

Cite this: *Energy Adv.*, 2023,
2, 398Received 9th September 2022,
Accepted 31st January 2023

DOI: 10.1039/d2ya00242f

rsc.li/energy-advances

Hydrogen sorption on microporous carbon/sulfur nanocomposite systems†

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Encapsulating sulfur in single-walled carbon nanotubes (S@SWCNTs) produces a composite material hitherto unexplored for hydrogen storage. Interactions between sulfur and carbon nanotubes modify the electronic properties of the composite, thus offering methods for improving hydrogen sorption in carbon nanotubes. Here we demonstrate that S@SWCNT composites can provide 35% greater gravimetric excess adsorbed hydrogen per unit specific surface area, and improved hydrogen uptake at lower pressures (<2 MPa), indicating higher enthalpies of adsorption. Through semi-empirical modelling of high-pressure gas sorption isotherms, it was determined that S@SWCNTs can provide 74% higher volumetric hydrogen density compared to an undoped equivalent at 2 MPa and 77 K.

1 Introduction

Poised to replace fossil fuels as a cleaner energy vector, hydrogen (H₂) offers several unique properties making it a seemingly ideal successor.¹ The potential for a zero-carbon emission, cyclic fuel economy with a relatively uniform global distribution has motivated researchers for several decades. However, the low-density storage of H₂ consistently impedes widespread adoption and commercial implementation. Currently, storage and transport methods rely on physical-based manipulation of H₂ *via* pressurising (up to 100 MPa), cryogenic cooling (typically between 20 K and 77 K) or a combination of the two to achieve a usable density.² These techniques though simple, are energy-intensive and raise safety concerns, especially when placed in a mobile setting. Physical adsorption onto a porous scaffold offers an alternative, where molecular H₂ is weakly bound and concentrated on the surface of an adsorbent.^{3,4} The spontaneous adsorption process has been observed to result in a higher density of H₂ than that of compressed H₂ under similar conditions of temperature and pressure.^{5–7} Moreover, when the adsorption conditions are reversed (*i.e.*, pressure decreased and/or temperature increased), a complete discharge of the

stored H₂ can be achieved. Generally, the gravimetric capacity of a physisorption material is dictated by the BET (Brunauer–Emmett–Teller) surface area, approximately 1 wt% of excess H₂ per 500 m² g^{−1} at 77 K (Chahine's Rule).^{8–11} However, materials with very high surface areas, such as metal–organic frameworks (MOFs), tend to have poor hydrothermal stabilities and are challenging to synthesise and scale up,¹² constraining commercial viability.

Carbonaceous scaffolds are promising sorptive materials for meeting the United States Department of Energy targets for H₂ storage (ultimately 6.5 wt% including all auxiliary equipment).¹³ Relatively high stability, low cost and a plethora of derivatives make porous carbons good candidates for practical implementation.¹⁴ Furthermore, the high microporosity and low density displayed by these materials offer high gravimetric uptakes, typically ranging between 0.2–5.5 wt% depending on temperature.¹⁵ carbon nanotubes (CNTs) (particularly single-walled carbon nanotubes (SWCNTs)) provide an excellent model system for exploring routes for increasing hydrogen storage densities, owing to their simple carbon structure, homogeneous surface and ability to incorporate additional heteroatoms. Single-walled, double-walled and multi-walled carbon nanotubes (SWCNTs, DWCNTs and MWCNTs) are allotropes of carbon that can be conceptualised as rolled graphite/graphene with narrow pseudo-1-dimensional channels on the nanometer scale. Due to their outstanding chemical/thermal stability, high mechanical strength and relatively high surface area (between 300–1300 m² g^{−1}),^{16–18} CNTs have attracted much attention in gas sorption and separation. However, compared to other porous carbons, SWCNTs provide relatively low adsorption gravimetric uptakes even under cryogenic conditions; this stems from the relatively weak binding strength of the H₂ molecules and

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In this report, SWCNTs infiltrated with sulfur (S@SWCNTs) are tested for their gravimetric H₂ sorption capacities. To the authors' knowledge, S@SWCNTs are yet to be experimentally investigated for their potential in H₂ storage applications, though these materials have previously been explored for lithium-sulfur batteries³⁷ and gas-sensing³⁸ applications. SWCNTs offer a good model system to investigate the interactions between the sulfur and carbon sub-systems and how this may modify the surface

2.1.3 Sulfur impregnation. Adapted from a method used by Fujimori *et al.*⁴² and later by Fu *et al.*,³⁷ the sulfur/carbon

composites were produced in a set-up similar to that used to produce carbon nanopeapods.⁴³ In a typical set-up, approximately 25 mg of porous carbon and 500 mg of powdered sulfur were loaded into separate compartments of a bespoke H-shaped quartz ampule with an internal volume of approximately 3 cm³ (see ESI,† Fig. S1). The ampule was evacuated to <1 Pa prior to sealing. The sealed samples were then placed in a tube furnace at room temperature and heated to 873 K at 5 K min⁻¹ for 48 h and allowed to cool to ambient temperature. External sulfur was removed by annealing the sulfur/carbon composites at 573 K for 10 h under an N₂ flow. Samples were stored in a dry N₂ glove box for testing.

2.2 Characterisation methods

2.2.1 Thermogravimetric analysis. Assaying the composition of the washed and doped materials was achieved through thermogravimetric analysis (TGA) using a Netzsch STA 449 F1 Jupiter (Netzsch, Germany). Samples were loaded into alumina crucibles heated under an inert atmosphere (50 cm³ min⁻¹, N₂) at 5 K min⁻¹ to a maximum of 1273 K. An isothermal dwell was maintained at 383 K for 30 min to remove any adsorbed moisture, which would potentially interfere with any mass loss due to degradation.

2.2.2 X-ray photoelectron spectroscopy. Insight into the chemical bonding and elemental composition of a separate batch of samples was obtained *via* x-ray photoelectron spectroscopy (XPS). Analysis was conducted using a Kratos Axis SUPRA XPS with a monochromated Al K α X-ray source (1486.7 eV), a spherical sector analyser and 3 multichannel resistive plates, and 128 channel delay line detectors. All data were recorded at 150 W and a spot size of 700 $\times$ 300 μ m. Survey scans were recorded at a pass energy of 160 eV, and high-resolution scans were recorded at a pass energy of 20 eV. Electronic charge neutralization was achieved using a magnetic immersion lens. Filament current = 0.27 A, charge balance = 3.3 V, filament bias = 3.8 V. All sample data was recorded at a pressure <133.3 Pa. Data were analysed using the Thermo Scientific Avantage software (v5.993). All spectra were charge-shifted to the C1s peak at 284.8 eV.

2.2.3 Raman spectroscopy. Raman Spectroscopy was conducted using a Horiba LabRam (Horiba, France) using a 532 nm (green) argon laser. The instrument was calibrated using a silicon standard at 521 cm⁻¹. Before analysis, no degas was conducted, and all measurements were taken under atmospheric conditions.

2.2.4 Nitrogen sorption. Surface and porosity properties were probed *via* Micromeritics 3Flex adsorption analyser (Micromeritics, USA). Before analyses, samples were dried *ex situ* for 4 h at 383 K within a vacuum oven. A thorough *in situ* degas was conducted under high vacuum (<1 $\times$ 10⁻⁴ Pa) at 623 K and 353 K for the undoped and doped materials, respectively. The specific surface area (SSA) was determined by applying the BET equation to the linear region of the BET plot obtained from N₂ isotherms collected at 77 K, using the Rouquerol criteria for microporous materials.⁴⁴ Pore volume was determined by conversion of the quantity of N₂ adsorbed

close to saturation ($P/P_0 > 0.94$) to a fluid volume. pore size distribution (PSD) was evaluated using non-local density functional theory (NLDFT), where the regularisation was chosen to minimise the standard deviation of the reconstructed adsorption isotherm.

2.2.5 Gravimetric hydrogen sorption. Gravimetric high-pressure gas sorption experiments were conducted up to 9 MPa at 77 K using a Hidden Isochema XEMIS-001 (Hidden Isochema, United Kingdom). Before analysis, the samples were degassed *in situ* by continuous exposure to a vacuum for 8 h at ambient temperature. Undoped materials were additionally heated to 623 K. The skeletal density of the samples was determined through helium pycnometry to account for the buoyancy force at high gas densities.

2.2.6 Semi-empirical modelling of hydrogen excess isotherms. Fitting eqn (1) to the H₂ sorption isotherms provides approximation of the adsorbate density at pore saturation, *i.e.* $\theta = 1$.

$$N_e = 100(\rho_a - \rho_b)V_p\theta \quad (1)$$

where N_e is the excess gravimetric uptake as a wt%. ρ_a and ρ_b are the adsorbate and bulk densities, respectively, in kg m⁻³. V_p is the pore volume in m³ kg⁻¹ and θ is the fill volume fraction which is the ratio of the adsorbate volume to the pore volume. Successful fitting of eqn (1) requires substituting an appropriate model of θ , in this report θ was substituted for the Tóth equation (see eqn (2)).⁴⁵

$$\theta = \frac{bP}{(1 + bP^c)^{\frac{1}{c}}} \quad (2)$$

where P is pressure in MPa, b is a temperature-dependent constant related to the enthalpy of adsorption (units in MPa⁻¹) and c is a unitless constant related to the heterogeneity of the surface. The Tóth equation was selected due to previous reports showing good fitting to a range of adsorbent materials.⁴⁶ ρ_b within eqn (1) should be expressed in terms of $\rho_b(P, T)$ using an appropriate equation of state (EoS). In this report, the Leachman EoS⁴⁷ was used by fitting a rational equation to density data provided by the National Institute of Standards & Technology (NIST) Chemical WebBook.⁴⁸ A detailed description can be found in the ESI† (see Page S-3).

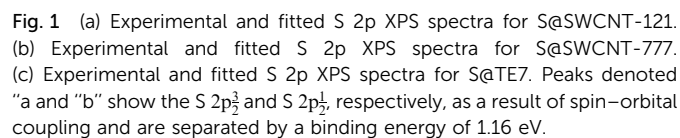
3 Results and discussion

3.1 Sulfur content and conformation

The sulfur content of the materials was estimated through the mass loss at 600 °C, determined *via* TGA. S@SWCNT-121 and S@SWCNT-777 and S@TE7 contain 9.1 wt%, 6.4 wt% and 23 wt% sulfur, respectively (see ESI,† Fig. S2). A direct comparison between the pristine materials and the sulfur encapsulating composites is challenging due to differences in the thermal history; the composite materials were additionally heated to 600 °C during the vapour deposition. However, it is assumed any mass loss event observed below 600 °C in the pristine carbon samples has already occurred during the vapour



After sulfur encapsulation, the Raman spectra (see Fig. 2) for all materials differ between the pristine and washed samples. New intense Raman peaks are observable at 320 cm^{-1} and 395 cm^{-1} within S@SWCNT-777, and 323 cm^{-1} and 394 cm^{-1} for S@SWCNT-121; these may provide insight into the conformation of the confined sulfur species. Previous reports have explored the origins of these doublet peaks located around 320 cm^{-1} and 400 cm^{-1} , in detail.^{49,51} Nascimento *et al.* predict that a strong doublet peak would be observed in a SWCNT of the chirality (7,6) and suggest these peaks arise from splitting from degenerate stretching modes of a polymeric sulfur chain due to quantum confinement effects enforced by the surrounding



Generally, all materials exhibit an increase in the I_D/I_G ratio with sulfur encapsulation (see Table 1), indicating a relative reduction in the sp^2 hybridised bonds⁵² or increase in defective sites along the SWCNT walls, following sulfur encapsulation, possibly suggesting the occurrence of a reaction between the sulfur and sp^2 graphitic material. Under the experimental conditions, the graphitic plates within the carbon material could form C-S_x-C bridges initiated by the diradical sulfur

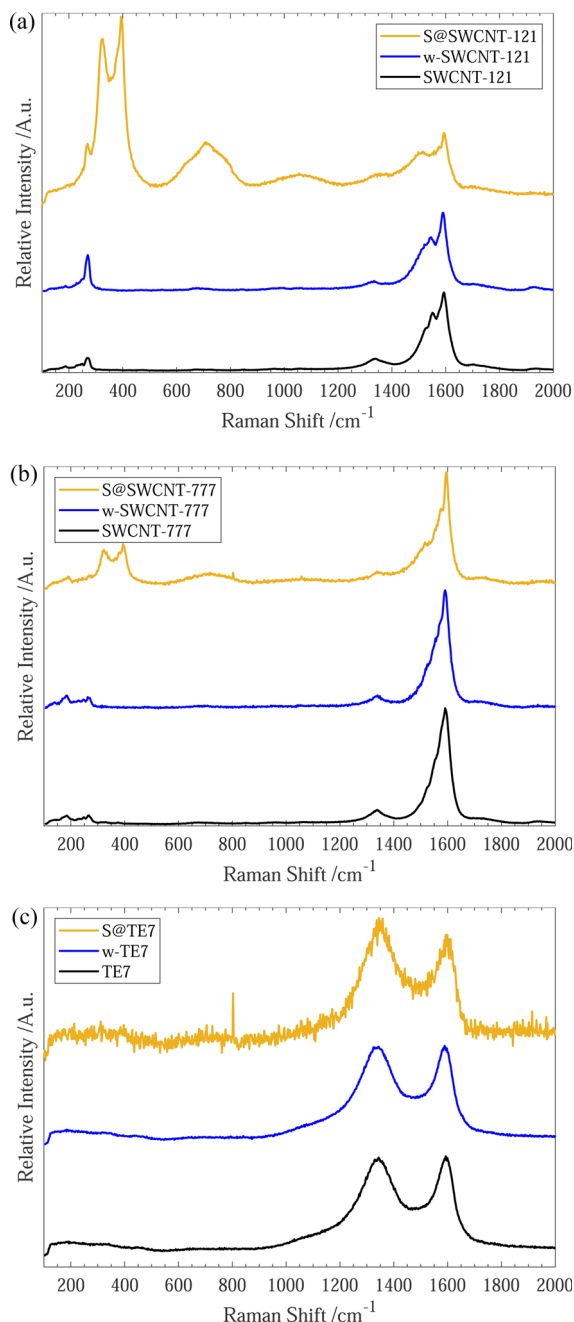


Fig. 2 (a) Raman spectra for SWCNT-121, w-SWCNT-121 and S@SWCNT-121, 532 nm excitation wavelength. (b) Raman spectra for SWCNT-777, w-SWCNT-777 and S@SWCNT-777, 532 nm excitation wavelength. (c) Raman spectra for TE7, w-TE7 and S@TE7, 532 nm excitation wavelength. All spectra are normalised to the intensity of the G-band for comparison. Each plot shows the as-purchased (black), washed (blue) and their sulfur composites (yellow).

species present in the vapour mixture.^{51,53,54} Evidence of a sulfur/carbon reaction occurring is given by the emergence of an infrared spectroscopy peak centered around 508 cm^{-1} (see ESI,[†] Fig. S7), where a series of alkyl/allyl/aryl disulfide and polysulfide responses are expected to occur⁵⁵ and is further corroborated by the peaks labelled 3a/3b and 4a/4b within the XPS spectra (see Fig. 1(c)). This is plausible for all samples.

Table 1 Summary of the G-band and D-band position and the ratio of the intensities for each sample

	ω_G/cm^{-1}	ω_D/cm^{-1}	I_D/I_G
SWCNT-121	1593	1339	0.1728
w-SWCNT-121	1589	1333	0.1430
S@SWCNT-121	1593	1359	0.4910
SWCNT-777	1590	1337	0.1359
w-SWCNT-777	1591	1339	0.1087
S@SWCNT-777	1595	1339	0.1400
TE7	1593	1345	0.9880
w-TE7	1589	1342	0.9920
S@TE7	1599	1344	1.1546

However, it is more likely for the S@TE7 sample, where no notable new Raman peaks are present in the spectra for S@TE7, compared to the pristine and washed samples—indicating that no polymeric sulfur species are present at a detectable depth within the sample, on the order of 100 nm (for 488 nm excitation wavelengths).^{56,57}

3.2 Surface and porosity measurements

After sulfur encapsulation, it is evident from the nitrogen sorption isotherms (see Fig. 3) that there is a loss of adsorption at low pressure ($P/P_0 < 0.05$) for all samples indicating a loss in observable microporosity, as expected. This is apparent in the pore size distribution (see Fig. 4) where the cumulative pore volume shows a reduced total volume in the microporous range ($< 2\text{ nm}$). S@SWCNT-121 demonstrates large reductions in pore volume within the sub-nanometer range (typically desirable for H_2 physisorption), where sulfur likely occupies deep sites between CNTs and the narrow endohedral channels. However, S@SWCNT-777 does not show the same reduction in pore volume. We hypothesise the larger diameters and lower sulfur loading of the SWCNTs present in S@SWCNT-777 still allow ingress of N_2 molecules to facilitate quantification of these pores. S@TE7 shows considerable loss in volume within the sub-nanometer pores (see Fig. 4(c)) with the emergence of larger micropores between 1–2 nm, this may indicate an expansion of the porous network *via* oxidation reaction with the sulfur vapour. The reduction in total micropore volume (μV_p) is corroborated using the Dubinin–Radushkevich method (see Table 2). Reductions of 13%, 23% and 22% in μV_p were found for S@SWCNT-121, S@SWCNT-777 and S@TE7, respectively, compared to the washed materials.

Additional reduction of the total pore volume within the mesoporous range (2–50 nm) is clear for both SWCNTs following sulfur encapsulation (see Table 2). Changes may result from exposure to molten sulfur during the synthesis procedure where changes in the SWCNT packing may have occurred.⁵⁸ S@SWCNT-777 shows a dramatic 39% reduction in total pore volume. Comparatively, S@SWCNT-121 shows only a 21% decrease in total pore volume. However, S@TE7 displays a +4.4% change in total pore volume, and shows an increase in the proportion of mesoporosity.

SSA for all sulfur composite materials decrease compared to the washed samples (see Table 2). This observation was expected



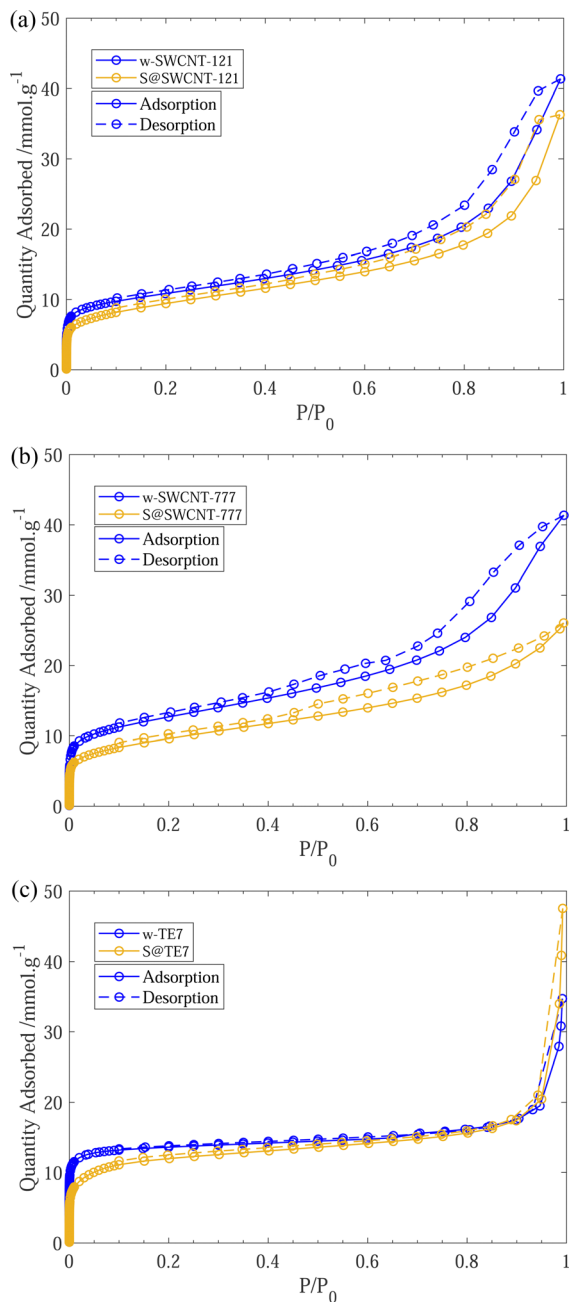


Fig. 3 (a) 77 K N₂ sorption isotherms for w-SWCNT-121 and S@SWCNT-121. (b) 77 K N₂ sorption isotherms for w-SWCNT-777 and S@SWCNT-777. (c) 77 K N₂ sorption isotherms for w-TE7 and S@TE7. Each plot shows adsorption (solid line) and desorption (dashed line) for the washed (blue) and sulfur composite (yellow).

as many of the pores are now occupied by the sulfur or sulfur is occluding pore entrances which can no longer be accessed by the N₂ molecules.

3.3 H₂ sorption

Supercritical high-pressure H₂ sorption isotherms were used to determine the excess gravimetric uptakes of the porous samples (see Fig. 5). w-SWCNT-121 and w-TE7 show relatively high

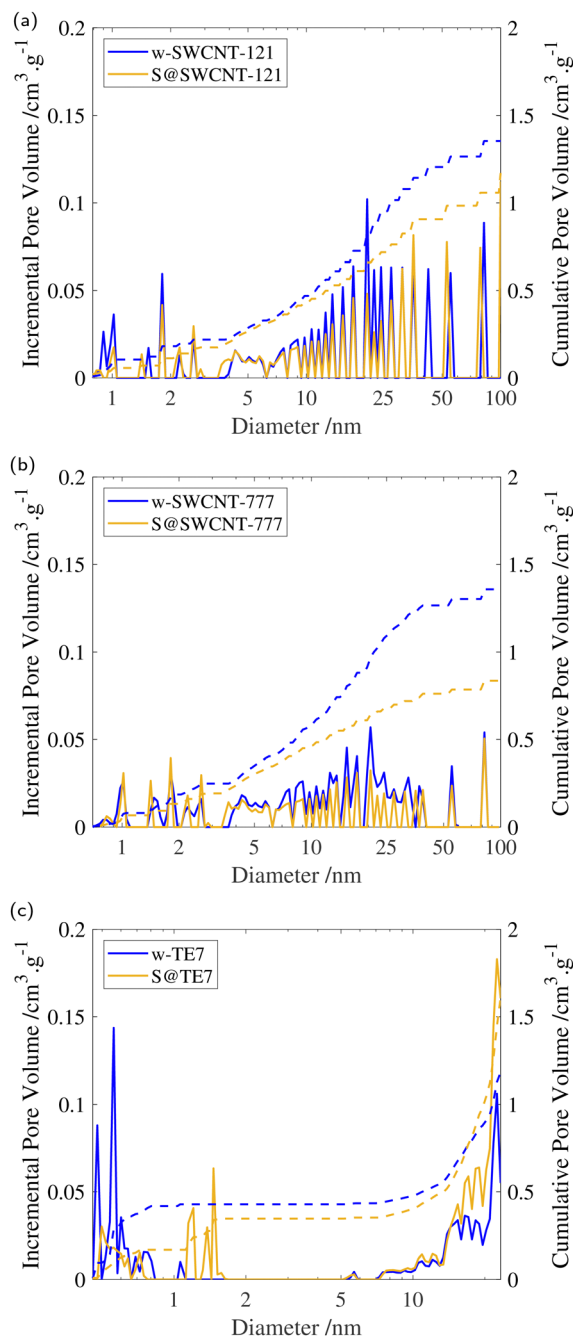


Fig. 4 (a) Incremental and cumulative pore volume for w-SWCNT-121 and S@SWCNT-121 determined via NLDFT using cylindrical pore model. (b) Incremental and cumulative pore volume for w-SWCNT-777 and S@SWCNT-777 determined via NLDFT using cylindrical pore model. (c) Incremental and cumulative pore volume for w-TE7 and S@TE7 determined via NLDFT using slit pore model. All plots show the incremental (solid line) and cumulative (dashed line) pore volume for the washed (blue) and sulfur composite (yellow).

maximum excess H₂ gravimetric uptakes at 77 K and surpass the forecasted value of 1 wt% per 500 m² g⁻¹, where w-SWCNT-121 and w-TE7 adsorbed 1.99 ± 0.03 wt% and 3.02 ± 0.03 wt%, respectively. In comparison, w-SWCNT-777 falls short of Chahine's rule and only adsorbs 1.67 ± 0.02 wt% of H₂. This

Table 2 Summary of surface area, pore volume and Dubinin–Radushkevich micropore volume determined from 77 K N₂ isotherms for all washed and sulfur composite samples

	^a SSA/m ² g ⁻¹	V _p /cm ³ g ⁻¹	μV _p /cm ⁻³ g ⁻¹
w-SWCNT-121	869 ± 2	1.19	0.31
S@SWCNT-121	752 ± 3	0.94	0.27
w-SWCNT-777	1014 ± 2	1.28	0.36
S@SWCNT-777	764 ± 2	0.78	0.28
w-TE7	1200 ± 2	0.68	0.46
S@TE7	1008 ± 6	0.71	0.36

^a Standard deviation values taken from the fitting of the BET equation.

may be attributed to the more significant proportion of ultra-micropores around the claimed optimum pore size of approximately 0.7 nm in the w-SWCNT-121 and w-TE7 (see Table 2), where increased overlap of electrostatic potentials from opposing walls generates stronger binding sites,^{5,25} thus, providing more

desirable adsorption sites and allowing for more significant H₂ densification.

Following sulfur encapsulation, both S@SWCNT-121 and S@TE7 show a reduction in maximum excess H₂ sorption by 32% and 50%, at 77 K, respectively. The decrease in the adsorbed quantity may originate from a reduction in available pore sizes around 0.7 nm shown by the N₂ sorption experiments. The higher sulfur loading may further exaggerate this reduction in adsorbed hydrogen within these samples, particularly in w-TE7, which displayed the largest sulfur content. In contrast, S@SWCNT-777 shows comparable maximum gravimetric excess sorption uptakes to the w-SWCNT-777 sample; this is made more remarkable due to the reduction in SSA induced by the presence of sulfur. This surprising enhancement to the H₂ per unit surface area (+33%) could originate from an increase in the enthalpy of adsorption. An enhancement to the enthalpy of adsorption is empirically suggested by

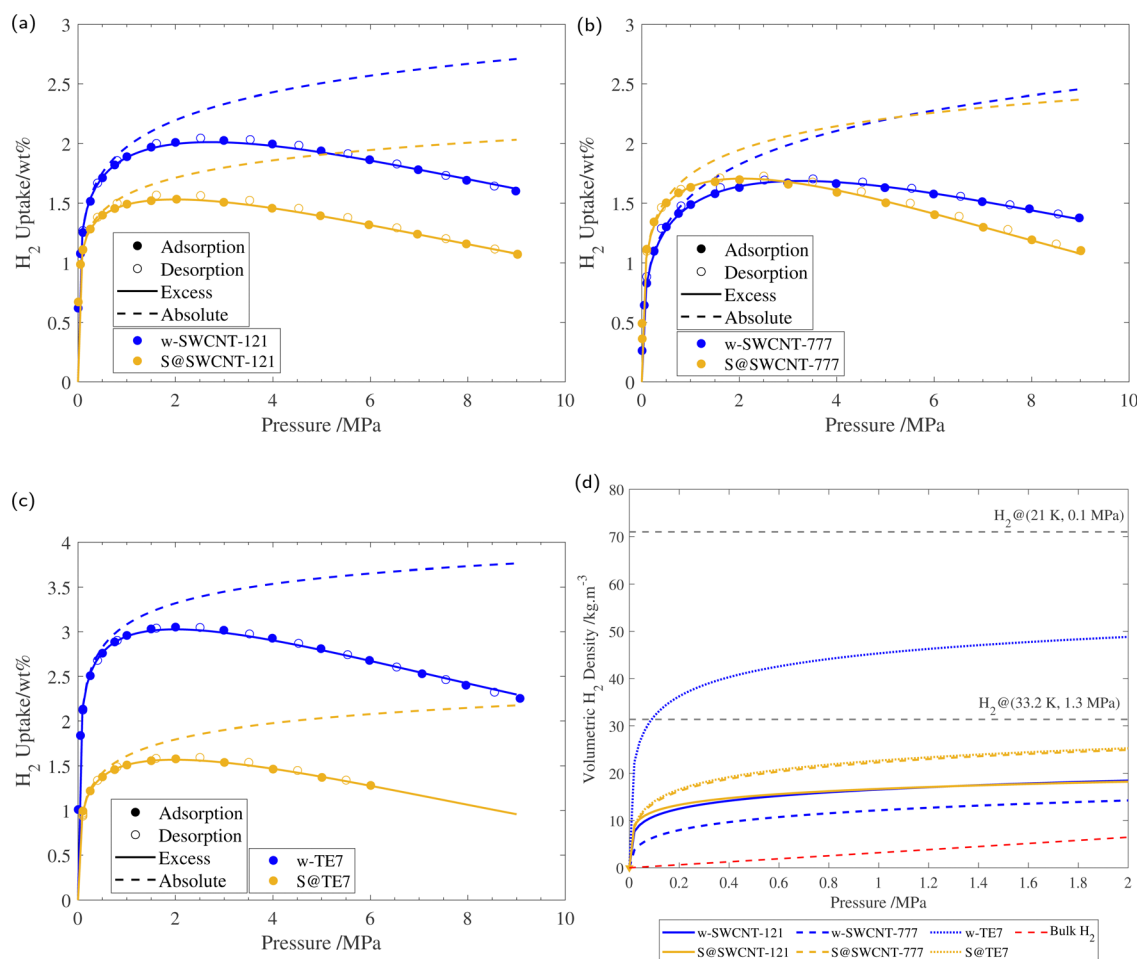


Fig. 5 (a) 77 K H₂ sorption isotherm of w-SWCNT-121 and S@SWCNT-121, with the respective excess isotherm determined through fitting and absolute isotherm, calculated using eqn (3). (b) 77 K H₂ sorption isotherm of w-SWCNT-777 and S@SWCNT-777, with the respective excess isotherm determined through fitting and absolute isotherm, calculated using eqn (3). (c) 77 K H₂ sorption isotherm of w-TE7 and S@TE7, with the respective excess isotherm determined through fitting and absolute isotherm, calculated using eqn (3). (d) Volumetric hydrogen density versus pressure up to 2 MPa for w-SWCNT-121 (yellow solid line), S@SWCNT-121 (yellow dashed line), w-SWCNT-777 (blue solid line), S@SWCNT-777 (blue dashed line), w-TE7 (blue dotted line), S@TE7 (yellow dotted line), calculated using eqn (4). NIST bulk hydrogen data at 77 K (red dashed line), Liquid hydrogen density (20.25 K, 0.1 MPa), and density of hydrogen at its critical point (33.20 K, 1.3 MPa) are shown for reference. Each isotherm shows the result of the 3rd repeat run, all isotherms can be found in the ESI† (see Fig. S8).



the steeper initial H₂ gravimetric uptake within the lower pressure regime; S@SWCNT-777 reaches the maximum excess gravimetric uptake at a lower pressure compared to w-SWCNT-777, excess sorption maxima are 2.0 MPa and 3.2 MPa, respectively. However, this effect is limited to the low-pressure regime where direct adsorbent-adsorbate interactions are prominent. At higher pressures, the H₂ uptake of S@SWCNT-777 can be seen to crossover with w-SWCNT-777 to a lower value. Here multi-layer formation in mesopores begins where substrate-adsorbate interactions are negligible. At this point, the quantity of hydrogen is then dictated by the total available pore volume remaining, which is reduced in the S@SWCNT-777 sample, resulting in the reduction in excess gravimetric uptake at higher pressures.⁵⁹ Mousavipour and Chitsazi computationally predicted increased binding energy (analogous to the enthalpy of adsorption) for H₂ on sulfur-decorated SWCNTs. Sulfur atoms decorated on the external surface increase the polarizability of the incoming H₂, thus increasing its interaction strength with the surface.^{36,60} Recently, Sedelnikova *et al.* demonstrated modification to the electronic surface where there is an electron accumulation on the external surface of (5,5) chirality CNTs (diameter approx. 0.73 nm) due to the encapsulation.³⁹ Higher enthalpies of adsorption are common in chemisorptive materials where chemical bonding occurs. However, the cryogenic conditions and lack of a desorption hysteresis suggest little to no chemical bonding between H₂ and adsorbent; therefore, this enhancement is deemed physisorption purely. From the PSD of S@SWCNT-777 and w-SWCNT-777, little to no reduction to the pore volume is observed in the ultramicroporous range (see Fig. 4), showing a synergistic effect between the high densification due to these sorption sites and modifications to the surface properties of the material.

A summary of other literature examples of sulfur-doped porous materials for hydrogen sorption at 77 K is given in the ESI† (see Table S3). Improved gravimetric uptakes are comparable to the improvements reported by Li *et al.* for sulfuric acid catalysed templated carbons, where the best performing material reported by Li *et al.* adsorbed approximately 59% more excess H₂ per surface area compared to a hydrochloric acid catalysed reference material (see ESI† Table S3). Despite similar SSA to the sulfur-containing materials described by Li *et al.* and Xia *et al.*,

the S@SWCNTs adsorb less H₂. It is well known that slit-pore materials generally perform better than cylindrical-pore materials for H₂ sorption and that cylindrical pores only demonstrate better performance at low pressures due to capillary condensation of H₂.^{61,62} This, coupled with potential pore blockages likely explains the difference between the samples reported here and other sulfur-doped carbons.

3.4 Estimation of hydrogen densities

Additional information can be extracted from the H₂ isotherms through implementing eqn (1). Semi-empirical modelling is a powerful tool to determine properties that would otherwise present significant challenges or costs to directly determine, such as adsorbate density, where the low atomic cross-section of H₂ makes it a challenging target for most experimental techniques. Excess isotherms shown in Fig. 5 reveal information regarding the quantity of H₂ as a direct result of the attractive electrostatic potential of the surface material. However, by adding the contribution of bulk H₂ within the V_p, the absolute quantity of H₂ can be estimated using the following equation (see eqn (3)).

$$N_a = N_e + \rho_b V_p \quad (3)$$

Following the introduction of sulfur to the porous system, there is a consistent decrease in the maximum absolute H₂ gravimetric uptake (see Fig. 5). This observation can be attributed to the change in the morphology (SSA and V_p) of the porous materials, simply no longer being able to accommodate large quantities of H₂ at higher bulk densities. This translates to a lower H₂ density at pore saturation (see Table 3). To obtain an estimate of volumetric density during pore filling (*i.e.* $\theta < 1$), $N_a(P)$ was simply divided by V_p (see eqn (4)).

$$\rho_{\text{vol}} = \frac{N_a(P)}{100 \times V_p} \quad (4)$$

where N_a is in wt%. V_p is in m³ kg⁻¹. 100 is used to convert N_a from a percentage.

At lower pressures (<2 MPa), ρ_{vol} of both S@SWCNT-121 and S@SWCNT-777 is greater than in SWCNTs without sulfur (see Fig. 5(d)). This suggests that in both SWCNTs, there is a stronger attractive electrostatic potential as a result of the

Table 3 Summary of gravimetric and volumetric H₂ densities determined through the semi-empirical model

	$a N_e^{\text{max}}/\text{wt}\%$	$b N_a^{(2 \text{ MPa})}/\text{wt}\%$	$c N_a^{(\theta=1)}/\text{wt}\%$	$d \rho_a^{(2 \text{ MPa})}/\text{kg m}^{-3}$	$e \rho_a^{(\theta=1)}/\text{kg m}^{-3}$
w-SWCNT-121	1.99 ± 0.03	2.16 ± 0.02	8.22 ± 0.19	18.19 ± 0.21	69.05 ± 1.61
S@SWCNT-121	1.35 ± 0.11	1.66 ± 0.21	5.40 ± 0.52	17.62 ± 2.21	57.49 ± 5.58
w-SWCNT-777	1.67 ± 0.02	1.82 ± 0.01	8.22 ± 0.06	14.24 ± 0.11	64.29 ± 0.48
S@SWCNT-777	1.70 ± 0.03	1.93 ± 0.03	4.17 ± 0.12	24.76 ± 0.33	53.52 ± 1.65
S2@SWCNT-777	0.66 ± 0.04	0.84 ± 0.02	1.72 ± 0.34	15.25 ± 0.37	31.38 ± 6.14
w-TE7	3.02 ± 0.03	3.29 ± 0.02	4.93 ± 0.04	48.37 ± 0.32	72.49 ± 0.61
S@TE7	1.52 ± 0.04	1.74 ± 0.05	3.50 ± 0.10	24.57 ± 0.67	49.26 ± 1.39

^a Maximum measured excess gravimetric uptake (average of all repeat measurements). ^b Absolute gravimetric hydrogen uptake at 2 MPa determined from fitting using eqn (1) (average of all repeat measurements). ^c Absolute gravimetric uptake at pore saturation determined from fitting using eqn (1) (average of all repeat measurements). ^d Volumetric hydrogen density determined using eqn (4) (average of all repeat measurements). ^e Volumetric hydrogen density at pore saturation using eqn (4) (average of all repeat measurements).



interactions between the sulfur and the SWCNT surface. The effect is more pronounced in S@SWCNT-777, likely owing to the preservation of the PSD within the sub-nanometer range, providing additional attraction. To test the effect of sulfur loading and microporosity, a second batch of S@SWCNT-777 (S2@SWCNT-777) was prepared with greater sulfur content and highly diminished total micropore volume (see ESI,† Fig. S9). The sulfur content of S2@SWCNT-777 was determined to be 19 wt% from TGA, and a Dubinin–Radushkevich μV_p of $0.16 \text{ cm}^3 \text{ g}^{-1}$ was calculated. Much of the loss in microporosity originates from the reduction of total pore volume in the ultra-microporous range ($<0.7 \text{ nm}$). S2@SWCNT-777 shows a severely reduced hydrogen density both at pore saturation and 2 MPa by 32% and 49.6%, respectively. S2@SWCNT-777 demonstrates that, while sulfur can improve adsorbate density, microporosity has a larger impact on densification. Many of the stronger binding sites for SWCNTs are located in exohedral grooves between adjacent CNTs.⁶³ Due to the greater sulfur loading, it is expected more exohedral sites within the bundle will be occupied by the sulfur; this prevents hydrogen from experiencing the improved electrostatic potential provided by the confined sulfur species.

4 Conclusion

Non-metal doping of existing porous materials offers an exciting and sustainable route to improved H_2 storage and densification. We report the increased H_2 surface packing and H_2 densities within sulfur vapour infiltrated SWCNTs at pressures up to 2 MPa. The enhanced properties are proposed to stem from the retention of ultra-micropore volume and modifications to the polarizability of the material surface through electrostatic interactions between the CNT surface and the encapsulated sulfur species, which produced greater densities of hydrogen. However, maintaining the ultra-micropores (approx. 0.7 nm) is imperative to achieving high densities of H_2 . Limiting the location of sulfur to the endohedral cavity of the SWCNTs while preserving high ultra-microporosity may provide the greatest enhancement to hydrogen densification. This is illustrated particularly by a comparative activated carbon sample (TE7 and S@TE7) and a second higher sulfur-loaded SWCNT-777, where the inclusion of the sulfur resulted in significant changes to the PSD, reducing the strong densification contributions from the desirable ultra-microporous sites. Future work will further explore the changes in the properties of the dense hydrogen adsorbate phase and identify the preferable adsorbate sites in these composites through neutron scattering and Raman spectroscopy, amongst other complementary techniques. Furthermore, experimental validation of increased enthalpy of adsorption may be provided through the application of the Clausius–Clapeyron method using additional adsorption isotherms at a range of temperatures.

Author contributions

CDB performed the experiments, data analysis and drafted the manuscript. LRT contributed to methodology, data analysis,

conceptualisation, supervision, and reviewing & editing of the manuscript. HVD contributed through the methodology and data analysis. SR contributed to data analysis, project supervision and reviewing & editing of the manuscript. VPT contributed to project conceptualisation, data analysis, supervision and reviewing & editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank the Engineering and Physical Science Research Council through the EPSRC Centre for Doctoral Training in Composites Science, Engineering and Manufacturing [EP/S021728/1] and an EPSRC Research Fellowship for VPT [EP/R01650X/1]. HVD thanks the Royal Society of Chemistry for the Research Fund grant [R20-8172]. HVD acknowledges support from the UK Engineering and Physical Sciences Research Council [EP/T517872/1]. SR acknowledges the support of the University of Bristol Dean's Fellowship. XPS experiments were performed at the Cardiff hub of the EPSRC National Facility for X-ray Photoelectron Spectroscopy ('HarwellXPS'), operated by Cardiff University and UCL under contract No. PR16195. Special thanks to Dr John Day (University of Bristol) for conducting the Raman Spectroscopy, Dr Mi Tian (University of Exeter) for consultation on this project, Dr Prasanth Prabhakaran (Teesside University) for training on the Hiden Isochema XEMIS-001 and Mr Duncan Tarling (University of Bristol) for manufacturing the H-shaped quartz ampule.

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