Nanostructured Carbon Networks as Electrically-Heatable Support for Layered Double Hydroxides

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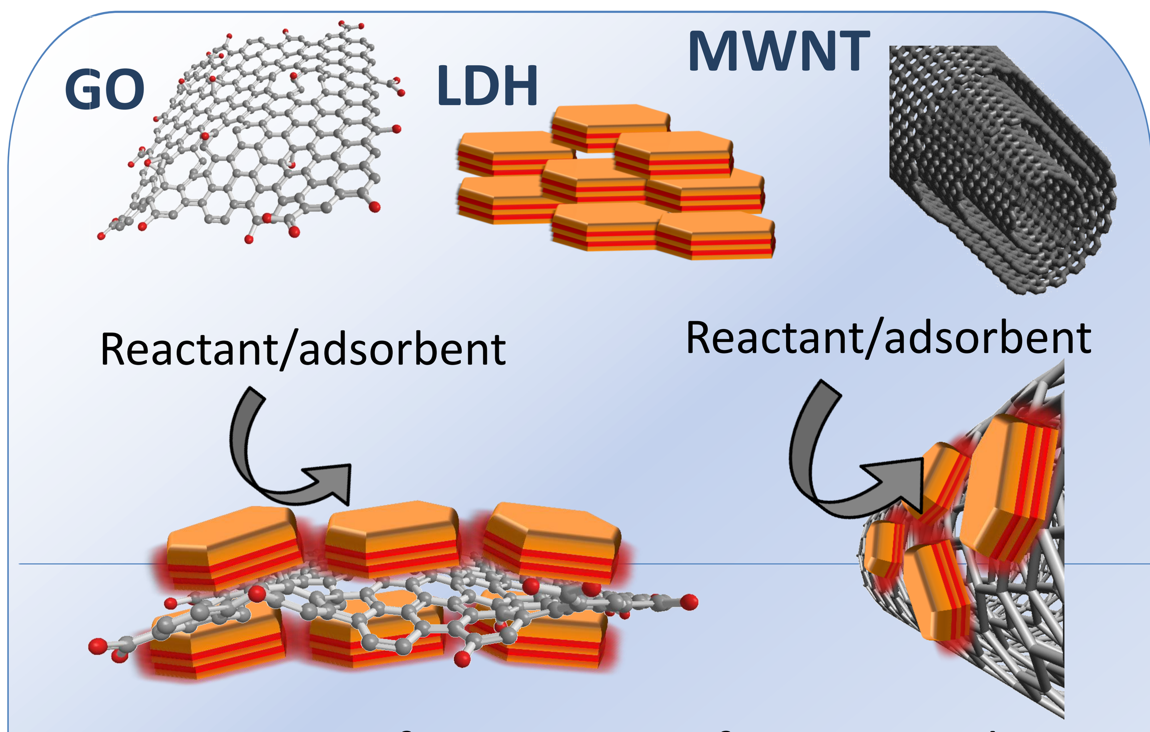
We explore the use of carbon nanotube (CNT) and graphene oxide (GO) networks, as porous support frameworks for layered double hydroxides (LDHs). CO_2 adsorption studies on MgAl LDHs have shown that nanocarbon-supported LDHs showed significantly improved properties. [1,2] In extension of this work, here, we study supporting a new class of metal-substituted LDHs (CuAl and CoAl LDHs) on GO and the performance of the resulting LDH/nanocarbon hybrids in heterogeneous catalysis. Further, we investigate how the unique thermal and electrical properties of the graphitic framework can be utilised for direct electrical heating. As a model system, we investigate the Joule-heating characteristics of a low-density, reduced graphene oxide (rGO) aerogel.

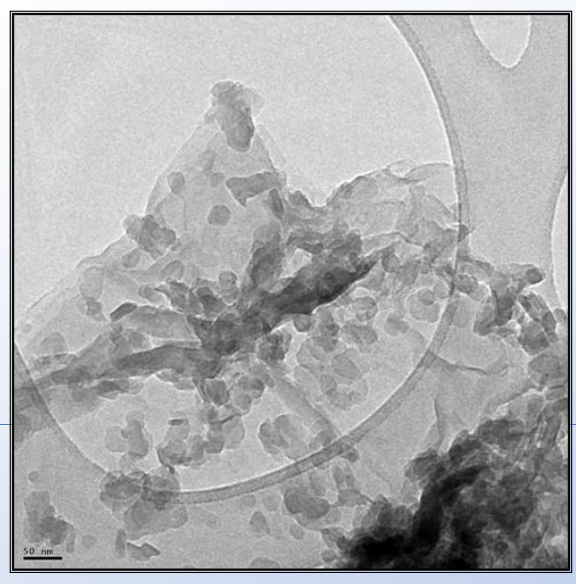
Nanocarbons as LDH supports

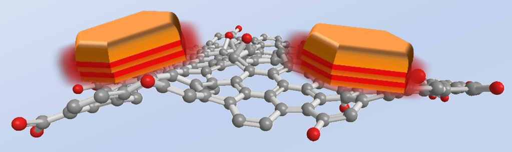


Improve performance of nanocarbon-supported LDHs in applications, such as CO_2 capture, catalysis and pollutant adsorption

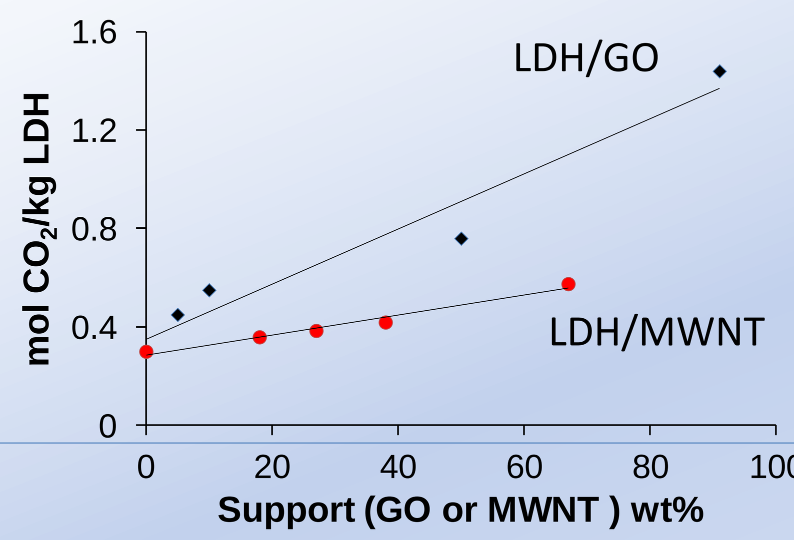
MgAl LDH/nanocarbon hydbrids for CO_2 adsorption [1,2]

MgAl LDH/GO hybrid

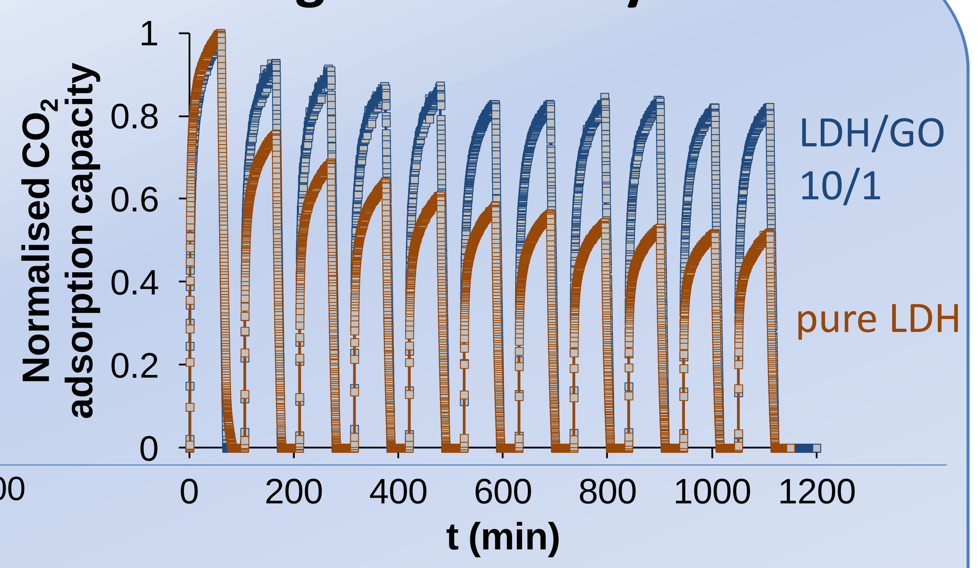




CO_2 adsorption capacity



Regeneration cycles

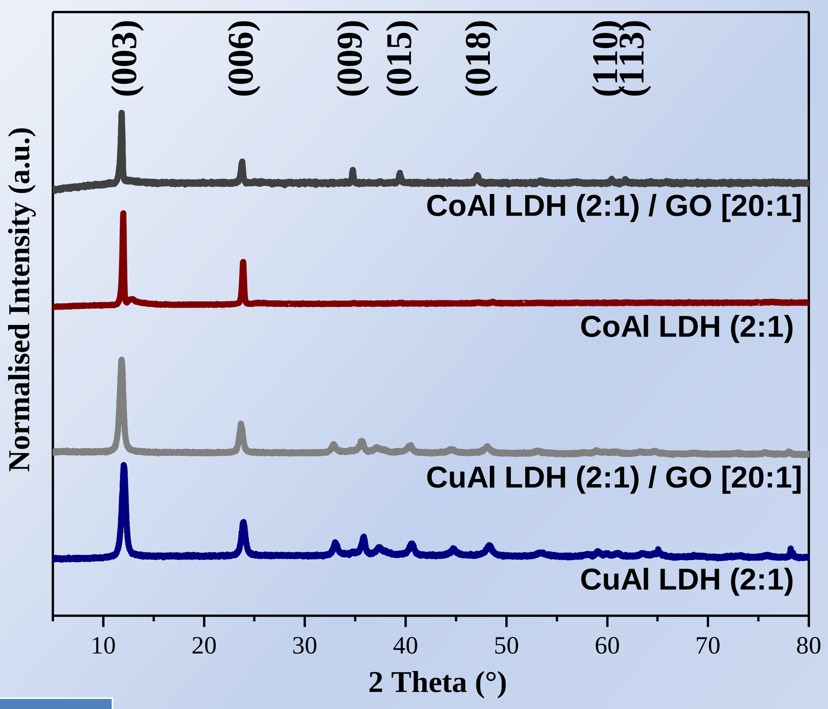


- Nanocarbon/MgAl LDH hybrids with different nanocarbon loadings were obtained via straightforward coprecipitation synthesis
- Supporting MgAl LDHs on nanocarbons results in increased CO_2 adsorption capacity and enhanced multicyling stability

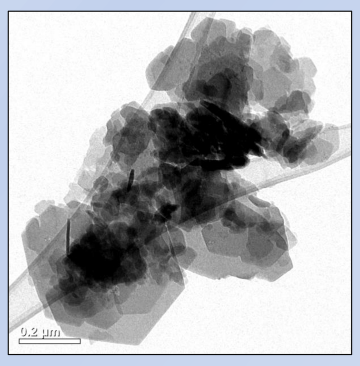
CoAl LDH/GO and CuAl LDH/GO for catalysis

CoAl/GO and CuAl LDH/GO synthesis

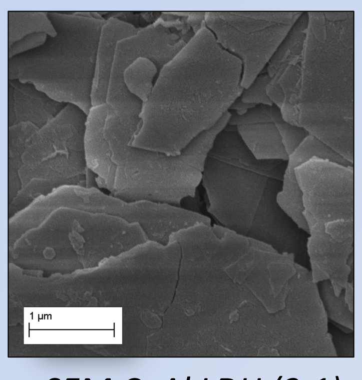
- Synthesis of **CuAl LDH (2:1)**, with and without GO support, via coprecipitation of $Co(NO_3)_2$ and $Al(NO_3)_3$ at constant pH of 10
- Synthesis of **CoAl LDH (2:1)**, with and without GO support, via reflux of aqueous solution of $CoCl_2$ and $AlCl_3$ in the presence of urea under nitrogen



Sample	TGA	BET		XRD
	GO content (wt%)	S_{BET} (m^2/g)	V_{Meso} (cm^3/g)	$D_{(003)}$ (nm)
CuAl(2:1) LDH	0	28.0	0.25	18.3
CuAl(2:1) LDH/GO	3	44.3	0.25	19.5
CoAl(2:1) LDH	0	9.9	0.10	43.8
CoAl(2:1) LDH/ GO	3	16.9	0.09	40.1



TEM CuAl LDH (2:1)

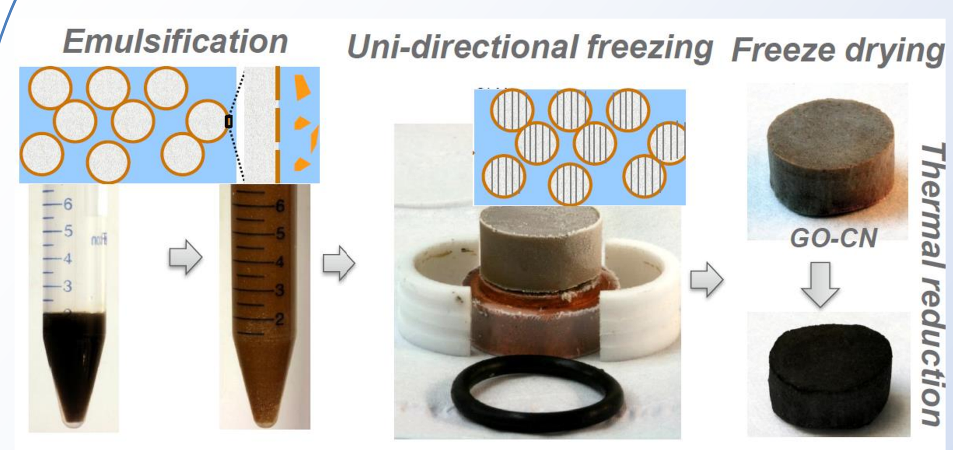


SEM CoAl LDH (2:1)

CoAl/GO and CuAl LDH/GO for catalysis

Electrically-heatable nanocarbon aerogels

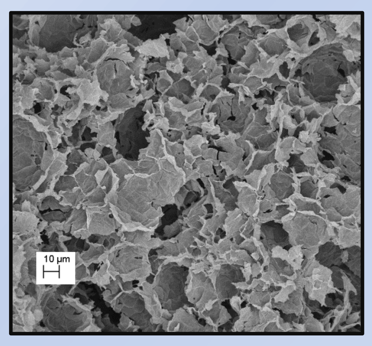
Fabrication of reduced graphene oxide (rGO) aerogel



Fabrication of rGO aerogel via emulsion templating [3]

rGO aerogel properties

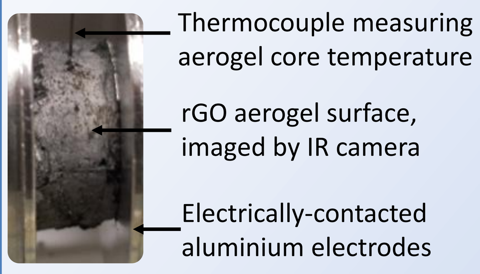
- monolith with defined shape
- ρ = 12 mg/cm^3
- σ = 0.64 S/cm
- open, cellular microstructure

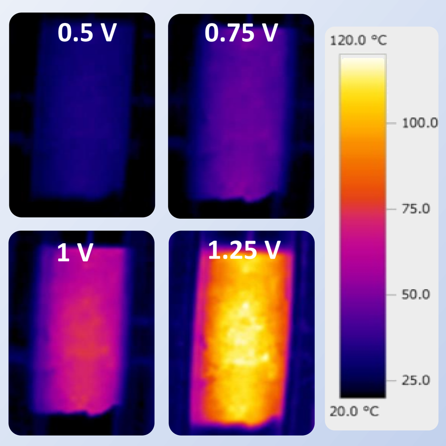


SEM rGO aerogel

Joule heating characterisation of rGO aerogel

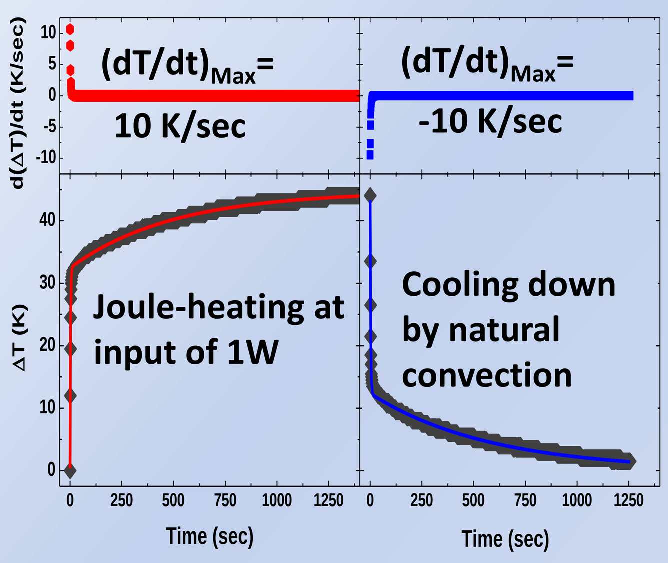
Aerogel Joule-Heating





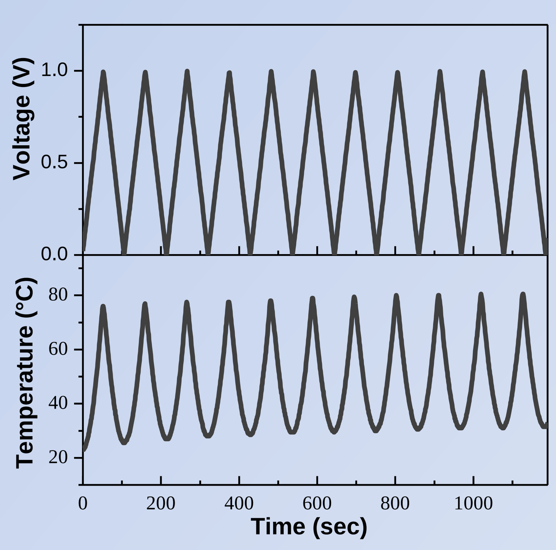
Thermal imaging of rGO surface

Heating and cooling kinetics

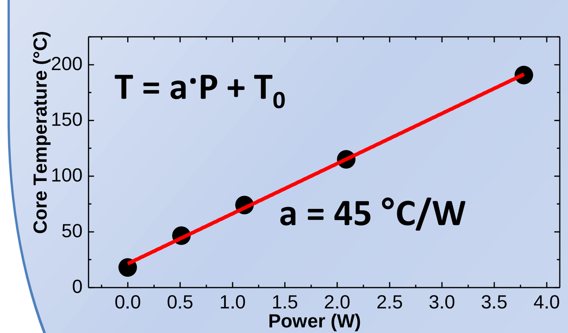


Change of rGO aerogel core temperature upon Joule-heating and cooling down.

Joule-heating Cycling



Joule-heating cycling between 0 and 750mV at 25mV/sec.



Monolith core temperature as function of power input

- Uniform Joule heating of rGO aerogel monolith up to temperatures of 200°C
- Fast adiabetic heating and cooling regimes (heating and cooling rates up to 10 K/min) followed by slower equilibration regimes
- Voltage cycling within the adiabetic time regime allows straightforward, repeatable control of the aerogel temperature

Conclusions

- Pure and nanocarbon-supported MgAl LDH, CoAl and CuAl LDH materials were successfully synthesised via various copreciptation approaches
- Nanocarbon-supported LDH particles showed improved performance in terms of activity and cyclabilty compared to the unsupported materials, due to improved particle dispersion, enhanced stabilisation against particle sintering and improved accessibility of active surface sites
- Fast and repeatable Joule heating of porous, low-density rGO aerogel was demonstrated which might be utilised for uniform, energy-efficient temperature control in gas-phase catalysis or for thermal cycling and regeneration of LDH solid adsorbers

References

[1] A. Garcia-Gallastegui, et al. *J. Mater. Chem.* **2012**, 22, 13932.
[2] A. Garcia-Gallastegui, et al. *Chem. Mater.* **2012**, 24, 4531.
[3] S. Barg et al. *Nature Comm.*, **2014**, submitted.

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