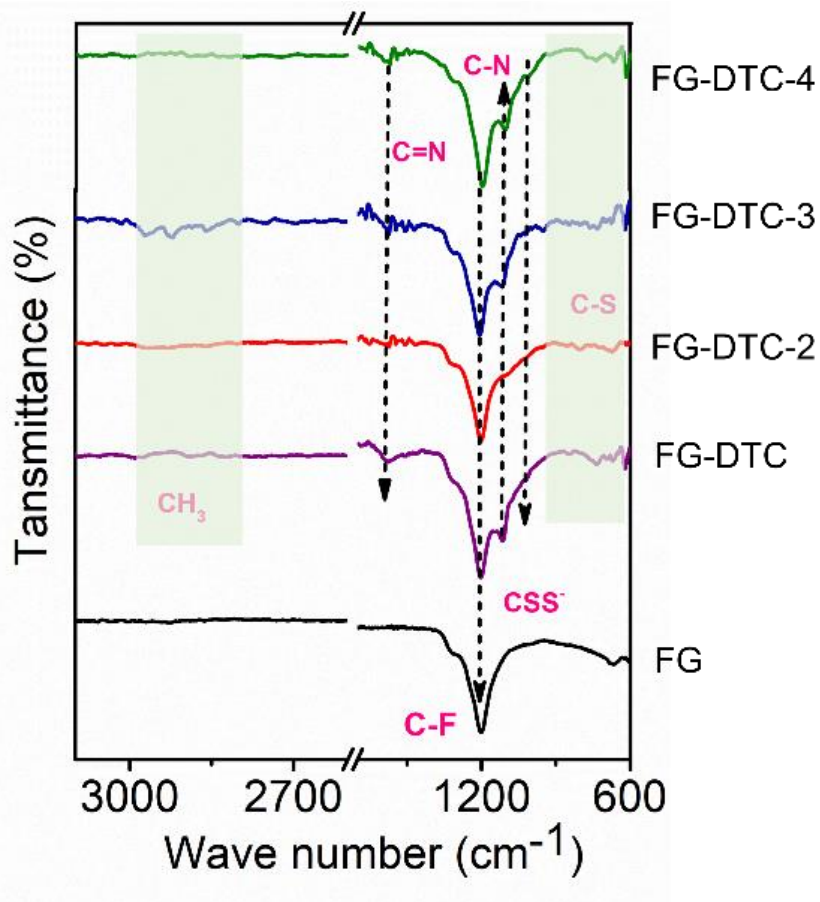


Figure S1: FTIR spectra of exfoliated FG and various FG-DTC samples

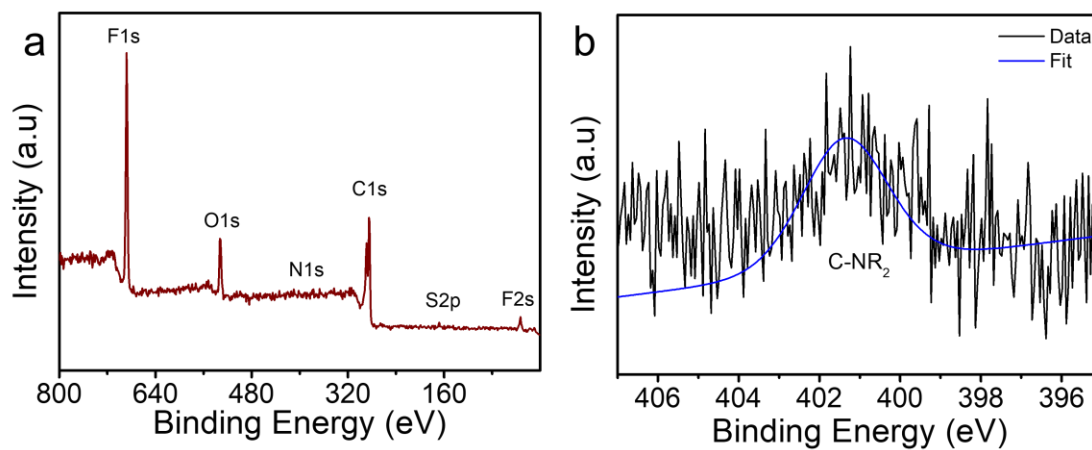


Figure S2: a) XPS survey spectrum and b) high resolution spectrum of N1s of FG-DTC

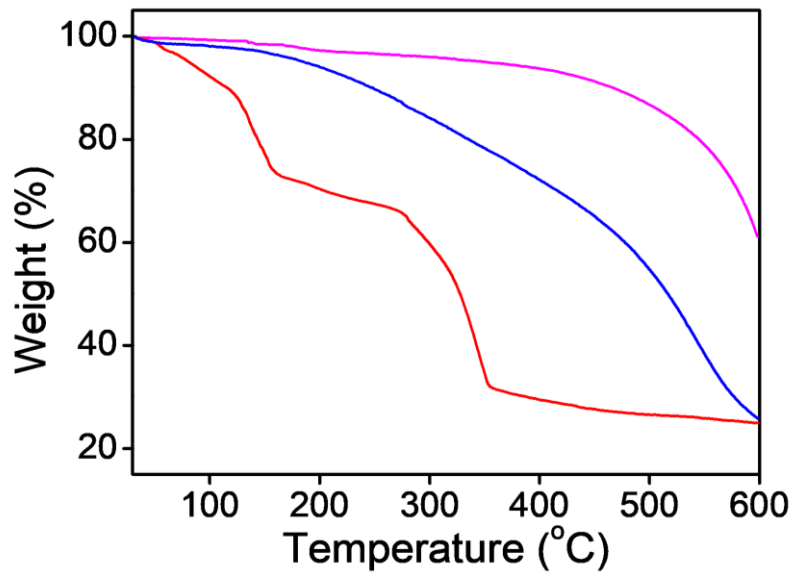


Figure S3: TG plots of FG-DTC (blue line), FG (violet line) and DTC (red line) samples

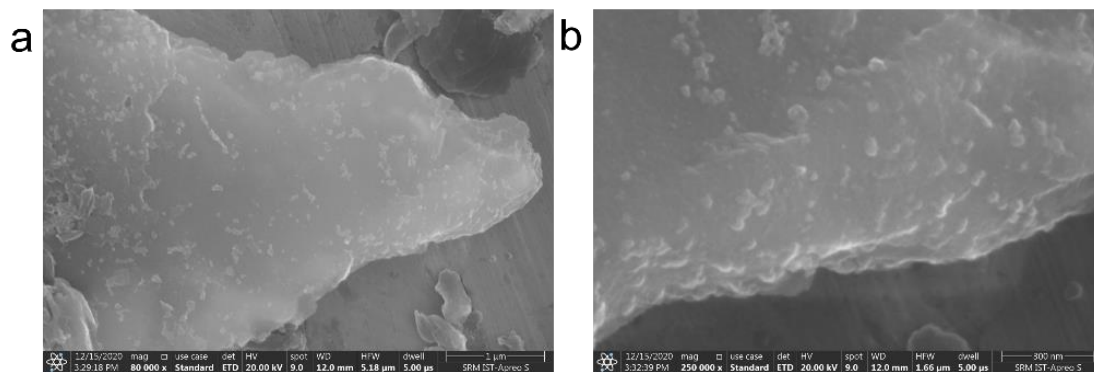


Figure S4: SEM images a) and b) of FG-DTC

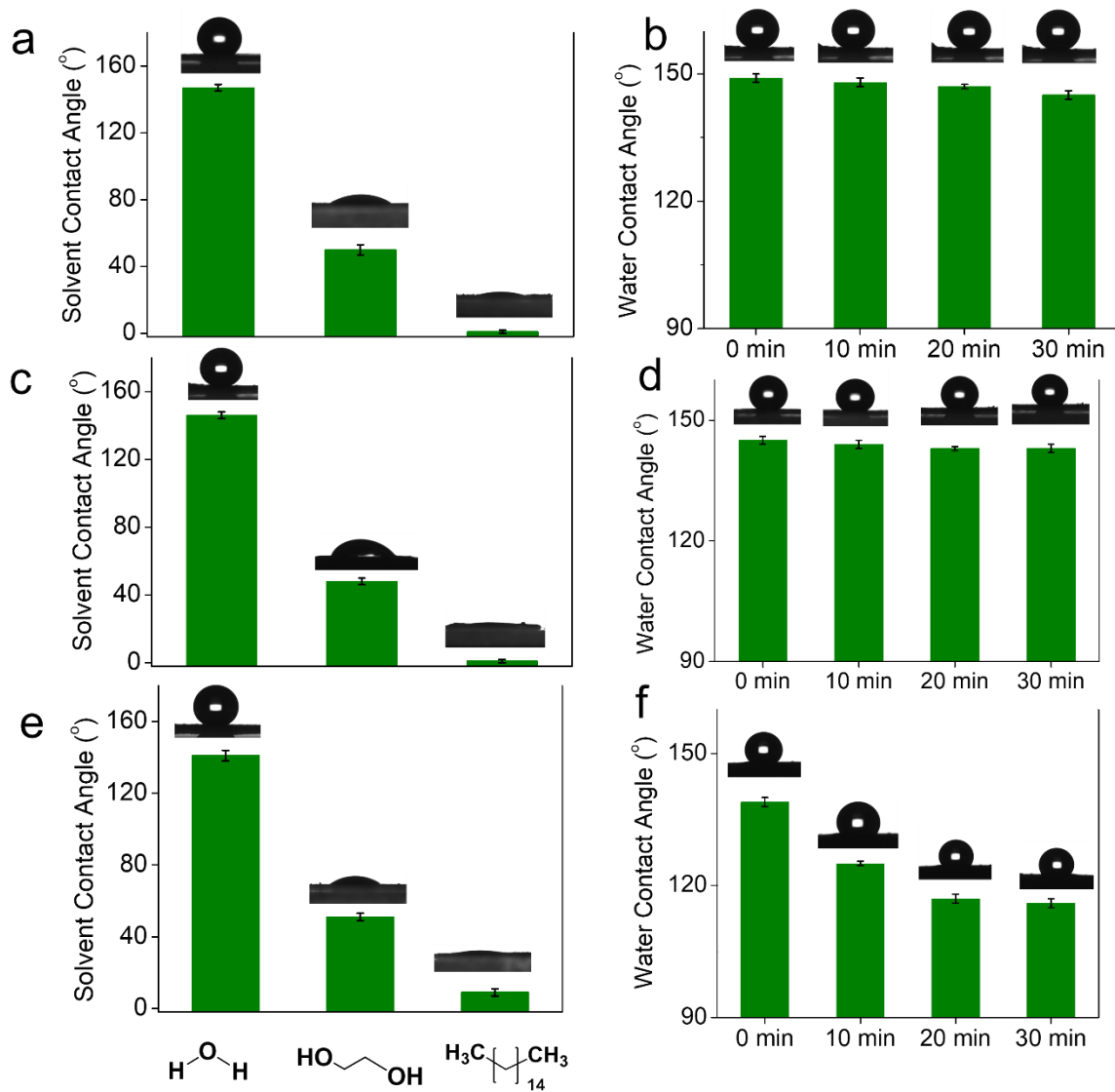


Figure S5: Plots and photos of a, c and e) solvent contact angles of water, ethylene glycol, and n-hexadecane b, d and f) WCA kinetics values measurements for every 10 minutes for FG-DTC-2, FG-DTC-3 and FG-DTC-4 samples

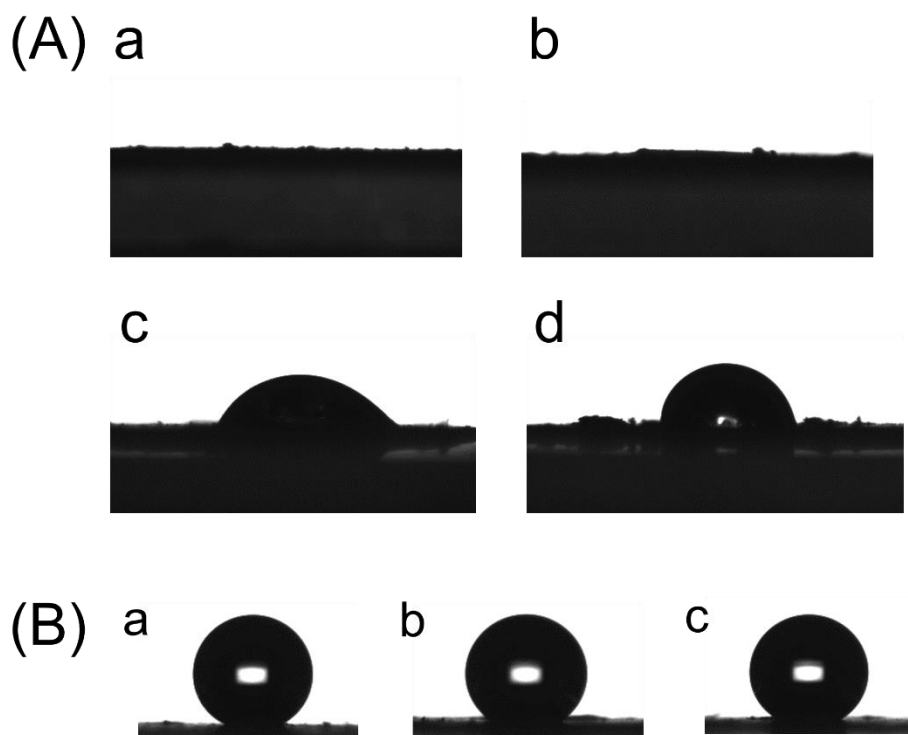


Figure S6: (A) FG+DTC mixtures prepared by (a-b) ex-situ synthesis* with WCA of 0° and (c-d) physically mixing 5 mg of exfoliated FG powder with 9 mg of DTC powder with WCA of $58\pm 2^\circ$ and $85\pm 1^\circ$ at different locations. (B) WCA measurements performed on FG-DTC samples (a) stored for 4 months ($151\pm 2^\circ$), (b) heated at 120°C for 3 hours ($148\pm 2^\circ$) and (c) kept under vacuum desiccator for one hour ($150\pm 1^\circ$).

* Synthetic procedure

250 mg of DTC was dissolved in 3 mL of methanol and mixed with 20 mL of exfoliated FG nanosheets dispersed in DMF and stirred at room temperature for 4 h followed by centrifugation and drying the mixture.

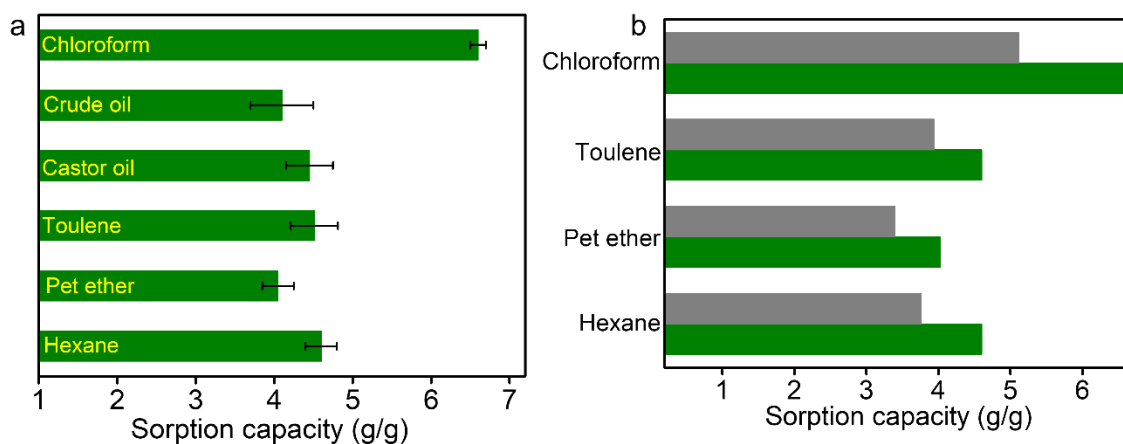


Figure S7: a) Plots showing sorption capacity of FG-DTC for oils and organic solvents and b) recyclability of FG-DTC samples for selected solvents.

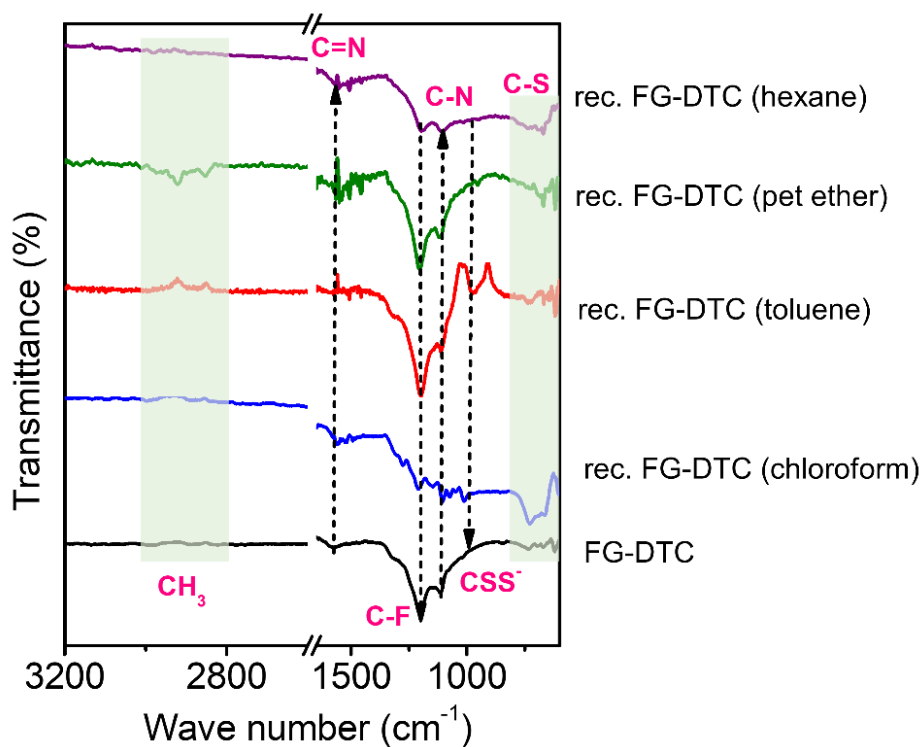


Figure S8: FTIR spectra of FG-DTC and recycled FG-DTC material after chloroform, toluene, pet ether and hexane sorption respectively.

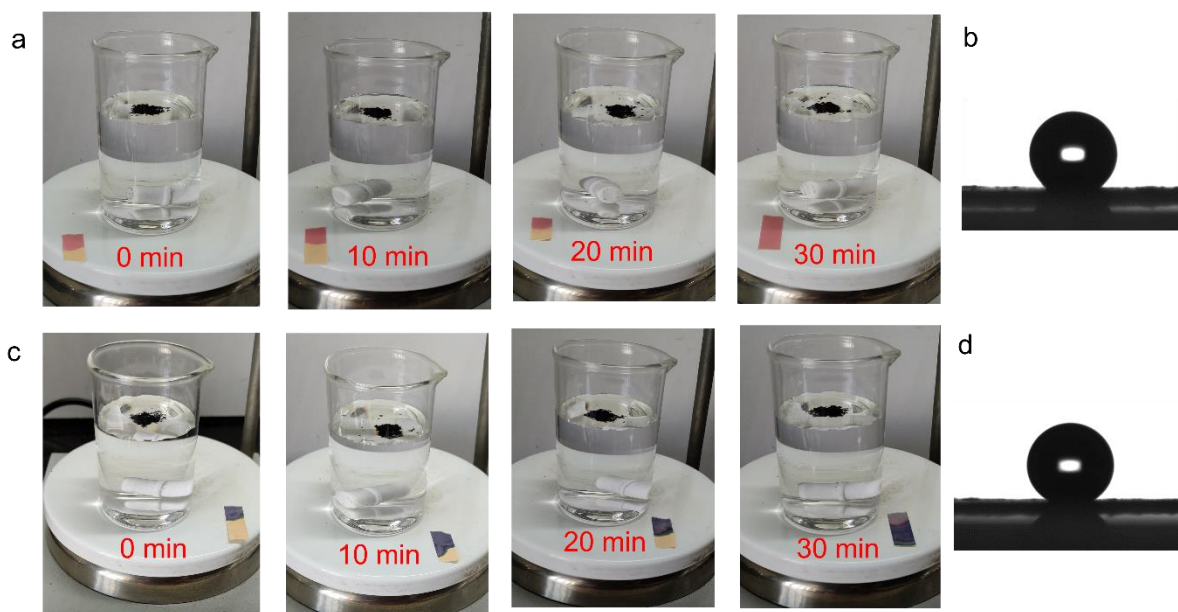


Figure S9: (a and c) Photos of FG-DTC powder dispersed in acidic (pH=1) and basic (pH=13) solution under constant stirring conditions, (b and d) WCA of the recovered powder after 30 min.



Figure S10: FG-DTC powder (5 mg) dispersed in 2 mL of polar, medium and non-polar solvents

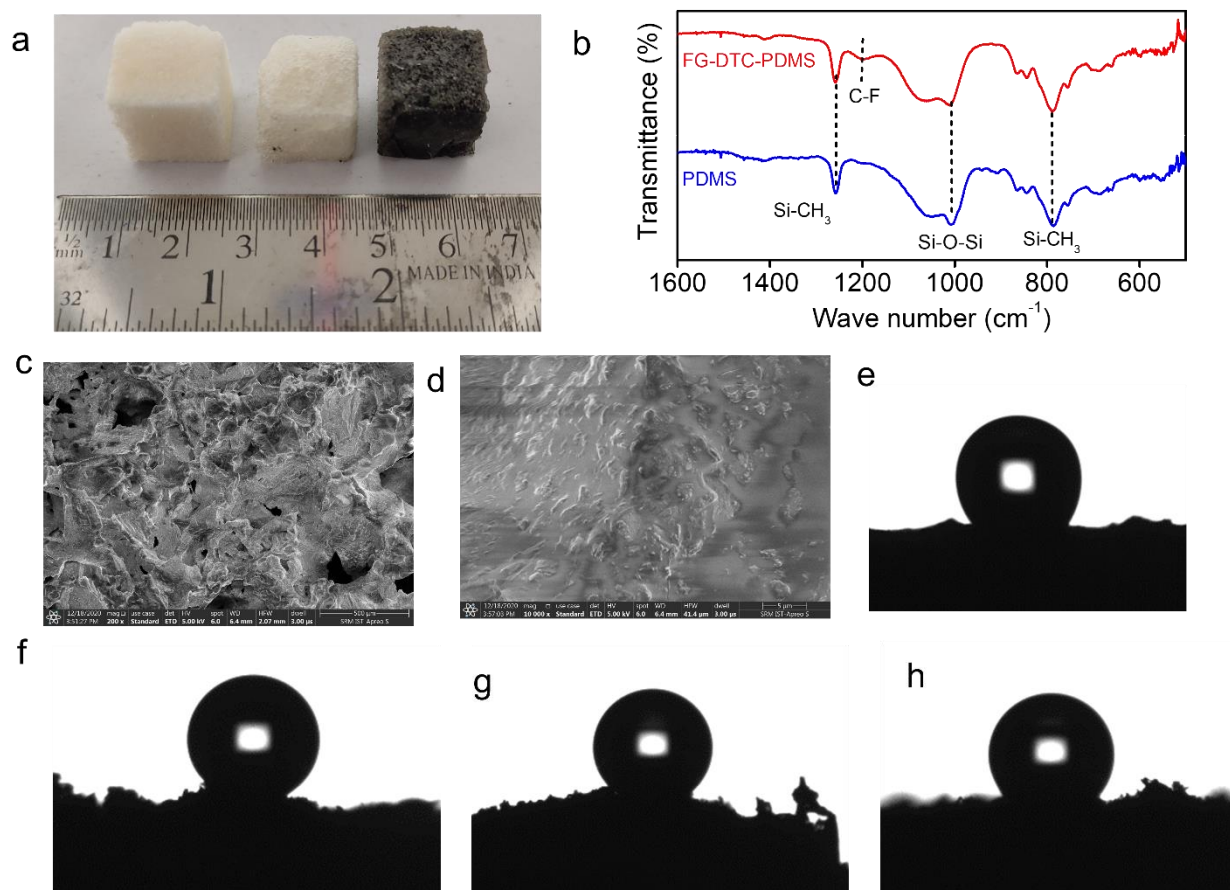


Figure S11: a) Photograph showing sugar cube, PDMS sponge and FG-DTC coated PDMS sponge b) FTIR spectra of PDMS sponge before and after FG-DTC coating, c-d) SEM images of FG-DTC-PDMS sponge and e) WCA of FG-DTC-PDMS sponge displaying a value of $140 \pm 5^\circ$, bulk hydrophobicity evaluated at f-g) center and edge and h) aged (for 3 months and dried) FG-DTC-PDMS sponge with WCA of $144 \pm 1^\circ$, $141 \pm 2^\circ$ and $137 \pm 1^\circ$ respectively

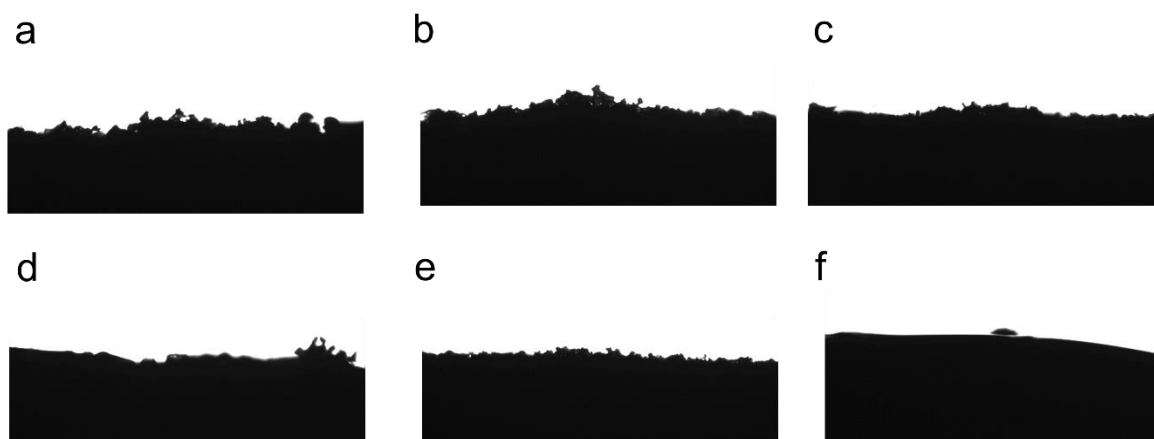


Figure S12: Wetting characteristics of FG-DTC-PDMS sponge with various solvents a) cyclohexane, b) dichloromethane, c) carbon tetrachloride d) tetrahydrofuran, e) xylene and f) hexadecane respectively.

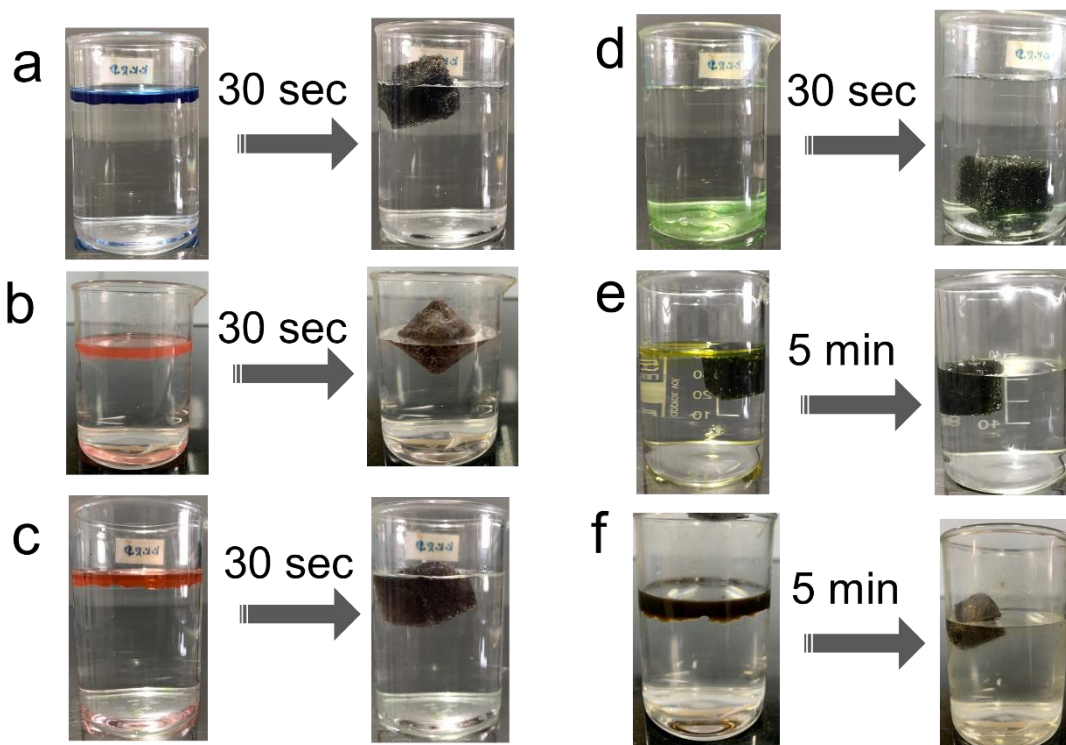


Figure S13: FG-DTC-PDMS sponge showing selective sorption of a) hexane, b) pet ether, c) toluene, d) chloroform, e) castor oil and f) crude oil respectively. 5 mL of solvent/oil spilled in 80 mL water.

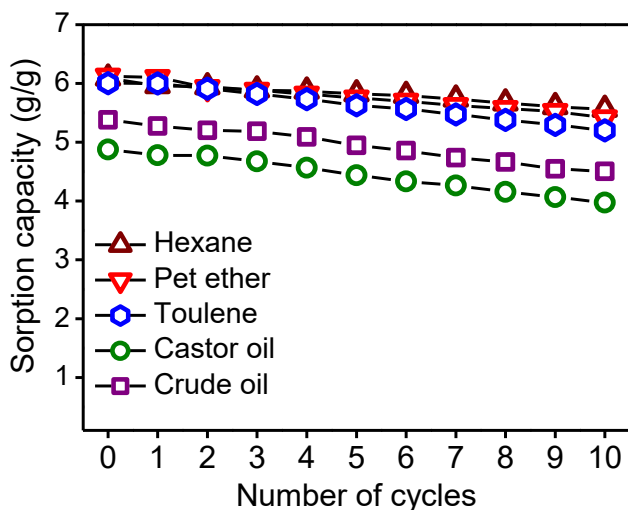


Figure S14: Graph showing adsorption capacity of FG-DTC-PDMS sponge for solvents and oils after 10 cycles.

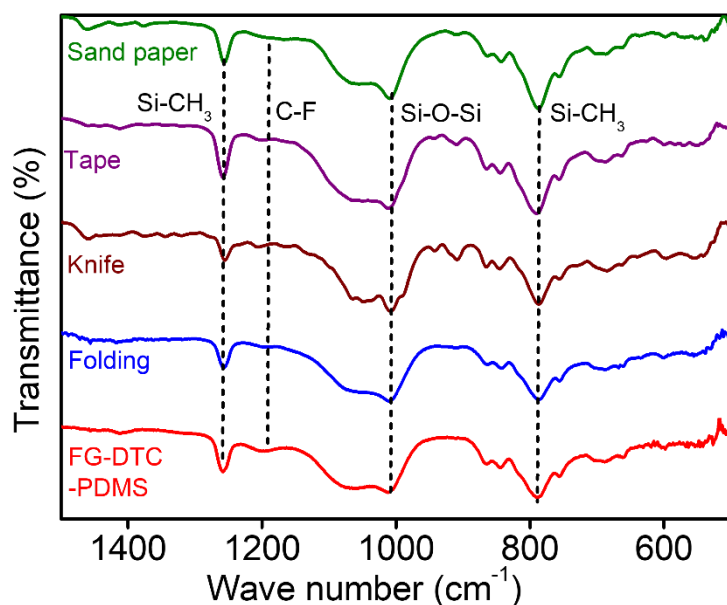


Figure S15: FTIR spectra of FG-DTC-PDMS (red line) and deformed and solvent adsorbed FG-DTC-PDMS after folding (blue line), knife scratching (brown line), tape peeling (violet line) and rubbing with sand paper (green) respectively. Note. After 40 times of mechanical deformations the corresponding FTIR has been measured.

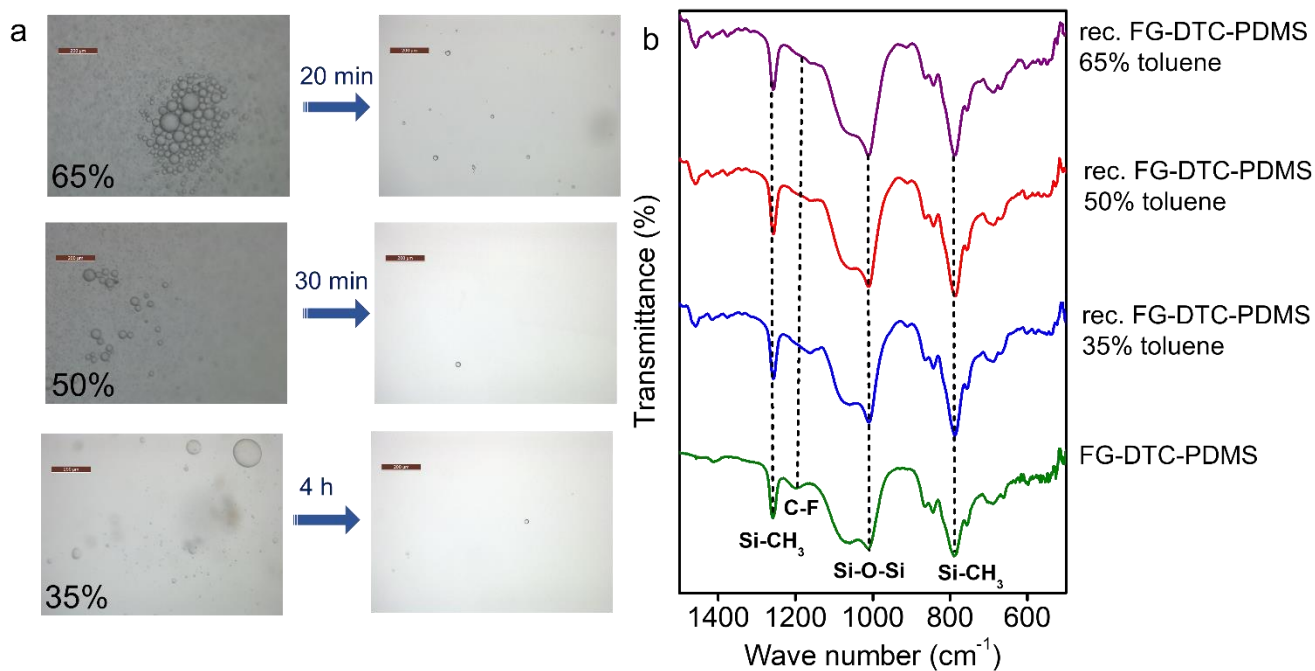


Figure S16: a) Microscopic images of toluene in water emulsions before and after separation using FG-DTC-PDMS sponge. b) FTIR spectra of FG-DTC-PDMS, and FG-DTC PDMS sponge recovered after separation of 35%, 50% and 65% of toluene-water emulsion.

Table S1: Literature reports on FG functionalization methods yielding diverse FG derivatives and comparison with the present work

#	Function alization	Key precursors	Reaction Conditions	Atomic %	Mechanism	Ref.
1	Dichloro carbene	Triethyl benzylammonium chloride (TBAC)	Fluorographite (0.01 g), TBAC were mixed in water/chloroform and sonicated followed by the NaOH addition under stirring at 80 °C for 1 day.	C: 67.1, F: 11.5, Cl: 7.6, O: 13.7	Partial defluorination of FG by base and cyclo addition	1
2	Hydrogenated FG	Sodium borohydride	FG dispersion in DMF (1 g/200 mL) was left for 4 days. FG dispersion was reacted with NaBH ₄ at room temperature for 3 days under sealed condition.	C: 74, F: 11.5, H: 9, O: 5	Partial defluorination occurring and hydride transfer via nucleophilic substitution	2
3	Urea	Urea	FG dispersion in NMP (0.1 g/20 mL) heated at 60 °C for 2 hours, washed and freeze dried. FG/urea in the ratio of 1:500 was ground and heated at 150° C for 4 hours under nitrogen flow.	C: 60.6, F: 17.4, O: 11.9, N: 9.9	Functionalization by urea via partial replacement of fluorine atoms	3
4	Thio fluoro	Sodium hydrosulfide	FG dispersion in DMF (0.25 g/50 mL) left for a day. Sodium hydrosulphide dissolved in DMF was mixed with FG dispersion for 3 days at room temperature.	C: 81.2, F: 6.8, O: 6.8, S: 4.9	Partial substitution of fluorine by nucleophilic sulphur resulting in sulfhydryl groups.	4
5	Thio fluoro	Potassium isopropyl xanthogenite (KIX)	FG (0.3 g) dispersion and KIX solution in acetonitrile was sonicated for 30 min and then heated 70° C for half day.	C: 64.6, F: 20.6, S: 5.1, O: 9.7	Defluorination of FG by base followed by nucleophilic attack	5
6	Octyl amine	Octylamine	FG dispersion in DMF (0.4 g/ 30 mL) left for 3 days followed by addition of octylamine at 130°C for 1 day under N ₂ atmosphere.	C: 80.8, F: 2.3, N: 8.1	Partial defluorination of FG followed by nucleophilic attack	6
7	Cyano Graphitic acid	Sodium cyanide, Nitric acid	G-CN: FG dispersion in DMF (0.12 g/15 mL) was mixed with NaCN and heated at 130°C for 1 day under (N ₂ atmosphere). G-COOH: HNO ₃ was added to G-CN and heated to 100° C for 1 day under stirring.	G-CN C: 78.6, N: 14.8, O: 6.0, F<1 G-COOH C: 70.6, N: 3.4, O: 25.8, F<1	G-CN: Reductive and defluorination of FG followed by cyanide substitution. G-COOH: Acid hydrolysis of -CN to -COOH groups	7
8	Grignard reagent	Pentyl (Pe), anisoyl (An), magnesium bromide and Allyl (Al) magnesium chloride	FG dispersion in dry THF (0.030 g/ 10 mL) was mixed with Grignard reagent and stirred for 5 hours under N ₂ condition.	Pe-FG C: 90.6, O: 5.2, F: 3.7 Al-FG C: 88.8, O: 5.2, F: 5.4 AnG C: 88.1, O: 8.3, F: 3.1	Reductive defluorination supplemented by nucleophilic substitution	8
9	Organo boric halide	Thiopheneboronic acid (TBA), Pyrimidinylboronic acid (PyBA), Phenylboronic acid (PBA)	Organic boric acid solubilized in dioxane followed by mixing FG (F/C=0.34) under N ₂ atm. in presence of catalytic amounts of Pd salt stirred at 100° C for 22 hours	FG-TBA F: 4.63, C: 78.43, O: 13.86, S: 1.94 FG-PBA F: 4.32, C: 85.83, O: 8.98 FG-PyBA F: 4.34, C: 85.30, O: 9.25, N: 1.03	Pd catalysed cross-coupling reaction between organic boron and organic halides. Defluorination followed by base activation of the boron compound	9
10	Aniline, aldehyde, ester	Pararosaniline, (PRA), 2-formyl-3-methylphenoxy-methyl)-benzoate, (FMP)	Partially defluorinated FG (PFG): FG dispersion in DMF (2 g/ mL) sonicated for 4 h under N ₂ atm. FG-PRA : PFG dispersion in DMF (0.030 g/20 mL) mixed with PRA and heated at 130 °C for 3 days under N ₂ atmosphere. FG-FMP : FG-PRA dispersion in acetonitrile mixed with FMP under N ₂ conditions and was irradiated at λ = 320 nm for 2 hours	FG-FMP C: 85, N: 12.4, F: 2.6 FG-FMP C: 81.8, N: 3.7, F: 14.5	Partially defluorinated graphene via thermal treatment at 550°C Photo-induced cycloaddition following amine nucleophilic substitution	10
11	Nitrogen doped	Sodium amide	FG dispersion in DMF (0.5 g/ 30 mL) was left for 2 days and then mixed with NaNH ₂ at 130 °C for 1 day	C: 78.8, N: 14.5, O: 7.7, F: 0.7	Nucleophilic attack at point defects	11

12	Alkynyl	Phenylacetylene (Pha), ethynyl aniline (Eta), and ethynylpyrimidine (Etp) Bis(triphenylphosphine)palladium dichloride, CuI	FG dispersion in dry DMF (0.031 g/ 5 mL) was mixed with catalytic amounts of Pd (0.0351g), CuI and triethylamine at room temperature for 3 days under nitrogen atmosphere	Pha-FG C: 76.3, N: 1.9, O: 10.3 F: 11.5 Eta-FG C: 76.6, N: 7.6, O: 12.5 F: 3.3 Etp-FG C: 69.2, N: 5.4, O: 4.7, F: 20.7	Sonogashira reaction of FG with terminal alkynes	12
13	Hydroxyl	Aqueous KOH, Toluene	FG dispersion in toluene (1 g/300 mL) was left for 1 day. Interfacial functionalization: Toluene and H ₂ O under basic pH (11-14) was mixed with FG dispersion at (60° C for 3 days).	Aqueous dispersion C: 64.5, O: 21 F: 13.3, N: 1.2 Toluene dispersion C: 48.4, O: 3.2 F:47.7, N:0.7	FG functionalization with hydroxyl groups via nucleophilic substitution of F atoms	13
14	Diethyl amino	Lithium diethylamide	FG dispersion in DMF (1.25 g/250 mL) of and left for 3 days.	DEA-FG C: 67.5, F: 26.5, O: 5.7 N: 2.1	Partial nucleophilic substitution of nitrogen	14
15	Thienyl/ Butyl	2-Thienyllithium, n-butyllithium	FG dispersion (0.062 g/10 mL) in anhydrous THF was mixed with organolithium reagent for 18 hours under N ₂ atmosphere at room temperature.	G-Th/Bu C: 89, N: 0.6 O: 5.1, F: 2.6 S: 2.7	Organometallic reagent resulted in elimination of fluorine followed by nucleophilic substitution	15
16	Thiophenol	Methoxy thiophenol (MTP) and dimethyl amino thiophenol (DMATP)	FG dispersion in DMF (1 g/200 mL) left for a day. MTP and DMATP was added to FG dispersion and was stirred for 3 days at room temperature.	MTP-FG C: 68.5, F: 27.1, O: 2.5 N: 0.9, S: 1 DMATP-FG C: 64.8, F: 30.7, O: 2.3 N: 1.7, S: 0.5	Partial nucleophilic substitution/reduction of FG by the thiophenols through C-S bonding	16
17	Dithiocarbamate	CS ₂ , diethylamine, KOH	FG dispersion in DMF (0.2 g/50 mL) was left for 15 minutes. FG dispersion was added to the mixture of CS ₂ and diethylamine under basic condition for 4 hours at room temperature.	C: 62.6, F: 27.2, O: 9.7, N: 0.3, S: 0.3	Partial defluorination by base followed by nucleophilic substitution of sulphur atoms	Present work

Table S2: Comparison showing graphene modified PDMS sponges with current work

#	Types of PDMS sorbents	Synthetic method	WCA (deg)	Separation of Oils/Organics	Absorbency (g/g)	Recyclability (Number of cycles)	Ref.
1	RGO	Reduction of GO to RGO: (solvothermal treatment at 180°C for 6 h under alkaline pH) Sugar cube template PDMS sponge 2.5 g/L of RGO dispersed in DMF was injected into PDMS sponge	126±1	DMF, vegetable oil, gasoline, toluene, THF Emulsion (Toluene-water 1-10% separation Separation time: 5 hours	2.2-7	7 sorption cycles for toluene-water mixture (~ 50 % decrease in sorption performance after 7 cycles)	17
2	RGO	Ultrasound assisted in-situ polymerization of PDMS dissolved in ethyl acetate with RGO (0-40 mg) along with salt particles (10 g) RGO loading (0, 1.5 and 3 wt%)	149±1	Paraffin oil, chloroform, hexane, pet ether	3 – 19 (3wt % RGO in PDMS)	10 sorption cycles for hexane (~ 10 % decrease in sorption performance after 10 cycles)	18
3	C ₃ N ₄	Carbonization of Melem 550°C (4 hours) to get carbon nitride Sugar cube template PDMS Injecting of C ₃ N ₄ dispersion into PDMS followed by annealing at 200°C for 2 hours	132±1	Chloroform, hexane, diethyl ether, pet ether Emulsion (Toluene-water) separation Separation time: 1 hour	1.7 – 8.6	10 sorption cycles for hexane and chloroform	19
4	Modified GO	Sugar templated PDMS cubes APTES modified PDMS sponge followed by dipping into GO dispersion subsequent covalent linkage with dicyclohexyl-carbodiimide and dimethylamino-pyridine at 70°C for 20 hours	147±1	DMF, THF, pump oil, soybean oil, chloroform	3.9-14.6	10 sorption cycles for toluene	20
5	FGO	Fluorinated graphene oxide (2.5 wt%) incorporated PDMS with tetraethylorthosilicate as cross linker and dibutyltindilaureate as catalyst Spray coating of PDMS-SiO ₂ composite over Al and glass substrates (8-10 µm thick film)	125-173±1 (23-60 wt % FGO in PDMS)	-	-	-	21
6	Vinyloxy-modified RGO	RGO modified with vinyloxybenzenediazonium tetrafluoroborate via aryl radical assisted addition reaction Vinyloxy modified RGO with trimethylsilyl and hydride terminated PDMS (catalytic amount of Pt) Spray coating (10 µL) over textile	125-150±1	-	-	-	22
7	EDC-NHS modified GO	PDMS (amino terminated) solution was mixed with GO, EDC, NHS and GA stirred at 35°C for 1 hour	117-120±1 (0.5-1.5 wt% of GO)	Silicone oil, THF, pet ether, chloroform and toluene	5.59-19.5	30 sorption cycles for petroleum ether	23
8	Graphene	Mould transfer-surface embedding method (drop coating of graphene dispersion onto cube sugar) PDMS dispersion poured onto graphene coated cube sugar and cured at 90°C followed by sugar removal	130±1	Engine oil, pump oil, hexane, soybean oil	4-15	15 sorption cycles for hexane and engine oil.	24

						(~ 35 % decrease after 15 cycles)	
9	FG-DTC	FG functionalized with dithiocarbamate. Room temperature in-situ synthesis (4 hours) Injecting FG-DTC dispersion onto PDMS	140±5	Crude oil, castor oil, chloroform, Toluene, pet ether, hexane Emulsion separation (Toluene-water) 35, 50 and 65 % toluene in water Separation time 20 min to 5 hours	4.8-12.1	20 sorption cycles for chloroform and 10 for oils and organics (~ 1% decrease for chloroform after 20 cycles and ~ 10 % decrease after 10 cycles for rest of the solvents and oils)	Present work

References

- 1 P. Lazar, C. K. Chua, K. Holá, R. Zbořil, M. Otyepka and M. Pumera, Dichlorocarbene-Functionalized Fluorographene: Synthesis and Reaction Mechanism, *Small*, 2015, **11**, 3790-3796.
- 2 I. Papadakis, Z. Bouza, S. Couris, A. B. Bourlinos, V. Mouselimis, A. Kouloumpis, D. Gournis, A. Bakandritsos, J. Ugolotti and R. Zboril, Hydrogenated Fluorographene: A 2D Counterpart of Graphane with Enhanced Nonlinear Optical Properties, *J. Phys. Chem. C*, 2017, **121**, 22567-22575.
- 3 X. Ye, L. Ma, Z. Yang, J. Wang, H. Wang and S. Yang, Covalent Functionalization of Fluorinated Graphene and Subsequent Application as Water-based Lubricant Additive, *ACS Appl. Mater. Interfaces*, 2016, **8**, 7483-7488.
- 4 V. Urbanová, K. Holá, A. B. Bourlinos, K. Čépe, A. Ambrosi, A. H. Loo, M. Pumera, F. Karlický, M. Otyepka and R. Zbořil, Thiofluorographene–Hydrophilic Graphene Derivative with Semiconducting and Genosensing Properties, *Adv. Mater.*, 2015, **27**, 2305-2310.
- 5 J. Sturala, S. Hermanová, L. Artigues, Z. Sofer and M. Pumera, Thiographene synthesized from fluorographene via xanthogenate with immobilized enzymes for environmental remediation, *Nanoscale*, 2019, **11**, 10695-10701.
- 6 A. Stathis, M. Stavrou, I. Papadakis, A. Bakandritsos, T. Steklý, M. Otyepka and S. Couris, Octylamine-Modified Fluorographenes as a Versatile Platform for the Efficient Engineering of the Nonlinear Optical Properties of Fluorinated Graphenes, *Adv. Photonics Res.*, 2020, **1**, 2000014.
- 7 A. Bakandritsos, M. Pykal, P. Błoński, P. Jakubec, D. D. Chronopoulos, K. Poláková, V. Georgakilas, K. Čépe, O. Tomanec, V. Ranc, A. B. Bourlinos, R. Zbořil and M. Otyepka, Cyanographene and Graphene Acid: Emerging Derivatives Enabling High-Yield and Selective Functionalization of Graphene, *ACS Nano*, 2017, **11**, 2982-2991.
- 8 D. D. Chronopoulos, A. Bakandritsos, P. Lazar, M. Pykal, K. Čépe, R. Zbořil and M. Otyepka, High-Yield Alkylation and Arylation of Graphene via Grignard Reaction with Fluorographene, *Chem. Mater.*, 2017, **29**, 926-930.
- 9 F. Huang, Y. Li, X. Liu, W. Lai, K. Fan, X. Liu and X. Wang, Suzuki–Miyaura reaction of C–F bonds in fluorographene, *Chem. Commun.*, 2021, **57**, 351-354.
- 10 H. Barès, A. Bakandritsos, M. Medved', J. Ugolotti, P. Jakubec, O. Tomanec, S. Kalytchuk, R. Zbořil and M. Otyepka, Bimodal role of fluorine atoms in fluorographene chemistry opens a simple way toward double functionalization of graphene, *Carbon*, 2019, **145**, 251-258.
- 11 D. Zaoralová, V. Hrubý, V. Šedajová, R. Mach, V. Kupka, J. Ugolotti, A. Bakandritsos, M. Medved' and M. Otyepka, Tunable Synthesis of Nitrogen Doped Graphene from Fluorographene under Mild Conditions, *ACS Sustain. Chem. Eng.*, 2020, **8**, 4764-4772.

- 12 D. D. Chronopoulos, M. Medved', P. Błoński, Z. Nováček, P. Jakubec, O. Tomanec, A. Bakandritsos, V. Novotná, R. Zbořil and M. Otyepka, Alkynylation of graphene via the Sonogashira C–C cross-coupling reaction on fluorographene, *Chem. Commun.*, 2019, **55**, 1088-1091.
- 13 A. Kouloumpis, D. D. Chronopoulos, G. Potsi, M. Pykal, J. Vlček, M. Scheibe and M. Otyepka, One-Step Synthesis of Janus Fluorographene Derivatives, *Chem. Eur. J.*, 2020, **26**, 6518-6524.
- 14 I. Papadakis, D. Kyrginas, A. Stathis, S. Couris, G. Potsi, A. B. Bourlinos, O. Tomanec, M. Otyepka and R. Zboril, Large Enhancement of the Nonlinear Optical Response of Fluorographene by Chemical Functionalization: The Case of Diethyl-amino-fluorographene, *J. Phys. Chem. C*, 2019, **123**, 25856-25862.
- 15 D. D. Chronopoulos, M. Medved', G. Potsi, O. Tomanec, M. Scheibe and M. Otyepka, Tunable one-step double functionalization of graphene based on fluorographene chemistry, *Chem. Commun.*, 2020, **56**, 1936-1939.
- 16 A. Stathis, I. Papadakis, N. Karampitsos, S. Couris, G. Potsi, A. B. Bourlinos, M. Otyepka and R. Zboril, Thiophenol-Modified Fluorographene Derivatives for Nonlinear Optical Applications, *ChemPlusChem*, 2019, **84**, 1288-1298.
- 17 D. N. H. Tran, S. Kabiri, T. R. Sim and D. Losic, Selective adsorption of oil–water mixtures using polydimethylsiloxane (PDMS)–graphene sponges, *Environ. Sci. Water Res. Technol.*, 2015, **1**, 298-305.
- 18 S. Qiu, H. Bi, X. Hu, M. Wu, Y. Li and L. Sun, Moldable clay-like unit for synthesis of highly elastic polydimethylsiloxane sponge with nanofiller modification, *RSC Adv.*, 2017, **7**, 10479-10486.
- 19 I. A. Abdelhafeez, X. Zhou, Q. Yao, Z. Yu, Y. Gong and J. Chen, Multifunctional Edge-Activated Carbon Nitride Nanosheet-Wrapped Polydimethylsiloxane Sponge Skeleton for Selective Oil Absorption and Photocatalysis, *ACS Omega*, 2020, **5**, 4181-4190.
- 20 J. Zhao, H. Chen, H. Ye, B. Zhang and L. Xu, Poly(dimethylsiloxane)/graphene oxide composite sponge: a robust and reusable adsorbent for efficient oil/water separation, *Soft Matter*, 2019, **15**, 9224-9232.
- 21 T. Bharathidasan, T. N. Narayanan, S. Sathyanaryanan and S. S. Sreejakumari, Above 170° water contact angle and oleophobicity of fluorinated graphene oxide based transparent polymeric films, *Carbon*, 2015, **84**, 207-213.
- 22 H. Yan, H. Zhou, Q. Ye, X. Wang, C. M. Cho, A. Y. X. Tan and J. Xu, Engineering polydimethylsiloxane with two-dimensional graphene oxide for an extremely durable superhydrophobic fabric coating, *RSC Adv.*, 2016, **6**, 66834-66840.

- 23 S. Mo, J. Mei, Q. Liang and Z. Li, Repeatable oil-water separation with a highly-elastic and tough amino-terminated polydimethylsiloxane-based sponge synthesized using a self-foaming method, *Chemosphere*, 2021, **271**, 129827.
- 24 Z. Pan, Y. Guan, Y. Liu and F. Cheng, Facile fabrication of hydrophobic and underwater superoleophilic elastic and mechanical robust graphene/PDMS sponge for oil/water separation, *Sep. Purif. Technol.*, 2021, **261**, 118273.