Supplementary information

Recyclable 3D Graphene Aerogel with Bimodal Pore Structure for Ultrafast and Selective Oils Sorption from Water

Muhammad Adil Riaz[†], Pejman Hadi[‡], Irfan H. Abidi[†], Abhishek Tyagi[†], Xuewu Ou[†] and Zhengtang Luo[†,*]

[†] *Department of Chemical and Biomolecular Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

[‡] *New York Center for Clean Water Technology, Stony Brook University, NY 11794, USA*

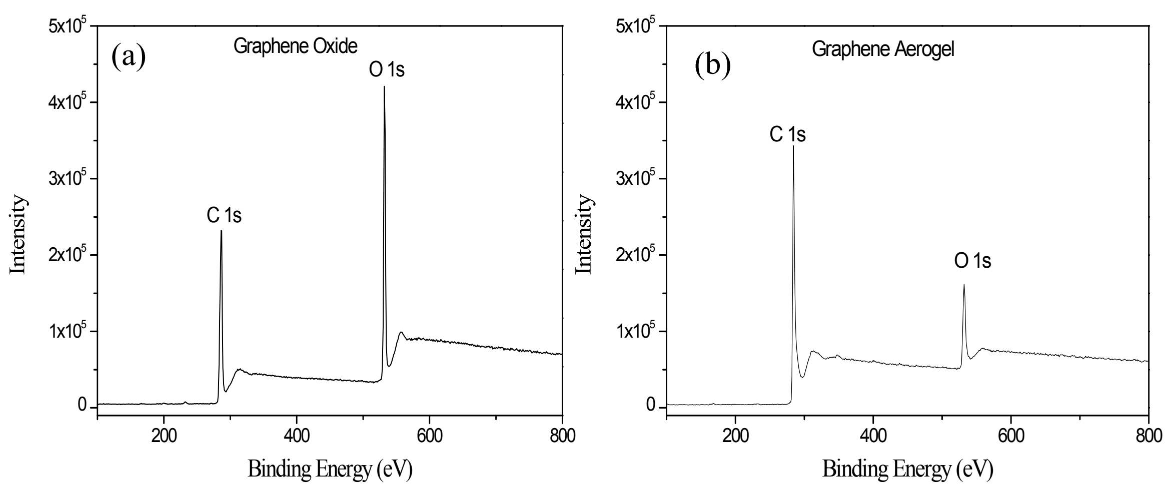

Figure S1. Full range XPS spectra for graphene oxide and graphene aerogel.

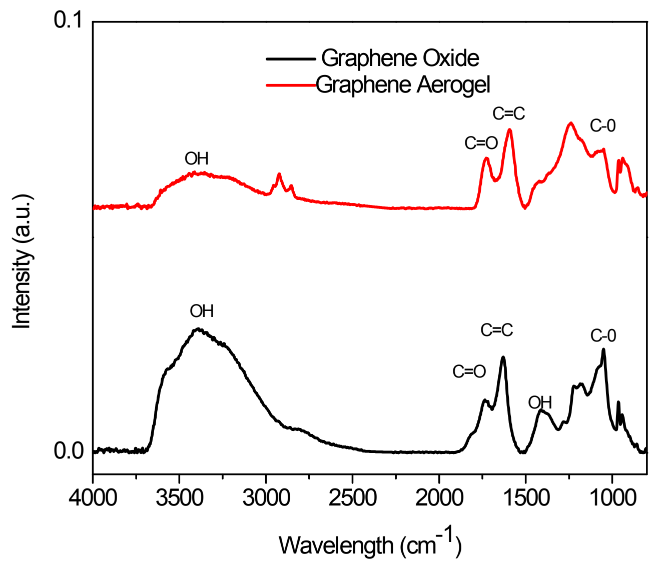

Figure S2. FTIR spectra for graphene oxide and graphene aerogel.

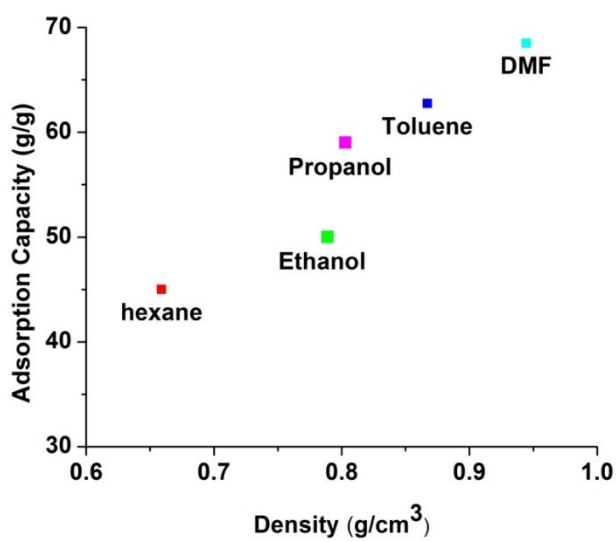

Figure S3. Effect of density on sorption capacity for organic solvents.

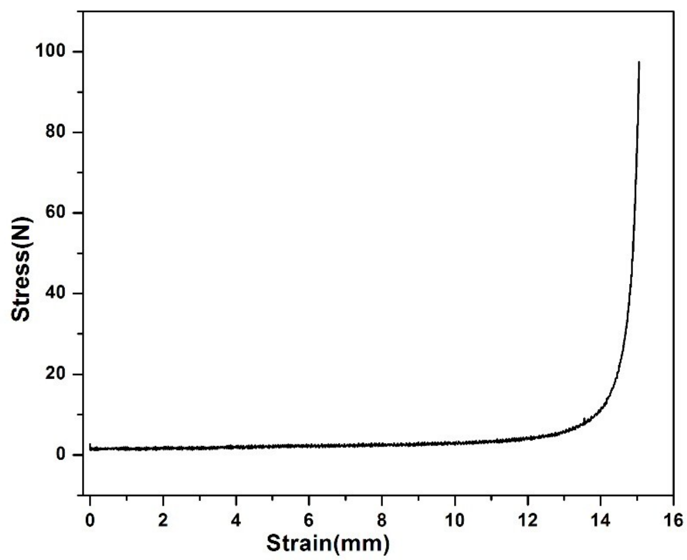

Figure S4. Stress strain curve of 3D graphene aerogel

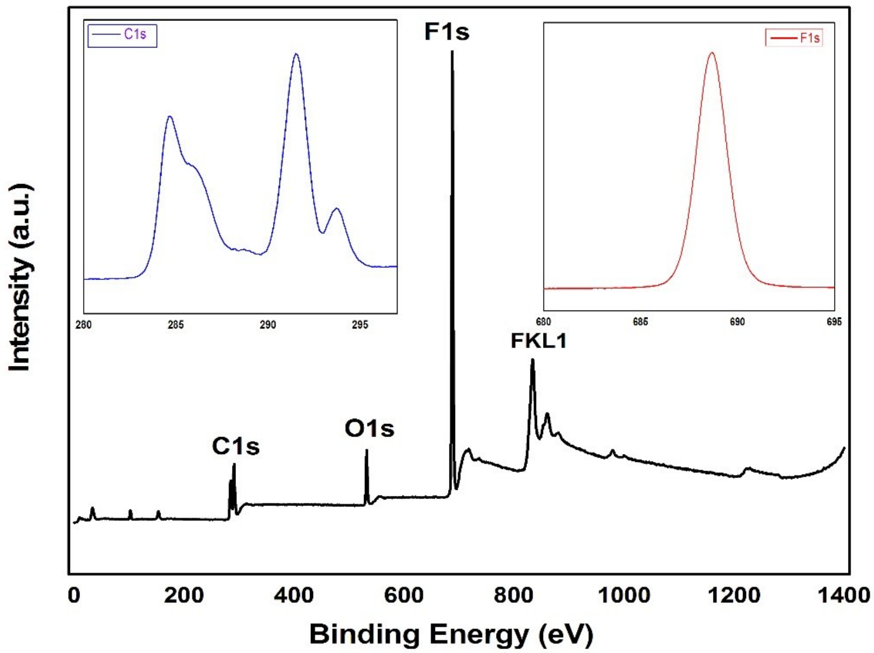

Figure S5. Full range XPS spectra of silane functionalized GA (insets show the C1s and F1s)

Table S1 Comparative study of sorption capacity of graphene aeorgel with other common sorbents

Sorbent	Oils	Capacity g/g	Organic liquid	Capacity g/g	Ref.
Graphene aerogel	Mineral oil, vegetable oil, motor oil, gear oil	60-70	All organic liquids	40-70	This work
Activated carbon	--	--	Benzene , toluene	<1	1
PDMS Sponge	Silicone oil, motor oil, transformer oil	4.5	Chloroform, dichloromethane,N-N DMF, toluene, methanol, ethanol,	4-11	2

			acetone		
Polyurethane sponge	Lubricating oil, dodecane	19,13	Octane, decane	14	3
Polypropylene	Diesel oil, crude oil, olive oil, fuel oil	9-16	Toluene	11.4	4
CNT Sponge	Mineral,oil vegetable oil, diesel oil	100-125	Octane , ethyl acetate	50	5
Silica Aerogel	Diesel oil	19	All organic liquids	9-21	6
Boron Nitride Sheets	Motor oil	20		5-14	
Fe/C, Co/C, Ni/C nanoparticles	Lube oil, crude oil , bean oil , dodecane	4.8-7.5	Decane	4.5	7
Nanocellulose aerogel	Dodecane, paraffin oil mineral oil	25-30	All organic liquids	20-40	8
Natural Wool	Diesel oil, crude oil	12.5	--	--	9
Cotton Fiber	Vegetable oil, mineral oil, fuel oil	17-20	Petroleum liquids	20	10

Table S2

Oil Type	Pseudo 1st Order			Pseudo 2nd Order			Intraparticle Diffusion		
	Q_e	K_1	R^2	Q_e	K_2	R^2	K_i	C	R^2
Mineral Oil	33.845	0.068	0.7829	66.622	0.005	0.9945	4.898	25.992	0.4664
Vegetable Oil	35.815	0.042	0.5735	71.327	0.007	0.9976	5.269	24.224	0.4854

Table S3 Comparative study of graphene aeorgel with previously reported 3D graphene sorbents for oils & organics

	Chemicals	**Synthesis Method**	**Performance**	**Recycling**	**Physical Properties**	**Ref.**
Spongy Graphene	GO, Ammonia	Hydrothermal 180 °C, 24 hr, Freeze drying	Capacity 20-86 g/g, no quantitative kinetic study (oil drop on water adsorbed in 80s	10 cycles by heating	(Surface area, contact angle) 432m²/g, 114 °	11
Spongy Graphene	GO only	Freeze casting, high temperature (1000°C) reduction & soot treatment	Capacity 120-616 g/g, no kinetic study	Burning & Heating	155°	12
Graphene Sponge	GO, Thiourea	Hydrothermal 180 °C, 4.5 hr, Freeze drying	Capacity 80-154 g/g, no quantitative kinetic study (diesel oil drop adsorbed in 10s	Burning	399 m²/g	13
Graphene oxide Aerogel	GO, Thiourea	Thermal Polycondensation, freeze casting	Capacity 50-90 g/g, no kinetic study	--	385 m²/g	14
Graphene Foam	GO, EDA, Copolymer (PV2P-b-PHA)	Chemical Reduction, Freeze drying	40-196 g/g, 2ml toluene adsorbed in 21s	Ph induced desorption for 10 cycles	152° (Ph=7)	15
Macroscopic	GO, Iron oxide Nanoparticles	Chemical Reduction	10-27g/g, no kinetic study	Burning for 6 cycles	--	16

graphene						
Graphene Aerogel	GO Only	Hydrothermal 180 °C, 2 hr, freeze drying, Silane treatment	40-70g/g oils/organics, Water sorption reduction from 20g/g to 5g/g , quantitative kinetic study for oils (uptake & desorption within 1min) & organics (sorption within 4 s)	Solvent extraction (oils) & heating(organics) for several cycles	$49 m^2/g$, 130°	**This work**

References:

(1) Lillo-Ródenas, M. A.; Cazorla-Amorós, D.; Linares-Solano, A. Behaviour of Activated Carbons with Different Pore Size Distributions and Surface Oxygen Groups for Benzene and Toluene Adsorption at Low Concentrations. *Carbon N. Y.* **2005**, *43*, 1758–1767.

(2) Choi, S.-J.; Kwon, T.-H.; Im, H.; Moon, D.-I.; Baek, D. J.; Seol, M.-L.; Duarte, J. P.; Choi, Y.-K. A Polydimethylsiloxane (PDMS) Sponge for the Selective Absorption of Oil from Water. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4552–4556.

(3) Zhu, Q.; Pan, Q.; Liu, F. Facile Removal and Collection of Oils from Water Surfaces through Superhydrophobic and Superoleophilic Sponges. *J. Phys. Chem. C* **2011**, *115*, 17464–17470.

(4) Ceylan, D.; Dogu, S.; Karacik, B.; Yakan, S. D.; Okay, O. S.; Okay, O. Evaluation of Butyl Rubber as Sorbent Material for the Removal of Oil and Polycyclic Aromatic Hydrocarbons from Seawater. *Environ. Sci. Technol.* **2009**, *43*, 3846–3852.

(5) Gui, X.; Li, H.; Wang, K.; Wei, J.; Jia, Y.; Li, Z.; Fan, L.; Cao, A.; Zhu, H.; Wu, D. Recyclable Carbon Nanotube Sponges for Oil Absorption. *Acta Mater.* **2011**, *59*, 4798–4804.

(6) Rao, V.; Hegde, N. D.; Hirashima, H. Absorption and Desorption of Organic Liquids in Elastic Superhydrophobic Silica Aerogels. *J. Colloid Interface Sci.* **2007**, *305*, 124–132.

(7) Chu, Y.; Pan, Q. Three-Dimensionally Macroporous Fe/C Nanocomposites as Highly Selective Oil-Absorption Materials. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2420–2425.

(8) Korhonen, J. T.; Kettunen, M.; Ras, R. H. a; Ikkala, O. Hydrophobic Nanocellulose Aerogels as Floating, Sustainable, Reusable, and Recyclable Oil Absorbents. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1813–1816.

(9) Radetić, M. M.; Jocić, D. M.; Jovančić, P. M.; Petrović, Z. L.; Thomas, H. F. Recycled

Wool-Based Nonwoven Material as an Oil Sorbent. *Environ. Sci. Technol.* **2003**, *37*, 1008–1012.

(10) Deschamps, G.; Caruel, H.; Borredon, M.-E.; Bonnin, C.; Vignoles, C. Oil Removal from Water by Selective Sorption on Hydrophobic Cotton Fibers. *Environ. Sci. Technol.* **2003**, *37*, 1013–1015.

(11) Bi, H.; Xie, X.; Yin, K.; Zhou, Y.; Wan, S.; He, L.; Xu, F.; Banhart, F.; Sun, L.; Ruoff, R. S. Spongy Graphene as a Highly Efficient and Recyclable Sorbent for Oils and Organic Solvents. *Adv. Funct. Mater.* **2012**, *22*, 4421–4425.

(12) Bi, H.; Xie, X.; Yin, K.; Zhou, Y.; Wan, S.; Ruoff, R. S.; Sun, L. Highly Enhanced Performance of Spongy Graphene as an Oil Sorbent. *J. Mater. Chem. A* **2014**, *2*, 1652–1656.

(13) Zhao, J.; Ren, W.; Cheng, H.-M. Graphene Sponge for Efficient and Repeatable Adsorption and Desorption of Water Contaminations. *J. Mater. Chem.* **2012**, *22*, 20197–20202.

(14) Wan, W. . b; Yu, S. .; Dong, F. .; Zhang, Q. .; Zhou, Y. . b. Efficient C3N4/graphene Oxide Macroscopic Aerogel Visible-Light Photocatalyst. *J. Mater. Chem. A* **2016**, *4*, 7823–7829.

(15) Zhu, H.; Chen, D.; Li, N.; Xu, Q.; Li, H.; He, J.; Lu, J. Graphene Foam with Switchable Oil Wettability for Oil and Organic Solvents Recovery. *Adv. Funct. Mater.* **2015**, *25*, 597–605.

(16) Process, S.; Cong, H.; Ren, X.; Wang, P.; Yu, S. Macroscopic Multifunctional Graphene-Based Hydrogels and Aerogels by a Metal Ion Induced. **2012**, 2693–2703.