Development of Mg-SWNT system for hydrogen storage

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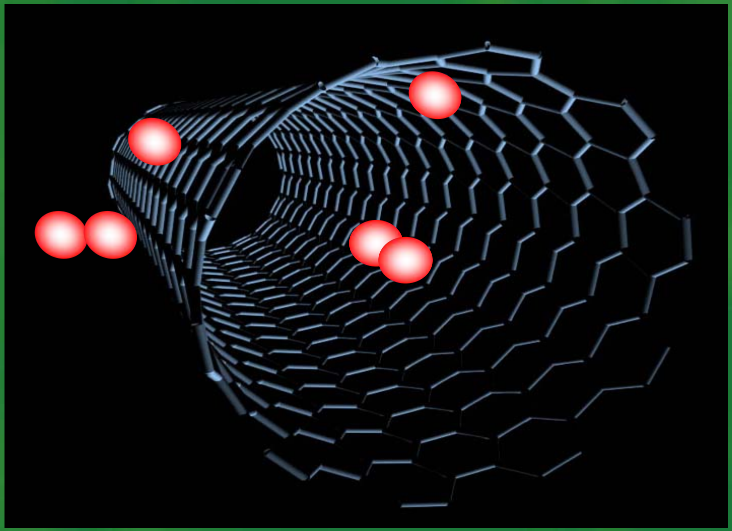
Outline

- Hydrogen storage in CNTs
- Hydrogen storage in Mg-CNT system
- Concluding remarks

1: Hydrogen Storage in Carbon Nanotubes



Summary of reported experimental results for hydrogen storage in CNTs/CNFs since 2002.

Sample	Synthesis technique	Diameter (nm)	Purity	Pre-treatment	Surface area ($m^2 g^{-1}$)	Storage method	Pressure and temperature	Result (wt%)	Reference nos
SWNT	HiPco	—	Purified	400°C vacuum	—	V	8 MPa, RT	0.43 (A)	[31]
MWNT	CVD	20–30	Purified	HF washing and air oxidation	33.7	V	100 bar, 298 K	3.3 (A)	[49]
SWNT	HiPco	—	Unpurified	CO_2 oxidation and 973 K under H_2 or He	—	G	48 bar, RT	1.2 (A)	[51]
MWNT	CVD	—	—	HNO_3 washing	—	V	145 bar, 300 K	3.7 (A)	[33]
MWNT	CVD	10–60	—	2200°C Ar	—	V	10 MPa, RT	3.98 (A)	[43]
MWNT	CVD	53	—	1037 K Ar	25	V	13.59 MPa, RT	4.6 (A) 3.2 (R)	[44]
MWNT	CVD	30	—	Acid washing, CO_2 oxidation, and compression	137	V	10 MPa, 77 K	0.45 (A)	[58]
MWNT (tip opened)	CVD (anodized Al_2O_3 template)	40	—	900°C Ar	840	V	10 MPa, 77 K and 10 MPa, RT	6.46 (A) 1.12 (A)	[34]
CNF	CVD	—	—	700°C H_2 *in situ*	242	V	69 bar, RT	3.8 (R)	[45]
SWNT	Arc discharge	1.2–1.5	—	Activated with KOH	1433	V	1 bar, RT 1 bar, 77 K	0.02 (A) 1.58 (A)	[57]
Mixed SWNT and DWNT	CVD	—	Unpurified	250°C vacuum	881	V	10 MPa, RT	0.51 (A)	[54]
MWNT	CVD	10	Unpurified	—	—	TDS	Desorbed up to 2000°C	8.6 (R)	[38]
SWNT	Laser ablation	1.4	Purified	NaOH treatment	—	V	9 MPa, RT	0.3 (A)	[66]
SWNT	HiPco	—	Purified	HF washing, heated under Ar	797	G	1 bar, 295 K, 1 bar, 77 K	0.2 (A) 1.7 (A)	[35]
SWNT	Arc discharge	1.2–1.5	Unpurified	Air oxidation, H_2 reduction	728	V	300 Torr, 77 K	3.0 (A)	[55]
SWNT	HiPco	—	Purified	Acid washing	710	V	3.5 MPa, 303 K	0.25 (A)	[91]
SWNT	HiPco	—	90 wt%	Vacuum degassed	800	V	300 atm, 294 K	0.91 (A)	[60]
SWNT	Arc discharge	1.2	75 wt%	Air oxidation, 400°C vacuum	—	V	25 bar, 77 K	2.4 (A)	[47]
MWNT	CVD	25–30	Purified	Ball milled	—	V	9 MPa, RT	0.69 (A)	[53]
SWNT	Arc discharge	0.7–1.2	12–15 wt%	873 K degassed	230	TDS	2 MPa	0.60 (R)	[36]
MWNT	CVD	60–100	—	400°C vacuum	—	V	10 MPa, RT	5.0	[50]
MWNT	CVD	10–30	85 wt%	NaOH washing 400°C vacuum	—	V	10.61 MPa, RT	0.272 (R)	[52]
CNF	CVD	250	—	150°C vacuum	—	V	80 atm, RT	17 (A)	[48]

Notes: RT, room temperature; V, volumetric; G, gravimetric; TDS, thermal desorption spectrum; A, adsorption; R, release.

Summary of reported theoretical results for hydrogen storage in CNTs/CNFs since 2002

Sample	Diameter (nm) or (*n*, *m*) indices	Intertube distance (nm)	Method	Temperature and pressure	Storage capacity (wt%)	Reference nos
CNT and CNF	—	—	GCMC	293 K, 10 MPa	0.6	[86]
SWNT	2.719	Isolated	Classical potential and DFT	77 K, 4 MPa	9.5	[76]
SWNT	2.719	Isolated	Classical potential and DFT	300 K, 20 MPa	1.0	[76]
SWNT	1.17	0.7	Tight-binding MD and GCMC	293 K, 10 MPa	3.4	[89]
Li-doped pillared SWNT	(10, 10) and 1 : 3 Li : C doping	0.9	Developed DFT and GCMC	50 bar RT	6.0 wt%, 61.7 kg m^{-3}	[87]

C. Liu & HM Cheng, Carbon Nanotubes for Clean Energy Applications, J Phys D: Appl Phys ***38***, 2005

Some perspectives obtained

- **The wide range of discrepancy has not been observed for any other hydrogen storage materials.**
- **Great efforts are made to identify influencing factors:**
  - **measurement methodology**
    - **Volumetric, gravimetric and thermal desorption spectrum (TDS) methods are most commonly used**
  - **synthesis techniques and post-treatment**
    - **Some synergitic effect between CNTs and nanosized metal hydrides**
    - **Acid or alkali treatment does not routinely improve the capacity**
    - **A suitable posttreatment or activation process may be beneficial**
  - **structural characteristics**
    - **SWNTs with larger diameter and MWNTs with worse structural perfection seem to be preferable**
  - **surface and pore characteristics**
    - **Pore structures of CNTs unique to ACs. Higher capacity observed**
    - **No perfect consistency in relationship between H capacity and SSA of CNTs**
  - **Adsorption sites**
    - **Four basic sites: inner cavity, interstitial channel, cylinder-shaped outer surface and groove site**
  - **Measurement pressure**
    - **Below 6MPa, almost no hydrogen can be stored**

SWNTs by sulfur-assisted arc discharge

（average diameter: ~1.7 nm)

39.5g; raw Mater.: Graphite

21.5g; raw Mater.: CNFs

Purification of SWNTs

SWNT products by hydrogen arc discharge

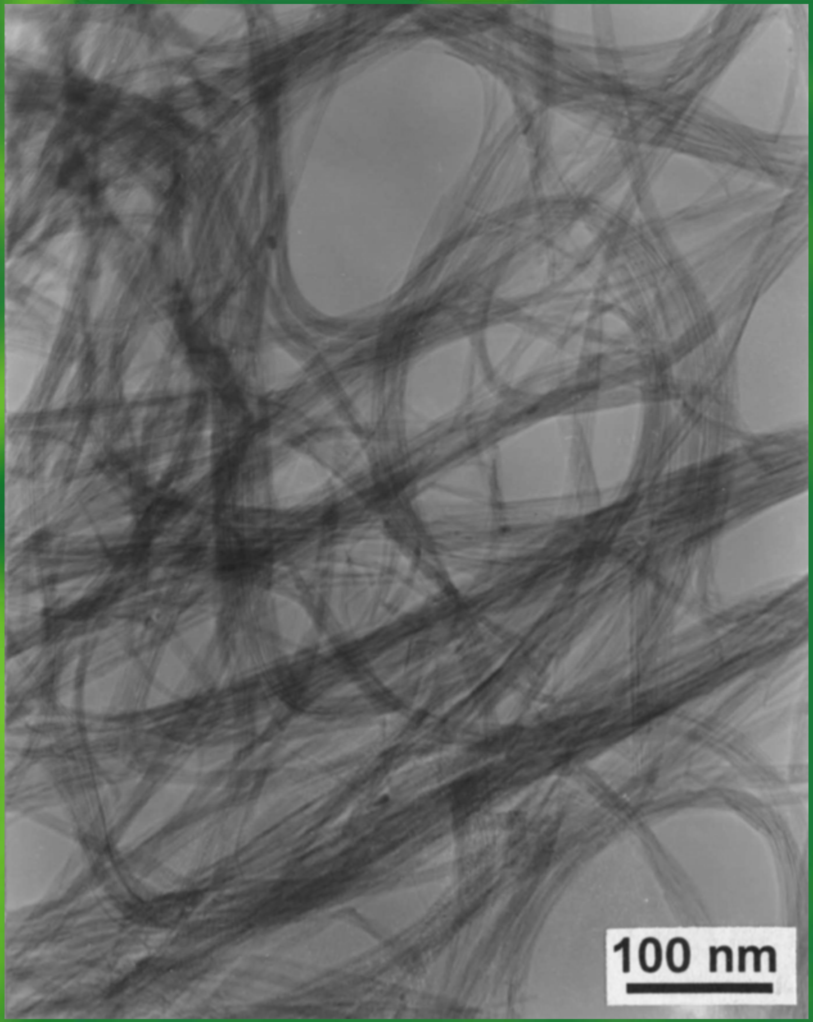
Ultrasonic vibration for 10 mins, separation of graphite particles, for 5 times

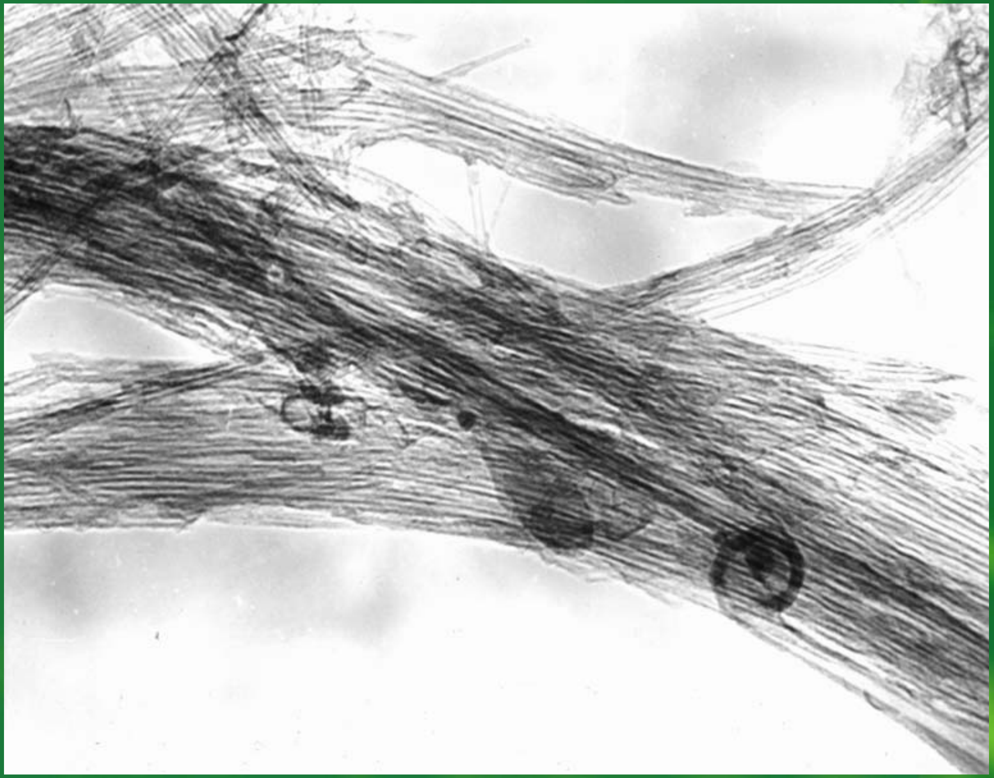
Boiling in water for 4 hrs for 3 times

Oxidation at 550 C in 3L air for 40 mins

Immersing in HCl acid

Washing to PH of 7 and drying





After purification (~4 wt% catalyst metal residue), part of the SWNTs were cut short and more defects are induced.

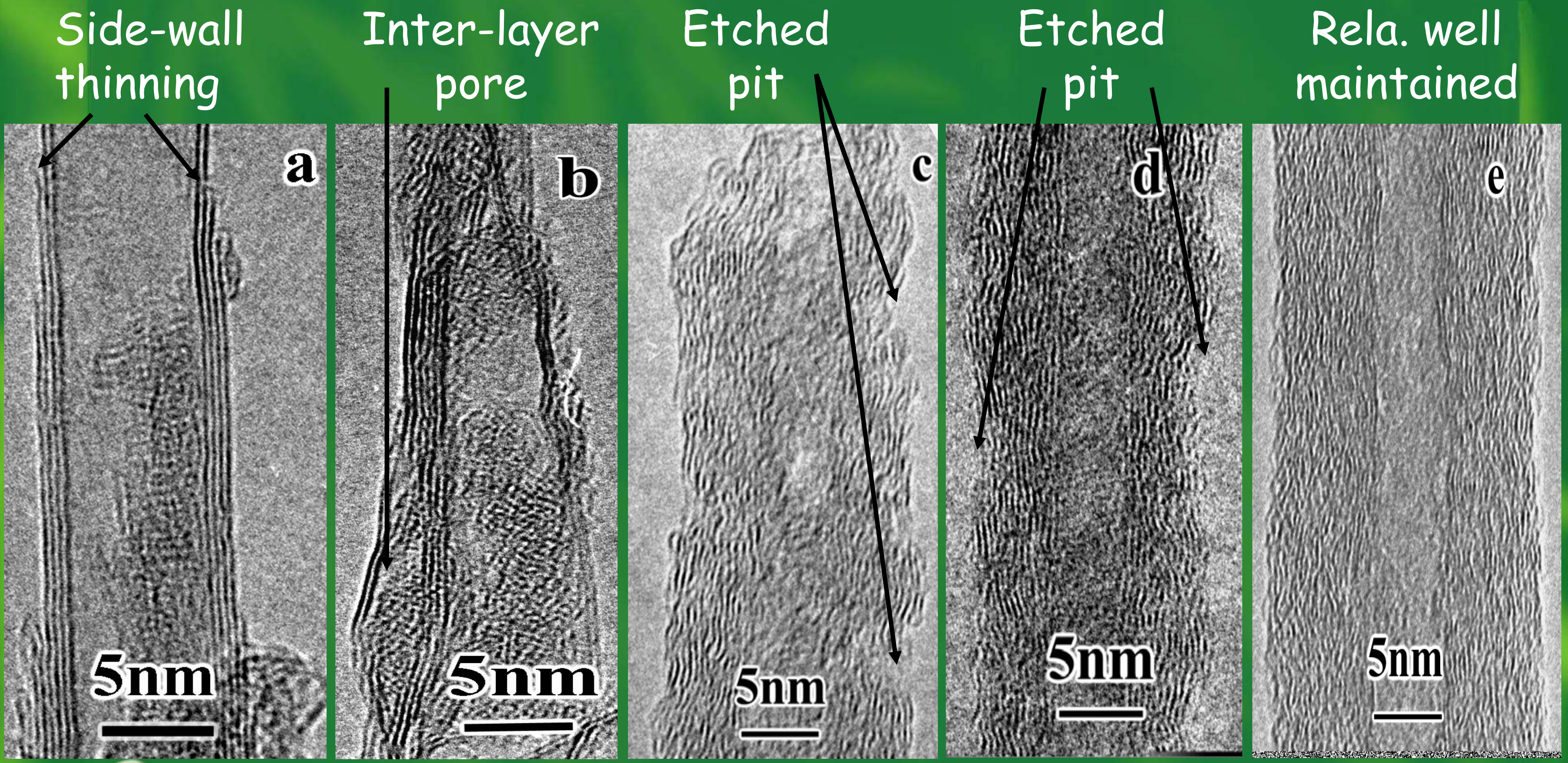
Experimental procedure of volumetric measurement method

- **Calibration of the setup**
  - **AC (Maxsorb): 0.6-0.8 wt% at 13 MPa and RT**
  - **$LaNi_5$: 1.34-1.44 wt% at 13 MPa and RT**
- **Heating the sample cell and vacuum degassing at 473 K**
- **Introduction of high purity H_2 (99.999~99.9999% purified by metal hydride)**
- **Measurements of pressure change**
- **Release of the adsorbed H_2**

Influence of purification and annealing on H-storage performance of SWNTs

Samples	Anneal. T (° C)	Meas. T (° C)	P_{H2} (MPa)	Sam.Weight (mg)	H-capacity (wt.%)
as-prepared	900	23	12.1	190	0.50
purified	500	24.5	12.1	214	1.05
purified	600	24.5	12.4	176	0.99
Purified	700	25.7	11.8	190	1.44
Purified	900	19	12.2	206	1.65

Activation of MWNTs: HRTEM observation



KOH-activated (a, b, c); CO_2-activated (d); air-activated MWNTs (e)

Hydrogen storage in the activated MWNTs

(~295 K, 13 MPa)

MWNTs	S_{BET} (m^2/g)	$V_{micro.}$ (cm^3/g)	$V_{meso.}$ (cm^3/g)	H-Capacity (wt.%)
As-prepared	65.7	0.009	0.118	0.24
Air-activated	270.4	0.056	0.555	0.90
CO_2-activated	429.1	0.102	0.582	1.01
KOH-activated	785.2	0.165	1.044	1.18

Activation is beneficial for hydrogen storage

2: Mg/SWNTs composite for hydrogen storage

Synergetic advantage

?

Effect of graphite addition

- **Hydrogen storage performance of Mg could be improved more or less by adding graphite.**

H. Imamura, et al, J. Alloys Comp. 293-295 (1999) 564-568.

H. Imamura, et al, Acta Mater. 51 (2003) 6407-6414.

J.-L. Bobet, et al, J. Alloys Comp. 366(2004)298-302.

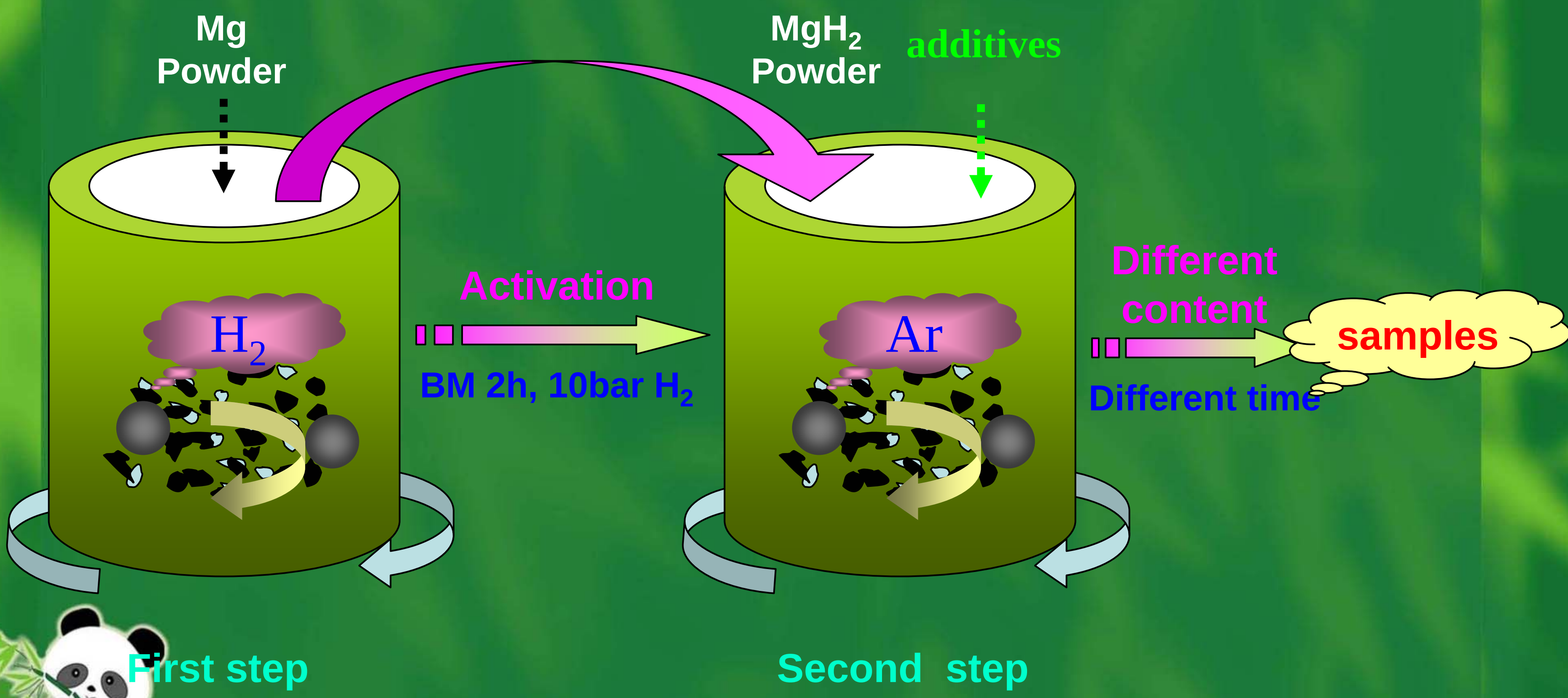
S. Bouaricha, et al, J. Mater. Res., 16(10)2893-2905

- **Graphite has little influence on the desorption properties of MgH2.**

C. X. Shang, Z.X. Guo, J. Power Sources, 129 (2004) 73-80.

Preparation of composite samples

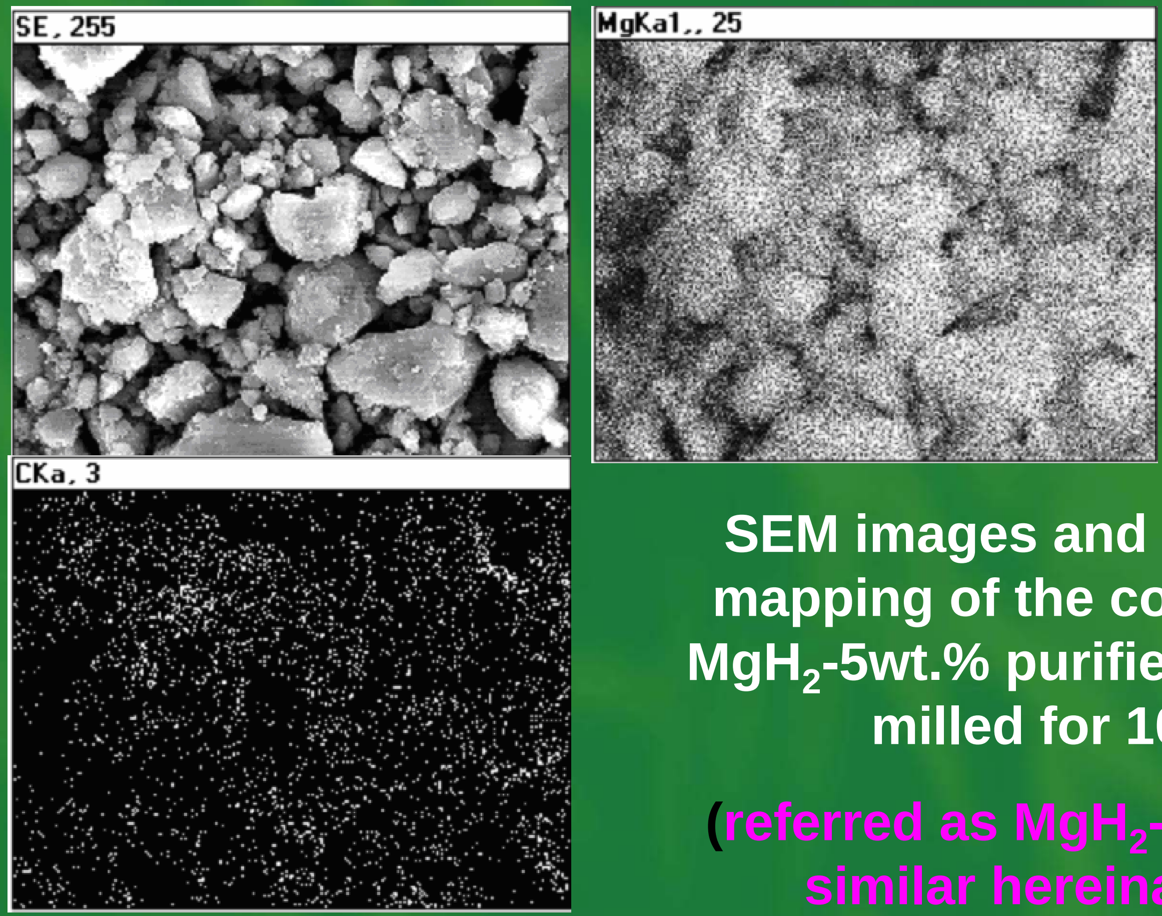
- reaction ball mill method



Addition of various carbon/non-carbon materials

- MgH_2 was mechanically ground for 10h with various additives below :
  - Carbon materials: purified SWNTs, activated carbon (Maxsorb), carbon black, graphite, and fullerene
  - Non-carbon materials: boron nitride nanotubes, and asbestos
- For the sake of comparison, MgH_2 also milled without additive for 10h

Dispersion of carbon nanotubes

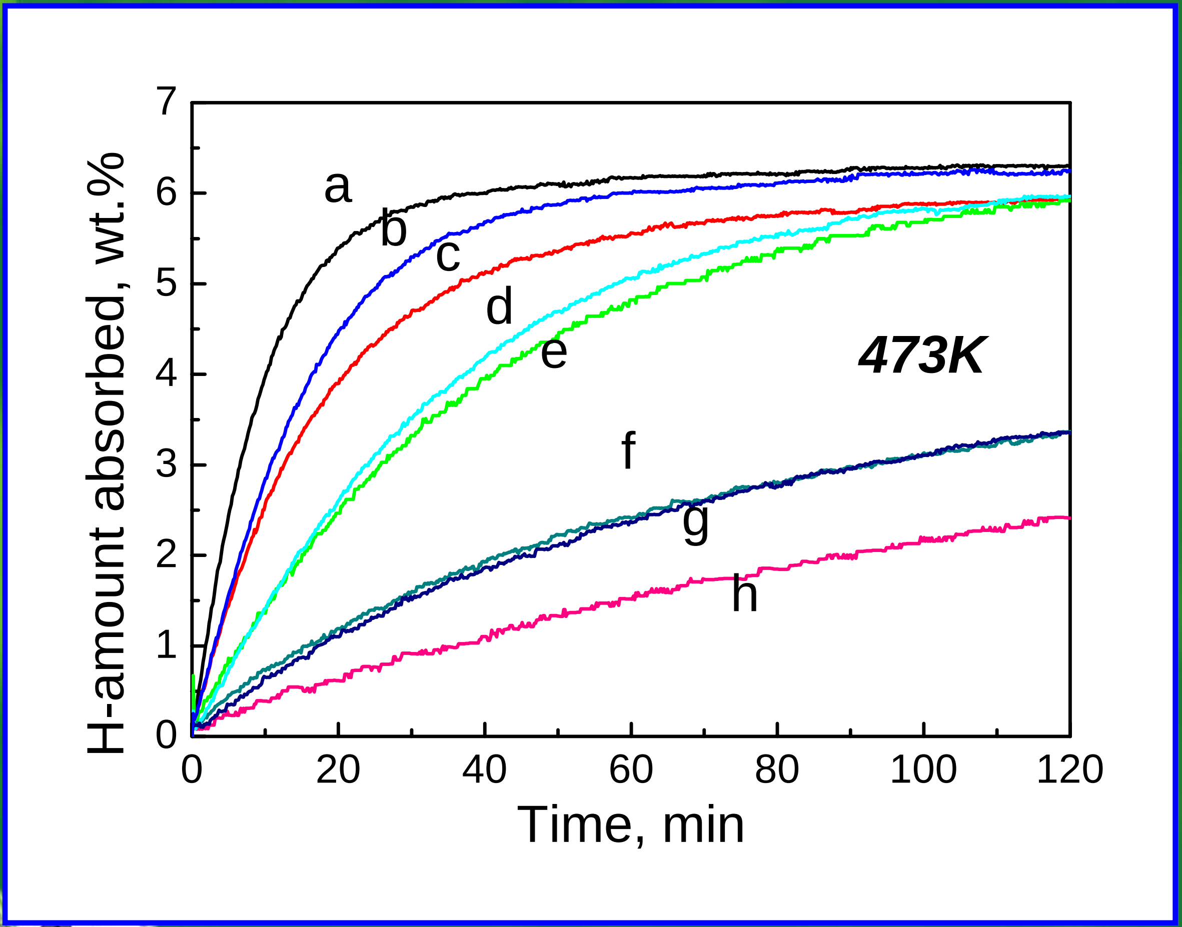


SEM images and element mapping of the composite MgH_2-5wt.% purified SWNTs milled for 10h

(referred as MgH_2-5ps-10h, similar hereinafter)

Dispersion seems to be quite uniform.

Addition of various carbon/non-carbon materials

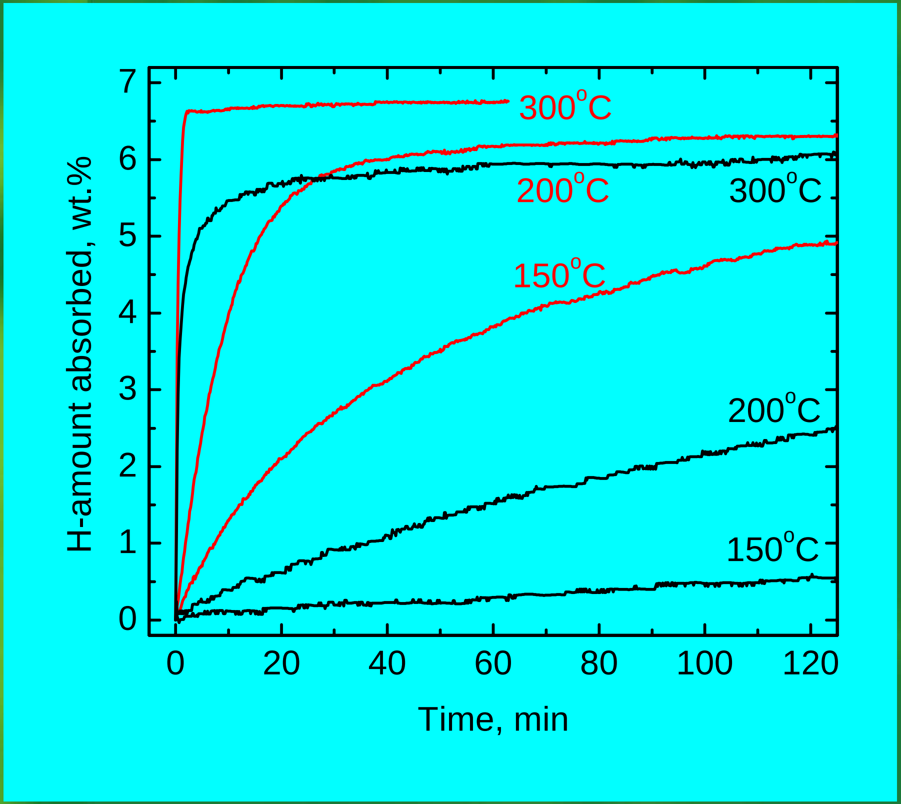


Hydrogen absorption profiles of the composite ***(a) MgH_2-5ps***, ***(b) MgH_2-5CB***, ***(c) MgH_2-5AC***, ***(d) MgH_2-5C_{60}***, ***(e) MgH_2-5G***, ***(f) MgH_2-5BNNTs***, ***(g) MgH_2-5Asbestos and (h) MgH_2*** (milled for 10h,respectively) at 473K with an initial hydrogen pressure of about 2.0 MPa.

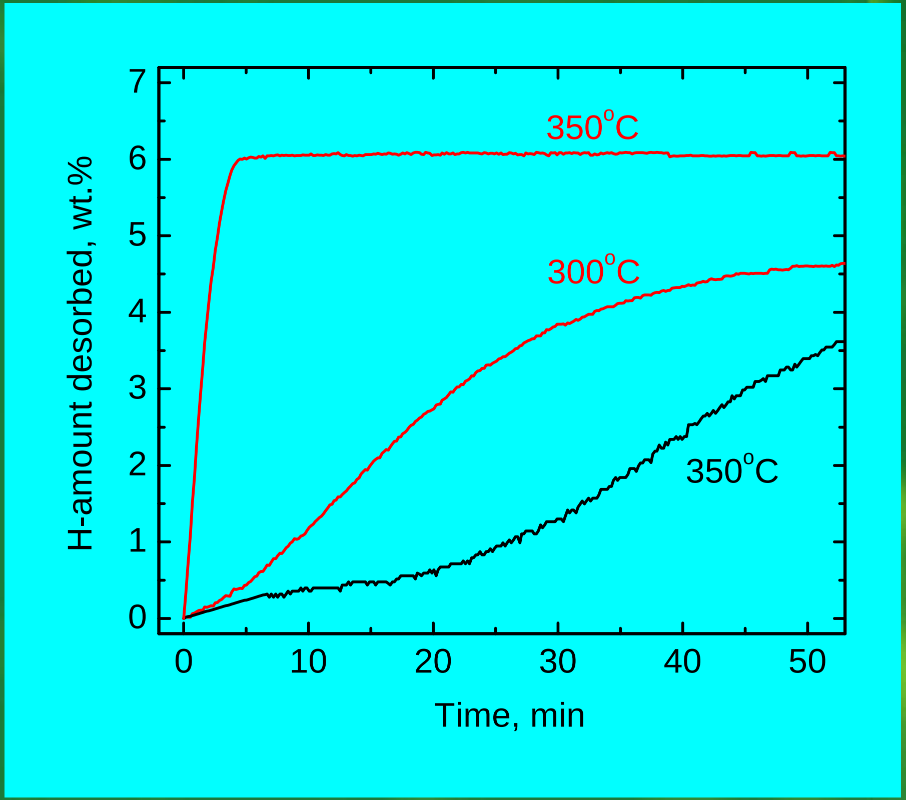
SWNTs are the most effective.

Enhanced de-/hydriding performance upon adding SWNTs (purified)

RH



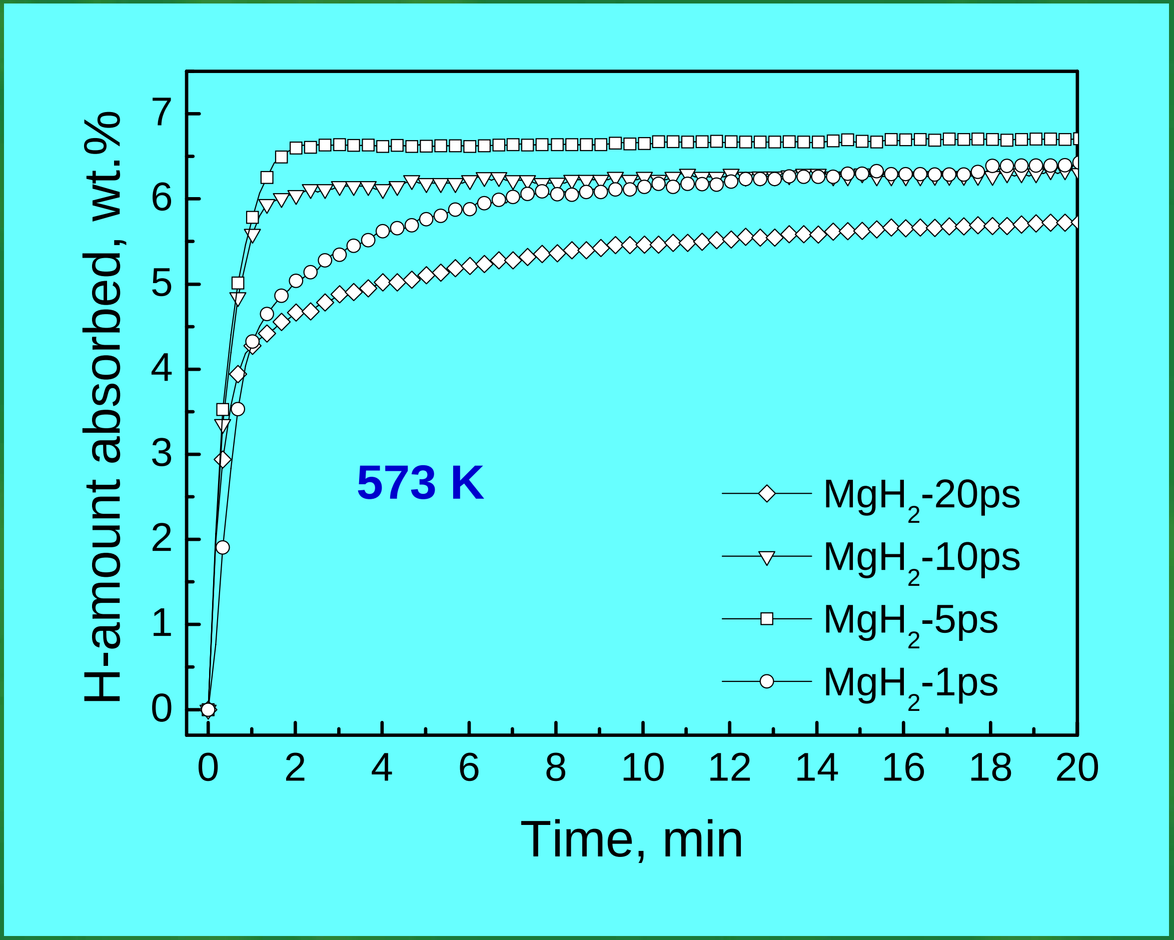
DH



— MgH_2+5wt.% SWNT, H_2, 10h; — MgH_2, H_2, 10h

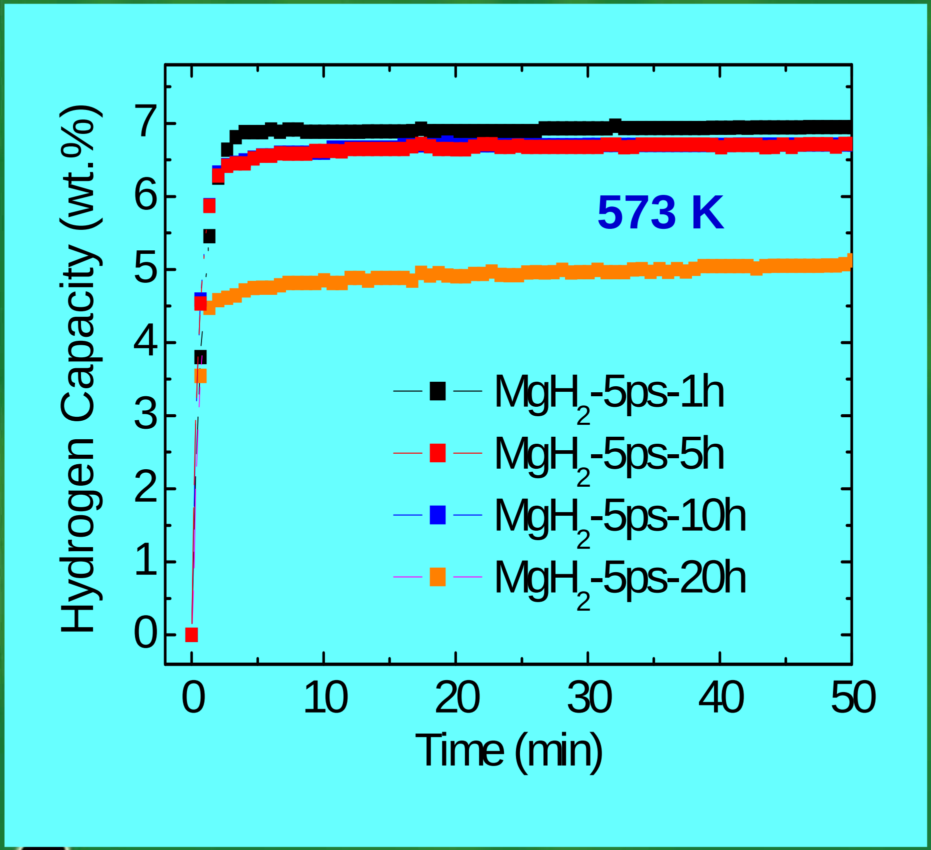
Both hydrogen capacity and hydrogenation kinetics of MgH_2 are markedly improved upon addition of SWNTs, especially at moderate temperature.

Dependence of H-storage performance of MgH_2/SWNTs composite on SWNT content



Hydrogen absorption profiles of the composite MgH2-*x* wt.% SWNTs ball milled for 10 h at 573 K with an initial hydrogen pressure of about 2 MPa.

Dependence of H-storage performance of MgH_2/SWNTs composite on milling time



Further ***increasing*** milling time from 10 to 20h

Destruction of C nano-structure or Local Mg-C interaction ?

Substantial ***decreased*** H-Capacity

Addition of pre-milled purified SWNTs

Purified SWNTs

Purified SWNTs milled for 30min

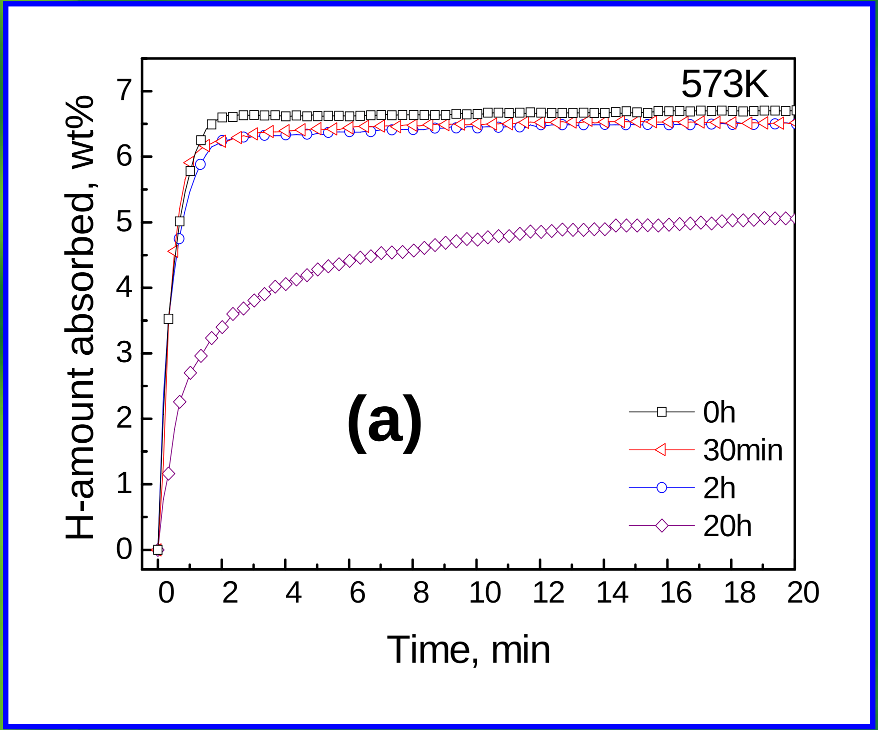
MgH_2+ ***+Milled for 10h***

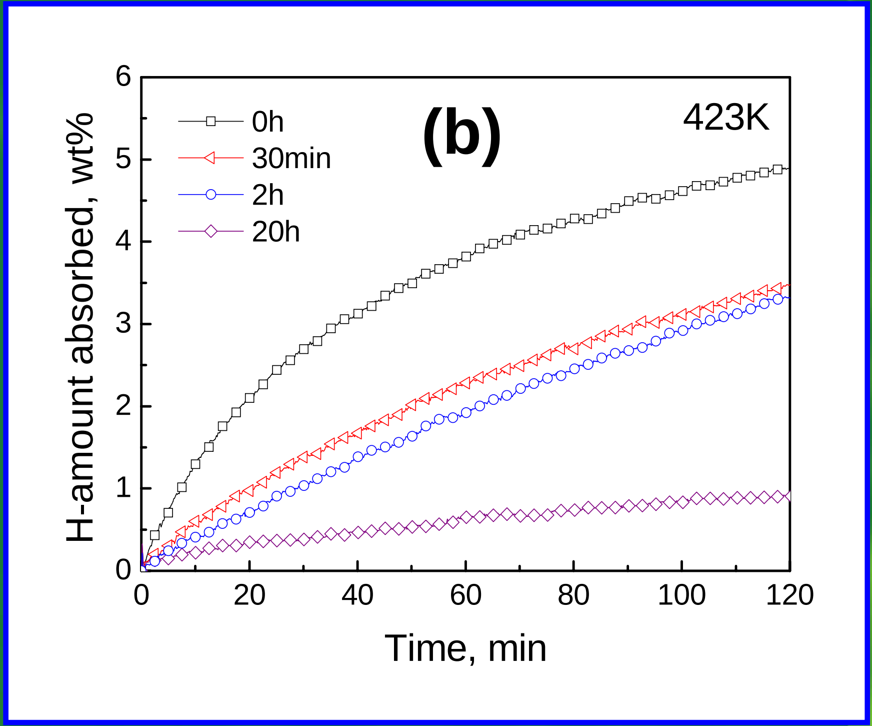
Purified SWNTs milled for 2h

Purified SWNTs milled for 20h

Objective: To investigate the function of SWNTs.

Addition of pre-milled purified SWNTs





Hydrogen absorption profiles of the composites MgH_2-5ps, MgH_2-5(ps-30min), MgH_2-5(ps-2h) and MgH_2-5(ps-20h) (milled for 10h, respectively) at (a) 573K and (b) 423K with an initial hydrogen pressure of about 2MPa.

Addition of as-prepared SWNTs

MgH_2-purified SWNTs

MgH_2-Fe,Co,Ni

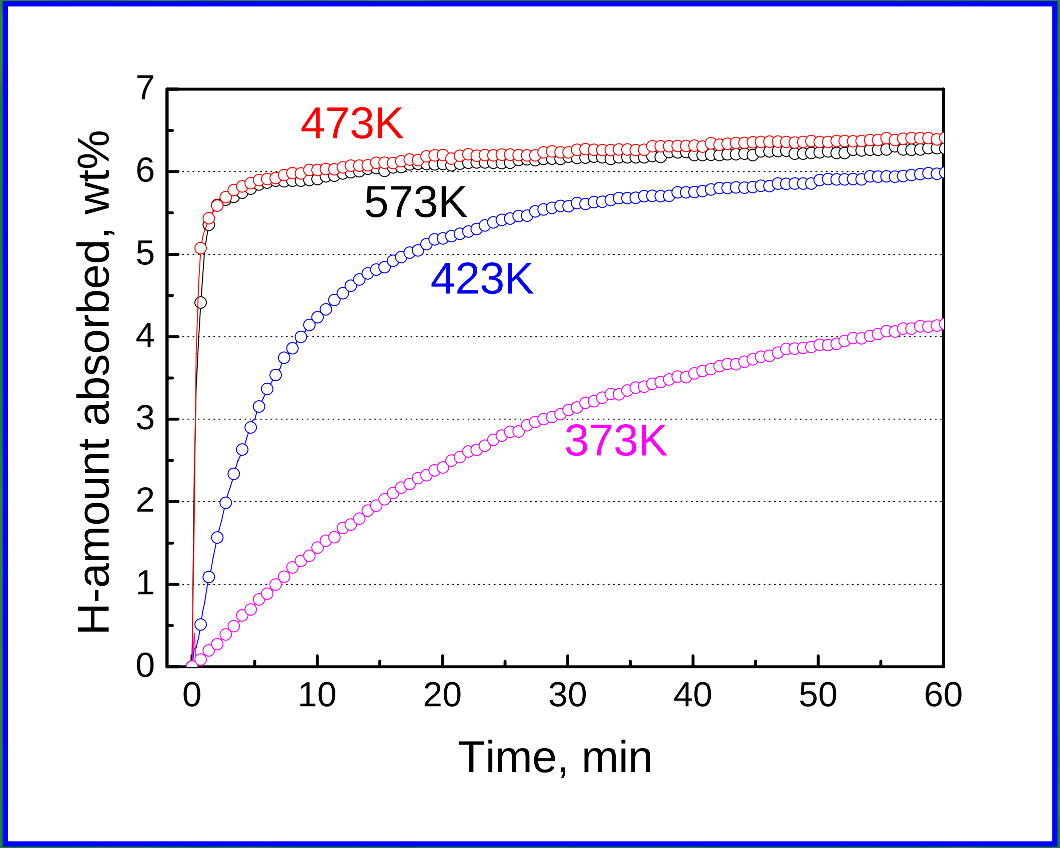
↓

MgH_2-5wt.% as-prepared SWNTs

↓

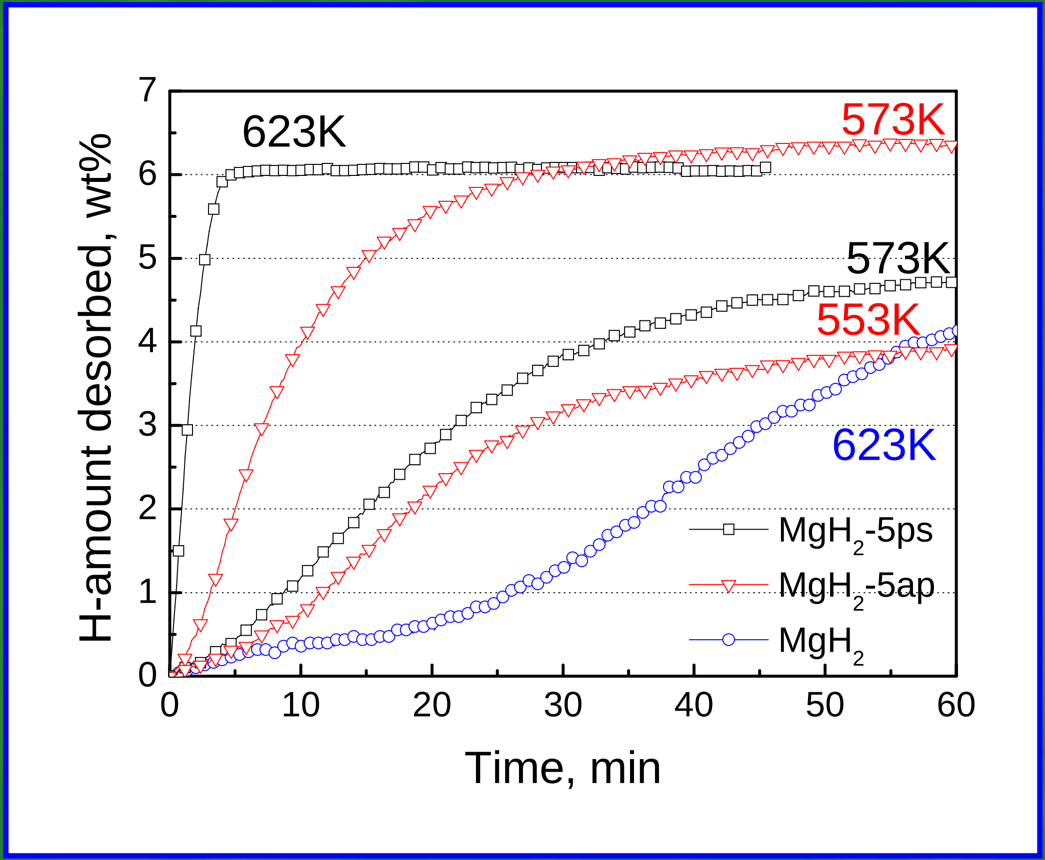
Positive Effect?

Addition of as-prepared SWNTs



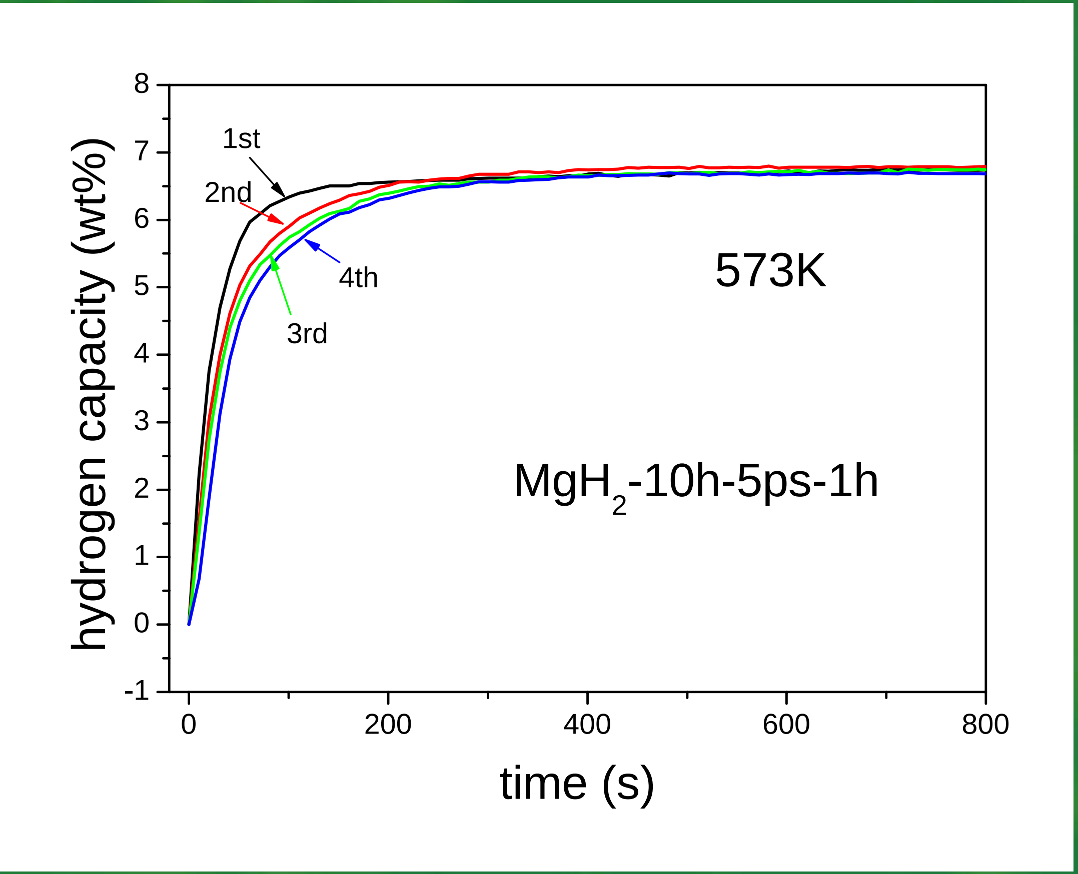
Hydrogen absorption profiles of the composite MgH_2-5ap-10h at the temperature range of 373K to 573K under 2.0 MPa hydrogen pressure

Comparison of hydrogen desorption of Mg/SWNT composites



Hydrogen desorption profiles of the composite ***MgH_2-5ps***, ***MgH_2-5ap***, ***and MgH_2*** at various temperature from 553K to 623K.

cycling stability of MgH_2-5% purified SWNT composites



With cycling, hydrogenation kinetics was somehow decreased, but the capacity was unchanged.

3. Concluding Remarks

- Efforts on CNTs are continuously made, and it is found that CNTs can absorb some amount of hydrogen.

- The hydrogen capacity of Mg can be considerably improved by addition of SWNTs
  ---Role of the novel carbon nanostructure?

- The utilization of as-prepared SWNTs leads to a more pronounced enhancement

  ---Function of metal catalyst nanoparticles?

- Mg-SWNT is a promising system for hydrogen storage. The systematic investigations including mechanism elucidation are on-going.

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Thank you very much for your attention!

Http:// carbon.imr.ac.cn