

Enhanced CO₂ Sorption Efficiency in Amine-Functionalised 2D/3D Graphene/Silica Hybrid Sorbents

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Supporting Information

Materials preparation

All chemicals were obtained from Sigma-Aldrich and used as received. SBA-15 was prepared with pluronic P123 block copolymer (EO₂₀PO₇₀EO₂₀) as the surfactant template, and tetraethylorthosilicate (TEOS, 98 wt%) as the silica source. Graphene oxide (GO) was prepared by the oxidation of graphite using the modified Hummers method. Graphene (G) was obtained by calcining as-prepared GO at 550 °C in N₂ atmosphere for 3h to remove the oxygen functional groups.

The TEPA functionalised 2D/3D graphene/silica hybrid sorbent was synthesized by the wet impregnation followed by the freeze-drying method. A desired amount of graphene was firstly dispersed in 10 mL water under ultrasonication for a period of 1h. Then, TEPA was dissolved in this mixture again under stirring for 10 min followed by the addition of calcined. The resultant mixture was kept under vigorous stirring for 24h at room temperature. Subsequently, the mixture was frozen in the liquid nitrogen and kept in a freeze drier at -65°C until the sample was completely dry. Similar procedure was also used to prepare SBA-15 and graphene samples impregnated with TEPA for comparison purpose.

Materials characterization and CO₂ sorption tests

Brunauer-Emmett-Teller (BET) surface area and pore volume were measured at 77 K by nitrogen sorption using a Micromeritics Tristar 3020. The pore size distribution was calculated using the non-local density functional theory (NL-DFT) method, a software available in the Micromeritics Tristar 3020. The same parameters in the NL-DFT model were used for the calculation of all pore size distributions. The samples were degassed at 90°C overnight prior to the measurements. Morphological features of the samples were examined using a Jeol JSM-7001F Scanning Electron Microscope (SEM) with a hot (Schottky) electron gun. Atomic force microscopy (AFM) images of GO and GO-Fe₃O₄ nanocomposites on a freshly cleaved mica surface were taken with a Veeco MultiMode AFM in tapping mode using OLTESPA-R3 silicon probe (Bruker). To get thermal decomposition properties, the samples were analysed with increasing the temperature from 25 to 550 °C in N₂ and from 550 to 700 °C in air at a rate of 10 °C min⁻¹ using a thermogravimetric analyser (TGA/DSC 1, Mettler-Toledo). CO₂ sorption experiments of composites were performed on the same

TGA/DSC 1. Firstly, the temperature of the furnace increased from ambient temperature to 90 °C and kept at 90 °C under pure N₂ (60 ml min⁻¹) for 30min to remove the adsorbed CO₂ and moisture. Subsequently, the gas is changed to 15 % CO₂/85 % N₂ (60 ml min⁻¹) to carry out the CO₂ adsorption process at 90°C for 30min. The temperature range was changed between 25 to 120 °C to investigate the effect of temperature on the cycle performance of the composites.

Tables

Table S1. CO₂ sorption capacity of functionalised amine mesoporous silica.

Sorbents	CO ₂ capacity (mmol g ⁻¹)	Testing conditions (Temp, P _{CO2})	Ref
2D/3D graphene SBA-15 (TEPA 80wt%)	5.45	90 °C, 0.15 bar	In this work
PEI graphene mesoporous silica sheet	3.89	75 °C, 1 bar	1
Triamine MCM-41	2.05	25 °C, 0.05 bar	2
PEI mesoporous silica nanotube	2.75	85 °C, 0.6 bar	3
3-Aminopropyl SBA-15	0.45	30 °C, 0.1 bar	4
APTES grafted KIT-6	1.56	30 °C, 1 bar	5
3-trimethoxysilylpropyl diethyltriamine (TA) SBA-15	3.5	40 °C, 0.15 bar	6
APTS and TEPA modified MCM-41	3.5	75 °C, 1 bar	7
Triamine SBA-15	1.88	25 °C, 0.05 bar	8
Pentaethylenehexamine (PEHA) KIT-6	4.18	105 °C, 1 bar	9
PEI SBA-15	3.18	75 °C, 0.15 bar	10
Amine-grafted SBA-15	1.6	25 °C, 0.15 bar	11

Table S2. Heat of sorption for amine functionalised silicas at maximum CO₂ sorption capacity.

Sorbents	Heat of sorption (kJ mol ⁻¹)	CO ₂ capacity (mmol g ⁻¹)	Ref
2D/3D hybrid sorbent (TEPA 30wt%)	40	2.5	In this work
2D/3D hybrid sorbent (TEPA 50wt%)	49		
2D/3D hybrid sorbent (TEPA 70wt%)	49		
2D/3D hybrid sorbent (TEPA 80wt%)	57		
2D/3D hybrid sorbent (TEPA 80wt%)	57		
Amine-Grafted SBA-15	70	1.1	12
Diamine SBA-15	48	0.79	13

Aminopropyl silica gel	90	0.8	14
Poly(ethylenimine) CARiACT G10 silica	50	2.9	15
APS mesoporous MSU-H silica	78	0.7	17
Aminopropyl mesoporous silica	60	1.59	18

Figures

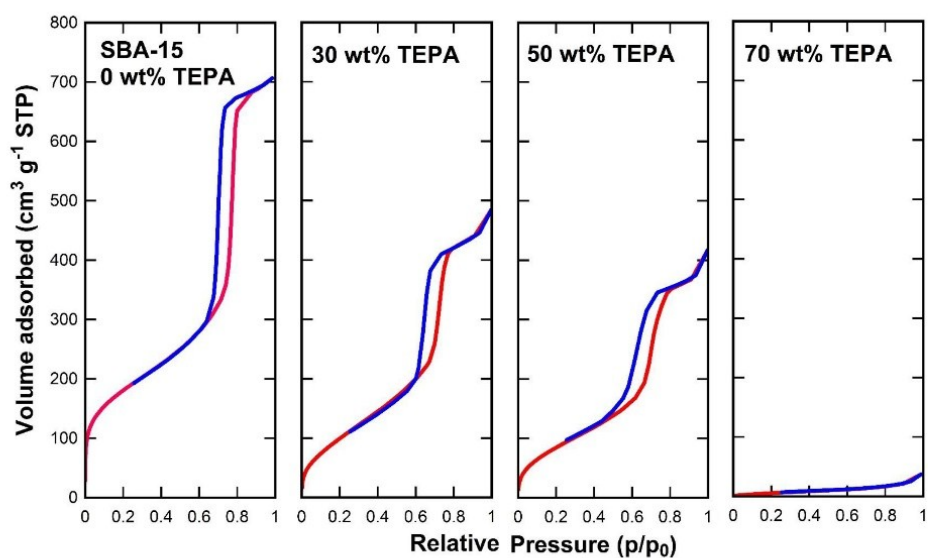
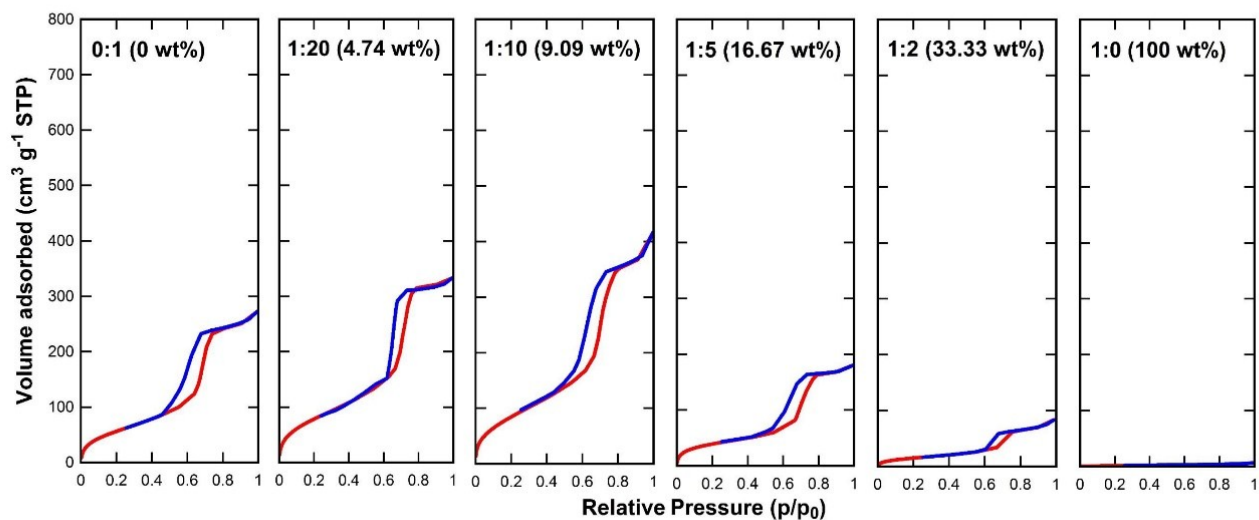


Fig. S1. N₂ sorption isotherms for sorbents with various graphene to SBA-15 ratio (1:0-0:1) and TEPA content (0-70 wt %) and SBA-15 loaded with TEPA (0-70 wt%) only. Adsorption (red line) and desorption (blue line).

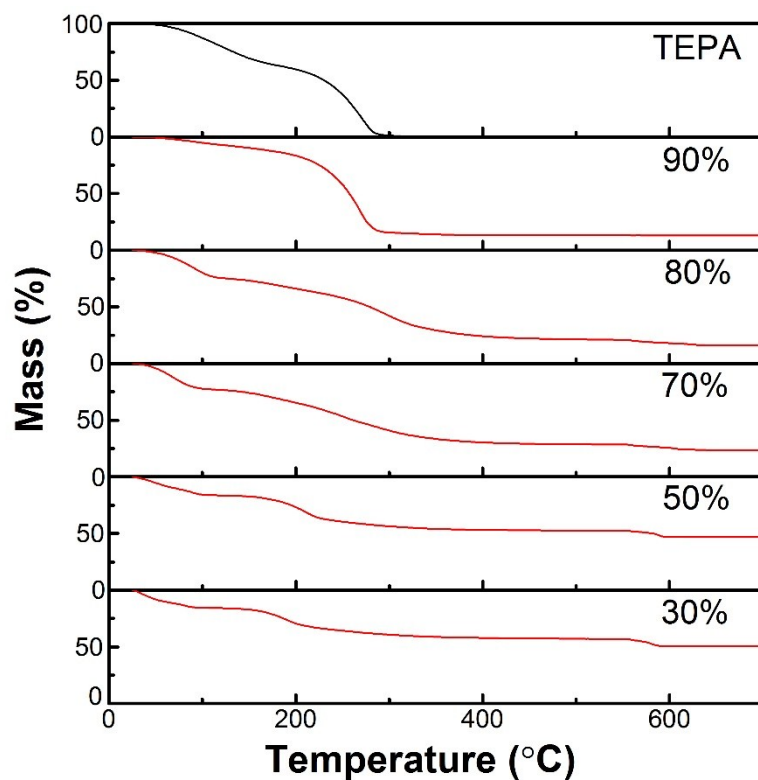


Fig. S2. TGA mass curves for 2D/3D graphene/SBA-15 (1:10 or 9.1 wt%) loaded with TEPA.

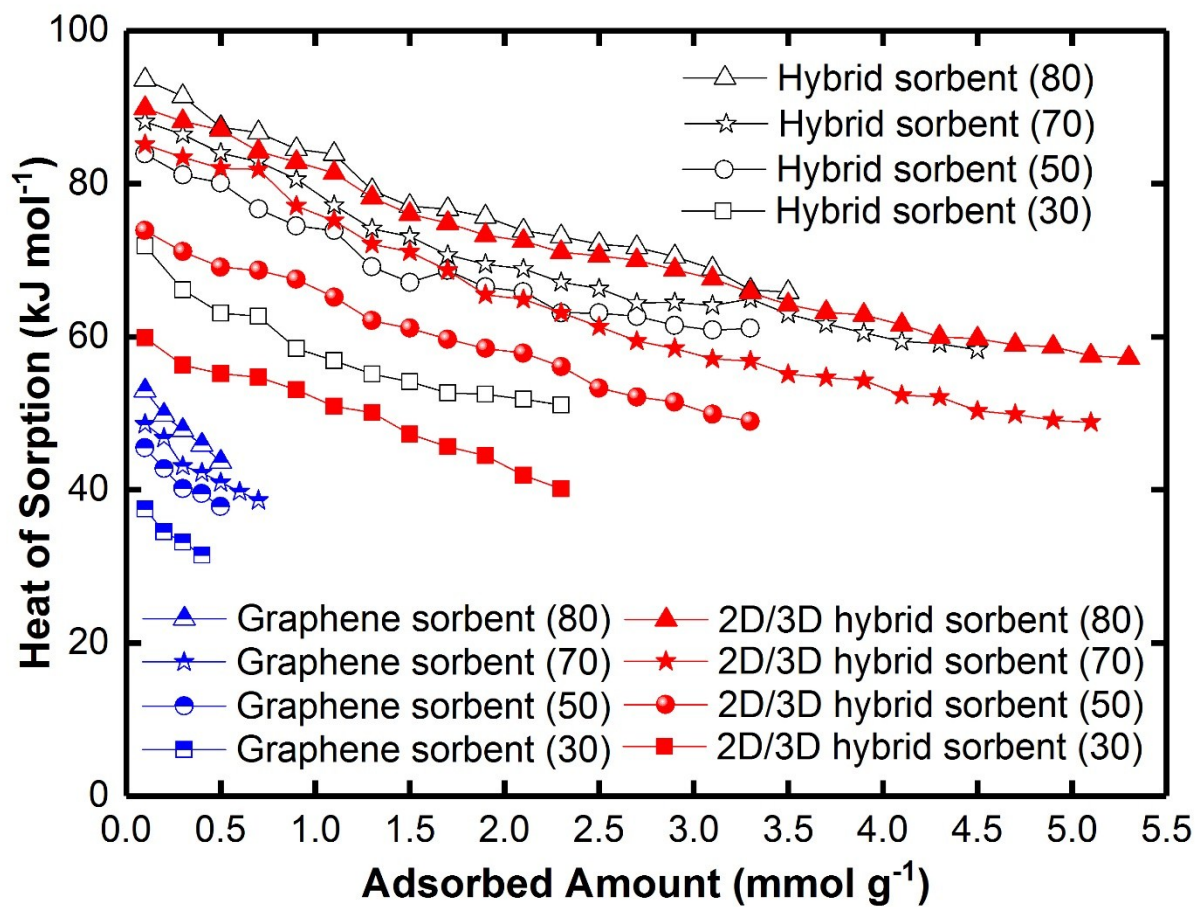


Fig. S3. CO₂ heat of sorption for various sorbents.

References

1. S. Yang, L. Zhan, X. Xu, Y. Wang, L. Ling and X. Feng, *Adv. Mater.* 2013, 25, 2130–2134.
2. Y. Belmabkhout and A. Sayari, *Adsorption*, 2009, 15, 318-328.
3. M. Niu, H. Yang, X. Zhang, Y. Wang and A. Tang, *ACS Appl. Surf. Interfac.* 2016, 8, 17312-17320.
4. M. A. Alkhabbaz, P. Bollini, G. S. Foo, C. Sievers and C. W. Jones, *J. Am. Chem. Soc.* 2014, 136, 13170-13173.
5. R. Kishor and A. K. Ghoshal, *Chem. Eng. J.* 2015, 262, 882-890.
6. K. Hori, T. Higuchi, Y. Aoki, M. Miyamoto, Y. Oumi, K. Yogo and S. Uemiya, *Microporous Mesoporous Mater.* 2017, 246, 158-165.
7. X. Wang, L. Chen and Q. Guo, *Chem. Eng. J.* 2015, 260, 573-581.
8. M. Jahandar Lashaki, H. Ziaei-Azad and A. Sayari, *ChemSusChem*, 2017.
9. R. Kishor and A. K. Ghoshal, *Energy Fuels*, 2016, 30, 9635-9644.
10. X. Ma, X. Wang and C. Song, *J. Am. Chem. Soc.* 2009, 131, 5777-5783.
11. L. Wang and R. T. Yang, *J. Phys. Chem. C* 2011, 115, 21264-21272.
12. L. Wang and R. T. Yang, *J. Phys. Chem. C* 2011, 115, 21264-21272.
13. R. A. Khatri, S. S. Chuang, Y. Soong and M. Gray, *Ind. Eng. Chem. Res.* 2005, 44, 3702-3708.
14. C. Knöfel, J. Descarpentries, A. Benzaouia, V. Zelenák, S. Mornet, P. Llewellyn and V. Hornebecq, *Microporous and Mesoporous Materials*, 2007, 99, 79-85.
15. A. D. Ebner, M. Gray, N. Chisholm, Q. Black, D. Mumford, M. A. Nicholson and J. A. Ritter, *Ind. Eng. Chem. Res.* 2011, 50, 5634-5641.
16. T. Watabe and K. Yogo, *Sep. Purif. Technol.* 2013, 120, 20-23.
17. G. P. Knowles, J. V. Graham, S. W. Delaney and A. L. Chaffee, *Fuel Proc. Technol.* 2005, 86, 1435-1448.