

## Supplementary Material

### **Simple method to evaluate material-enhanced hydrogen storage capacity: route to end controversies.**

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#### **Table of Contents**

1. Details of materials synthesis.
2. Details of definitions, calculations and formula derivations.
3. Sources of errors in GT method.
4. Examples of data sheets with GT measurements of hydrogens storage.
5. Example of calculation of tank volume using GT method with helium.

#### **Experimental Procedures.**

##### **1. Materials and methods.**

Following materials were tested for hydrogen storage performance in this study:

- Graphite powder, flake (-325 mesh purchased from Alfa Aesar
- Commercial reduced graphene oxide (rGO) provided by Graphenea
- Highly purified carboxylic single-walled carbon nanotubes (CNT) by ACS Material (USA)
- Iron(III) carboxylate (MIL-100) synthesized according to procedure reported elsewhere ref <sup>1</sup>;
- 1,4-benzodicyclohexadiene (MOF-5) synthesized using procedure reported in ref <sup>2</sup>;
- Copper benzene-1,3,5-tricarboxylate Basolite<sup>®</sup> C 300 (Cu-BTC MOF) was purchased from Sigma-Aldrich,
- Activated carbon (AC) provided by ACS Materials;
- High surface area “graphene scaffolds” prepared using KOH activation of thermally exfoliated rGO (a-rGO).

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## **KOH Activated rGO (a-rGO)**

In order to produce sufficient amount of a-rGO the activation procedure was slightly modified compared to our earlier reported procedure.<sup>3</sup> Commercial Hummers GO (HGO, Abalonyx, Oslo, Norway) was used as a precursor. Powder HGO was rapidly inserted into a hot furnace at 300-320 °C to produce rGO. Water/ethanol (30%/70%) mixture was used for KOH soaking instead of toxic methanol. Pure ethanol could not provide desirable solubility of KOH to achieve required ratio of reduced HGO and KOH. Higher temperature of 80-100 °C was used during drying step to achieve a full evaporation. Larger diameter tube furnace was used for annealing of rGo-KOH under argon flow at 850°C. Following this procedure several portions of a-rGO with SSA around 2700 m<sup>2</sup>/g and amount 450mg per portion were prepared for H<sub>2</sub> tests.

## **Synthesis of MOF-5<sup>1</sup>**

Terephthalic acid (5.065 g, 30.5 mmol) was dissolved in 400 ml DMF with 8.5 ml of triethylamine. Then, a solution of Zn(OAc)<sub>2</sub> (16.99 g, 77.4 mmol) in 500 ml DMF was added dropwise to the reaction mixture over 30 min. The solution was stirred for 2 h and the precipitate was then filtered. The resulting white powder was washed with twice 100 ml DMF, twice 100 ml CHCl<sub>3</sub> and twice 100 ml CH<sub>2</sub>Cl<sub>2</sub> (10 minutes washing under stirring each time) and dried under vacuum.

## **Synthesis of MIL-100(Fe)<sup>2</sup>**

To a first solution, containing FeCl<sub>2</sub> (2.26 g, 11.4 mmol) in 97 ml water, was added a second solution containing NaOH (0.96 g, 24 mmol) and trimesic acid (1.68 g, 7.6 mmol) in 24 ml H<sub>2</sub>O. The solution was stirred in the presence of air during 4 hours and then the precipitate was separated by centrifugation. The obtained solid was then washed three times with water and twice with ethanol. Finally, the powder was dried at 70°C under vacuum using a rotary evaporator.

## **BET surface area analysis**

The Specific Surface Area (SSA) of these materials was verified using analysis of nitrogen sorption isotherms recorded (Quantachrome Nova 1200e surface area analyzer) before and after hydrogen storage tests to detect possible effect of pore structure collapse related to degassing procedures or pressure driven effects. The SSA remained unchanged or slightly decreased (<5 % change) after H<sub>2</sub> testing for all studied materials.

## **Hydrogen storage tests using standard volumetric and gravimetric methods.**

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The excess hydrogen sorption (wt%) was verified using standard gravimetric and volumetric methods routinely used in our laboratory over past decade.<sup>4-6</sup> Rubotherm GmbH gravimetric sorption analyzer and Hiden Isochema IMI volumetric systems were used, see details elsewhere.<sup>4-6</sup>

## 2. Details of definitions, calculations and formula derivations.

### 2.2 Definitions and calculations of TSD and Gain.

The weight of material filled and degassed tank closed under vacuum is  $M_{ref}$ . The weight of the same material tank filled with  $H_2$  at given P-T is  $M_{mat}$ . The total amount of hydrogen store in material filled tank is then  $m_{total} = M_{ref} - M_{mat}$

Total Storage Density (TSD) specific for the test tank is defined as:

$$TSD_{tank} = m_{total}/V_{tank} \quad (0)$$

where  $V_{tank}$  is total volume of test tank.

The total amount of hydrogen stored inside of the tank of arbitrary size could be calculated by multiplication of TSD value with volume of tank if the measurement was done for the tank completely filled with powder. However, due to the specific design we have relatively large part of tank which is not filled by powder. This includes dead volume ( $V_{dead}$ ) in connection pipes and inside of the valve. In some experiments we have not had sufficient amount of material to fill the whole space inside of the sample cell. For these samples the volume of tank not occupied by the material is also included into  $V_{dead}$ .

Material related Tank Storage Density ( $TSD_{mat}$ ) is defined as a density of  $H_2$  gas within the volume occupied by sample (useful volume  $V_u$ , see **Figure 1**).  $TSD_{total}$  is the value which includes characteristics of certain tank design, including some dead volume. In order to exclude the part which is not related to the properties of materials ( $V_{dead}$ ) we introduce another parameter which is related to useful volume of tank, the volume which can be filled with material:

$$TSD_{mat} = m_{total}/V_{useful} \quad (1)$$

The useful volume of tank  $V_{useful}$  is calculated as mass of material multiplied with bulk density of material  $\rho_{mat.bulk}$ . The total weight of hydrogen in material filled volume can be then calculated by

subtracting amount of hydrogen stored as gas in the dead volume from the total storage  $m_{total}$ .  $TSD_{mat}$  can be then calculated as following:

$$TSD_{mat} = (m_{total} - V_{dead} * \rho_{H_2}(P, T)) / V_{useful} \quad (2)$$

Note that we used some silica wool displacer to cover the sample (to prevent loss of material in process of gas dozing and release) which occupies certain volume of the tank and not occupied by hydrogen gas. Therefore, it is necessary to calculate the volume occupied by the displacer ( $V_{displ}$ ) using known density and weight of displacer and subtract it from the total volume of tank:

$$V_{dead} = V_{tank} - V_{useful} - V_{displ} = V_{tank} - m_{sample} / \rho_{mat.bulk} - m_{displacer} / \rho_{displacer} \quad (3)$$

The useful volume  $V_{useful}$  is calculated using known mass and bulk density of material:

$$V_{useful} = m_{sample} / \rho_{mat.bulk} \quad (4)$$

The  $TSD_{mat}$  is then the density of hydrogen in the volume occupied by material. Using this density it is possible to calculate hydrogen storage capacity of any material filled tank with arbitrary useful volume.

$$m_{total} = TSD_{mat} * V_{useful} \quad (5)$$

Note that ideal tank is filled completely by material while certain dead volume will always be present.

The  $TSD_{mat}$  can be higher or lower compared to the density of compressed hydrogen at the same P,T conditions.

The hydrogen storage (or storage of any gas) performance of the given material can be then estimated using simple parameter which we propose to name as Hydrogen (Gas) Storage Gain (or simply *Gain* in following discussions) expressed in units of percents (%).

$$Gain(P, T) = 100 * (TSD - \rho_{H_2}(P, T)) / \rho_{H_2}(P, T) \quad (6)$$

Materials capable to store hydrogen better compared to compressed gas (at the same P,T conditions) provide positive *Gain*. Materials which store hydrogen less good compared to compressed gas exhibit negative *Gain*. By definition, the *Gain* value shows the change in density of hydrogen inside of test tank due to addition of material relative to the density of hydrogen gas and expressed in percent's. In this case the meaning of gain is rather clear and informative for the practical applications. Note the *Gain* calculated using total volume of tank ( $TSD_{tank}$ ) is specific only for certain construction of the test vessel.

In order to provide parameter characteristic of the material we introduce Material-related *Gain* ( $G_{mat}$ ). In this case we take into account only volume occupied by the material and use  $TSD_{mat}$  in the equation (6).

Inserting  $TSD_{mat}$  into equation (6) with  $V_{dead}$  from (3) and  $V_{useful}$  from (4) :

$$G_{mat}(P,T)=100*((m_{total}-(V_{total}-V_{useful})*\rho_{H_2}(P,T))- \rho_{H_2}(P,T))/(\rho_{H_2}(P,T)*V_{useful}) \quad (7)$$

If the silica wool displacer is added to the tank, the calculation needs to take into account that the volume occupied by displacer is not included into the total volume of tank and  $V_{total}= V_{tank}- V_{displ.}$  will be used in (7)

Note that  $G_{mat}$  is parameter includes both volumetric and gravimetric characterization of the hydrogen storage since it depends on the bulk density of material.

Excess hydrogen uptake in wt% can be calculated using data provided by GT method by subtracting the weight of hydrogen stored as a gas in pores and free volume from the  $m_{total}$ . The volume not occupied by material multiplied with density of hydrogen gas will provide the part of hydrogen storage not included in the excess sorption.

The excess of hydrogen sorbed by the material ( $m_{excess}$ ) and wt% can be then calculated as following:

$$m_{excess}=m_{total}-\rho_{H_2}(P,T)*V_{free} \quad (8) \quad or$$

$$m_{excess}=m_{total}-(V_{tank}-m_{sample}/\rho_{sample}) \rho_{H_2}(P,T) \quad (9)$$

$$Wt\%= 100*m_{excess}/m_{sample} \quad (10)$$

### 2.3. Derivation of formula connecting Gain and excess Wt%.

Derivation for the formula (9) from the main part of the paper. The formula relates the values of wt% and *Gain*. We assume ideal tank where TSD values and Gain are calculated for 100% filling of all space with material (assuming  $V_{dead}=0$ ). The volume not occupied by material (total pore volume) is  $V_{free}$

According to definitions *Gain* and wt% are found as following :

$$Gain(P,T) = 100 * (TSD - \rho_{H_2}(P,T))/\rho_{H_2}(P,T) \quad (6) \quad and \quad Wt\% = 100 * \frac{m_{excess}}{m_{sample}} \quad (11)$$

According to definition TSD=  $m_{total}/V_{tank}$  (3) and  $m_{total} = m_{excess} + V_{free}\rho_{H_2}(P,T)$  (8)

At the same time  $m_{sample} = V_{skeletal} / \rho_{sample}$  and

$V_{tank} = V_{free} + V_{skeletal}$  (Total - skeletal volume of the sample),

$$Gain = 100 \left( \frac{m_{total}}{V_{tank}} - \rho_{H_2}(P,T) \right) / \rho_{H_2}(P,T)$$

Thus and with (8) it can be rewritten as following:

$$Gain = 100 \left( \frac{m_{excess}}{V_{tank}} + \left( \frac{V_{tank} - V_{skeletal}}{V_{tank}} \right) \rho_{H_2}(P,T) - \rho_{H_2}(P,T) \right) / \rho_{H_2}(P,T) = 100 \left( \frac{m_{excess}}{V_{tank}} + \frac{V_{skeletal}}{V_{tank}} \rho_{H_2}(P,T) \right) / \rho_{H_2}(P,T)$$

Inserting wt% into the equation as  $m_{excess} = wt\% * m_{sample} / 100$

and inserting  $V_{skeletal} = m_{sample} / \rho_{sample}$

Gain can be presented as:

$$Gain = \frac{V_{skeletal}}{V_{tank}} (wt\% \rho_{sample} - 100 \rho_{H_2}(P,T)) / \rho_{H_2}(P,T) \quad (12)$$

### 3. Sources of errors in GT method.

The GT method (like any other) has own sources of errors which must be taken into account. Starting from simplest procedure we learned about several types of errors which may dramatically decrease precision of method if not accounted properly. However, these errors can be minized using relatively simple procedures.

#### a) Precision and repeatability of the weight measurements provided by balance.

It is important to emphasize that we used rather standard commercial mass produced balance and not even the most expensive for the given maximal load and accuracy. What we want to prove here is that even using that kind of affordable balance it is possible to make reliable estimation of hydrogen storage and to avoid controversies typical for hydrogen storage measurements. The hydrogen storage tests using proposed method can be arranged even in small budget laboratories.

The tests performed in our study showed that the balance provides excellent repeatability over short periods of time. Maximal deviation in weight measurements was  $\pm 0.2$  mg, see example of measurement sheets below. Note that the repeatability of weight measurements is the most important parameter in our method, not the accuracy for the measurements of total weight of the test tank (~330 g). The balance was also regularly calibrated and verified using the standard with the weight similar to the weight of test tank.

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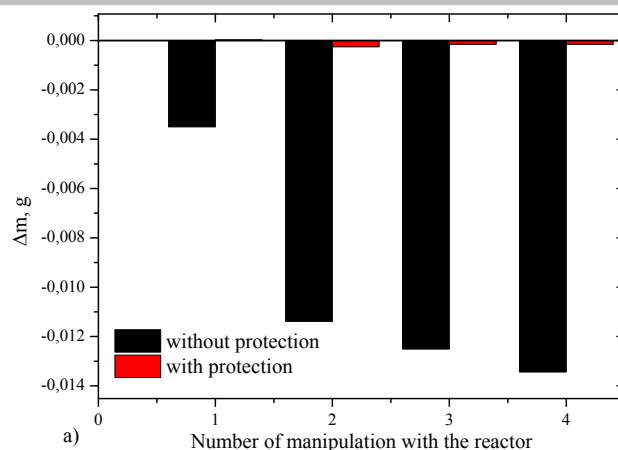
It is important to emphasize that total weight of hydrogen inside of the tank is directly measured quantity and excess wt% is secondary parameter in the GT method. Note that even for the sample with zero excess sorption some change in the  $m_{\text{total}}$  will be observed: the weight of hydrogen inside of the tank will be smaller by the value which is provided by skeletal volume of the material and density of hydrogen gas which correspond to this volume.

The accuracy of GT method measurements is provided by  $m_{\text{total}}$  in relation to error in weight measurements  $\pm 0.2$  mg. Therefore the error increases when total amount of stored hydrogen is smaller. The weight of hydrogen in the material free tank used in our experiments was  $\sim 95$  mg at 120 bar and 23°C. At 10 bar the density of hydrogen is approximately 10 times smaller and the total measured amount would be only  $\sim 9.5$  mg which is still measured with the same repeatability of  $\pm 0.2$  mg thus making experimental errors in evaluation of TSD and Gain (especially for material-related quantities) unacceptably high.

These example illustrates that GT method provides reliable estimation of hydrogen storage for high pressures but will never replace accurate measurements of sorption isotherms for low pressure part. However, the method could provide reliable isotherms for pressures above 100 bar, something which is very difficult for e.g. standard volumetric and gravimetric methods. The great value of GT method is that it will completely exclude strong overestimations of hydrogen storage for various novel materials at near ambient temperatures and pressures in the range close to application demands. For example, some literature claims of hydrogen sorption on the level of 3- 5 wt% would be extremely easy to verify using gram amount of material and pressures above 100 bar.

#### ***b) Contamination and mechanical damage.***

The test tank should be operated using gloves to prevent contamination, the temperature in the laboratory must be stable to prevent moisture condensation. We have not experienced any problems related to moisture condensation in our laboratory due to stable (within required few hours time) temperature and relatively low humidity (20-30%). The tank must be annealed 2-3 times at temperature above 100°C prior using for complete removal of surface contamination. The tank must be operated only using soft tools to prevent scratching, that is especially critical for the connecting/disconnecting the tank from the dosing system. Metallic wrenches must be wrapped with soft fabric or rubber when operate don the tank connections. Examples of errors experienced in practical tests are shown in **Figure 1S**.



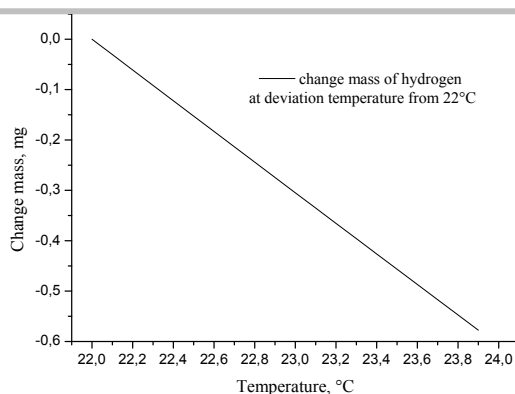
**Figure 1S** Change of the test tank weight due to connection and disconnection of tank to/from gas dozing system. Using rubber strip between wrench and metallic tank parts as a protection against mechanical improves quality of data

### c) Other sources of errors

The temperature stabilization during loading of H<sub>2</sub> is very important. The density of H<sub>2</sub> depends on the temperature and loading the tank without temperature control will result in different hydrogen loading. One degree difference in temperature results for our tank in 0.3 mg error in the weight of loaded hydrogen. Thermal stabilization was performed using circulating liquid thermostat and homemade cell which provided exactly the same conditions for hydrogen loading independently on the value of temperature in the room. Insertion of compressed H<sub>2</sub> into the test tank results in temperature increase and it is important to wait at least 5-10 minutes for thermal stabilization of the system before closing the valve and disconnecting the tank. Using thermal stabilization (circulating water bath) and increasing the loading time noticeably reduced the experimental errors.

Introducing and removing gas may result in loss of material, especially in case of rather fine powders. Therefore, we used silica wool displacer as a protection. However, the same problem (but in smaller scale) is possible with displacer as well. To prevent outflow of sample in process of gas release we used manual controlled fine sensitive valve and manometer. Slow filling of tank and slow release of pressure can be achieved after some training. The weight change due to sample outflow is easily detected by the weighting of the tank after release of hydrogen and can be avoided using accurate gas dozing.





**Figure S1.** Weight change of our tank due to unstable temperature at 120 bar H<sub>2</sub> pressure.

The weight measurements with gas-free tank and gas-filled tank need to be performed with shortest possible time intervals to provide as identical as possible environmental conditions (room temperature, humidity etc). The environmental conditions might affect e.g. performance of balance. Making measurements within 1-2 hours' time allows to achieve the best repeatability of the weight measurements.

The method allows to control leaks in very easy way. The tank shows notable change of weight if any meaningful leak is present. Repeating the weighting at least 10 times allows not only to provide better repeatability but also gives control over possible leaks.

#### 4. Examples of data sheets with GT measurements of hydrogens storage

**Table S1.** Example of GT method measurements datasheet for activated carbon (AC) sample. The measurement was tested with and without thermal stabilization at ambient temperature. Total weight of the tanks was measured 9-10 times, average value and standard deviation calculated. The weight is first measured for the tank with loaded sample and vacuum inside. On the second step the tank is connected to dynamic vacuum and degassed at 150°C for several hours, disconnected with vacuum inside and weighted again to evaluate mass loss due to degassing. Excellent repeatability of the weight measurements is observed.

AC without thermal stabilization			
Mass sample before degas = 1.4479g. m <sub>displ</sub> = 0.4671g			
	Under vacuum before heating	Under vacuum after heating	At 120bar H <sub>2</sub> 23.7 °C
	331.1579	331.1331	331.2297
	331.1577	331.1332	331.2296
	331.1576	331.1332	331.2294
Weight			At 120bar H <sub>2</sub> 24.0 °C
			331.2295
			331.2296
			331.2295

g	331.1581	331.1331	331.2295	331.2294
	331.1579	331.1328	331.2295	331.2296
	331.1581	331.1327	331.2293	331.2298
	331.1581	331.1329	331.2294	331.2297
	331.1579	331.1330	331.2294	331.2294
	331.1580	331.1330	331.2292	331.2295
Average weight, g	331.1579	331.1330	331.2294	331.2296
Standard deviation, g	0.0002	0.0002	0.0002	0.0001

AC with thermal stabilization  
Mass sample before degas = 1.1055g,  $m_{displ} = 0.3432g$

	Under vacuum before heating	Under vacuum after heating	At 120bar H <sub>2</sub> 23.0 °C	At 120bar H <sub>2</sub> 23.0 °C
	330.7212	330.7044	330.8006	330.8003
	330.7211	330.7044	330.8006	330.8001
Weight, g	330.7211	330.7045	330.8006	330.8005
	330.7210	330.7045	330.8004	330.8003
	330.7211	330.7041	330.8002	330.8003
	330.7210	330.7040	330.8004	330.8001
	330.7208	330.7040	330.8004	330.8002
	330.7208	330.7043	330.8002	330.8004
	330.7210	-	330.8002	330.8003
Average weight, g	330.7210	330.7043	330.8004	330.8003
Standard deviation, g	0.0001	0.0002	0.0002	0.0001

Example of measurement using material free tank weighted with vacuum inside and with hydrogen at 120 bar at 23°C.

	Under vacuum	At 120bar H <sub>2</sub>
	329.2951	329.3897
	329.2950	329.3897
Weight, g	329.2949	329.3898
	329.2949	329.3895
	329.2945	329.3895
	329.2950	329.3895
	329.2949	329.3894
	329.2947	329.3895
	329.2950	329.3895
Average weight, g	329,2949	329.3896
Standard deviation, g	0.0002	0.0002

Empty tank after week

	Under vacuum	At 120bar H <sub>2</sub>
	329.2998	329.3950
	329.2999	329.3949
Weight, g	329.2996	329.3950
	329.2997	329.3950
	329.2996	329.3949
	329.2996	329.3949
	329.2998	329.3949
	329.2997	329.3948
	329.2996	329.3948
Average weight, g	329.2997	329.3949

Standard deviation, g	0.0001	0.0001
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Example of calculation for sample which does not fill tank to maximum – Cu-BTC-MOF without thermal stabilization:

**Table S2.** Parameters of tank and sample are necessary for calculation.

Parameters of tank and sample are determined before start degas	$V_{\text{tank}} = 10.3151\text{mL}$
	mass sample before degas = - 1.1221g
	$\rho_{\text{bulk mat.}} = 0.44\text{g/cm}^3$
	$m_{\text{displacer}} = 0.4818\text{g}$
Parameters of tank and sample are determined after degas	$m_{\text{sample}} = 1.0706\text{g}$
	$V_{\text{skeletal}} = 0.437\text{cm}^3$
	$V_{\text{dead}} = 9.670\text{mL}$
	$V_{\text{displ}} = 0.197\text{mL}$
	Mass of tank after heating under vacuum = 330.8340g
	Masses of tank after heating at 120 bar and 1-23.7°C = 330.9291g; 2- 23.2 = 330.9293g; 3 - 23.3°C = 330.9293g

**Table S3.** Example of calculation.

Name	Formula	Result
$m_{\text{total}}$	Weight under vacuum after heating – Weight at 120 bar and T °C $330.9291 - 330.8340$	0.0951g with $\rho_{\text{H}_2}(120, 23.7) = 9.1368\text{mg/mL}$
	$330.9293 - 330.8340$	0.0953g with $\rho_{\text{H}_2}(120, 23.2) = 9.1514\text{mg/mL}$
	$330.9293 - 330.8340$	0.0953g with $\rho_{\text{H}_2}(120, 23.3) = 9.1479\text{mg/mL}$
Excess wt%	$(m_{\text{total}} - V_{\text{dead}} * \rho_{\text{H}_2}(p, T)) / m_{\text{sample}} * 100$	
	$(0.0951 - 9.670 * 0.0091368) / 1.0706 * 100$	0.63%
	$(0.0953 - 9.670 * 0.0091514) / 1.0706 * 100$	0.64%
	$(0.0953 - 9.670 * 0.0091479) / 1.0706 * 100$	0.64%
$G_{\text{mat}}$	$((m_{\text{total}} - (V_{\text{tank}} - V_{\text{displ}} - m_{\text{sample}} / \rho_{\text{bulk mat.}}) * \rho_{\text{H}_2}(p, T)) / (m_{\text{sample}} / \rho_{\text{bulk mat.}} - \rho_{\text{H}_2}(p, T)) / \rho_{\text{H}_2}(p, T)) * 100$ $((0.0951 - (10.3151 - 0.197 - 1.0706 / 0.44) * 0.0091368) / (1.0706 / 0.44) - 0.0091368) /$	

	0.0091368 *100	12,1% average by 3
Tank specific Gain	$\frac{(m_{total})/(V_{tank} - V_{displ}) - \rho_{H_2}(p,T)}{(0.0951/(10.3151-0.197) - 0.0091368) / 0.0091368} *100$	2.92% average by 3
TSD <sub>mat</sub>	$\frac{((m_{total} - (V_{tank} - V_{displ} - m_{sample} / \rho_{bulk\ mat}) * \rho_{H_2}(p,T)) / (m_{sample} / \rho_{bulk\ mat}))}{((0.0951 - (10.3151-0.197 - 1.0706/0.44) * 0.0091368) / (1.0706/0.44))}$	10.23 mg/mL
	$((0.0953 - (10.3151-0.197 - 1.0706/0.44) * 0.0091514) / (1.0706/0.44))$	10.27 mg/mL
	$((0.0953 - (10.3151-0.197 - 1.0706/0.44) * 0.0091479) / (1.0706/0.44))$	10.28 mg/mL
TSD <sub>tank</sub>	$\frac{m_{total}/(V_{tank} - V_{displ})}{0.0951/(10.3151-0.197)}$	9.40 mg/mL
	0.0953/(10.3151-0.197)	9.42 mg/mL
	0.0953/(10.3151-0.197)	9.42 mg/mL

## 2. Expanded table with summary of measurements which include additional sample-related information and all measurements averaged for the Table 1 in the main part of paper.

**Table S1.** Characterization of sorption properties for several common physisorption materials at 120 bar and 23 °C. From left to right:  $G_{mat}$ - Material related *Gain*;  $G_{tank}$ - *Gain* specific for whole tank (includes volume not occupied by material); TSD<sub>t</sub>-tank storage density TSD<sub>mat</sub> – material specific storage density. BET and Cumulative SSA determined using analysis of nitrogen sorption isotherms. excess wt% of hydrogen sorption; mass of material loaded into the test tankl. Results of two measurements are provided for AC material. where AC<sub>T=const</sub> with thermal stabilization..

Name	$G_{mat}$ , %	$G_{tank}$ , %	TSD <sub>tank</sub> , mg/cm <sup>3</sup>	TSD <sub>mat</sub> , mg/cm <sup>3</sup>	BET SSA, m <sup>2</sup> /g	Cum. SSA, m <sup>2</sup> /g	Wt%	m <sub>sample</sub> , g	$\rho_{real}$ , g/cm <sup>3</sup>	$\rho_{bulk}$ , g/cm <sup>3</sup>	F u l l
Gr	-10.47±0.05	-2.82±0.007	8.87±0.02	8.17±0.04	0	0	0.00±0.02	0.9812	2.230	0.36	-
rGO	-11.15±0.07	-6.43±0.02	8.55±0.02	8.12±0.05	445	473	0.13±0.01	1.9654	2.135	0.33	-
rGO	-11.50±0.07	-6.64±0.02	8.53±0.02	8.09±0.05	445	473	0.12±0.01	1.9654	2.135	0.33	-
rGO	-9.81±0.06	-5.66±0.02	8.61±0.02	8.23±0.05	445	473	0.16±0.01	1.9654	2.135	0.33	-
MIL-100	-2.88±0.02	-1.316±0.003	9.03±0.02	8.89±0.05	1467	1051	0.37±0.02	0.9043	1.799	0.19	-
MIL-100	-3.35±0.02	-1.530±0.003	9.01±0.02	8.84±0.05	1467	1051	0.35±0.02	0.9043	1.799	0.19	-
MIL-100	-3.58±0.02	-1.637±0.004	9.00±0.02	8.82±0.05	1467	1051	0.34±0.02	0.9043	1.799	0.19	-
CNT	2.90±0.02	1.792±0.004	9.33±0.02	9.44±0.07	1093	1136	0.46±0.02	0.9088	3.348	0.04	+
CNT	3.53±0.02	2.177±0.005	9.37±0.02	9.49±0.07	1093	1136	0.50±0.02	0.9088	3.348	0.04	+
CNT	2.99±0.02	1.845±0.004	9.34±0.02	9.44±0.07	1093	1136	0.46±0.02	0.9088	3.348	0.04	+
MOF-5	1.07±0.01	0.343±0.001	9.17±0.02	9.23±0.06	2604	2348	0.51±0.02	1.2095	1.908	0.37	-
MOF-5	2.03±0.01	0.651±0.002	9.20±0.02	9.32±0.06	2604	2348	0.53±0.02	1.2095	1.908	0.37	-
MOF-5	2.71±0.02	0.868±0.002	9.22±0.02	9.39±0.06	2604	2348	0.55±0.02	1.2095	1.908	0.37	-
AC	7.12±0.04	4.03±0.01	9.50±0.02	9.79±0.06	2007	1778	0.66±0.01	1.423	2.270	0.17	+
AC	7.50±0.05	4.24±0.01	9.52±0.02	9.82±0.06	2007	1778	0.68±0.01	1.423	2.270	0.17	+

AC	7.12±0.04	4.03±0.01	9.50±0.02	9.79±0.06	2007	1778	0.67±0.01	1.423	2.270	0.17	+
AC	7.67±0.05	4.34±0.01	9.52±0.02	9.83±0.06	2007	1778	0.69±0.01	1.423	2.270	0.17	+
AC <sub>T=const</sub>	5.04±0.04	3.14±0.01	9.44±0.02	9.62±0.07	2007	1778	0.67±0.02	1.0958	2.294	0.17	-
AC <sub>T=const</sub>	5.04±0.04	3.14±0.01	9.44±0.02	9.62±0.07	2007	1778	0.67±0.02	1.0958	2.294	0.17	-
Cu-BTC-MOF	12.0±0.06	2.87±0.01	9.40±0.02	10.23±0.06	1593	2132	0.63±0.02	1.0706	2.450	0.44	-
Cu-BTC-MOF	12.2±0.07	2.92±0.01	9.42±0.02	10.27±0.06	1593	2132	0.64±0.02	1.0706	2.450	0.44	-
Cu-BTC-MOF	12.3±0.07	2.96±0.01	9.42±0.02	10.28±0.06	1593	2132	0.64±0.02	1.0706	2.450	0.44	-

**Table S2.** Characterization of sorption properties for materials, which maximum loaded mass is lower than 1g, at 120 bar and 23 °C. From left to right:  $G_{mat}$ - Material related Gain;  $G_{tank}$ - Gain specific for whole tank (includes volume not occupied by material);  $TSD_{tank}$ -tank storage density  $TSD_m$  – material specific storage density. BET and Cumulative SSA determined using analysis of nitrogen sorption isotherms. Excess wt% of hydrogen sorption; mass of material loaded into the test tank. Results of two measurements are provided for AC material. where AC<sub>T=const</sub> with thermal stabilization. a-rGO\* was prepared from manufactured thermally reduced Abalonyx graphene oxide. a-rGO has different SSA, because to be able repeat test it was not enough material and it was added a new portion of material, obtained by same procedure

Name	$G_{mat}$ %	$G_{tank}$ %	$TSD_{tank}$ , mg/cm <sup>3</sup>	$TSD_{mat}$ , mg/cm <sup>3</sup>	BET SSA, m <sup>2</sup> /g	Cum. SSA, m <sup>2</sup> /g	Wt%	$m_{sample}$ g	$\rho_{real}$ , g/cm <sup>3</sup>	$\rho_{bulk}$ , g/cm <sup>3</sup>	F u l l
a-rGO	2.74± 0.02	1.780±0.004	9.35±0.02	9.44±0.07	2719	2218	0.68±0.04	0.5952	2.29	0.09	+
a-rGO	2.93± 0.02	1.907±0.004	9.36±0.02	9.46±0.07	2719	2218	0.70±0.04	0.5952	2.29	0.09	+
a-rGO	2.52± 0.02	1.641±0.004	9.34±0.02	9.42±0.07	2719	2218	0.66±0.04	0.5952	2.29	0.09	+
a-rGO	5.24± 0.04	3.16±0.007	9.43±0.02	9.62±0.07	2812	2260	0.94±0.03	0.6351	1.90	0.10	+
a-rGO	5.06± 0.03	3.05±0.007	9.42±0.02	9.60±0.07	2812	2260	0.93±0.03	0.6351	1.90	0.10	+
Average	3±1	2.3±0.7	9.38±0.04	9.5±0.1	-	-	0.8±0.1	-	-	-	+
a-rGO*	1.84± 0.01	1.075±0.002	9.22±0.02	9.29±0.06	2263	-	0.87±0.03	0.6300	2.350	0.10	+
a-rGO*	1.86± 0.01	1.083±0.002	9.23±0.02	9.30±0.06	2263	-	0.85±0.03	0.6300	2.350	0.10	+
a-rGO*	2.23± 0.01	1.29±0.002	9.25±0.02	9.34±0.06	2263	-	0.82±0.03	0.6300	2.350	0.10	+
a-rGO*	3.84± 0.03	2.298±0.005	9.37±0.02	9.50±0.07	2263	-	1.05±0.05	0,4810	1,835	0.08	+
a-rGO*	2.93± 0.02	1.753±0.004	9.32±0.02	9.43±0.07	2263	-	0.94±0.05	0,4810	1,835	0.08	+
a-rGO*	3.47± 0.02	2.075±0.005	9.35±0.02	9.47±0.07	2263	-	1.01±0.05	0,4810	1,835	0.08	+
Average	2.7±0.9	1.6±0.5	9.29±0.06	9.39±0.09	2263	-	0.9±0.1	0,4810	-	-	

## 5. Example of calculation volume by weighting of tank with helium.

Weight tank, g	Under vacuum	At 120bar He and 23°C ( $\rho_{He}=0,018472$ g/mL)
	329,2396	329,4309
329,2396	329,4308	
329,2394	329,4307	
329,2396	329,4309	
329,2396	329,4308	

	329,2395	329,4308
	329,2396	329,4308
	329,2395	329,4309
	329,2396	329,4307
Average weight, g	329,2396	329,4308
Standard deviation, g	0.0001	0.0001

Weight of helium inside of the tank= 329.4308-329.2396=0.1912 g Density of He (120 bar,23°C)  $\rho_{\text{He}}=0,018472 \text{ g/mL}$

Volume of tank= 0.1912g/0.018472 g/ml= 10.35 ml

Volume of tank found by pycnometry =10.31 ml

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