Supporting information

Bud Type Carbon Nanohorns. Materials for High Pressure CO₂ Capture and Li-Ion Storage

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High-pressure gas adsorption setup

High-pressure CO_2 adsorption measurements were carried out on a self-built volumetric setup. A schematic of the setup is shown in **Figure S1**. The all-stainless steel construction is designed for a pressure of up to 100 bar and is made from Swagelok® tubes and fittings. Three pressure transducers in the range 0 - 3 bar, 0 - 30 bar and 0- 100 bar with an accuracy of 0.05 % of maximum pressure rating are used for greater accuracy in the respective pressure regimes. The adsorption chamber and the storage vessels are equipped with separate K-type thermocouples. A water bath is used for providing isothermal conditions and the entire setup except for the body of the pressure transducer is immersed in the water bath. The fluctuations in pressure readings caused by the exposed transducer body are minimized by the use of a water jacket maintained at the same temperature as that of water bath.



Figure S1: Schematic of the high pressure volumetric setup

Calibration of volumetric setup

After checking the system for any possible leakages, the different colored sections were calibrated separately. Calibration measurements were carried out at 298 K and pressures up to 50 bar using high purity N₂ (99.999 %). Stainless steel balls (type 1.4301) of known density $(\rho = 7.9 \text{ g/cm}^3)$ and mass were used as the known volume for the calibration measurements. The volume of the adsorption chamber was determined from mass balance calculations by carrying out expansion measurements with and without the known volume, more details of which can be found in the reference [1]. Density values were obtained from the NIST webbook database [2]. From the schematic it can be seen that the pressure transducers are attached to the section Va. Since 3 pressure transducers were used, the section volume is calibrated individually for each pressure transducers as Va1 (0 - 100 bar), Va2 (0 - 30 bar)and Va3 (0 - 3 bar). For single component gas adsorption measurements, depending on the pressure, only sections Va (Va1, Va2, Va3), Vb (adsorption chamber), Vc (storage vessel 1), and Vd (storage vessel 2) were used. A cylindrical stainless steel cell (Vsc) was used for placing the sample inside the adsorption chamber. At least 5 expansion measurements were carried out for determining the volumes and the calibrated volumes of each section are listed in table S1.

The calibrations were cross-verified by measuring the adsorption isotherm of an extensively studied adsorbent/adsorbate system. CO_2 adsorption on microporous activated carbon Norit R1 extra was chosen as the standard as its adsorption values are extensively reported in literature [3-5]. The specific volume of the sample was determined by helium (99.999 %)measurement and was found to be 0.4595 cm³/g, consistent with the earlier reports. High purity CO_2 (99.998 %) was used for the adsorption measurements. Since in a volumetric measurement the errors accumulate and rise exponentially with each successive measurement, only 3 measurements were performed in a given cycle. The sample was then evacuated overnight at 150°C and the process was repeated. Whenever possible, the initial pressure in

the consecutive cycles were so chosen such that the points in the graph falls between the values from the previous cycle. The isotherm thus obtained is shown in **Figure S2**. The adsorption values are found to be in very good agreement with the reference data up to the maximum studied pressure of 43 bar.

Section	Volume (cm ³)
Val	12.6138 ±0.006
Va2	12.6576 ± 0.002
Va3	12.6996 ± 0.008
Vb	32.7417 ± 0.030
Vc	15.8568 ± 0.038
Vd	15.7795 ± 0.025
Vsc	2.0521 ± 0.003

Table S2: Calibrated volumes of different sections of volumetric setup



igure S2: CO₂ adsorption on Norit R1 extra at 25°C.



Figure S3: TEM image of CO_2 treated CNH

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Electrochemical measurements



Figure S4: Discharge curves of the measurements for a) as-prepared CNH and b) an enlarged section of the last cycles at 1C. For the discussion measurement 3 was chosen.



Figure S5: a) Discharge profiles of CO_2 treated CNH at a rate of 1C and b) the last cycles in detail. Measurement 3 was used for the discussion.



Figure S6: a) Optical microscope image of as-prepared CNH showing some whitish spots in otherwise black CNH material (scale bar = $150 \mu m$) b) Characteristic micro Raman spectrum obtained on of these spots. The large variations observed in the electrochemical measurements are most propably due to such inherent inhomogenities in the CNH sample.

References

- J. U. Keller, R. Staudt, Gas Adsorption Equilibria: Experimental Methods and Adsorptive Isotherms; Springer, 2005.
- [2] Thermophysical Properties of Fluid Systems. NIST http://webbook.nist.gov/chemistry/fluid/
- [3] F. Dreisbach, R. Staudt, J. U. Keller, Adsorption 1999, 5, 215.
- [4] S. Beutekamp, Adsorptionsgleichgewichte der reinen Gase Methan, Kohlendioxid, Stickstoff und deren binärer Gemische an verschiedenartigen porösen Stoffen, University of Leipzig, 2001.
- [5] J. Möllmer, Adsorption der reinen Gase CO₂, CH₄ und N₂ sowie deren Gemische an mikroporösen Koordinationspolymeren., University of Leipzig, 2012.