The Hydrogen Storage Performance of Magnesium Based Nanostructures Prepared by Oblique Angle Deposition

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Outline:

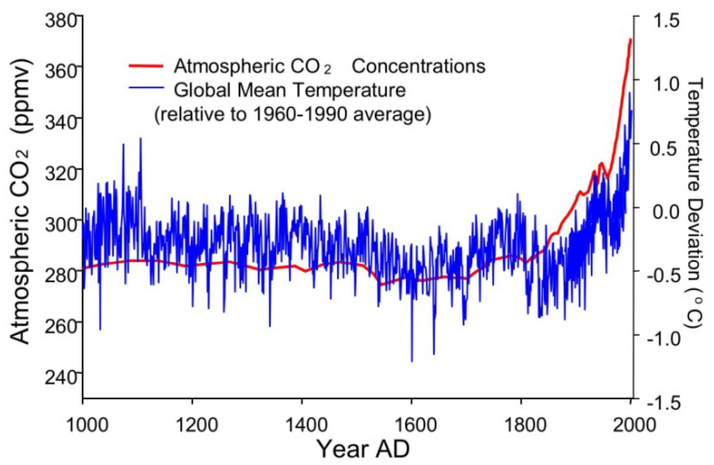
- Introduction
- Hydrogenation behaviors

  1. Mg film versus Mg nanoblade array
  2. V decorated Mg nanoblade array
  3. Mg nanostructures with differently distributed V nanocatalysts
- Conclusions

Hydrogen Economy: Drivers

Fossil Fuels

- Potential exhaustion
- Pollution: CO, CO_2, SO_2, NO_x, dust
- Global warming



Hydrogen

- Abundant: 75% in universe; H_2O on earth as raw materials
- Clean: H_2+O_2 -> H_2O +energy
  Only produces energy and water, zero emission
- Renewable energy

Hydrogen Economy: Four Aspects

- Hydrogen production

  Today: Reform Fossil Fuels

  Tomorrow: Splitting H_2O

- Hydrogen storage

  Today: Gas and liquid

  Tomorrow: Solid state

- Hydrogen transportation
- Hydrogen use

  Today: Combustion H_2 -> heat -> electricity

  Tomorrow: Fuel cells H_2 -> electricity

Hydrogen Storage

Hydrogen storage is the bottleneck for hydrogen energy applications

- Pressurized gas
- Cryogenic liquid
- Solid-state storage
  - Metal hydrides
  - Complex hydrides
  - Carbon-based materials

Solid-state storage is the safest and most efficient method.

Revised Performance and Cost Targets

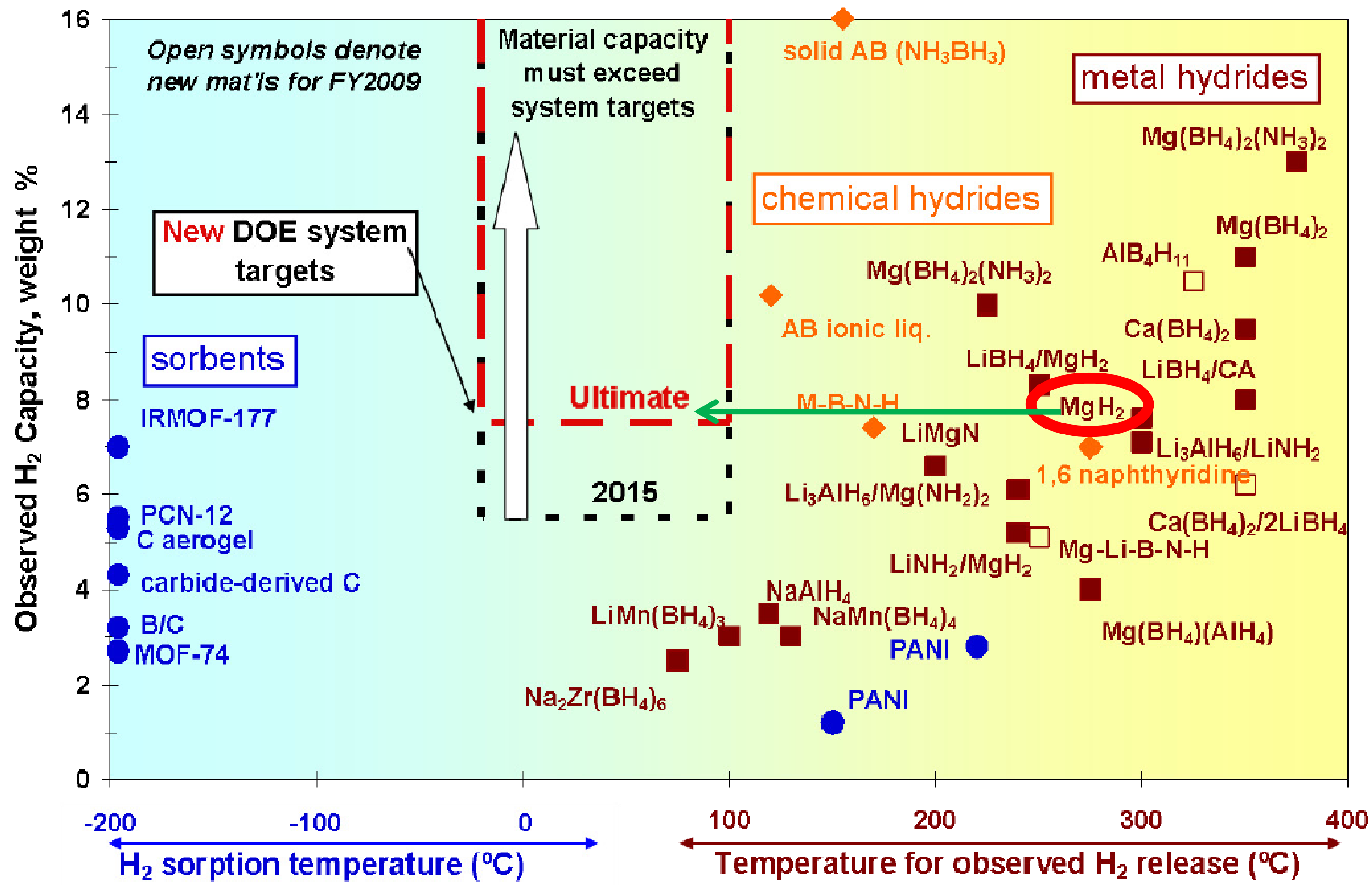
U.S. DEPARTMENT OF ENERGY

Performance targets revised in 2009 based on real-world experience with hydrogen fuel cell vehicles.

Target	**2015**	2015	**Ultimate***
	new	*old*	***new***
System Gravimetric Density [wt.%] (kWh/kg)	**[5.5] (1.8)**	[9] (3.0)	**[7.5] (2.5)**
System Volumetric Density [g/L] (kWh/L)	**[40] (1.3)**	[81] (2.7)	**[70] (2.3)**
System fill time for 5-kg fill [min] (kgH_2/min)	**[3.3] (1.5)**	[2.5] (2.0)	**[2.5] (2.0)**
System cost [$/$kgH_2$] ($/kWh_{net})	**TBD**	[67] (2)	**TBD**

***Ultimate** targets are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models

Progress: Material Capacity vs. Temperature



- Currently no technology is able to meet the revised 2015 targets
- New Ultimate targets remain very challenging
- Focus is on materials-based technologies that have potential to meet Ultimate targets and revised 2015

Mg-Based Hydrogen Storage

MgH_2 is very promising for solid-state hydrogen storage

Advantages (Mg):

- ✓ Low cost
- ✓ Lightweight
- ✓ Nontoxic
- ✓ High hydrogen storage capacity: 7.6 wt% in MgH_2

Problem

- ✗ Poor hydrogen sorption thermodynamics and kinetics
  (MgH_2 is very stable, $T \geq 300^{\circ}C$ is needed to release H_2)

Improvement

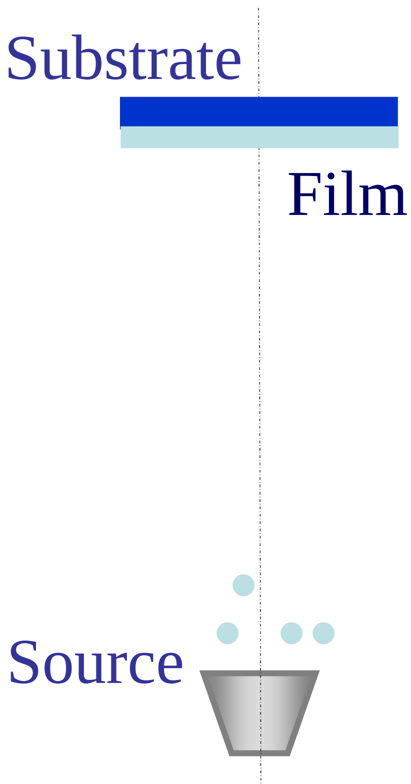
? Tailor Mg into nanostructures

? Add an appropriate transition metal catalyst

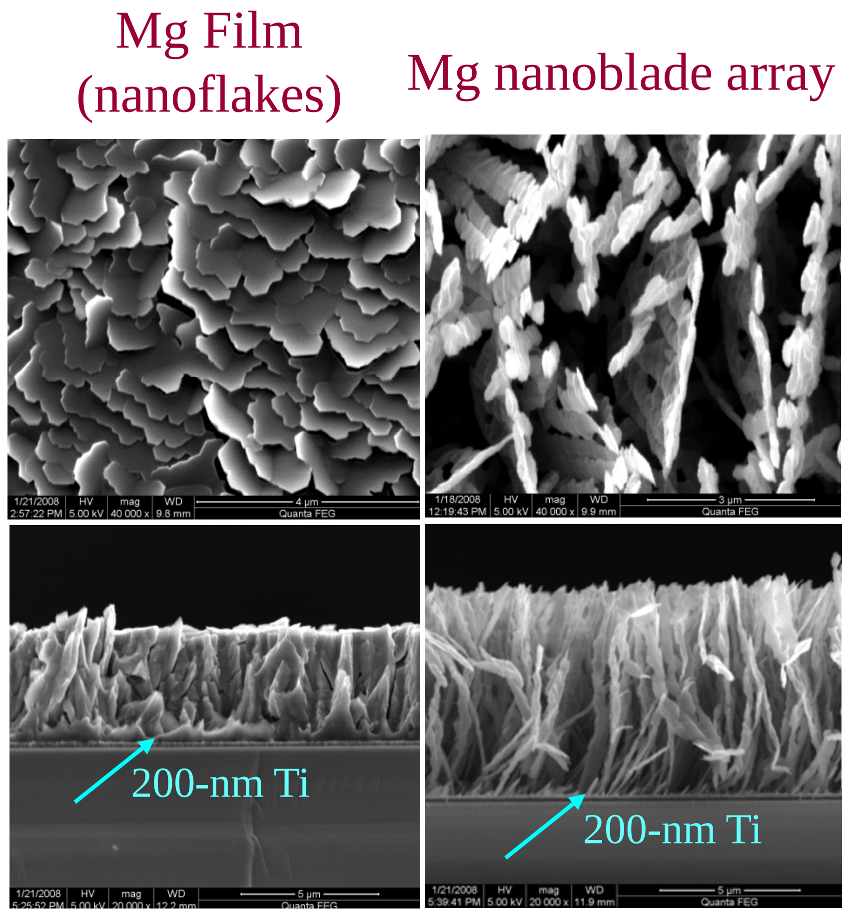
Tailor Mg into nanostructures

Conventional method: mechanical alloying or ball milling

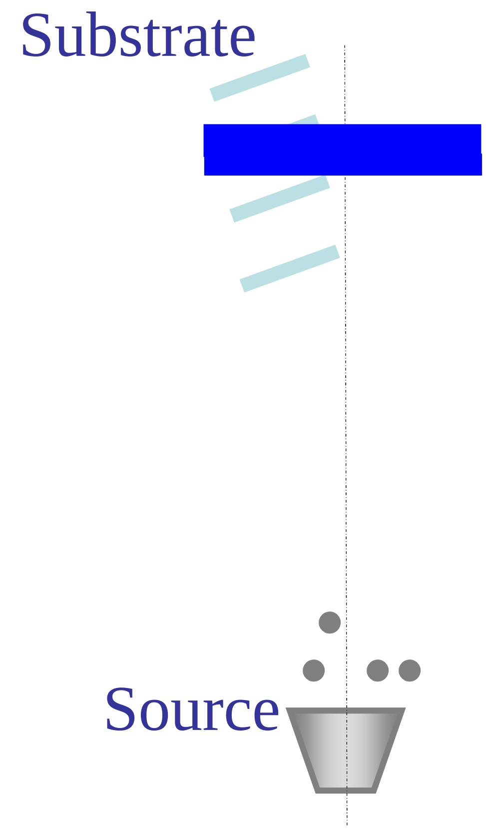
Fabrication of Mg Film and Mg Nanoblade Array



Normal deposition



Hydrogenation (PCT Pro-2000):
20 bar H-pressure
2000 minutes
200°C, 250°C, 300°C, 350°C



Oblique angle deposition (OAD)

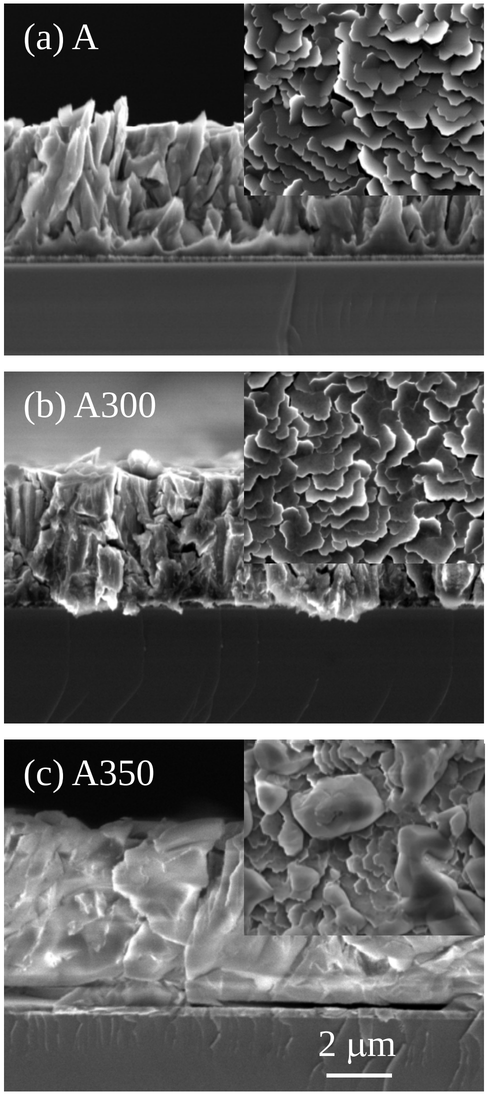
He *et al.*, APL 2008, 93, 163114.

Fabrication and Characterization Systems

Hydrogenation at Different Temperatures

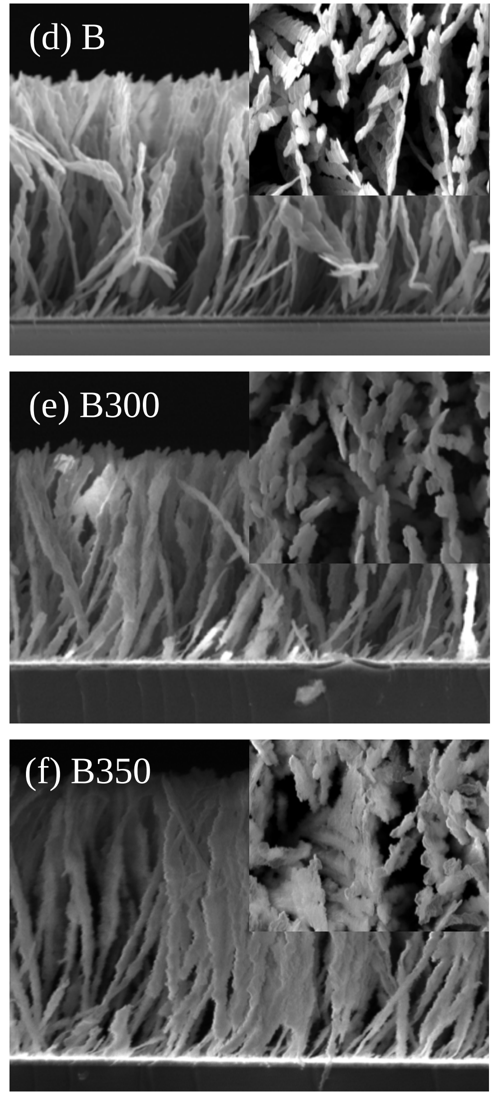
Mg Thin Film

Sample height
$h \approx 4$ μm



$h \approx 6.2$ μm
$\eta \approx 55\%$
Volume expansion η

Mg Nanoblades



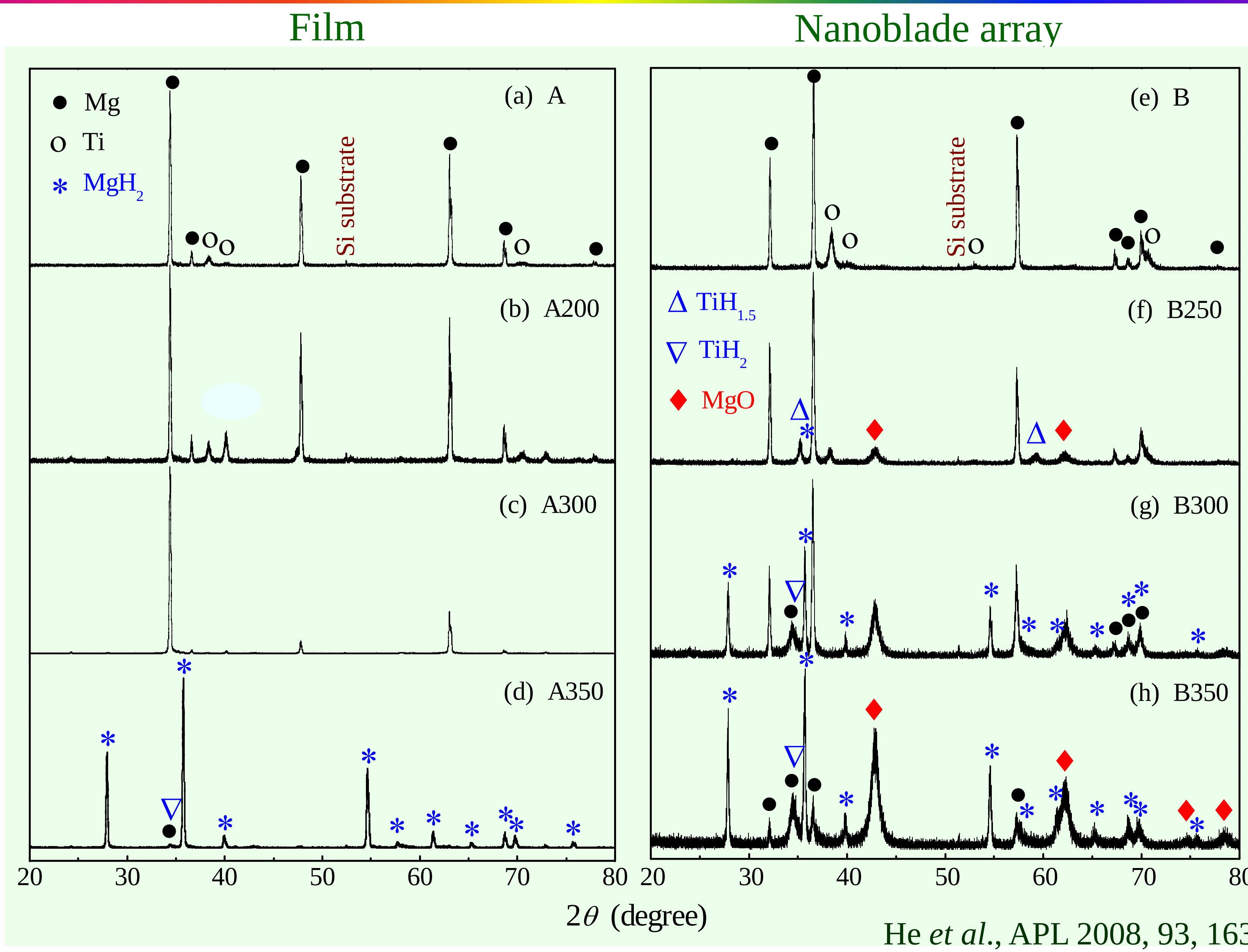
$h \approx 7.1$ μm
$t \approx 160$ nm
Blade thickness t

$h \approx 7.3$ μm
$t \approx 220$ nm
$\eta \approx 41\%$

$h \approx 7.7$ μm
$t \approx 250$ nm
$\eta \approx 69\%$

He *et al.*, APL 2008, 93, 163114.

Hydrogenation at Different Temperatures



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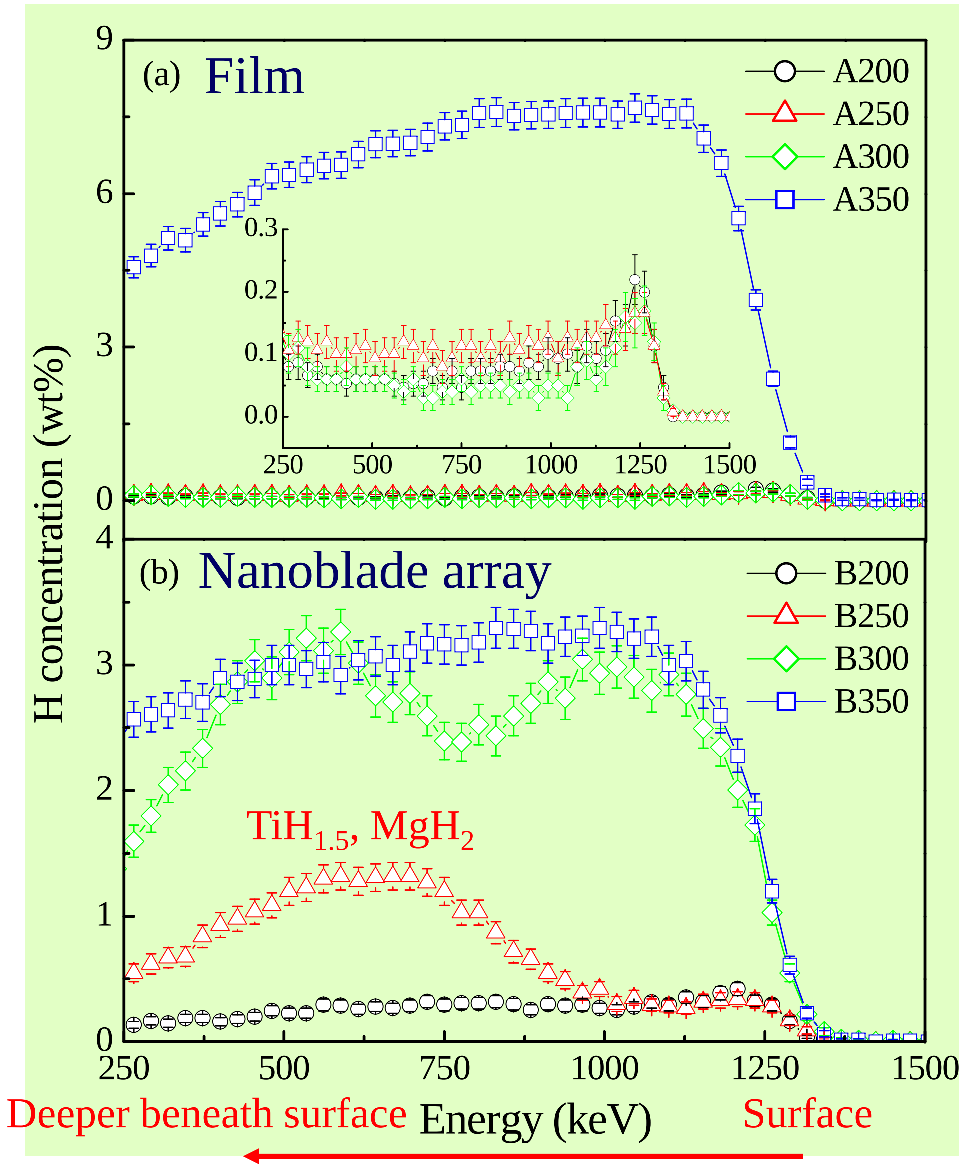
FRES (Forward REcoil Spectrometry)



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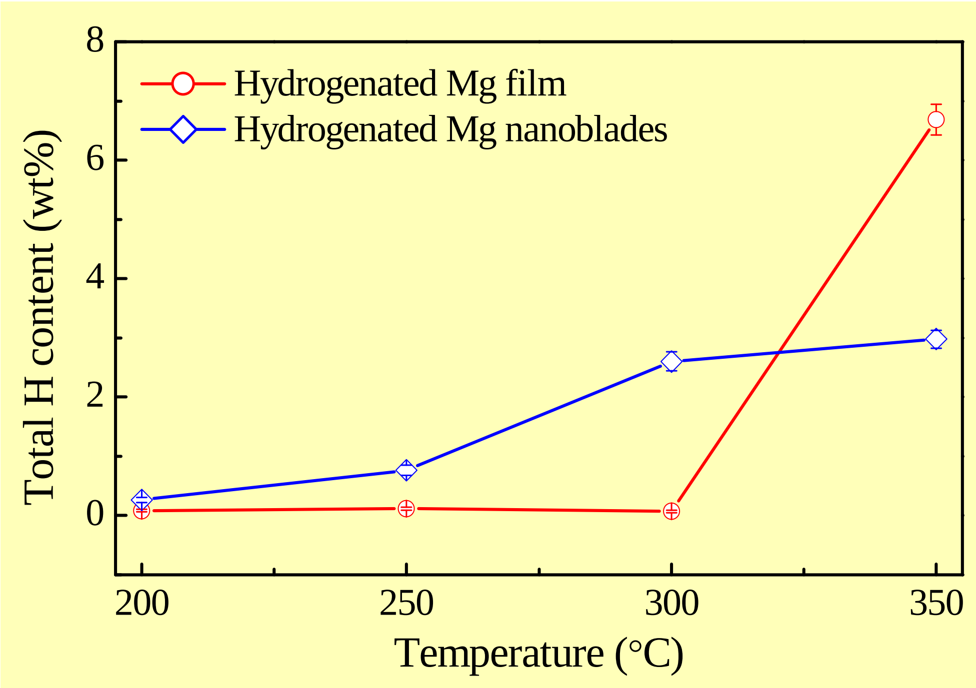
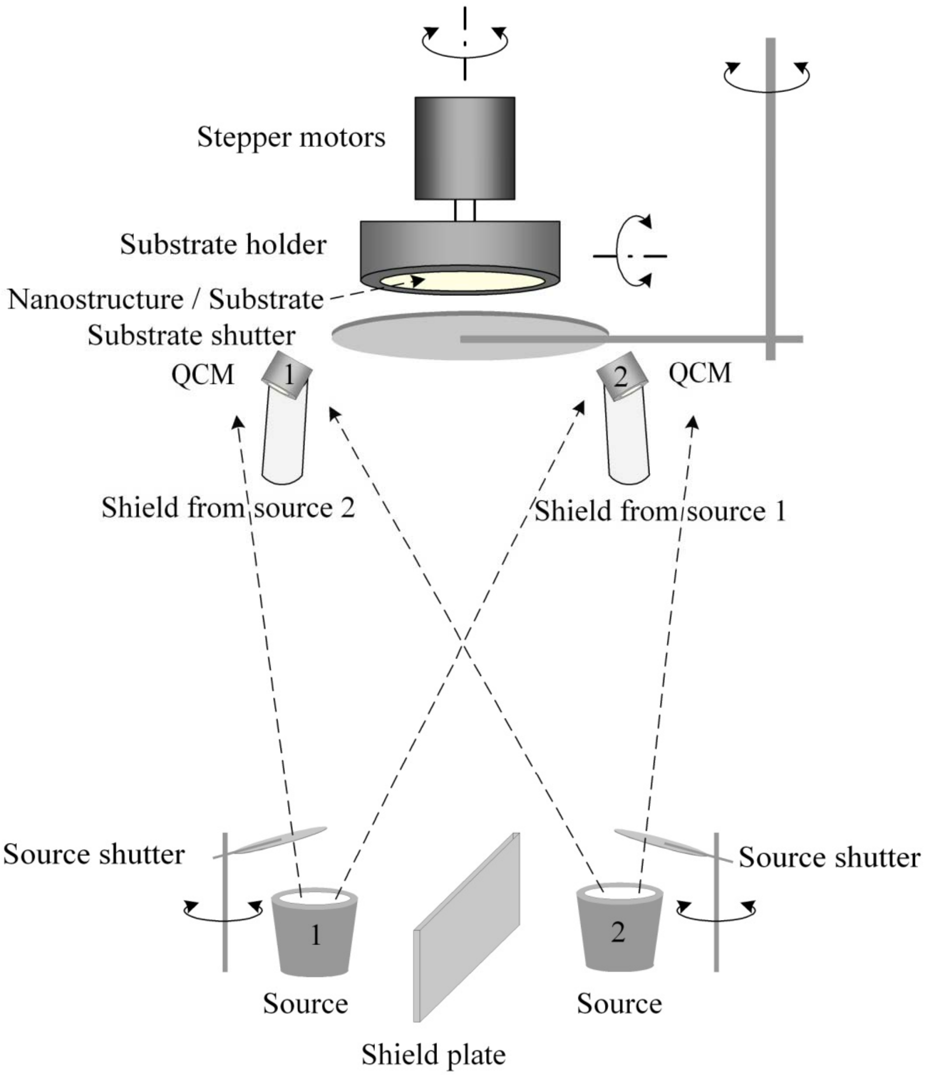


- $T \approx 250°C$ (blades) vs $T \approx 350°C$ (film)
- MgO→ small H amount in blades
- The unique nanoblade morphology and catalysis of Ti layer → nanoblade hydrogenation behavior.

He *et al*., APL 2008, 93, 163114.

Add an appropriate transition metal catalyst

Fabrication of V-Decorated Mg Nanoblade Arrays



He *et al.*, Phys Chem Chem Phys 2009, 11, 255
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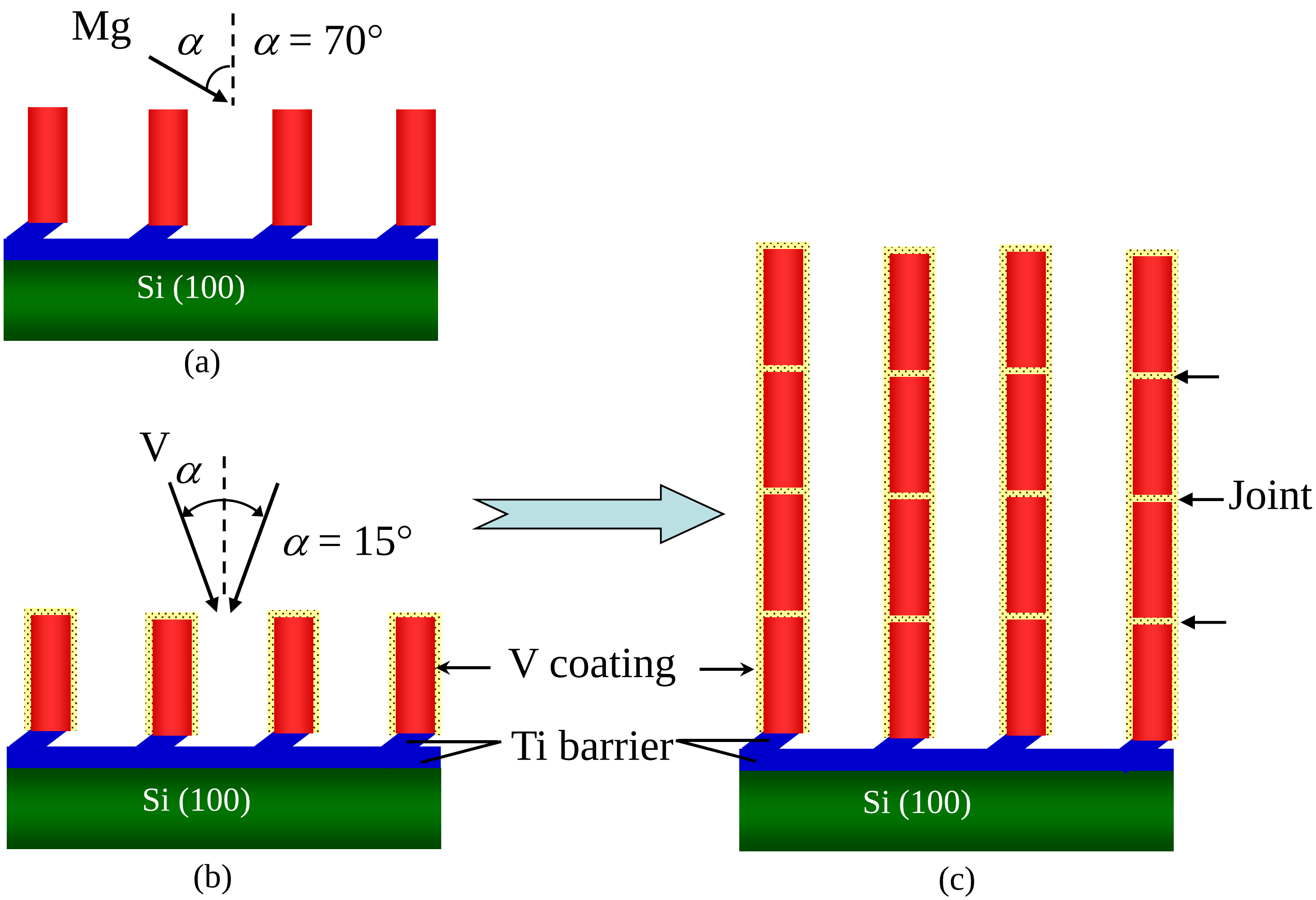

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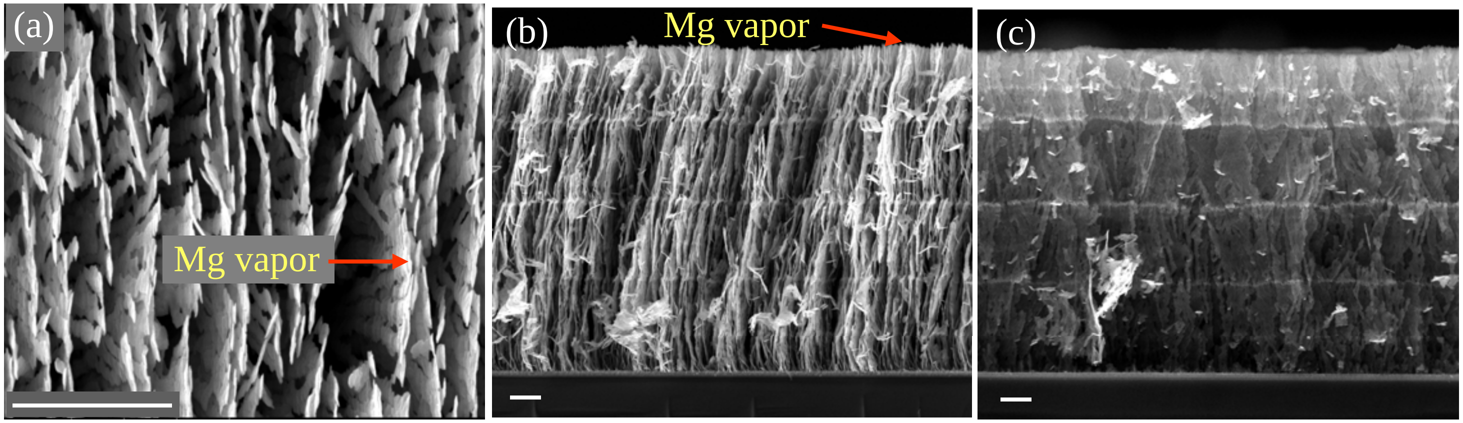
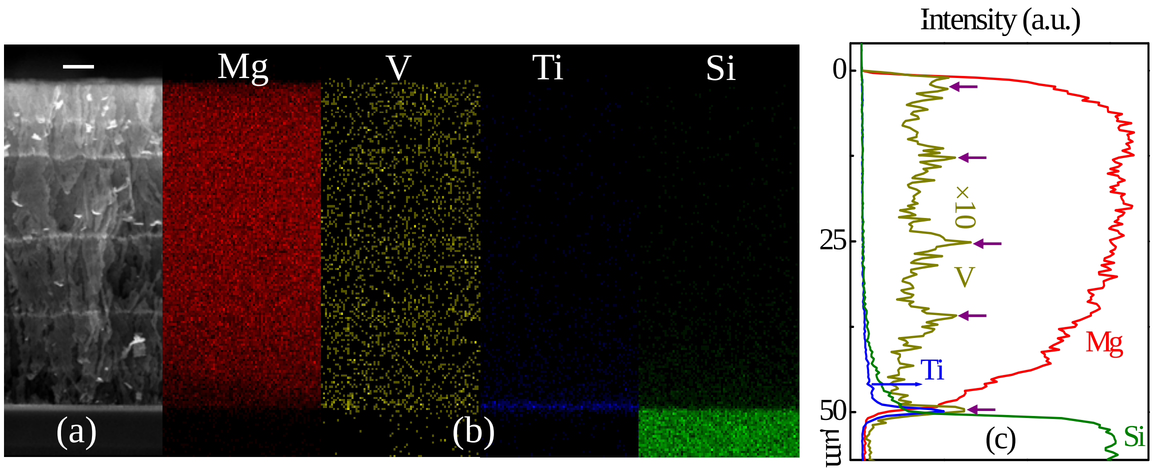
Characterizations: SEM and EDX

Scale bars: 5 µm



h ≈ 50 µm
t ≈ 65 nm



V/(Mg+V) ≈ 2.25 at.%

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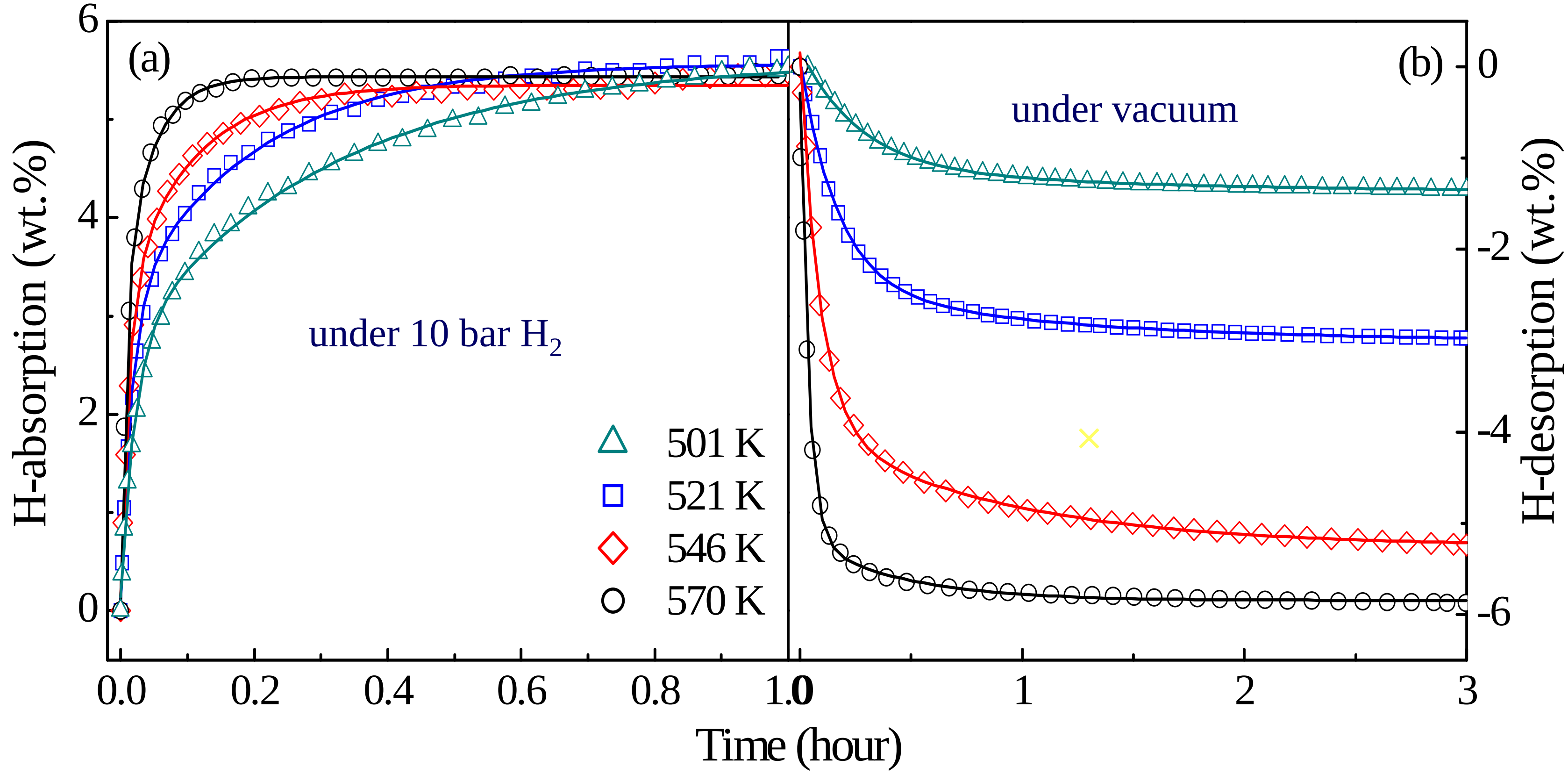
Hydrogen Storage Performance

Kinetic curves



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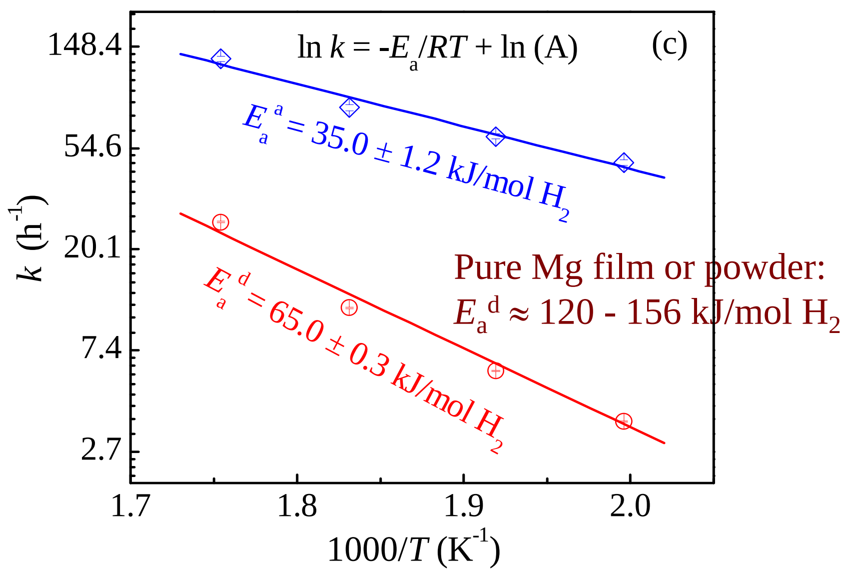
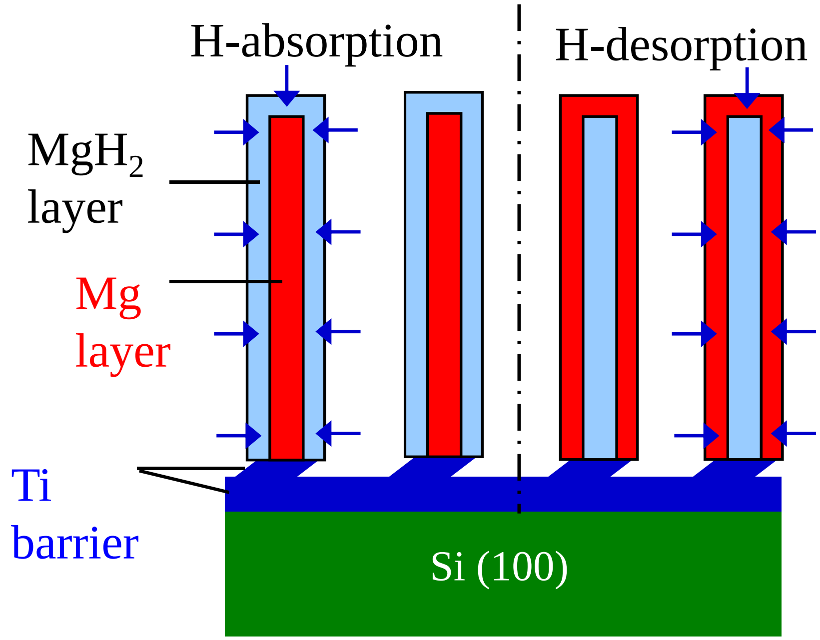
Hydrogen Storage Performance

Arrhenius plots





Spherical particle (radius *R*) model

$$\frac{\partial C_H}{\partial t} = -k_H C_H + D_H \nabla^2 C_H$$

$$\begin{cases} C_H(r < R, t = 0) = C_0 & \text{Initial condition} \\ C_H(r = R, t > 0) = C_s & \text{boundary condition} \end{cases}$$

$$\frac{C_H - C_0}{C_s - C_0} = 1 + \frac{2R}{\pi r}\sum_{m=1}^{\infty}\frac{(-1)^m}{m}\sin\frac{m\pi r}{R}\exp[-(\frac{D_H m^2\pi^2}{R^2} + k_H)t]$$

The larger k_H & D_H, and smaller *R*, the faster the kinetics

- The V coating
- The unique nanoblade morphology:
  1. large surface area
  2. small H-diffusion length.

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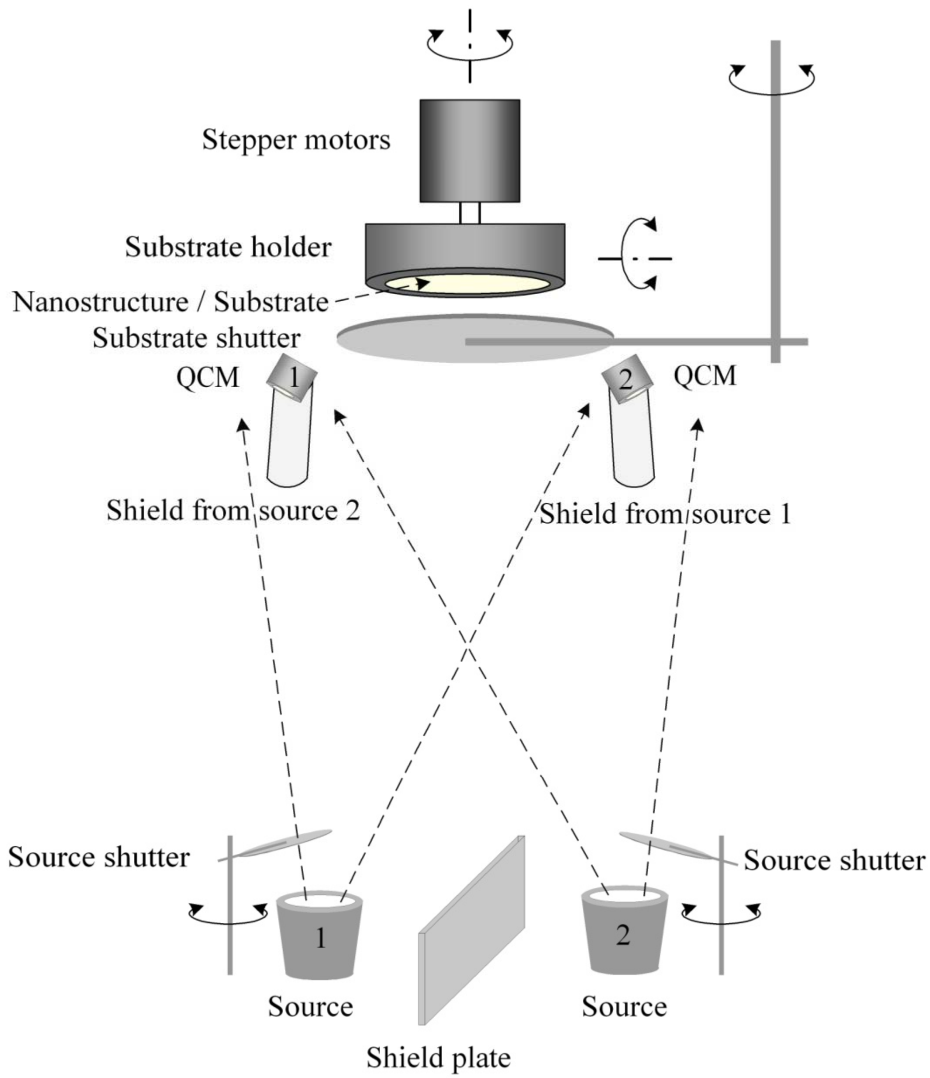
Mg nanostructures with differently distributed V nanocatalysts

He *et al*., Int J Hydrogen Energy 2010, 35, 4162

Fabrication of V-Decorated Mg Nanoblade Arrays



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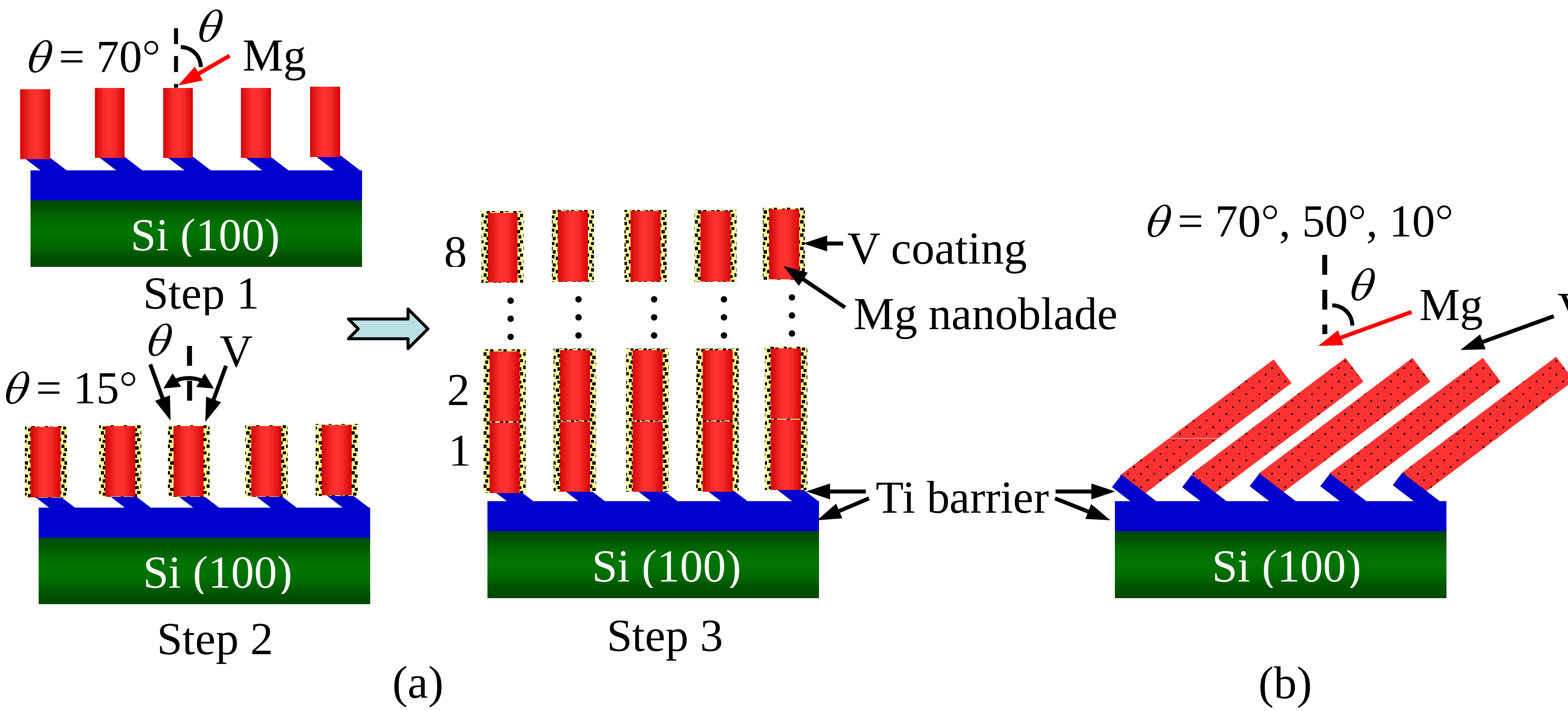
Fabrication of V-Incorporated Mg Nanostructures

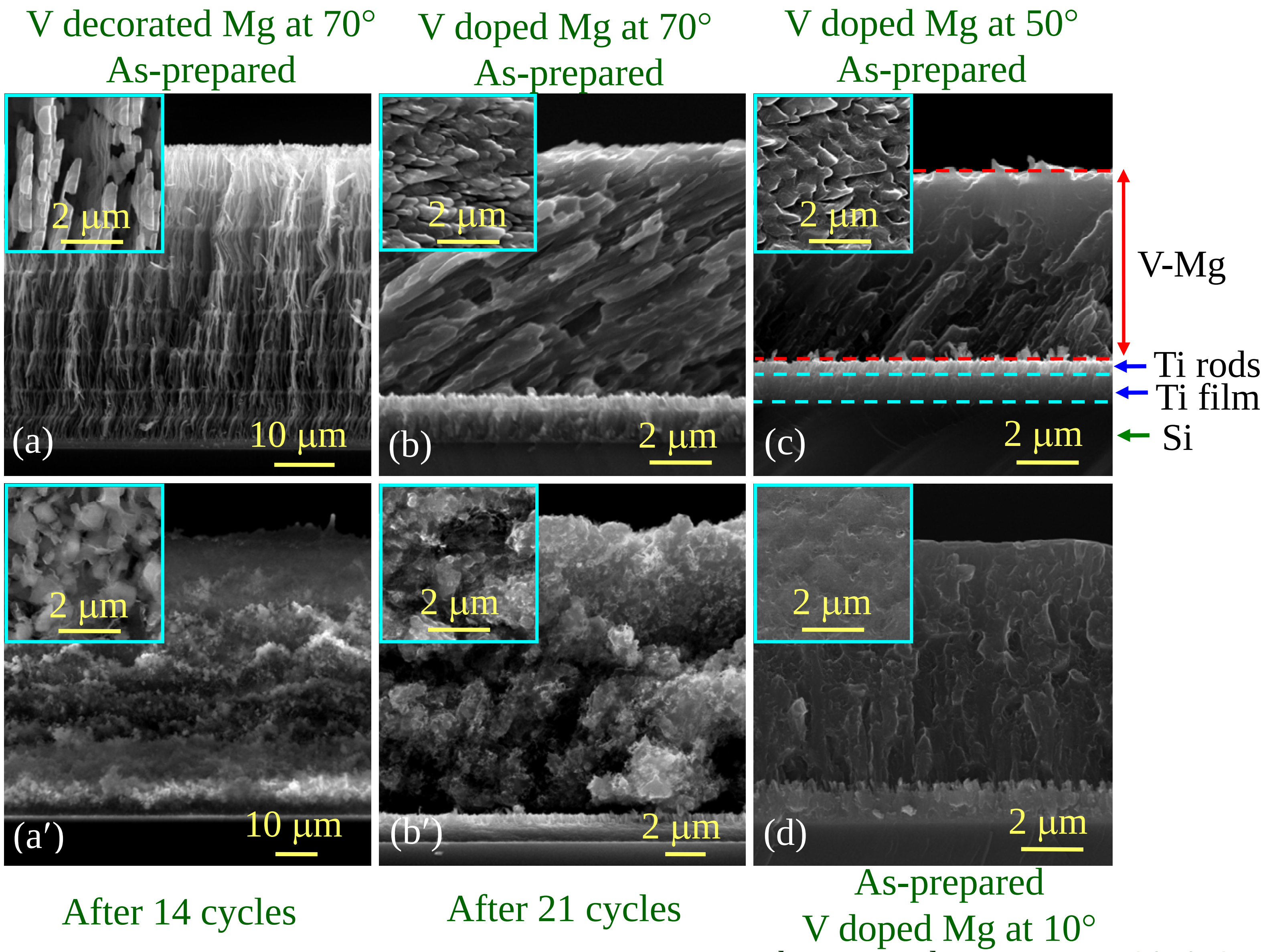


V decorated Mg at 70°

V doped Mg at 10°, 50°, 70°

He *et al*., Int J Hydrogen Energy 2010, 35, 4162

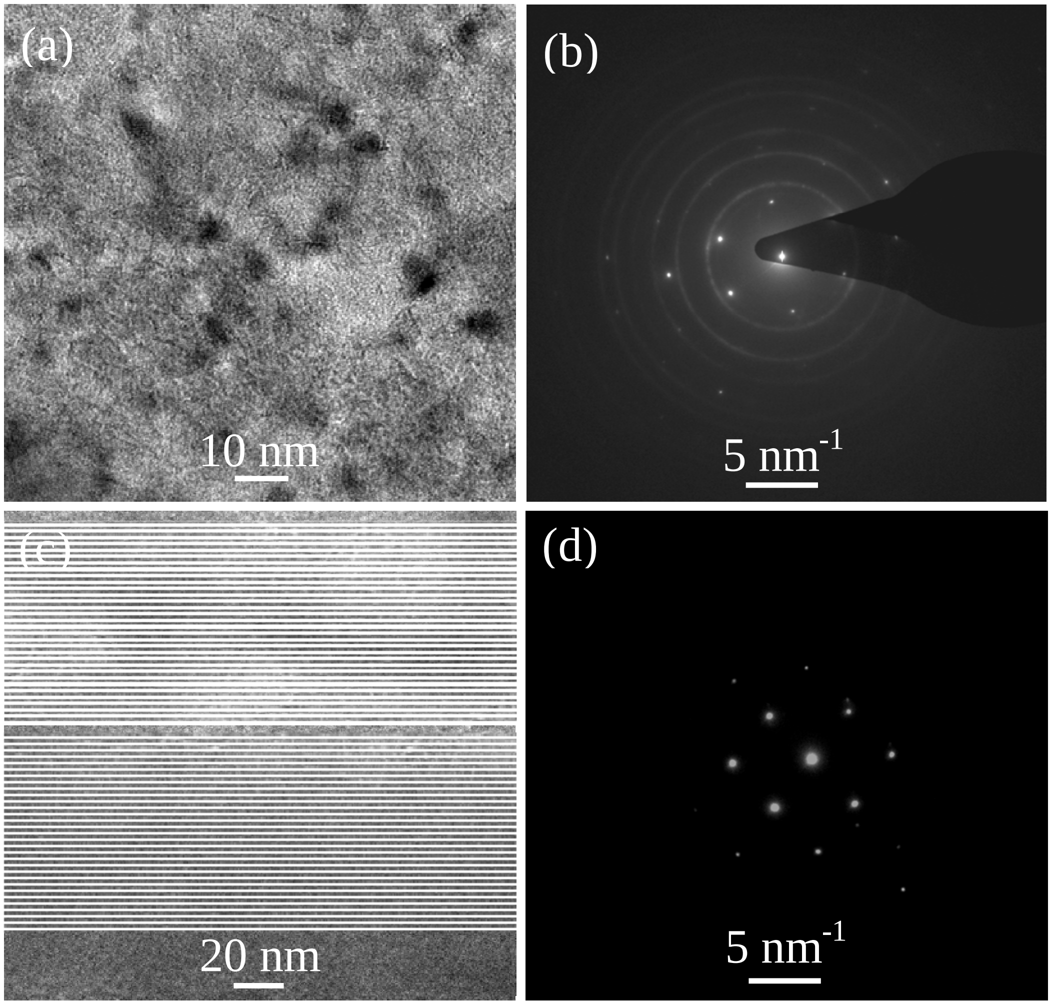
Morphological Characterizations



4.6 at% V

He *et al.*, Int J Hydrogen Energy 2010, 35, 4162

TEM and ED (As-Prepared Samples)



V decorated Mg at 70°:

- V crystals in Mg matrix
- Rings (V) + spots (Mg) in ED

V doped Mg at 70°:

- No V signal is detected
- Only Mg diffraction pots in ED

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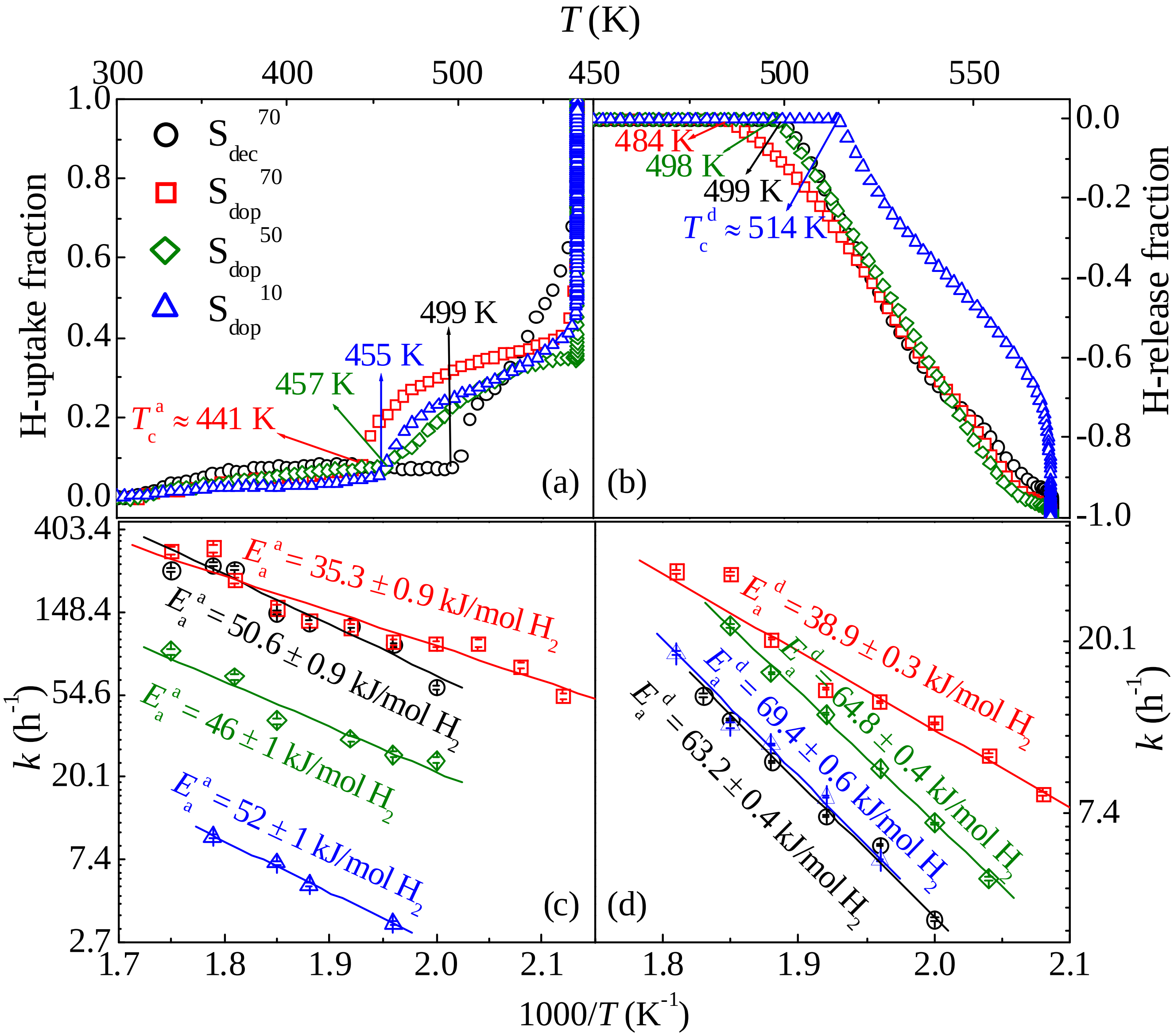
Hydrogen Storage Performance



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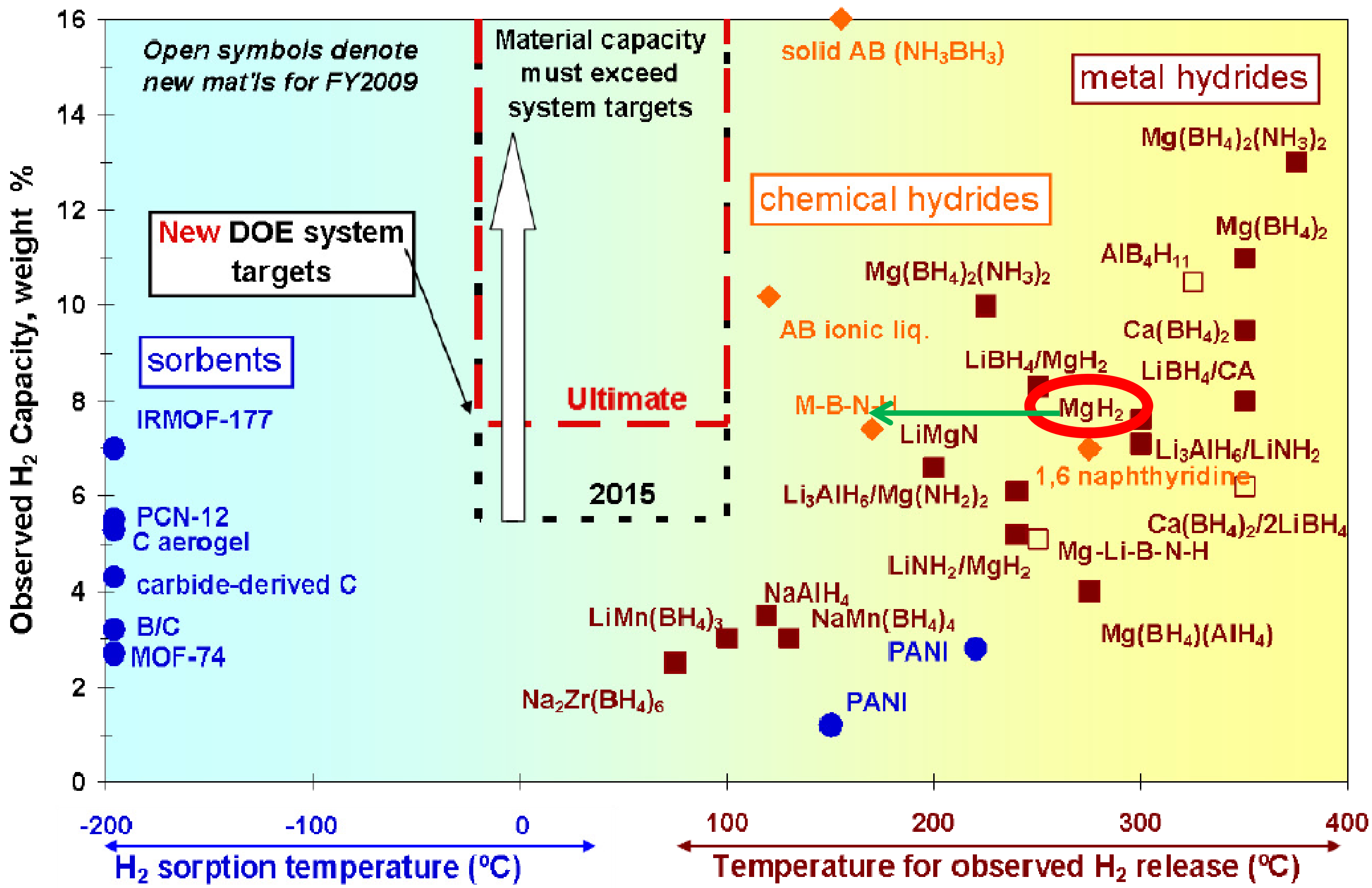
Progress: Material Capacity vs. Temperature



Conclusions

The H-storage performance of Mg can be improved by

1. Tailoring Mg into nanoblades
2. Coating a layer of V on the surface of individual Mg nanoblades

The H-storage performance of V-Mg depends strongly on the distribution of V nanocatalyst

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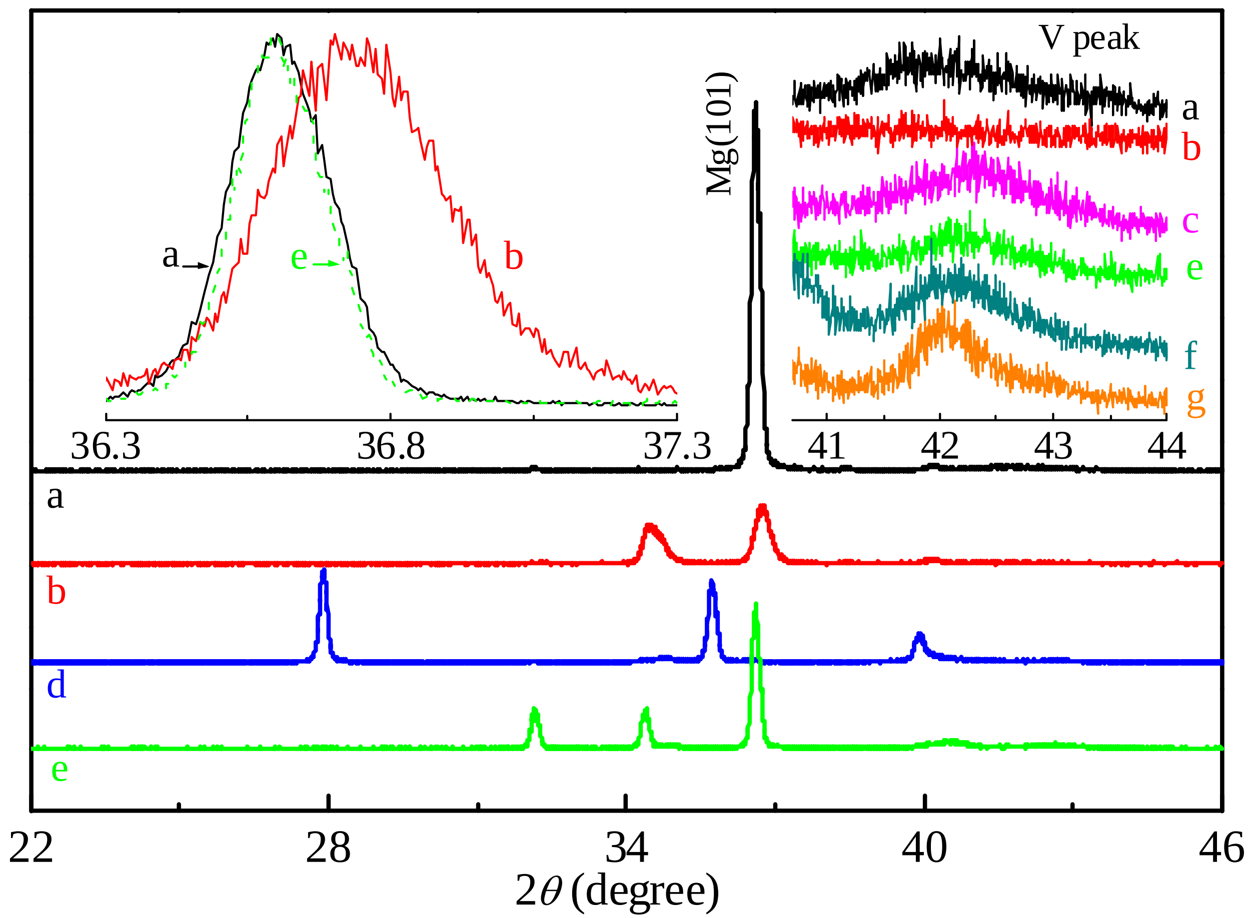
XRD



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