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De Marco, M, Menzel, R, Bawaked, SM et al. (4 more authors) (2017) Hybrid effects in graphene oxide/carbon nanotube-supported Layered Double Hydroxides: Enhancing the CO₂ sorption properties. *Carbon*, 123. pp. 616-627. ISSN 0008-6223

<https://doi.org/10.1016/j.carbon.2017.07.094>

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PII: S0008-6223(17)30777-7

DOI: [10.1016/j.carbon.2017.07.094](https://doi.org/10.1016/j.carbon.2017.07.094)

Reference: CARBON 12260

To appear in: *Carbon*

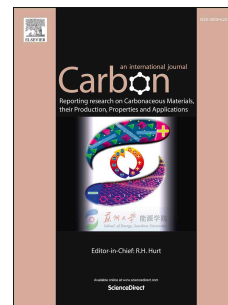
Received Date: 17 April 2017

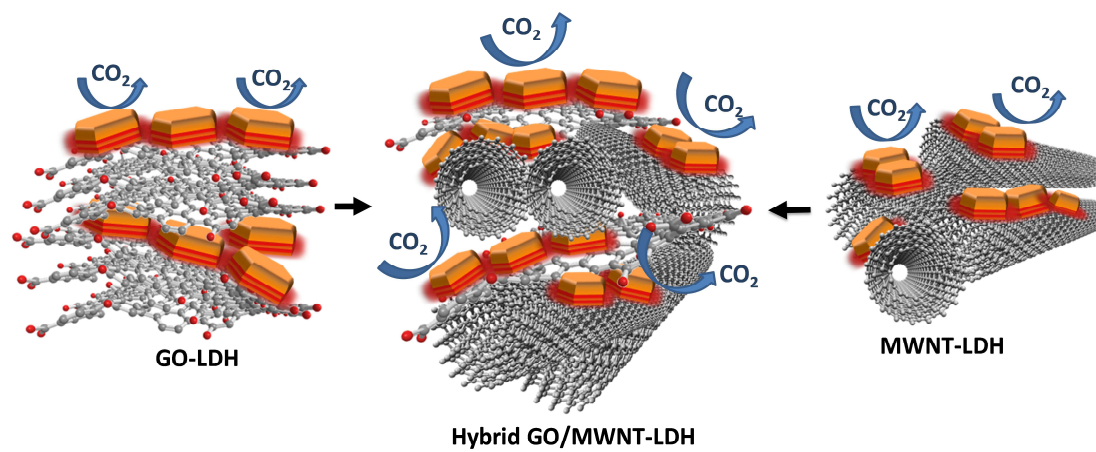
Revised Date: 29 July 2017

Accepted Date: 31 July 2017

Please cite this article as: M. De Marco, R. Menzel, S.M. Bawaked, M. Mokhtar, A.Y. Obaid, S.N. Basahel, M.S.P. Shaffer, Hybrid effects in graphene oxide/carbon nanotube-supported Layered Double Hydroxides: Enhancing the CO₂ sorption properties, *Carbon* (2017), doi: 10.1016/j.carbon.2017.07.094.

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ACCEPTED MANUSCRIPT

1 Hybrid Effects in Graphene Oxide/Carbon Nanotube-Supported Layered Double 2 Hydroxides: Enhancing the CO₂ Sorption Properties

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9

10 Graphene oxide (GO) and multi-walled carbon nanotubes (MWCNT) have been previously used
11 independently as active supports for Layered Double Hydroxides (LDH), and found to enhance the
12 intrinsic CO₂ sorption capacity of the adsorbents. However, the long-term stability of the materials
13 subjected to temperature-swing adsorption (TSA) cycles still requires improvement. In this contribution,
14 GO and MWCNT are hybridized to produce mixed substrates with improved surface area and
15 compatibility for the deposition of LDH platelets, compared to either phase alone. The incorporation of a
16 robust and thoroughly hybridized carbon network considerably enhances the thermal stability of
17 activated, promoted LDH over twenty cycles of gas adsorption-desorption (96% of retention of the
18 initial sorption capacity at the 20th cycle), dramatically reducing the sintering previously observed when
19 either GO or MWCNT were added separately. Detailed characterization of the morphology of the
20 supported LDH, at several stages of the multicycle adsorption process, shows that the initial morphology
21 of the adsorbents is more strongly retained when supported on the robust hybrid GO/MWCNT network;
22 the CO₂ adsorption performance correlates closely with the specific surface area of the adsorbents, with
23 both maximized at small loadings of a 1:1 ratio of GO:MWCNT substrate.

24 1. Introduction

25 Layered double hydroxides (LDH) are lamellar hydroxides of the family of hydrotalcites (HT), with
26 general formula $(M^{2+}_{1-x}M^{3+}_x(OH)_2)^{x+}(A^{m-}_{x/m}nH_2O)^{x-}$, where M^{2+} , M^{3+} and A^{m-} most commonly
27 represent Mg^{2+} , Al^{3+} and CO_3^{2-} respectively (Brucite), although many other compositions occur.¹
28 Brucite-like sheets of octahedrally-coordinated divalent cations (typically Mg^{2+}) undergo a partial
29 substitution by the trivalent cations (typically Al^{3+}), generating a net positive charge that is balanced by
30 the intercalated anions (typically CO_3^{2-}). The intrinsic properties of these compounds have stimulated

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31 interest in a diverse range of applications, including as catalysts (aldol condensation, epoxidations,
32 alkene isomerisations reactions, *etc.*),² biomedical vectors,^{3, 4} flame retardants,⁵ adsorbents⁶ and
33 nanocomposite reinforcements.⁷ In particular, the Mg/Al LDH family (with Mg:Al ratios of 2 and 3) has
34 been extensively studied in the past years, and recognised as an excellent composition for CO₂
35 adsorption applications.⁸ The gas adsorption properties are manifested after thermal treatment of the
36 material, that evolves into an active mixed metal oxide (MMO) form with finer particle size and
37 increased surface area compared to the original structure. The associated progressive dehydroxylation
38 and decarbonation of the structure generates the basic sites responsible for the subsequent (acid-base
39 type) interaction with the CO₂ molecules.⁹ Compared to known low temperature CO₂ solid adsorbents
40 (such as zeolites, activated carbons, and metal organic frameworks), thermally-activated LDH typically
41 manifest a lower intrinsic specific CO₂ adsorption capacity, but can operate at higher temperatures.¹⁰ On
42 the other hand, they manifest faster adsorption kinetics and much better regenerability than other high
43 temperature solid adsorbents (such as lithium zirconates and calcium oxides).¹¹ LDH are frequently
44 supported on high surface area substrates in order to improve adsorption capacity and stability over
45 prolonged use, aspects that still hamper practical industrial implementation.

46 Amongst the materials tested as supports in these applications, carbon nanostructures (CN), including
47 carbon nanofibers (CNF),¹² multi walled-carbon nanotubes (MWCNT)^{13, 14} and graphene oxide (GO),^{15,}
48 ¹⁶ have shown the most promise, particularly compared to more conventional systems based on alumina
49 or zeolites.^{17, 18} These carbon allotropes exhibit an intriguing combination of mechanical,^{19, 20} thermal,²¹
50 and electrical²² characteristics, as well as high aspect ratios and surface areas,²³ which make them
51 suitable for preparing robust, porous and high surface supporting networks.²⁴ Activated carbons are a
52 possible alternative high surface area substrate,^{25, 26} but tend to have relatively inaccessible slit
53 micropores that are readily blocked by LDH deposition.²⁷ The use of LDH/ nanocarbons composites has
54 been considered for a wide range of applications,^{28, 29} but here we focus on CO₂ sorption. Mg/Al LDH
55 platelets loaded dilutely on CNF (up to 90 wt% carbon), were reported to manifest an order of
56 magnitude increase in the CO₂ adsorption capacity compared to the unsupported counterparts.¹²
57 Oxidized MWCNT were subsequently adopted as supports,¹³ where the acidic surface was used to drive
58 nucleation of the positively-charged LDH platelets through electrostatic interactions; once activated,
59 these MWCNT-LDH exhibited significant enhancement of the first-contact gas adsorption capacity
60 compared to the unsupported material. In addition, an improvement in the multicycle stability was
61 observed over twenty continuous cycles of gas adsorption-desorption.¹³ The improvements were

62 attributed to a reduction in the LDH particle size and an associated increase in the basic site
63 concentration available for gas adsorption.³⁰ Subsequently, 2 - 30 wt% of a GO substrate was found to
64 be even more effective than the other CN for improving the CO₂ adsorption performance of LDH;^{16, 31}
65 the improvement was attributed to the two-dimensional geometric compatibility of the GO nanosheets
66 with LDH platelets. Small loadings of GO were found to be most promising, with benefits plateauing at
67 higher concentrations due to apparent restacking of the carbon sheets. However, it is not clear whether
68 the GO only promotes multicycle stability or also first-contact adsorption capacity.^{16, 32} In addition to the
69 use of a support, the CO₂ adsorption capacity of LDH can be improved by doping with alkali metals.^{33, 34}
70 The benefits of alkali metal promotion have been confirmed with both CNF-LDH³⁴ and GO-LDH¹⁶
71 materials; in general, residual sodium from the LDH synthesis may remain in the LDH, resulting in a
72 significant enhancement of the first-contact adsorption capacity.¹⁶ Whilst the literature identifies
73 consistent trends for the adsorption capacity of CN-LDH hybrids, the absolute capacities vary due to the
74 specific adsorption conditions adopted, including adsorption temperature and pressure, presence of
75 water, concentration of carbon support and degree of doping.

76 Overall, the multicycle stability of CN-LDH still has considerable scope for improvement; for instance,
77 for the best materials reported so far (GO-LDH), the loss of CO₂ adsorption performance over 20 cycles
78 of gas adsorption-desorption under dry conditions remained a significant 15 - 40% (though improved
79 compared to the 50 - 60% loss for pure LDH).^{16, 31} Despite their promise, neither MWCNT nor GO are
80 ideal supports: MWCNT, though offering a mechanically strong network for LDH deposition, require
81 higher loadings to match the performance improvement provided by GO, as the surface area is not as
82 intrinsically high, and the geometry less well matched. Increased CN loading negatively impacts the
83 overall cost and weight of the final sorbent. On the other hand, GO alone has poor network forming
84 ability, limiting benefits even at modest carbon loadings due to restacking of the sheets.

85 Recently, hybrid GO/MWCNT systems have been reported to exhibit interesting synergistic effects in
86 certain applications.³⁵⁻³⁸ Most studies focus on improvements in the properties of electrochemical double
87 layer (EDLC) supercapacitors using hybrid GO/CNT electrodes, compared to carbon nanotubes (CNTs)
88 and GO used independently.^{39, 40} Hybrid GO/CNT electrodes have also been found to offer superior drug
89 and gas sensing performance.⁴¹ GO/CNT hybrids are compatible chemically due to the π - π attractions
90 between basal planes and the hydrogen bonding between acidic functional groups.⁴⁰ Geometrically,
91 CNTs act as spacers between the graphene sheets, preventing restacking and agglomeration. The
92 enhanced overall surface area of the structure facilitates the access of electrolytes (for electrochemical

93 applications) and may improve the transport of gases (in adsorption applications). GO can help to form
94 intimately mixed hybrid structures by acting as a dispersing agent for unoxidized-SWCNT⁴² or
95 MWCNT⁴³.

96 In principle, hybridized GO/MWCNT constructs are appealing as LDH supports, but have not yet been
97 thoroughly studied because of the complexity of the resulting three-phase mixture (GO/MWCNT/LDH),
98 although some recent reports have indicated promising potential for the use of hybrid graphene/nanotube
99 systems to support LDH for catalytic (NiFe-LDHs)⁴⁴ or electrochemical (NiAl-LDH)⁴⁵ applications. Our
100 aim was to explore GO/MWCNT hybrids in more detail, and specifically in the context of CO₂ sorption,
101 in order to overcome the limitations identified for LDH supported on either GO or oxidized MWCNT,
102 separately. We promoted the material with a small amount (5 wt%) of potassium to improve the absolute
103 performance and avoid variations due to low loadings of adventitious alkali metal. The materials were
104 tested for CO₂ adsorption properties, and were fully characterized to understand the deactivation
105 mechanism over several temperature-swing (TS) adsorption-desorption cycles.

106 2. Experimental

107 2.1 Materials

108 For this work, CVD-grown, multi-walled carbon nanotubes (MWCNT) were purchased from ARKEMA
109 (Graphistrength), with an average diameter of 10 - 15 nm. Graphene oxide (GO) was purchased as single
110 layer water dispersion of 10 mg mL⁻¹ (flake size 0.5 - 2.0 μm and size 0.6 - 1.2 nm) from ACS Materials.
111 Mg(NO₃)₂·6H₂O (99%) and Al(NO₃)₃·9H₂O (98%) were purchased from Sigma-Aldrich; NaOH, H₂SO₄
112 (95%), HNO₃ (65%), Na₂CO₃ and K₂CO₃ were purchased from VWR international. Polycarbonate (PC)
113 membranes were purchased from Millipore (HTTP Isopore membrane, pores diameter 0.45 μm).

114 2.2 Oxidation of MWCNT

115 In a typical oxidation procedure, 17.5 mL of concentrated H₂SO₄/HNO₃ (3:1 mixture) were added for
116 every 500 mg of MWCNT. The mixture was stirred and refluxed for 30 min at 120 °C. After cooling,
117 MWCNTs were vacuum-filtered over a 0.45 μm PC membrane, and base-washed with 1 L of
118 0.01 M NaOH. The base washing procedure assists the removal of molecular oxidation debris (also
119 known as carboxyated carbonaceous fragments, which are thought to be related to humic or fulvic

120 acids),⁴⁶ produced during the oxidation treatment.^{47, 48} In this work, only oxidized MWCNT were used,
121 and will be referred simply as to 'MWCNT'.

122 2.3 Synthesis of Mg/Al LDH

123 LDH platelets were synthesized by co-precipitation method; typically, aqueous solutions of
124 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 and 0.05 mol respectively) were mixed and co-precipitated
125 onto a basic solution of NaOH and Na_2CO_3 (0.35 mmol and 0.09 mmol respectively). The resulting
126 white suspension was heated for 24 hours at 60 °C under vigorous stirring. The precipitate was filtered
127 using a PC membrane and washed with 1 L of water at 60 °C, in order to completely remove residual
128 sodium. The samples were then dried for 24 - 48 hours at 100 °C.

129 2.4 Preparation of the CN supports

130 Aqueous solutions (1 mg mL^{-1}) of GO and MWCNT were mixed at 300 rpm for 4 hours at GO/MWCNT
131 ratios of 1:0 (pure GO), 10:1, 3:1, 1:1, 1:3, 1:5 and 0:1 (pure MWCNT). The mixed solutions were then
132 filtered on PC membrane until a wet carbon paste was obtained, and used directly for LDH deposition.

133 2.5 Deposition of LDH on CN substrates

134 MWCNT-supported-LDH (MWCNT-LDH) and GO-supported LDH (GO-LDH) were prepared using
135 the following procedure. 100 mL of a 1 mg mL^{-1} solution of either MWCNT or GO were vacuum-
136 filtered over a $0.45 \mu\text{m}$ PC membrane until the desired low volume of carbon solution was obtained. The
137 MWCNT- (GO-) wet paste was then transferred to a 100 mL round bottom flask and 9.9 mmol of NaOH
138 and 2.5 mmol of Na_2CO_3 added. Subsequently, 1.4 mL of a salt solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and
139 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.8 mmol and 1.4 mmol respectively) was added. The resulting black suspension was
140 aged at 60 °C for 12 hours, under vigorous stirring. The sample was filtered and dried as explained
141 above for the preparation of unsupported LDH.

142 The same procedure was applied for the preparation of hybrid GO/MWCNT-LDH materials. In order to
143 achieve a homogeneous hybridization of MWCNT and GO, the corresponding aqueous solutions were
144 mixed in the desired amounts (typically for a total volume of 200 mL) for 4 hours at room temperature.
145 The mixed solution was then filtered as described previously, and transferred to a round-bottom flask for
146 the co-precipitation of the Mg and Al salts, under basic conditions. The name of the samples includes: 1)

147 type of substrate (GO, MWCNT or hybrid GO/MWCNT); 2) numbers in brackets, indicating the relative
148 proportion of GO and MWCNT; 3) subscript numbers, indicating the weight percentage (wt%) of carbon
149 substrate (GO, MWCNT or GO+MWCNT) in the sample. For example, GO/MWCNT(1:1)₅₀-LDH
150 refers to a material containing 50 wt% of a hybrid carbon substrate constituted of GO and MWCNT
151 mixed in a ratio 1:1.

152 CN-LDH samples were doped with an aqueous solution of K₂CO₃ by a modified incipient wetness
153 procedure. 1.5 mL of aqueous K₂CO₃ (0.48 M, 5% to LDH mass) were added to a fixed 100 mg of LDH
154 and stirred for 4 hours before drying in vacuum oven at 100 °C for 24 hours.

155 *2.6 Calcination of CN-LDH*

156 Prior to CO₂ adsorption measurements, CN-LDH were calcined in a tubular quartz reactor (5 cm internal
157 diameter), for 4 hours at 400 °C, under a 100 mL min⁻¹ of nitrogen flow. Freshly calcined samples were
158 submitted immediately to CO₂ adsorption measurements, or used within a day to avoid structure
159 reconstruction driven by spontaneous adsorption of atmospheric moisture and CO₂. Further conditioning
160 (2 h, 400 °C, 20 mL min⁻¹ of nitrogen flow) occurred in the TGA before measurement.

161 *2.7 CO₂ adsorption measurements*

162 Multicycle CO₂ adsorption measurements were performed within a TGA (Perkin Elmer 4000) equipped
163 with a CO₂ gas line. The sample was heated from 25 ° to 400 °C at 10 °C min⁻¹ under a nitrogen flow of
164 60 mL min⁻¹, and held for 2 hours. Temperature was then decreased to 300 °C and the gas feed was
165 switched to a premixed gas of 20% CO₂/N₂ and held for 1 hour. The multicycle stability of the
166 adsorbents was assessed by performing repeated steps of CO₂ adsorption at 300 °C for 1 hour and
167 desorption at 400 °C for 30 minutes, under nitrogen. The flow rate was kept constant at 60 mL min⁻¹
168 throughout the experiment. Adsorption capacities were calculated from the change in mass of the
169 adsorbents before and after the adsorption step. This response was corrected by subtracting the
170 equivalent data from a blank empty TGA crucible, in order to take into account mass fluctuations due to
171 change in gas density and viscosity at the feed switch and throughout the adsorption. Under the
172 operating conditions, the fluctuation of the blank was negligible.

173 *2.5 Measurements and characterization*

174 Thermogravimetric analysis (TGA) was performed using a METTLER TGA/DSC1 machine (Mettler-
175 Toledo International, Beaumont Leys Leicester, UK). Typically, 2 mg of sample were first dried at
176 100°C under nitrogen for 20 min and then heated from 100° to 800° at 10°C min⁻¹ in 20 mL min⁻¹ of air.
177 X-ray diffraction (XRD) was carried out with a PANalytical X'Pert Pro Multi Purpose Diffractometer
178 (Cu K_α radiation) in reflection mode, with angle (2θ) varying between 5 ° and 80 °. Transmission
179 electron microscopy (TEM) images were obtained on a JEOL 2010, operating at 200 kV. Samples were
180 prepared by dispersion in isopropanol (0.01 mg mL⁻¹ of CN-LDH, and allowing a drop to dry onto a
181 holey carbon copper grid (300 mesh, Agar Scientific). Scanning Electron Microscopy (SEM) images
182 were collected using a Gemini 1525 FEGSEM, fitted with an Oxford Instruments INCA energy
183 dispersive X-ray spectrometer (EDS). Raman spectroscopic characterisation was carried out on a
184 Renishaw InVia Confocal Raman microscope (Renishaw plc, Wotton-under-Edge, UK). The system
185 calibration was performed using an integrated silicon wafer prior to measurement; Raman spectra were
186 obtained using a green laser (wavelength 532 nm, intensity 1 %, 10 seconds) in edge mode (2400
187 lines mm⁻¹ diffraction grating); for the determination of the I_D/I_G ratio, Raman mapping was performed
188 in StreamLine acquisition mode at *ca.* 10 μm intervals on an area of *ca.* 500 μm² for an acquisition of
189 1600 independent spectra between 1220 – 2700 cm⁻¹, using a green laser (wavelength 532 nm, 2.33 eV)
190 1% laser power, 10 s of exposure. The elemental composition of the adsorbents was measured by
191 inductively coupled plasma-optical emission spectroscopy (ICP-AES) in a PerkinElmer Optima
192 2000 DV apparatus. The carbon component of CN-LDH samples was combusted in TGA; the metal
193 residue was dissolved in 5 mL of *aqua regia* for 24 hours. 2 mL of the digested solution were diluted to
194 20 mL in deionized water, and submitted to analysis. Nitrogen adsorption and desorption isotherms were
195 measured using a Micromeritics Tristar 3000 apparatus on 50 mg of CN-LDH samples, dried at 100°C
196 and held overnight under N₂ prior to adsorption measurements. Specific surface areas were calculated
197 according to the Brunauer–Emmett–Teller (BET) equation. The pore-size distribution of the samples
198 was calculated from desorption branch using the Barrett–Joyner–Halenda (BJH) method.

199 3. Results and discussion

200 Initially, the hybrid substrates were analyzed without depositing LDH platelets; mixed substrates were
201 prepared at different GO/MWCNT ratios of 10:1, 3:1, 1:1, 1:3, 1:5, and compared to the pure GO (1:0)
202 and MWCNT (0:1) forms. In the XRD patterns (Fig.1a), the intensities of GO (11.3 °) and MWCNT
203 graphitic carbon peaks (25.8 °) reflect their relative proportions in the substrates. The mean measured

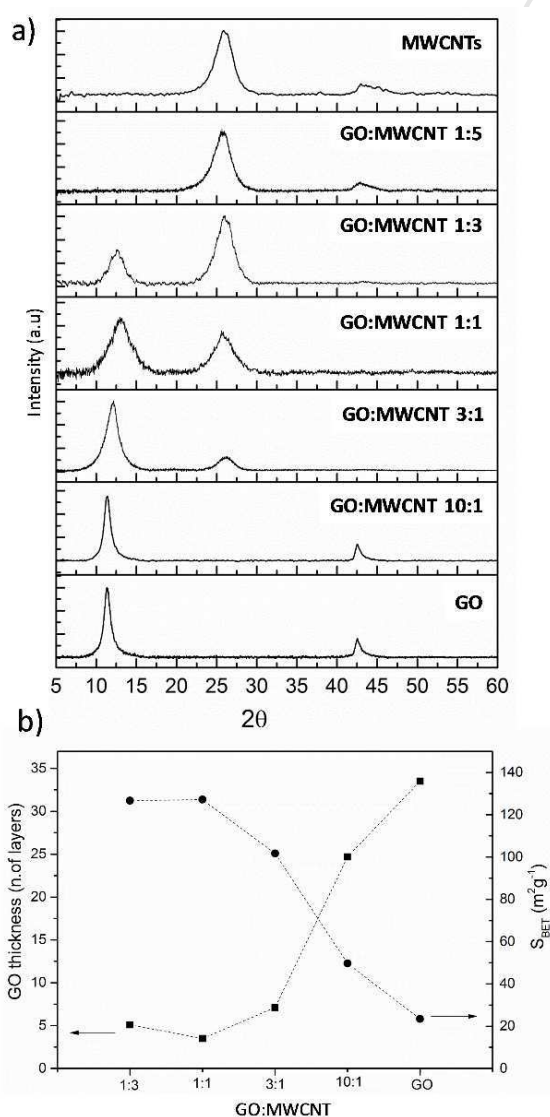
204 thickness of the dried GO stacks was calculated from the width of the interlayer reflection using the
205 Scherrer equation.⁴⁹ Although hybrid GO/CNT materials have been recently studied,^{42, 50, 51} the degree
206 of GO delamination, at different GO/CNT ratios, has not been reported systematically. The pure GO
207 sample restacks on drying to an average 33 layers; however, on hybridizing with MWCNT at an
208 optimum 1:1 ratio, the average number reduces to only 3 - 4 layers (Table 1). Hybrids with similar
209 degree of GO layering (4 - 32 sheets) have been previously prepared by controlled LbL assembly,⁵¹
210 however, the level of exfoliation reached in the present work is attributed only to the spontaneous
211 interactions between the GO and MWCNT. This improved exfoliation, retained within the dried hybrids,
212 is reflected in the specific surface areas calculated from N₂ adsorption-desorption measurements (Fig.1b

213 and Table 1). The pure MWCNT have a higher surface area than the pure GO, as they are less prone to
 214 restacking/repacking; however, their intrinsic potential surface area is lower due to the multiple shells
 215 within their structure.

216 **Fig.1.** a) XRD patterns of GO/MWCNT substrates at different compositions; b) correlation between GO
 217 exfoliation (number of layers, left axis) and specific surface area ($\text{m}^2 \text{g}^{-1}$, right axis).

218 **Table 1**

219 XRD calculated thickness of GO stacks, interlayer spacing and nuber of layers. Overall specific surface areas of



220 GO/MWCNT hybrid samples.

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<i>GO:MWCNT</i>	<i>GO (002) (°)</i>	<i>GO stack thickness (± 0.1 nm)</i>	<i>Interlayer spacing (nm)</i>	<i>GO layers (± 0.1)</i>	<i>S_{BET} (m² g⁻¹)</i>
MWCNT	/	/	/	/	90.34 ± 0.43
1:5	n/a	/	/	/	73.71 ± 0.19
1:3	12.67	3.6	0.70	5.1	126.63 ± 0.72
1:1	12.95	2.4	0.70	3.5	127.16 ± 0.51
3:1	12.16	4.9	0.70	7.1	101.72 ± 0.32
10:1	11.38	19.2	0.78	24.7	49.66 ± 0.19
GO	11.33	26.1	0.78	33.5	23.41 ± 0.59

The

addition of a proportion of the increasingly exfoliated GO raises the average surface area, reaching a maximum for the 1:1 hybrid (127 m² g⁻¹). The synergistic improvement in surface area for mixed materials can be attributed to the MWCNT acting as spacers for the GO sheets,³⁹ forming a network that evenly supports the high surface area exfoliated GO layers (SEM, Fig.S1b). Similar results have been observed previously for GO/MWCNT hybrids prepared with mixing approaches,⁵² although the surface areas reported are generally lower due to post-processing reduction of GO, for use in electrodes. As a control, solid GO powder was added into a MWNCT suspension to produce a phase separated network, with a distinctly different appearance (Fig.S2). TGA traces of the mixed substrates reflect the differences in their compositions (Fig.S1a); the weight loss at 200 °C of highly concentrated GO systems is associated with the removal of the surface oxides, and systematically disappears for the lower GO/MWCNT ratios.

Initially, the effects of hybridizing LDH with CN were explored using three key examples as the carbon supports: GO-, MWCNT-, and the optimal GO/MWCNT(1:1)- mixture; in each case 50 wt% LDH was combined with 50 wt% CN, to form the samples termed GO₅₀-LDH, MWCNT₅₀-LDH, and GO/MWCNT(1:1)₅₀-LDH, respectively. TGA profiles of these samples and of a reference unsupported LDH control (Fig.S3b) confirm the presence of the expected carbon and LDH components;¹³ the estimated proportions (wt%, Table 2) match the nominal loadings, assuming that the combustion residues of each phase are simply additive.¹³ From ICP analysis, the average Mg/Al ratio of the as-synthesized CN₅₀-LDH materials was determined as 2.1 ± 0.1, which is very close to the nominal ratio of 2; the mean potassium doping was found to be 5.1 ± 0.14 %, (Table 2), confirming the straightforward nature of the synthesis process. The LDH content is essentially determined by the proportion of salt precursors to nanocarbon, due to near quantitative conversion. The XRD pattern of the

252 unsupported LDH reference (Fig.S3a), exhibits the expected features, with narrow, symmetric and
 253 strong lines at low 2θ angles, and weaker lines at high 2θ values. The (00 l) reflections (003), (006),
 254 (009) are easily recognized, as well as the two reflections of (110) and (113), clearly distinguished
 255 between 60° and 63° (JCPDS No. 14-191). The basal reflection (003) at 11.8° falls approximately at
 256 the same 2θ angle as the GO layer spacing (11.4°), although the GO peak is weak and tends to diminish
 257 further after hydrothermal treatment (LDH synthesis conditions),¹⁵ due to elimination of the oxidative
 258 debris. The graphitic carbon (002) at 26.3° is isolated from the other peaks. For CN₅₀-LDH, the (003)
 259 peak broadens compared to the unsupported sample (Table 2). This effect can be attributed to a reduced
 260 crystallite size in the stacking direction (*c*-direction) from 22 nm for pure LDH to 5.7 - 15 nm for CN₅₀-
 261 LDH, due to CN modifying the nucleation/growth conditions.^{13, 15}

262 **Table 2**

263 Summary table of samples composition, morphologic characteristics and CO₂ adsorption properties.

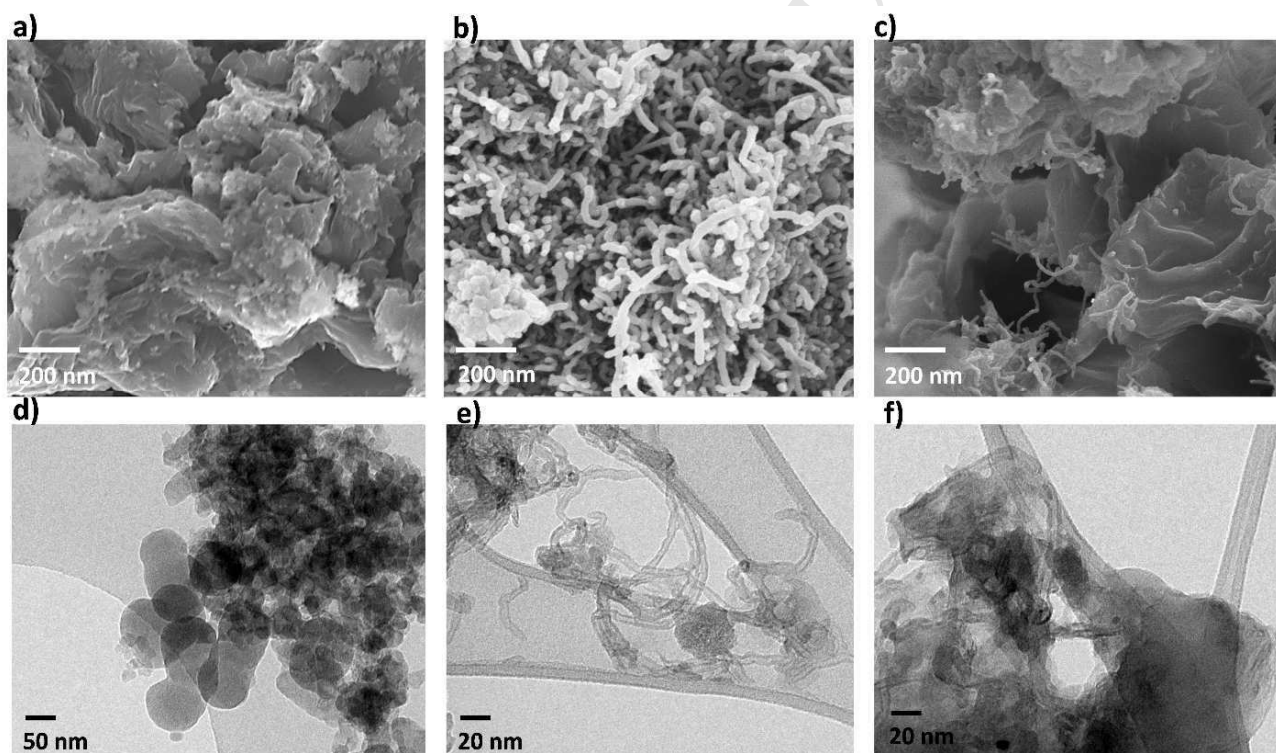
264 ^a LDH platelet thickness calculated from the (003) peak by Scherrer equation. ^b gas adsorption capacity relative to
 265 the 1st adsorption cycle.

Sample	C wt% (nom)	C wt% (actual)	Mg/Al (mol/mol)	K (wt%)	LDH platelet thickness ^a (nm)	S _{BET} (m ² g ⁻¹)	V _{pores} (cm ³ g ⁻¹)	CO ₂ adsorbed (mol kg ⁻¹ LDH)	Rel capacity ^b 20 th cycle (%)
LDH	0	0	2.2	5.1	22.8	49.31 ± 0.63	0.32	0.18 ± 0.02	50
MWCNT ₅₀ -LDH	50	48	2.1	4.9	15	77.69 ± 1.98	0.31	0.24 ± 0.03	77
GO ₅₀ -LDH	50	46	2.2	5.3	5.7	84.89 ± 0.17	0.27	0.27 ± 0.02	65
GO/MWCNT(1:1) ₅₀ -LDH	50	46	1.9	5.1	13.7	103.51±0.36	0.41	0.49 ± 0.01	96

266

267 A change in crystallinity may also contribute to the peak width, although LDH crystallinity is usually
 268 dictated by temperature, ageing time, pH and mixing rate,^{53, 54} factors that were kept consistent between
 269 batches. Peak broadening is much more noticeable for the GO₅₀-LDH sample than for MWCNT₅₀-LDH
 270 (LDH platelet thickness of 5.7 nm and 15 nm, respectively); the two dimensional GO sheets should be
 271 more compatible with the LDH platelets than the MWCNT.¹⁵ The LDH platelet thickness of the
 272 GO/MWCNT₅₀-LDH hybrid (13.7 nm) is intermediate between GO- and MWCNT-LDH. No crystalline
 273 signal for the potassium carbonate promoter was detected, consistent with the low loading introduced

274 (5%) and a homogenous distribution. In principle TEM can help to confirm platelet thickness, but is
 275 difficult to apply, with statistical significance to LDH supported on convoluted GO; qualitatively,
 276 however, TEM (Fig.S4) indicates a similar LDH platelet thickness as the XRD results. SEM and TEM
 277 images confirm an intimate association between LDH particles and the carbon substrates, with LDH
 278 aggregates covering the surface of the GO (Fig.2a,d), MWCNT (Fig.2b,e) and the hybrid (Fig.2c,f).
 279 Importantly, the GO/MWCNT₅₀-LDH hybrid manifests enhanced specific surface area compared to both
 280 GO₅₀-LDH and MWCNT₅₀-LDH (Table 2), continuing the trend identified above for the supports in the
 281 absence of LDH (Fig.1). Previous work suggests that the 2D geometry of GO sheets may offer a more
 282 compatible nucleation surface for the LDH platelets,¹³ however, there is no evidence of selective growth
 283 in the GO/MWCNT-LDH material. The similar concentration of oxygen functionalities (1 - 2 mmol g⁻¹)

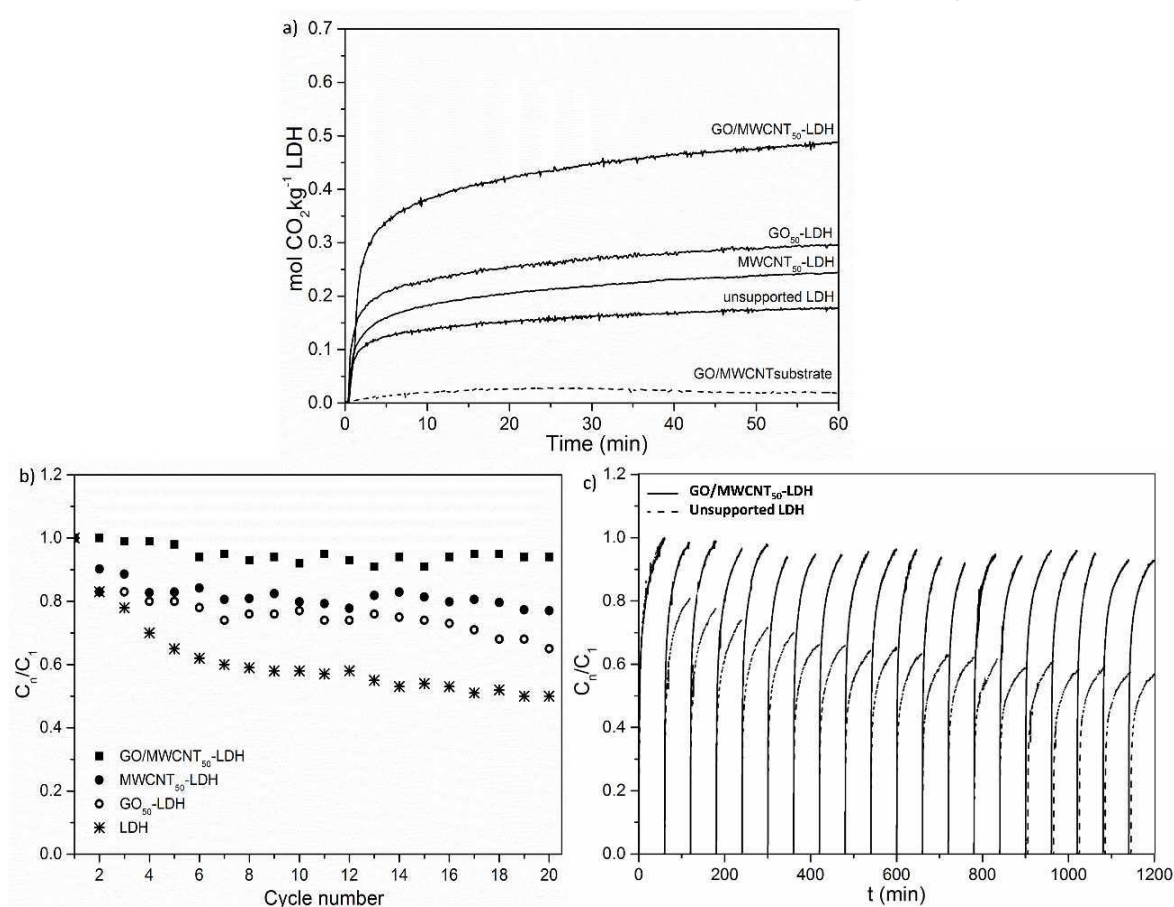


284 for both GO and MWCNT,^{15,47} may dominate the nucleation process.

285 **Fig.2.** SEM and TEM images of a,d) GO₅₀-LDH; b,e) MWNT₅₀-LDH; c,f) GO/MWCNT(1:1)₅₀-LDH samples.

286 The properties of the CN₅₀-LDH materials as CO₂ adsorbents were assessed over 20 cycles of gas
 287 adsorption-desorption. All the samples manifested fast intrinsic CO₂ adsorption kinetics (Fig.3a),
 288 achieving more than 80% of their equilibrium capacity within 30 minutes. Critically, the

289 GO/MWCNT₅₀-LDH hybrid exhibited the highest gas adsorption capacity (0.49 mol CO₂ kg⁻¹LDH),
 290 more than twice the value of unsupported LDH (0.18 mol CO₂ kg⁻¹LDH), and significantly higher than
 291 LDH supported on GO and MWCNT independently (0.27 and 0.24 mol CO₂ kg⁻¹LDH, respectively).
 292 The first-contact adsorption capacity of the GO₅₀-LDH sample is higher than the MWCNT₅₀-LDH one,
 293 in accordance with previous results.¹⁵ Under these operating conditions, the GO/MWCNT substrate
 294 alone has a negligible CO₂ adsorption (0.02 mol CO₂ kg⁻¹ carbon) compared to the LDH component
 295 (Fig.3a). Previous studies have also shown very low capacity on either raw or acid treated nanocarbons,
 296 and have ruled out any contribution potentially arising from residual catalyst particles.⁵⁵

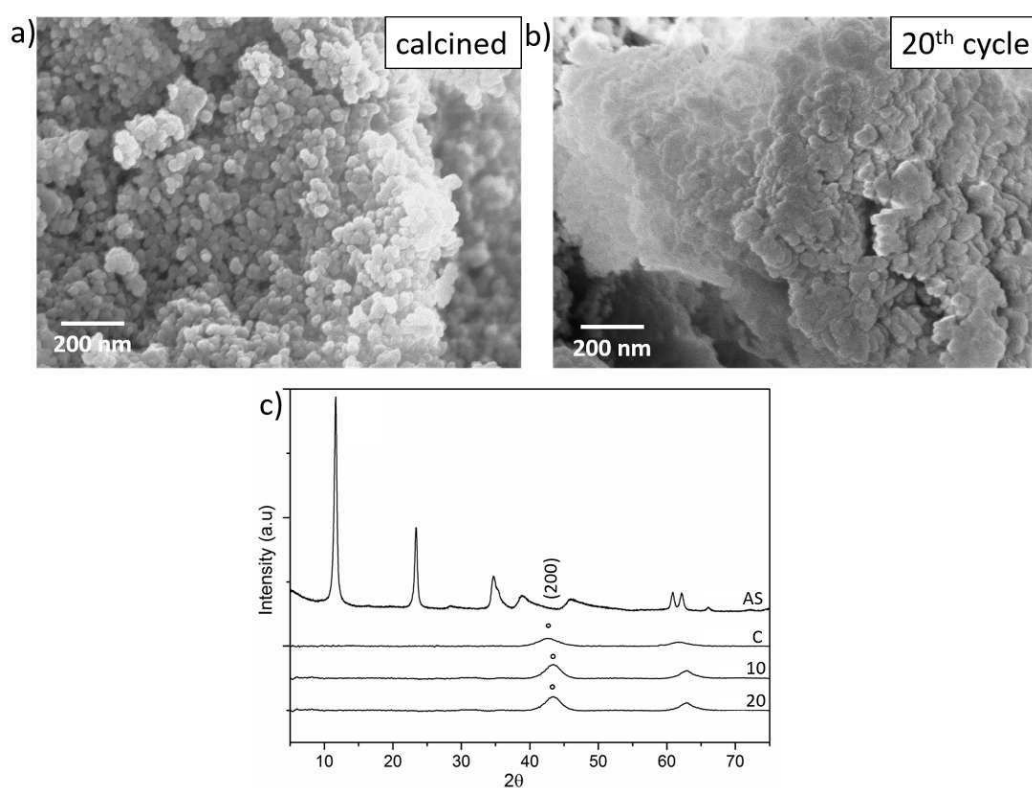


297

298 **Fig.3.** a) First-cycle CO₂ adsorption profiles of unsupported/supported LDH and GO/MWCNT (1:1) substrate, at
 299 300 °C and P_{CO₂}= 0.2 bar, after blank subtraction (pan+substrate). Substrate curve refers to mol CO₂ kg⁻¹ of
 300 carbon; b) normalized CO₂ adsorption capacity over 20 adsorption-desorption cycles; c) multicycle profiles of
 301 activated GO/MWCNT(1:1)₅₀-LDH and unsupported-LDH samples. Values are listed in Table 2

302

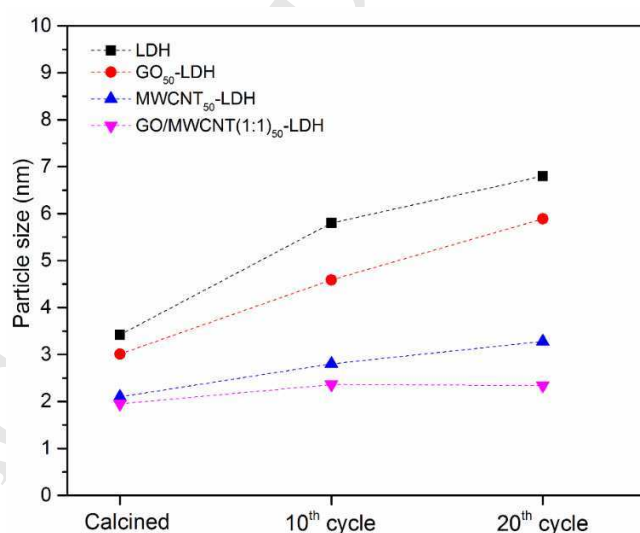
303 The adsorption capacity of all the samples showed good reproducibility among three repeated
 304 measurements for each sample (standard deviation of 0.01 - 0.03 mol CO₂ kg⁻¹LDH). The improved gas
 305 adsorption capacity manifested by GO/MWCNT₅₀-LDH can be attributed to the presence of the high
 306 surface area hybrid support and the enhanced effective LDH surface area, due to changes in crystal size
 307 and quality (Table 2). Smaller supported-LDH platelets are thought to have a higher concentration of
 308 active edge sites, which were previously shown to provide the binding sites for CO₂ adsorption.⁹ There is
 309 a synergy between the MWCNT, which provide a robust open network, and the GO, which is
 310 geometrically compatible with LDH.



311 **Fig.4.** SEM images of unsupported LDH materials: a) calcined, b) at the 20th cycle of gas adsorption-desorption;
 312 c) XRD evolution of unsupported LDH at different stages of the adsorption-desorption test: as-synthesised (AS),
 313 calcined (C) materials, after 10, and after 20 cycles.

314 The regeneration and stability of the adsorbents were also assessed by carrying out continuous
 315 adsorption-desorption cycles under dry conditions (Fig.3b-c). Unsupported LDH materials are known to
 316 suffer from irreversible declines in the adsorption capacity over cycling,¹⁶ due to chemisorption
 317 phenomena and particle sintering.⁵⁶ The present, unsupported LDH sample follows a similar decreasing

318 trend to previous reports (Fig.3b,c), exhibiting a loss of *ca.* 50 % of adsorption capacity at the 20th cycle.
 319 This trend is associated with a progressive sintering of the LDH platelets (SEM images, Fig.4), which
 320 likely contributes to the loss of surface area and basic site availability. However, this poor multicycle
 321 stability is mitigated by supporting LDH on either GO or MWCNT, but only partially. In contrast, the
 322 GO/MWCNT(1:1)₅₀-LDH hybrid retains up to 96% of its initial CO₂ adsorption capacity throughout all
 323 the 20 cycles of testing. This exceptionally stable behavior has not been observed before for adsorptions
 324 under dry conditions, and suggests the presence of a synergistic effect of the MWCNT and GO. The
 325 presence of modest levels of dopants were previously shown not to affect the multicycle stability of the
 326 materials, but only the absolute capacity.¹⁶
 327 To provide an explanation for this retained stability, the morphological evolution of LDH and CN₅₀-
 328 LDH samples was studied, *via* XRD, SEM and Raman spectroscopy (Fig.5,6,7), at different stages of the
 329 multicycle adsorption tests, specifically as-synthesized (AS), calcined (C), after 10 cycles and after 20
 330 sorption cycles. Cycling adsorption-desorption tests on unsupported LDH caused the structure to
 331 progressively lose surface area, likely due to continuous decarbonation, irreversible chemisorption
 332 effects, sintering or carbon deposition.⁵⁶ The calcined particles were found to sinter into larger
 333 structures, as calculated from the width of the (200) peak of periclase in XRD (Fig.5, and Table in
 334 Fig.S4), eventually halving the initial adsorption capacity.



335 **Fig.5.** Graph of MMO particle size for calcined unsupported LDH and CN₅₀-LDH at different stages of the
 336 multicycle adsorption process. The reduced slope of the curve evidences reduced sintering effects.

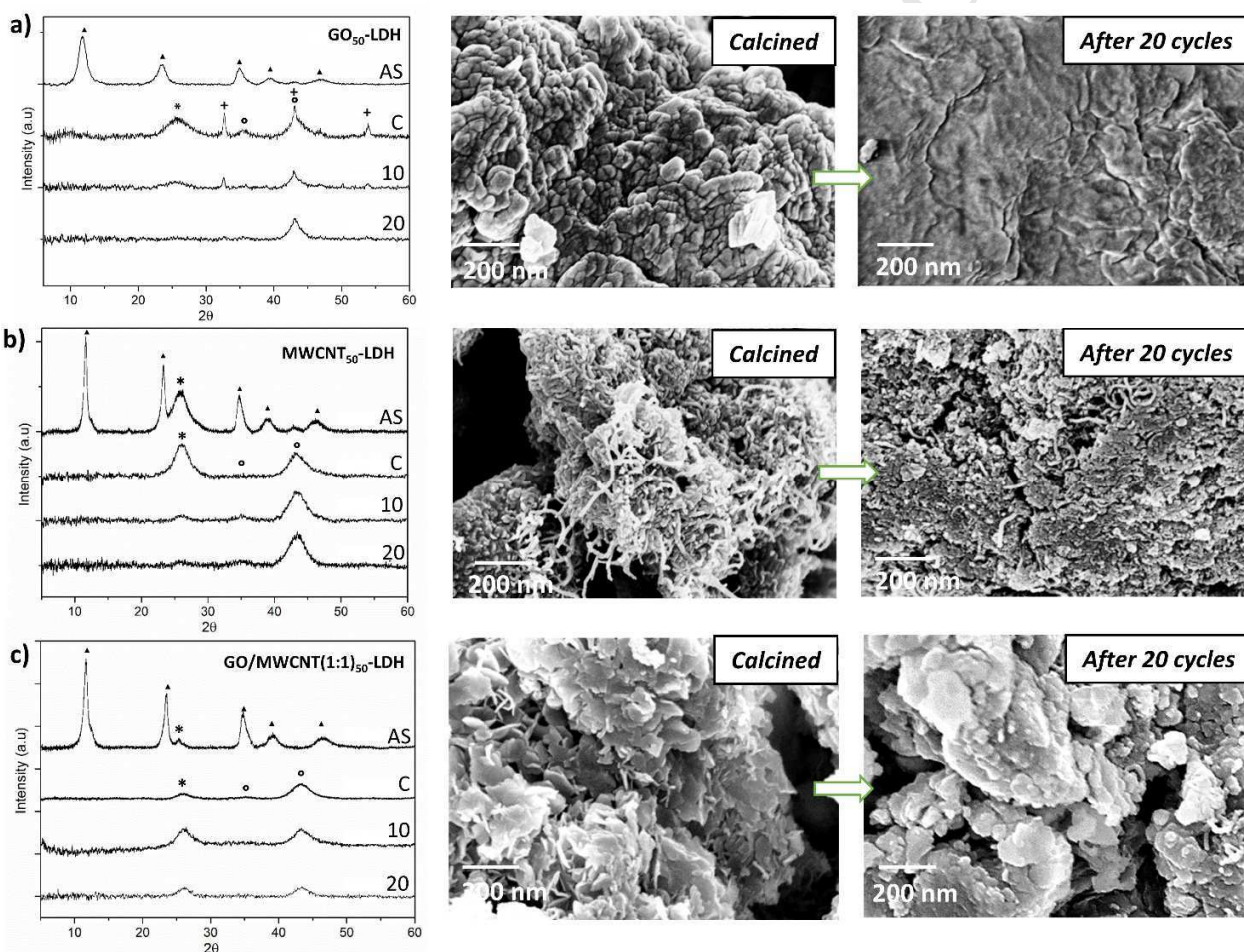
337

338 The GO₅₀-LDH material exhibits significant structural changes following the thermal cycling (Fig.6a).
339 On calcination, GO is thermally 'reduced' leading to restacking and the appearance of the (002)
340 graphitic peak at $\sim 26.4^\circ$; at the same time, peaks associated with free K₂CO₃ appear, indicating that
341 some of the impregnated salt was associated with the lost GO oxygen moieties, as expected due to acid-
342 base interactions. By the 10th cycle, the intensity of the graphitic (002) peak is significantly decreased
343 and eventually lost by the 20th cycle, consistent with the disappearance of the characteristic G and D
344 bands from the Raman spectra, which are normally associated with graphitic structures (Fig.7a).
345 Previous work reported that heat treatments of Ni/Mn LDH/GO hybrids at high temperatures
346 (450 - 800 °C) in inert atmosphere caused gasification and removal of the graphitic material.⁵⁷ Here, the
347 temperature is modest, but apparently sufficient to cause a similar loss of the graphitic component. The
348 loss of carbon is supported by TGA (Fig.S5), showing that the carbon content in the GO-LDH material
349 drops from 46 wt% before cycling (Table 2) to *ca* 6 wt% afterwards. Towards the end of the cycling
350 experiment, the potassium redistributes into the periclase phase,⁵⁸ indicated by the disappearance of the
351 initial K₂CO₃ peaks in XRD pattern (Fig.6a). The degradation of the GO substrate and associated loss of
352 support, allows the MMO particles to sinter, increasing their size as estimated from peak width (Fig.5
353 and S4), though at a slower rate than the pure LDH. These observations account for the 30% capacity
354 loss measured for GO₅₀-LDH after 20 cycles. Although GO appears not to be an ideal substrate for
355 LDH, it slows the deactivation of the adsorbent due to sintering, both in rate and in extent.

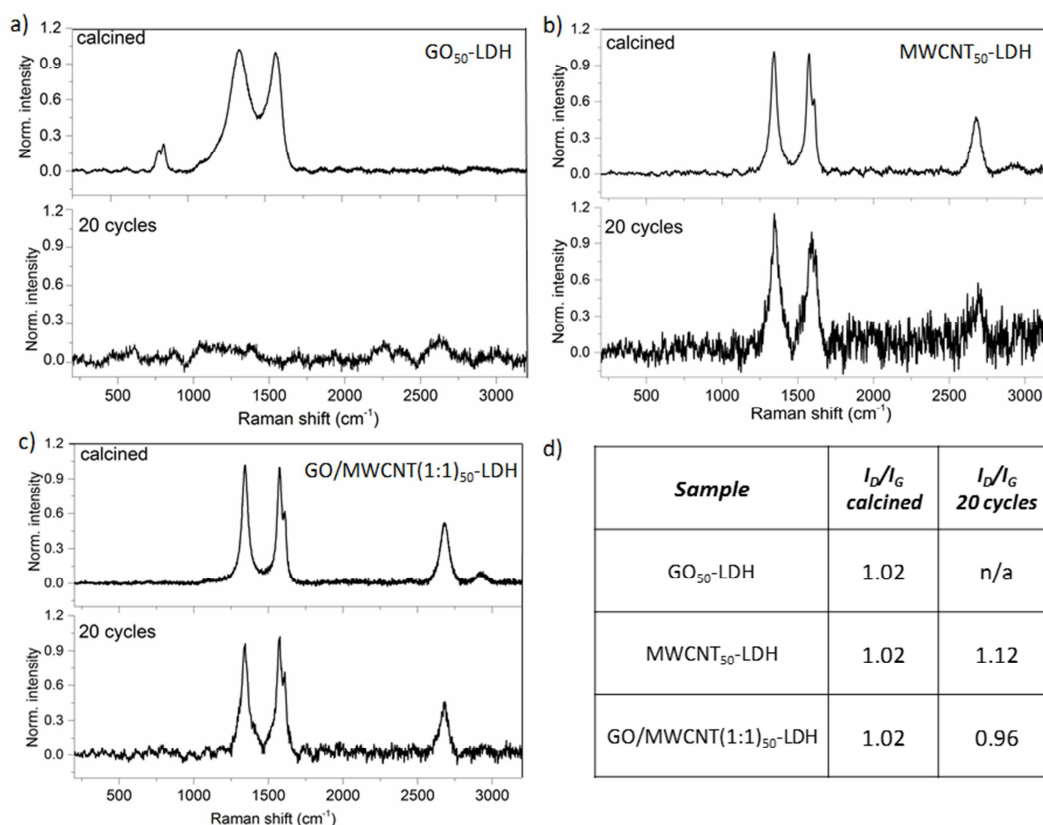
356 For MWCNT₅₀-LDH (Fig.6b), the initial calcined structure is better retained over cycling compared to
357 GO₅₀-LDH, as the carbon (002) and periclase (200) reflections are present in all the XRDs. Though
358 reduced in intensity, the XRD carbon peak and the typical Raman features of MWCNT are still detected
359 at the final adsorption cycle (Fig.7b). However, a more defective structure is confirmed by the increased
360 I_D/I_G ratio of the cycled sample (Table Fig.7d), and the partial loss of G band splitting. There appears to
361 be insufficient K₂CO₃ associated with the much smaller oxidized MWCNT surface, to nucleate separate
362 salt crystals. Overall, the MWCNT network is more robust than GO, unsurprisingly as only the surface
363 is initially oxidised, leaving a lower surface area and more perfect graphitic core that appears not to
364 gasify as readily as the GO. Thus, the sintering of the sorbent particles is reduced compared to
365 unsupported LDH and GO₅₀-LDH (Fig.4 and 5). These observations are in turn reflected by the greater
366 retained adsorption capacity (75%) manifested by the MWCNT₅₀-LDH sample in the last cycle.

367 The GO/MWCNT(1:1)₅₀-LDH hybrid benefits from the presence of both types of CN. Whilst the GO is
368 reduced (no layer peak at 11.4°), the XRD pattern of the calcined hybrid is relatively little altered during

369 subsequent cycling (Fig.6c), and the graphitic Raman band is better retained compared to either pure
 370 case (Fig.7c). In the GO/MWCNT(1:1)₅₀-LDH hybrid, the MWCNT and the GO appear to act
 371 synergistically. One possible explanation is that the large flat GO flakes, coated in LDH, provide a
 372 barrier offering a degree of protection to the MWCNT, whilst the MWCNT maintain a network
 373 scaffolding that limits sintering of the LDH/periclase that otherwise leads to exposure of the (reduced)
 374 GO framework. The microstructure of the hybrid, shown in the SEM images (Fig.6c), indeed exhibits
 375 much coarser plate-like features than the MWCNT₅₀-LDH, but more separated into discrete particles
 376 than the GO₅₀-LDH. This stable, hybrid support shows very little sintering of the periclase particles
 377 (Fig.5 and S4), consistent with the excellent retention of the capacity (96%) across the 20 cycles.



378 **Fig.6.** XRD patterns of a) GO₅₀-LDH, b) MWCNT₅₀-LDH, c) GO/MWCNT(1:1)₅₀-LDH at different stages: as-
 379 synthesized (AS) and calcined (C) materials, after 10, and after 20 cycles of gas adsorption-desorption. (▲) LDH
 380 reflections, (*) graphitic carbon, (°) periclase, (+) potassium carbonate. SEM images of calcined samples and after
 381 cycling 20 times.



382 **Fig.7.** Raman spectra at λ_{laser} of 532 nm of activated (calcined) materials and after 20 cycles of gas
 383 adsorption/desorption for a) GO₅₀-LDH, b) MWCNT₅₀-LDH and c) GO/MWCNT(1:1)₅₀-LDH materials. Spectra
 384 are normalized to the G mode at *ca.* 1575 nm. d) Table with calculated I_D/I_G ratios.

385

386 Having established a synergistic response, the influence of different ratios of GO and MWCNT on the
 387 final CO₂ adsorption properties were explored at a range of GO/MWCNT compositions (1:5, 1:3, 1:1,
 388 3:1). The GO/MWCNT substrate of composition 10:1 resulted in poor hybridization and low surface
 389 area (see Fig.1), and was not investigated further. The other hybrid substrates were added to LDH at
 390 various fractions (50, 30, 20 carbon wt%), producing supported hybrids denoted as
 391 GO/MWCNT₅₀-LDH, GO/MWCNT₃₀-LDH and GO/MWCNT₂₀-LDH, respectively. Lower loadings of
 392 the inert supports are more appealing industrially speaking, since they reduce the size of the adsorption
 393 units and limit the overall costs; in addition, the previous optimums for the pure GO and pure MWCNT
 394 supports were at 50 wt% carbon, or less. Generally, these three phase hybrids were formed successfully
 395 (XRD, Fig.S6). LDH grown on low GO/MWCNT ratio supports display broader XRD (003) peaks, and

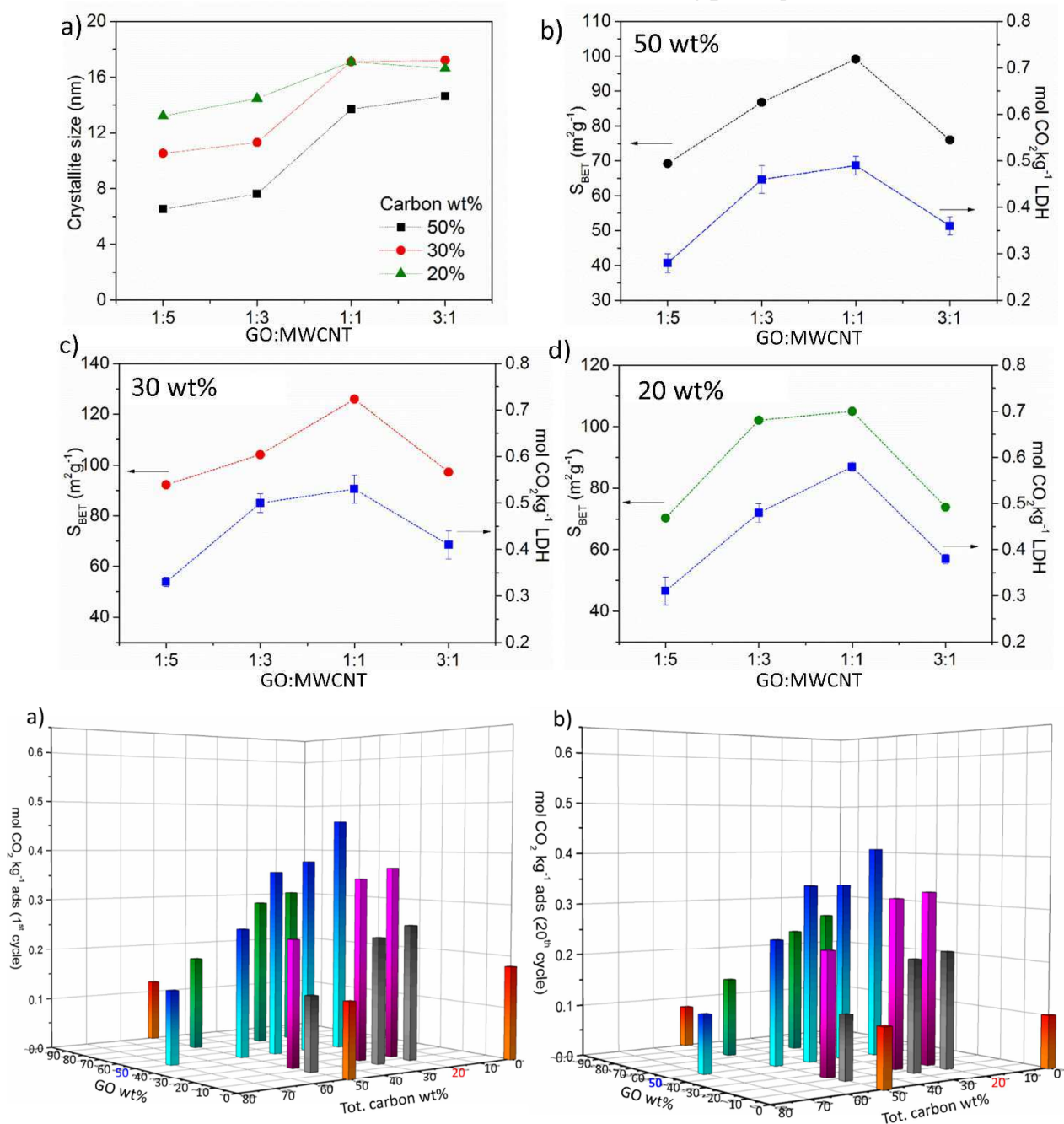
396 thus smaller platelet thickness in the *c*-direction (Fig.8a and S6), which is consistent with the formation
397 of a well hybridised material and the initial trends discussed above.

398 First contact CO₂ adsorption capacity and multicycle stability were assessed as previously, and
399 compared to BET surface area data (Fig.S7). The results can be summarized as follows: 1) the
400 adsorption kinetics for all the adsorbents is very fast, with 80% of the equilibrium capacity reached
401 again in the first 10 minutes of gas exposure (Fig.S8a,c,e); 2) regardless of the proportion of the support
402 added to the LDH phase, the highest intrinsic CO₂ adsorption capacity is always exhibited by LDH
403 supported on a GO/MWCNT substrate of composition 1:1 (Fig.8b-d); 3) LDH deposited on the
404 GO/MWCNT (1:1) substrate also manifest the highest surface areas within each set of carbon loadings;
405 4) for each set of samples, the CO₂ uptake trend is consistent with the BET surface area of the
406 adsorbents (Fig.8b-d).

407 **Fig.8.** a) Crystallite size of the adsorbents per support type. Specific surface area (m² g⁻¹) and CO₂ uptake (mol
408 CO₂ per mass of LDH) vs support type for b) GO/MWCNT₅₀-LDH, c) GO/MWCNT₃₀-LDH, d)
409 GO/MWCNT₂₀-LDH (values in Table S2). The error bars for the BET are very small (as indicated in the tabulated
410 data, Table S1), and mostly negligible on the scale of the plots.

411

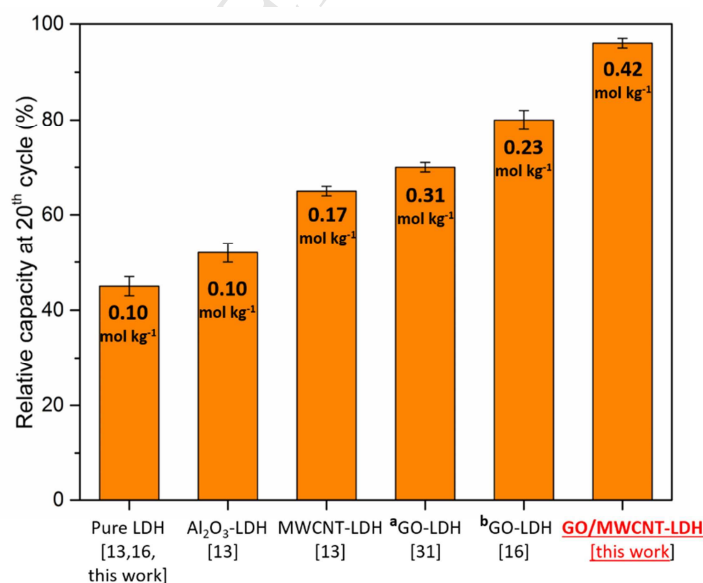
412 The specific surface area of the hybrids is related to the level of GO exfoliation/MWCNT intercalation
 413 achieved, and reflects the results for the pure nanocarbon blends. The enhancement in the intrinsic
 414 adsorption capacity (*i.e.* per mass of LDH) is important from a fundamental perspective; however, in
 415 practical terms, it is also important to consider the adsorption capacity per mass of total adsorbent (*i.e.*
 416 LDH+GO+MWCNT). The 3d plots of all the sorption data (Fig.9) confirm the optimum substrate
 417 composition GO/MWCNT 1:1 (blue bars), and highlights that, across all the GO/MWCNT ratios, the
 418 optimum carbon loading is between 10 - 20 wt% ($0.46 \text{ mol CO}_2 \text{ kg}^{-1}$ ads for the
 419 GO/MWCNT(1:1)₂₀-LDH hybrid), lower than previously used support fractions.^{12, 13} This range takes
 420 advantage of improved dispersion and gas accessibility without increasing significantly the total mass of



421 adsorbent. The existence of an optimum carbon loading, when normalising to the total mass of sorbent,
 422 was reported previously both for the pure MWCNT-LDH (optimum at 35 – 50 wt% MWCNT)¹³ and
 423 pure GO-LDH (optimum at 5 - 10 wt% GO)¹⁵ systems. As expected, the optimum loading for the hybrid
 424 GO/MWCNT-LDH falls between the two previous values, although much closer to the GO-LDH, due to
 425 the greater specific surface area of GO once restacking is prevented. Once isolated, a relatively small
 426 fraction of GO is sufficient to support all the LDH platelets. After 20 cycles (Fig.9b and S8), the
 427 adsorption capacity per mass of adsorbent continues to exhibit a marked improvement for all
 428 GO/MWCNT supported LDH samples compared to both pure LDH and LDH supported on only GO or
 429 MWCNT (red bars). The optimum performance is still observed for equal proportions of GO and
 430 MWCNT, for all contents of LDH. The capacity loss in the best cases, was only between 4% and 9%,
 431 much lower than previous reports for other supported HTs, under dry conditions.

432 **Fig.9.** CO₂ adsorption capacity per total mass of *adsorbent* at a) 1st cycle and b) 20th cycle, for all the samples.
 433 The data show consistent trends across a large number of samples, confirming the hybrid effect.

434 The absolute CO₂ adsorption capacity of the CN-LDH hybrids, though greatly improved compared to
 435 unsupported LDH, remains on an average 0.4 - 0.5 mol CO₂ kg⁻¹ adsorbent. This range is lower than
 436 other types of commercially-available solid adsorbents, for example 0.1 - 5 mol CO₂ kg⁻¹ zeolite and
 437 0.1 - 3.5 mol CO₂ kg⁻¹ activated carbons, tested at their active temperature of 5 – 100 °C.¹⁰ However, as



438 noted in the introduction, CN-LDH materials can successfully operate at much higher temperatures
 439 (200 – 400 °C), with good kinetics and potentially over long cycle lives. Moreover, they require low

440 energy in regeneration (300 - 400 °C), as opposed to other high temperature solid adsorbents (LiZrO₃
441 and CaO systems) which, although possessing higher adsorption capacities, can be regenerate only
442 above 600 – 800 °C, and manifest slower adsorption kinetics. The 20 cycles tested in this study were
443 selected to allow practical evaluation of a large number of hybrids, using a common range in the
444 scientific literature; clearly industrial evaluation would require extensive studies across a range of more
445 realistic conditions. Nevertheless, the 96 % retention of sorption capacity is a striking improvement over
446 previous studies (Fig.10), and the absolute amount gas sorption in the last cycle is also significantly
447 higher (0.42 mol CO₂ kg⁻¹ ads) than recent reports. It is worth noting that Meis *et al.* reported a stable
448 cycling behaviour of their CNF-supported LDH,¹² but under wet conditions (wet CO₂ gas feed (83%
449 N₂/12 % H₂O/5 % CO₂), which are known to obscure any specific stabilising effect of the support.⁴⁸ In
450 the present case, the increased stability in dry-feed conditions can be directly attributed to the presence
451 of the carefully designed high surface area and robust substrates.

452 **Fig.10.** Summary of comparable data for recently reported Mg/Al CO₃ LDH materials: CO₂ adsorption capacity
453 retention (per mass of total adsorbent and relative to the 1st contact adsorption) at the 20th adsorption cycle.
454 Examples considered include only materials tested under similar operative conditions (dry gas feed, 1 atm,
455 medium temperatures of 200-400 °C). ^a Mg/Al NO₃ LDH type, ^b Mg/Al CO₃ LDH type.

456

457 4. Conclusions

458 The use of a hybrid GO/MWCNT support for Layered Double Hydroxides offers a clear synergistic
459 benefit in CO₂ adsorption applications. This synergy can be considered as a true “hybrid effect”,
460 highlighting the benefit of combining phases such that the mixed phase performs better than either pure
461 phase or a simple rule of mixtures. Compared to substrates consisting of a single nanocarbon species, the
462 mixed GO/MWCNT systems are more effective, more stable, and offer a higher specific surface area for
463 the active LDH material. Systematic investigation consistently identified equal proportions of GO and
464 MWCNT (ratio 1:1) as the optimum composition to maximize both accessible surface area and sorption
465 performance. Indeed, the surface area was found to correlate directly with the CO₂ uptake. Both
466 MWCNT and GO contribute to the surface area and can support the LDH platelets; however, the
467 primary role of the MWCNT is to form a compatible, robust network, preventing restacking of the GO; a
468 high degree of exfoliation is therefore retained in the GO phase, providing a large surface anionic area
469 with a 2d geometry, particularly suited to the nucleation and growth of smaller cationic LDH platelets.

470 When exfoliated, GO sheets are a more efficient support than MWCNT. The presence of an open,
471 accessible, high surface area network stabilizes the final adsorbent, minimizing the deactivation and
472 sintering effects normally observed for unsupported LDH. Careful processing was required to generate
473 the intimate, uniform, three phase mixture that ensures an effective hybrid response. The best hybrid
474 identified (GO/MWCNT(1:1)₂₀-LDH) had an intrinsic adsorption capacity of 0.58 mol CO₂ kg⁻¹ LDH,
475 corresponding to 0.46 mol CO₂ kg⁻¹ of total adsorbent. The good performance per overall weight of
476 sorbent is particularly noteworthy, since many previous studies used much higher dilutions of LDH on
477 the support, increasing the weight significantly. Most strikingly, the intrinsic CO₂ adsorption capacity of
478 the hybrids was exceptionally consistent over repeated cycles of gas adsorption-desorption, even under
479 dry conditions, retaining up to 96% of the initial sorption capacity after twenty cycles, significantly more
480 than both unsupported LDH (50% retained) and previous reports for supported LDH (60 - 85%). This
481 type of hybrid sorbent may be considered, in the long term, for targeted pre-combustion carbon capture
482 applications, for instance in sorption enhanced water gas shift reactions and sorption enhanced methane
483 reforming, but may also be applied to smaller scale sorption problems. The improved performance of the
484 supported LDH is likely to be relevant to other known LDH applications, including as heterogeneous
485 bases for catalysis, as sorbents for the desulphurization of fuel,⁵⁹ and in pseudocapacitors.²⁹ In addition,
486 the concept of a GO/MWCNT hybrid network as substrate can be readily extended to other adsorbent
487 materials, particularly where problems of sorbent degradation over use are still present.⁶⁰ Other forms of
488 1d/2d hybrid materials can also be considered, drawing on the growing body of nanomaterial feedstocks
489 considered to be analogous to graphene/nanotubes.⁶¹⁻⁶³

490

491 **Acknowledgements**

492 The authors would like to thank prof. David Chadwick for help and discussion and Dr Hannah Leese for
493 TEM images acquisition. Financial support for this project was provided by the Deanship of Scientific
494 Research at King Abdulaziz University (Grant D-1- 434), and EPSRC grant EP/L001896/1.

495

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