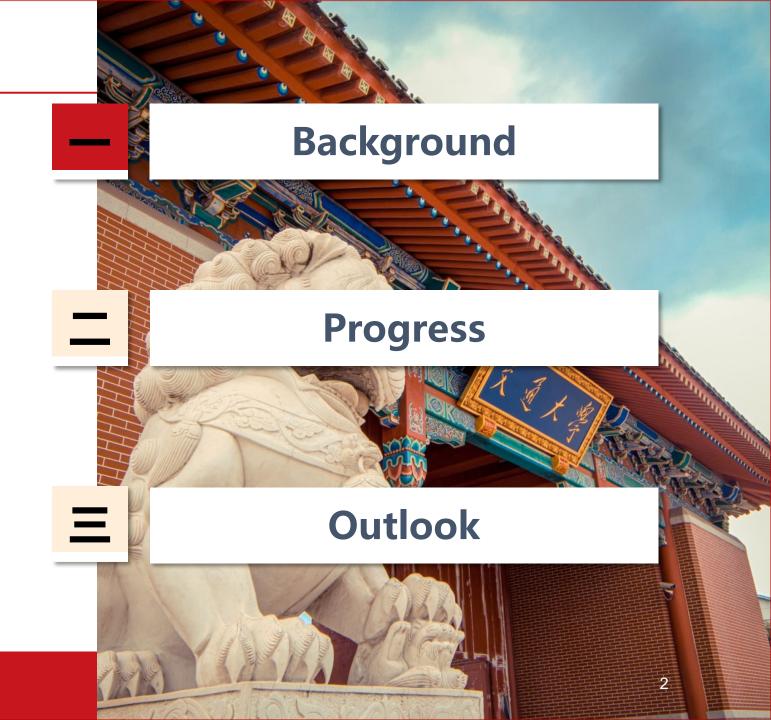


## Development of Mg-Based Materials for Hydrogen Storage

Jianxin Zou, Wenjiang Ding

**Shanghai Jiao Tong University** 







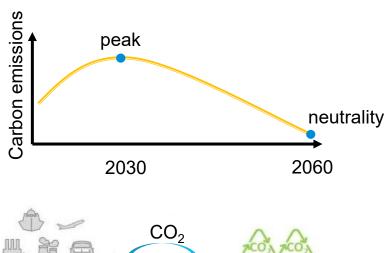


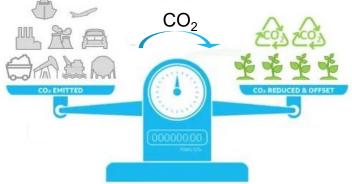




### **Hydrogen energy**

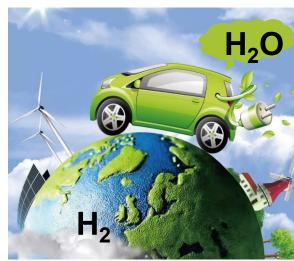
- ☐ China is actively promoting green and low-carbon development and is committed to achieving carbon peaking by 2030 and carbon neutrality by 2060
- Hydrogen energy the ideal energy carrier to achieve the goal of carbon peaking/carbon neutrality





Urgent need for systemic change in decarbonization



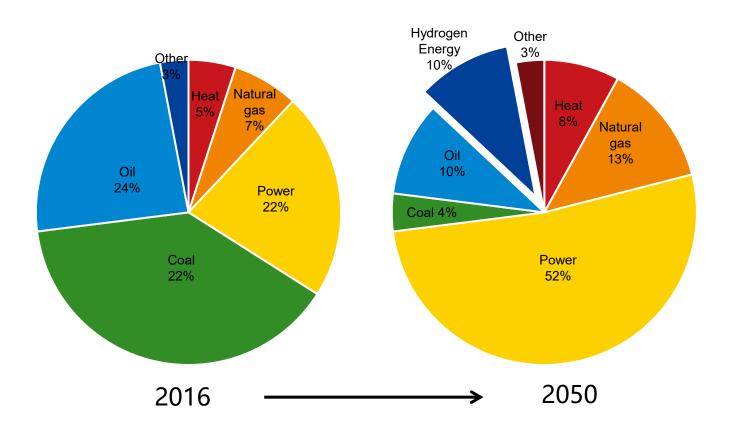


- Characteristics of hydrogen
- A secondary energy source with high calorific value;
- Wide range of resources, clean and non-polluting;
- Wide range of applications: transportation, energy, metallurgy



### **Hydrogen energy**

A conservative estimation shows that hydrogen will account for 10% (possibly 18%) of the end-use energy in 2050 in the world.



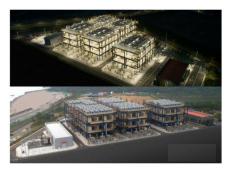
### ■ Applications



Transportation



**Energy Systems** 



Power and heat supply



Metallurgy



### **Hydrogen energy**



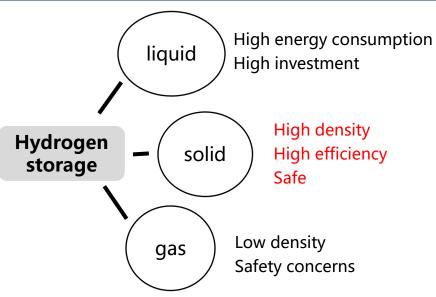
### Hydrogen production

### Hydrogen ultilizations

#### Hydrogen production

- From fossil fuels
- Clean energy (hydropower, solar, wind power)
- Industrial by-product











Energy storage



Industry



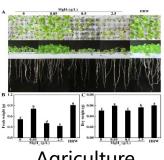
Backup power



On-board energy



Health/Medical

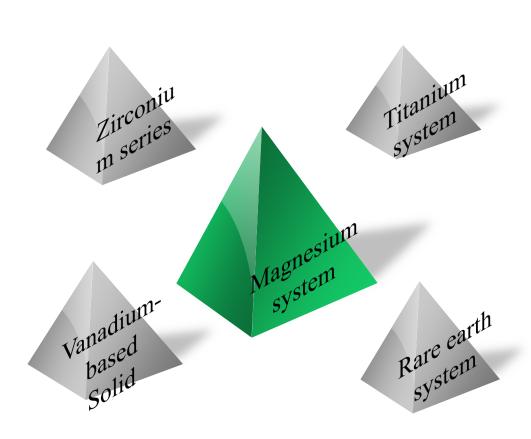


Agriculture



### Solid-state hydrogen storage materials





Solid-state hydrogen storage materials

Туре	Intermetallic compounds	Hydride	Hydrogen capacity			Desorption temperature (@1 Bar)		
A <sub>2</sub> B	Mg2Ni	Mg2NiH4		3.6			528	
AB	FeTi	$FeTiH_2$		1.86			265	
AB	ZrNi	$ZrNiH_3$		1.85			565	
$AB_2$	$ZrMn_2$	$ZrMn_2H_{3.6}$		1.77			440	
$AB_5/MmB_5$	LaNi <sub>5</sub>	LaNi <sub>5</sub> H6		1.49			285	
$AB_2$	$\mathrm{TiV}_2$	TWMaH		2.15			267	
	$(TiV_{0.62}Mn_{15})$	TiV <sub>0.62</sub> Mn <sub>15</sub> H <sub>25</sub>		2.15				

Table 1 Hydrogen storage properties of intermetallic compounds

#### Mg-based hydrogen storage materials

- > Mig≑±a715akih/eneahttip mestetable wheosto alpuandarst → desorption
- > teghperatghegra623etric (7.6 wt%), and volumetric (110 kg/m³)
- > Bludgggenkstærtage; saparcdtffusion rate of hydrogen
- > Weater land rexpossibility national transfer in the stability
- > Stable and safe at room temperature



### Mg-based hydrogen storage materials

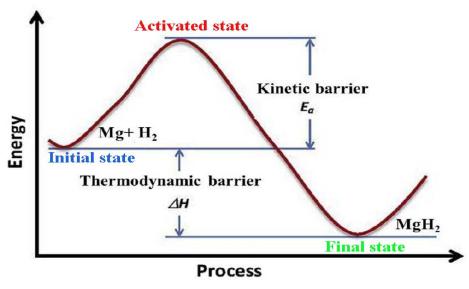


The improvement of thermodynamic and kinetic properties of MgH<sub>2</sub>/Mg systems mainly focuses on **alloying**, **catalyzing and nano-structuring** 

### **Alloying**

### Catalyzing

Nanostructuring



Change of free energy in the transformation from initial to final state for the hydrogenation/de-hydrogenation process of MgH<sub>2</sub>/Mg

Improvement of the thermodynamics:

Forming the alloy phase, changing the reaction path, reducing the reaction temperature

The loss of capacity and deterioration of the cycle stability

Improvement of the kinetics:

Agglomeration and growth of catalysts seriously reduce their catalytic efficiency.

Difficulty: Uniformly distributed nanoscale catalysts

Improvement of the thermodynamics and kinetics:

Unstable of Mg/MgH<sub>2</sub> NPs Agglomeration and growth result in deterioration of performance.

Nanoconfinement: inhibits the growth of nanocrystals. Carbonbased and silica-based frameworks lack catalytic ability.





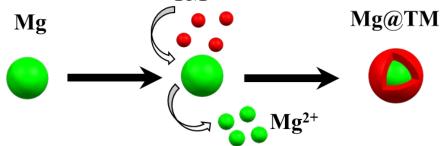




## Synthesis Strategies



Core-shell structured
Mg@TM



 $TM^{x+}$ 

➤ Ball milling of MgH<sub>2</sub> with catalysts

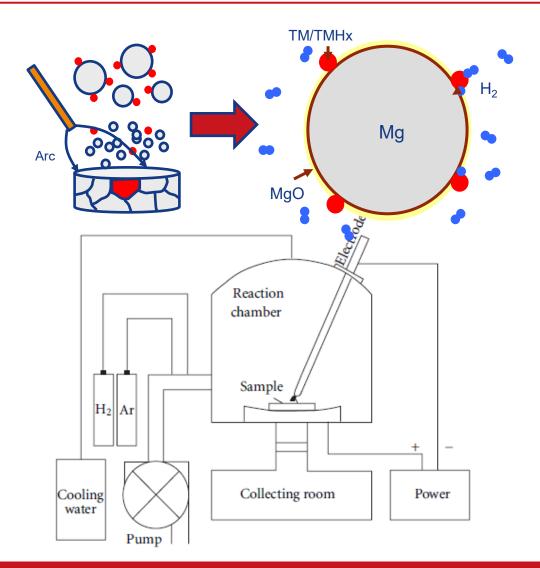
➤ Nano-confinement of MgBu<sub>2</sub>
MgH<sub>2</sub>

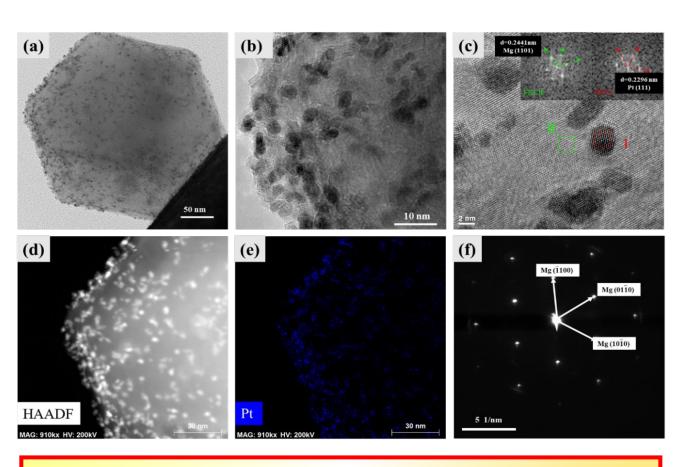




## 1.Core-shell structured Mg@TM







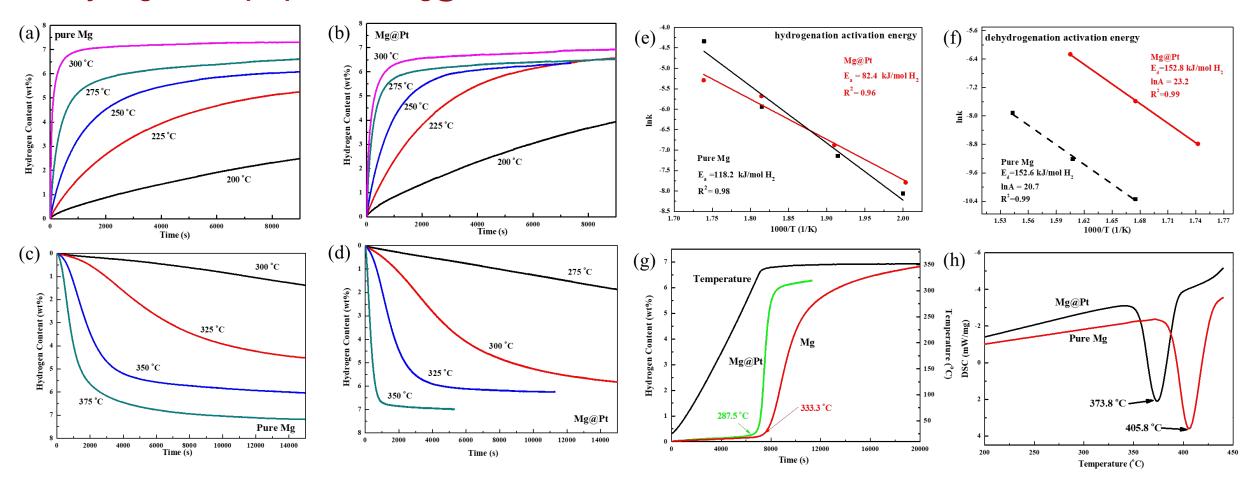
The Pt nanoparticles were distributed on the surface of Mg, forming the core-shell structure.





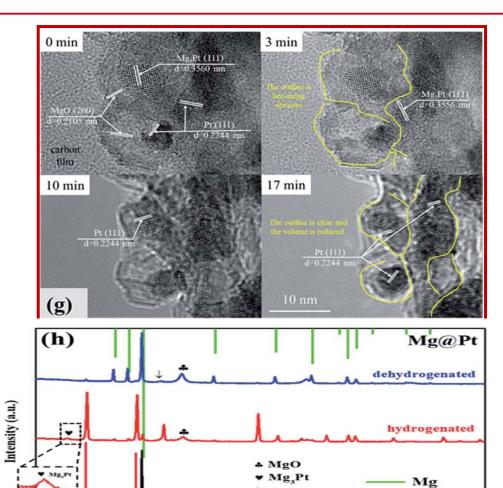


#### The hydrogenation properties of Mg@Pt









<sup>50</sup>2θ (°)

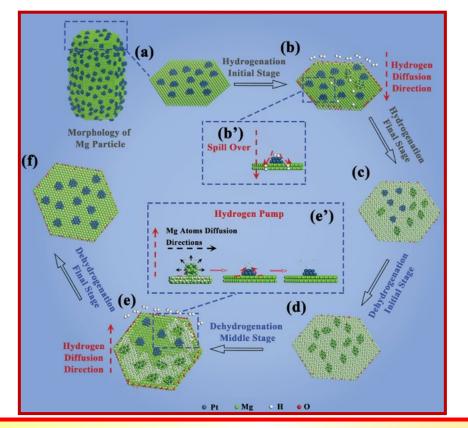
60

70

- MgH,

80

as-prepared



In situ TEM observations demonstrated that the H-stabilized Mg<sub>3</sub>Pt acted as a "hydrogen pump" for the dehydrogenation of MgH<sub>2</sub> and then transformed into Pt after desorption. Through this effect, the dehydriding kinetics of the hydrogenated Mg@Pt composite was improved and the onset dehydrogenation temperature was reduced compared to that of the pure MgH<sub>2</sub> powder.

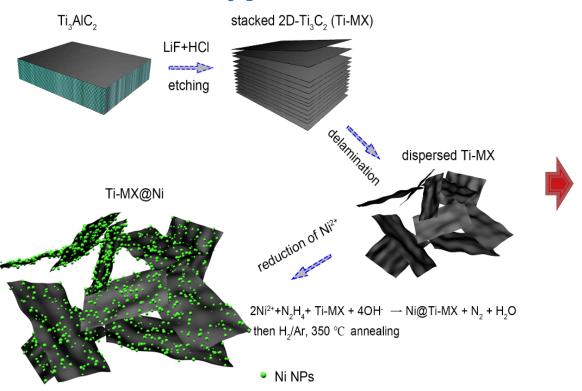


30

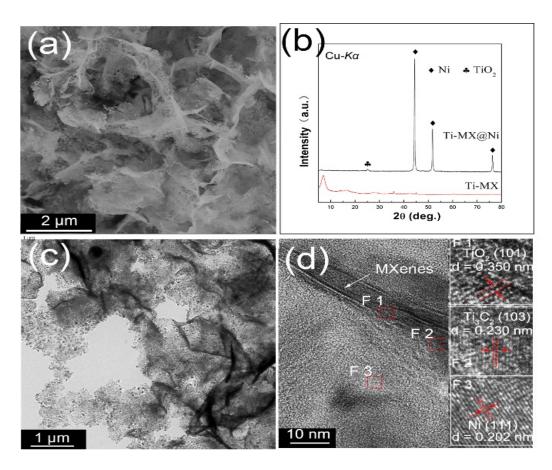
40



#### The Synthesis of 2D-Ni@Ti<sub>3</sub>C<sub>2</sub> (Ni@Ti-MX)



Typical micromorphology of Ni@Ti-MX is mainly consisted of uniform distribution of numerous Ni nanoparticles anchored on the surface of Ti-MXene sheets.

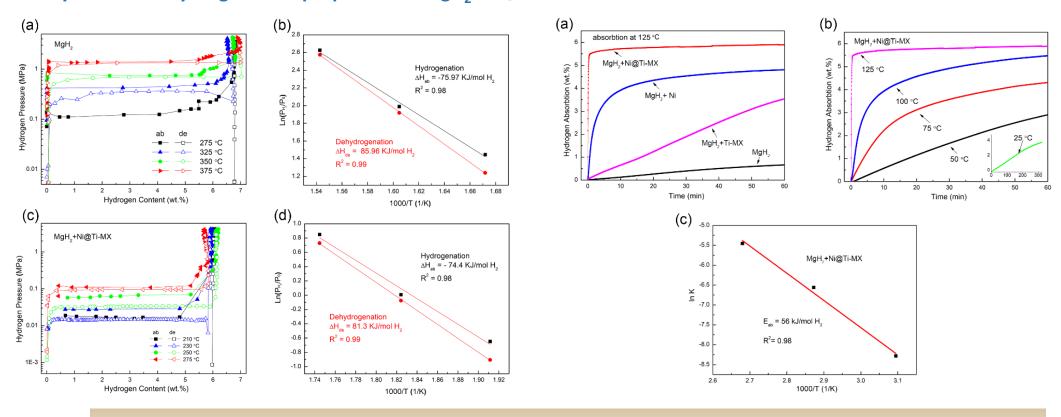


SEM (a), TEM (c) and HRTEM image (d) images of Ni@Ti-MX, (b) XRD patterns of Ni@Ti-MX samples,





#### The thermodynamic and hydrogenation properties of MgH<sub>2</sub>+Ni@Ti-MX

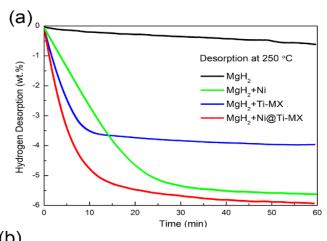


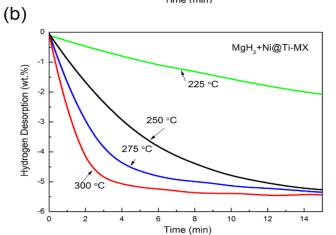
- > The PCT results show no improvement in thermodynamic property.
- ➤ The MgH<sub>2</sub>+Ni@Ti-MX composite can absorb 5.4 wt.% H<sub>2</sub> in 25 s at 125 °C. Interestingly, it can uptake 4 wt.% H<sub>2</sub> in 5 h even at room temperature.

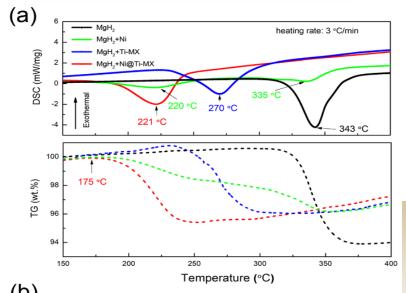


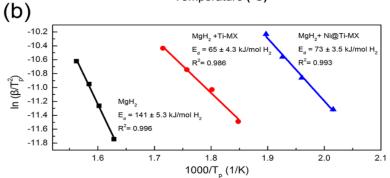


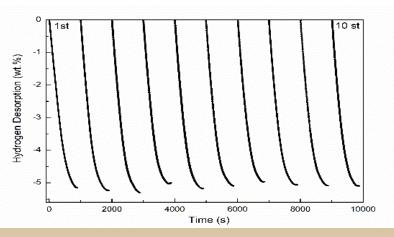
#### The dehydrogenation properties of MgH<sub>2</sub>+Ni@Ti-MX









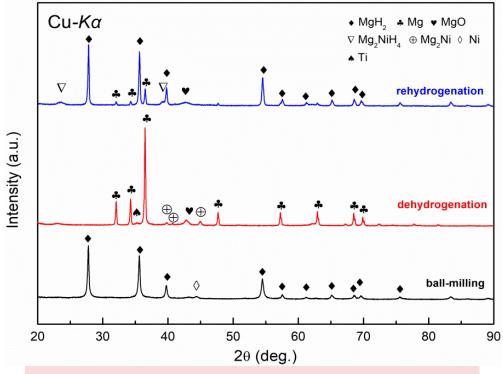


- The MgH<sub>2</sub>+Ni@Ti-MX composite can absorb 5.4 wt.% H<sub>2</sub> in 25 s at 125 °C and release 5.2 wt.% H<sub>2</sub> in 15 min at 250 °C.
- ➤ The dehydrogenation peak temperature of the MgH<sub>2</sub>+Ni@Ti-MX composite is about 221 °C, which is 50 °C and 122 °C lower than that of MgH<sub>2</sub>+Ti-MX and MgH<sub>2</sub>, respectively.
- ➤ The storage capacity (~ 5.2 wt.% H<sub>2</sub>) of the composite remain unchanged after 10 cycles.



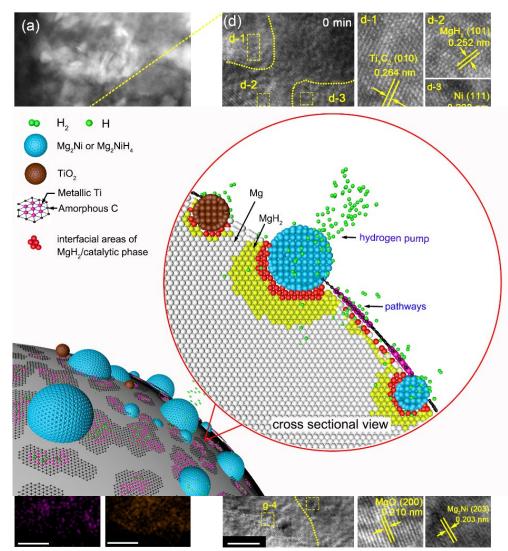


#### The XRD and the in-situ TEM results



The XRD and the in-situ TEM results reveal the microstructure evolution from initial MgH<sub>2</sub>+Ni@Ti-MX to the multiple-phase system:

$$Ni+MgH_2 \longrightarrow Mg_2Ni+H_2 \rightleftharpoons Mg_2NiH_4$$
  
 $Ti_3C_2 \longrightarrow TiH_2 \rightleftharpoons Ti+H_2$ 

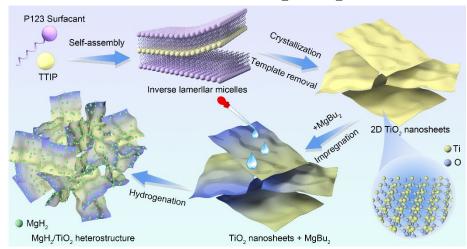




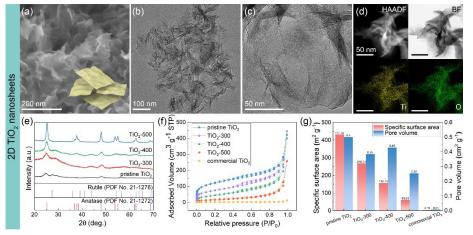
### 3. MgH<sub>2</sub>/TiO<sub>2</sub> NS nanocomposites



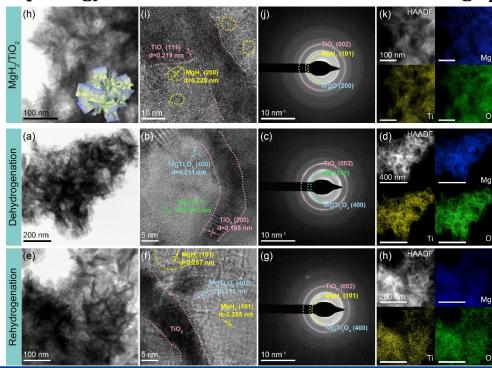
Schematic synthesis of MgH<sub>2</sub>/TiO<sub>2</sub>



Morphology and structural characterization of TiO<sub>2</sub>



➤ Morphology and structural characterization of MgH<sub>2</sub>/TiO<sub>2</sub>



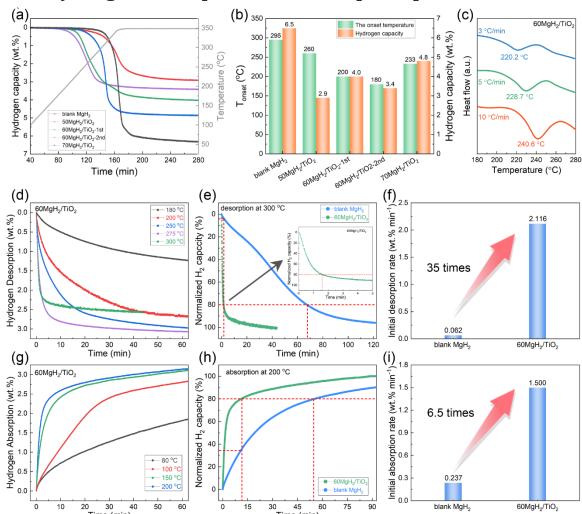
- The 2D TiO<sub>2</sub> nanosheets have a high specific surface area of up to 431 m<sup>2</sup>/g
- MgH<sub>2</sub>/TiO<sub>2</sub> was synthesized by a solvothermal method using MgBu<sub>2</sub> as the precursor and 2D TiO<sub>2</sub> nanosheets as the carrier
- MgH<sub>2</sub> is uniformly dispersed on the surface of TiO<sub>2</sub> nanosheets and assembled into flower-like structures



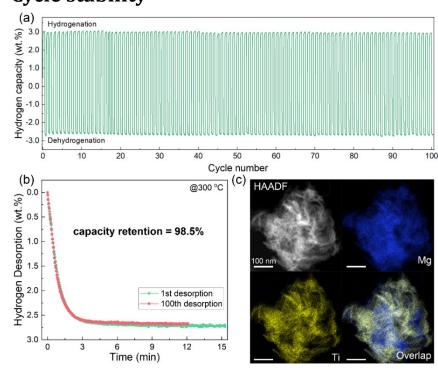
### 3. MgH<sub>2</sub>/TiO<sub>2</sub> NS nanocomposites



#### Hydrogen absorption and desorption performance



#### Cycle stability



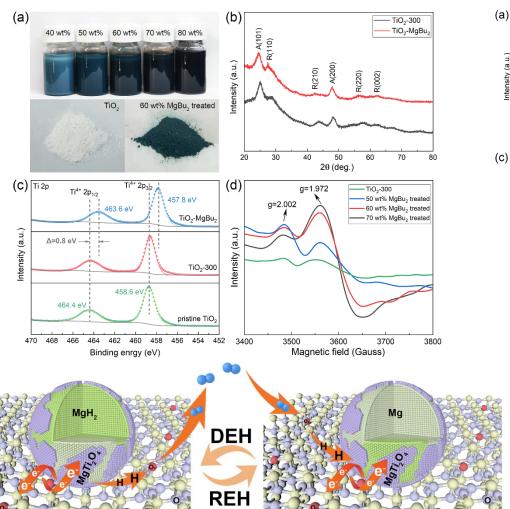
- $T_{onset}$ : 180 °C;  $E_{de}$ : 106.7 kJ mol<sup>-1</sup> H<sub>2</sub>
- The initial hydrogen release rate of 60MgH<sub>2</sub>/TiO<sub>2</sub> is 35 times that of pure MgH<sub>2</sub> (300 °C), and the initial hydrogen absorption rate is 6.5 times (200 °C) of pure MgH2
- Capacity retention up to 98.5% after 100 cycles at 300 °C



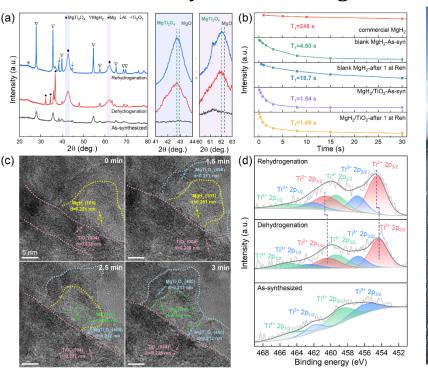
### 3. MgH<sub>2</sub>/TiO<sub>2</sub> NS nanocomposites

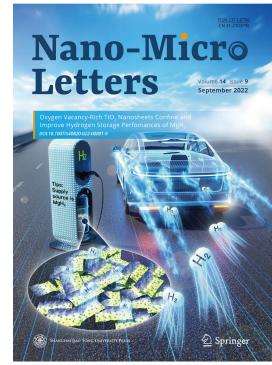


#### Formation of oxygen vacancies



#### Catalytic action of Mg-Ti ternary oxides





- Two birds with one stone: MgBu₂: ① acts as a precursor to MgH₂; ② serves as a reducing agent to make oxygen-vacancy TiO₂ NS
- Abundant oxygen vacancies: enhance the conductivity of TiO<sub>2</sub> NS
- Mg-Ti oxide: hydrogen diffusion channel; buffers the volume expansion and contraction during the hydrogen absorption and release process of MgH<sub>2</sub>



### **Conclusions**





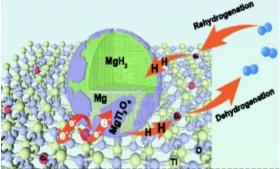
- Ni, Co, TiLa<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>
- **≻**High catalytic efficiency
- **≻**High capacity
- absorption **≻Low**

temperature

Mg@TM, Mg@TMOx

**Core-shell structure** 

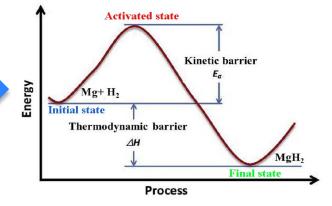




**Nanoconfinement** 

- **MXene**
- TiO<sub>2</sub> nanosheets
- **≻**High stability
- desorption >Low temperature
- **≻In-situ catalysis**

Nano-confinement



Improved performances





## Production of Mg based hydrogen storage materials

□ Production of MgH<sub>2</sub> powder (10 ton/y) and Mg alloy pellets (100 ton/y)





















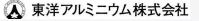


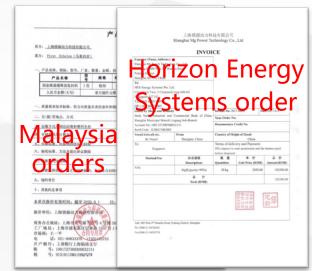




















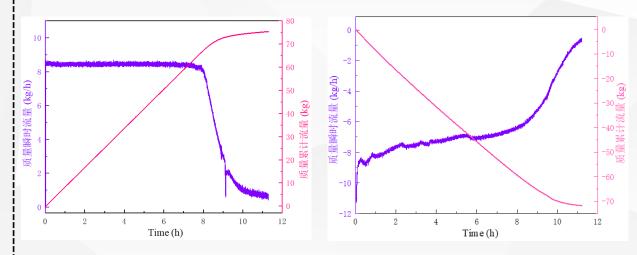
### Test and simulation



□ Prototype testing of a 75 kg Mg-based solid-state hydrogen storage tank

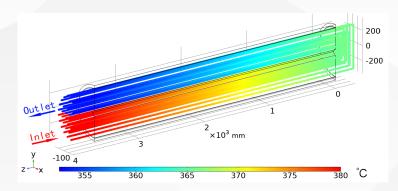


Mg-based solid-state hydrogen storage tank and its test system

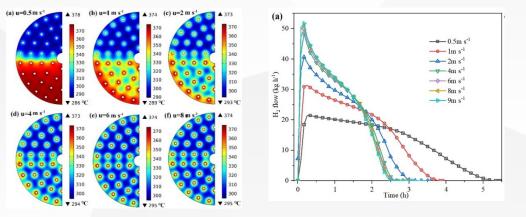


Test results of Mg-based solid state hydrogen storage tanks

□ Numerical simulation of Mg-based solidstate hydrogen storage tank



Temperature distribution of heat transfer medium for 2 m/s flow rate



Influence of different flow rates of heat exchange media on temperature and hydrogen release rate

## **Application**



□ Tonnage Mg based solid state hydrogen storage trailer





- 40-foot container & 14.4 t Mg-Ni alloy
- 1t of hydrogen storage & purification

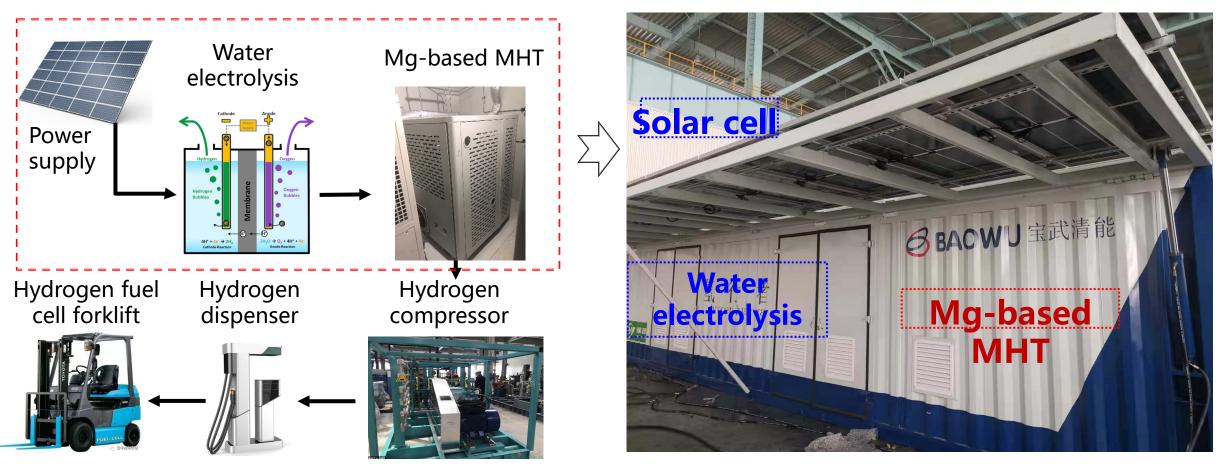
Hydrogen supply & storage in Refueling station



## **Application**



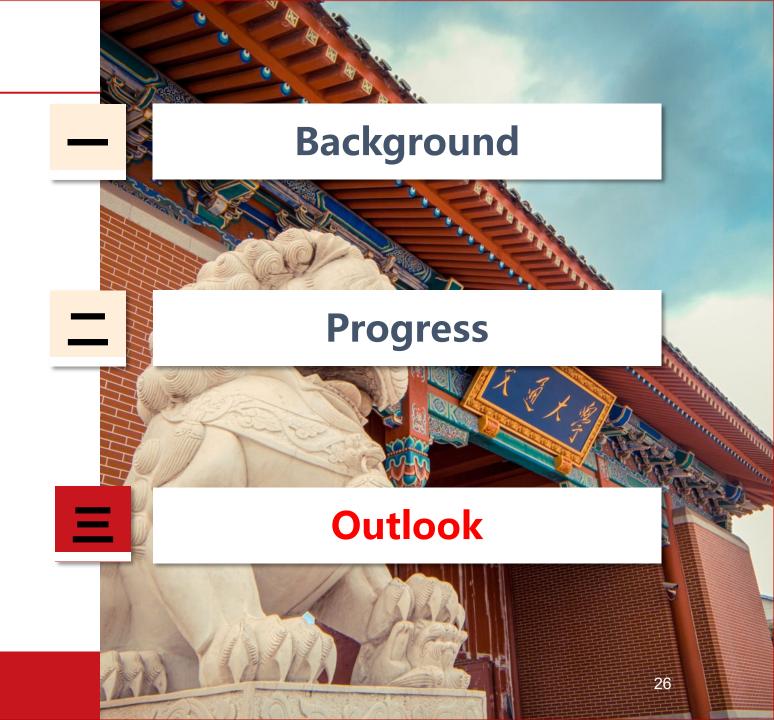
### □ The demonstration project: "Hydrogen Quadriga" in China Baowu Steel Group



The demonstration facility using Mg-based hydrogen storage system named "Hydrogen Quadriga"











## **Development trend**



### □ Hydrogen refueling station/hydrogen-electric energy storage station

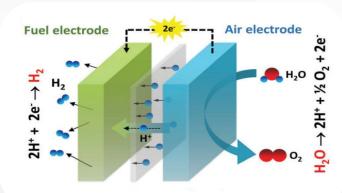




Thyorogen Control of the Control of

Hydrogen refueling station/
hydrogen-electric energy storage station

Mg-based solid- state hydrogen storage trailers



Hydrogen production by electrolysis of water



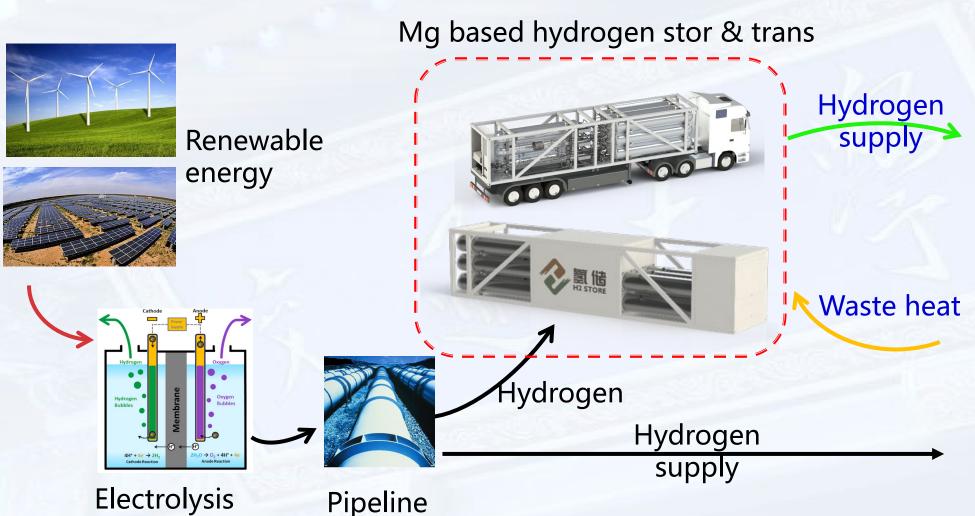
**Hydrogen energy vehicles** 



**Stable power supply** 

### **Hydrogen Metallurgy & Chemical Engineering**

☐ There will be a demand of >130 million ton/y



Hydrogen Metallurgy



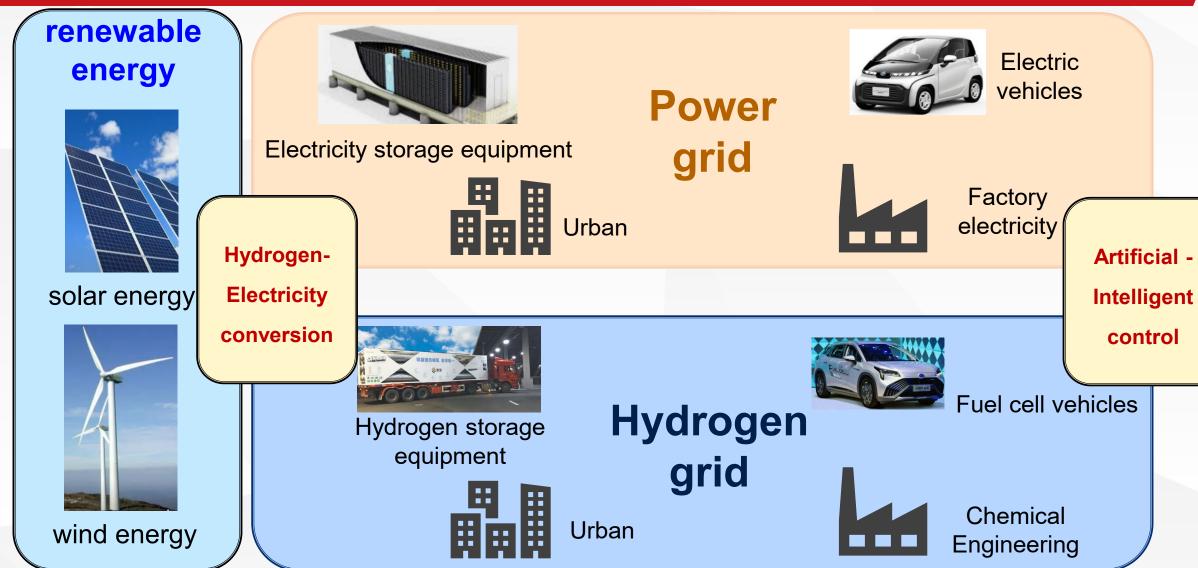


Chemical Engineering



### **Prospectives**





Future: Hydrogen-electricity coupling mode for utilization of renewable energy



### Center of Hydrogen Science, SJTU



The world's top experts in the field of hydrogen energy, hydrogen medicine, hydrogen ag riculture, and other hydrogen science



**Academician Wenjiang Ding Director of the Center** 



Hydrogen energy



Prof. Tao Deng
Specially appointed expert
of the Ministry of
organization
Hydrogen

medicine

Prof. Jianxin Zou Chief scientist



Science Hydrogen

Hydrogen



Prof. Wenbiao Shen Hydrogen agronomy leaders The laboratory has gathered more than 60 experts in the field of hydrogen science, including one academician of the Chinese Academy of Engineering, 26 young and middle-aged leaders. The number and age structure of discipline leaders, academic backbone and permanent research staff are very reasonable.

Prof. Qianjun He Hydrogen medicine leaders







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# Thanks for your attention!



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