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## Quantum effects in sonochemistry

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# Magnetic Nitinol: New Efficient Photothermal Catalyst

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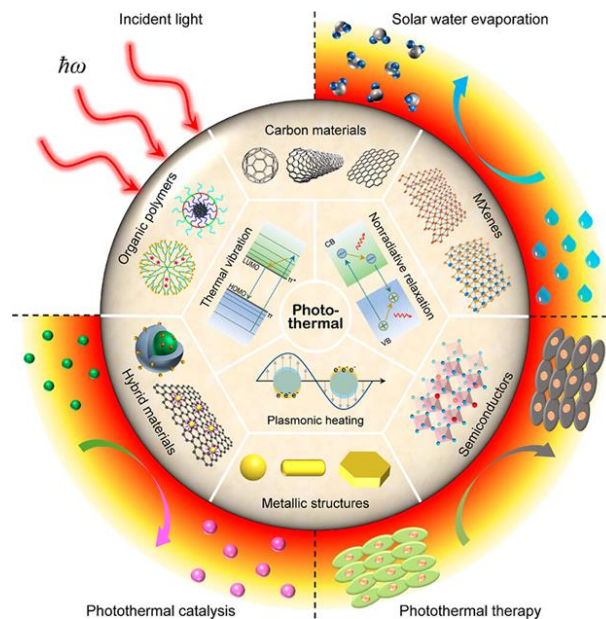
# Ascending photothermal catalysis



➤ *Introducing heat into photocatalytic processes can significantly improve the photoconversion efficiency*

➤ *Self-heating of the photocatalytic systems can reduce energy consumption required for the photothermal processes*

❖ *Preparation of cost-effective photothermal catalysts from earth-abundant elements is of prime importance for heterogeneous catalysis driven by concentrated solar light*



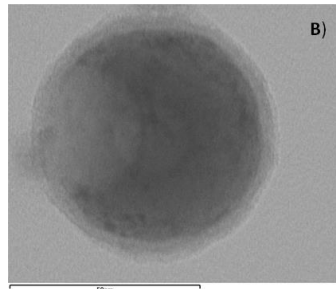
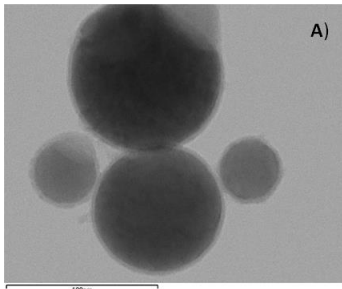
# Nitinol as a photothermal catalyst?



Nitinol, NiTi, is a famous shape-memory alloy widely used in medicine, aerospace industry, instrumentation etc.

**But what about the catalysis with NiTi?**

NiTi NPs



Particle size 20-100 nm,  
≈ 2-4 nm passivation layer: [TiO<sub>2</sub>] > [NiO] (XPS data)



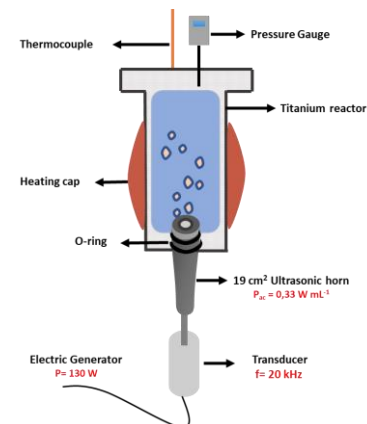
# Preparation of core-shell-satellite NiTi@TiO<sub>2</sub>/Ni nanoparticles



- ✓ Sonohydrothermal (SHT) treatment of pristine NiTi NPs in pure water (200°C, autogenic pressure P= 14 bar, US: 20 kHz, P<sub>ac</sub>=17 W, t = 3 h)

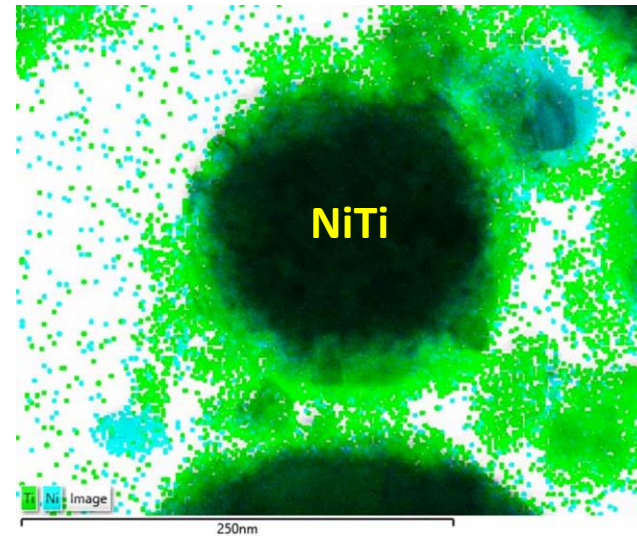
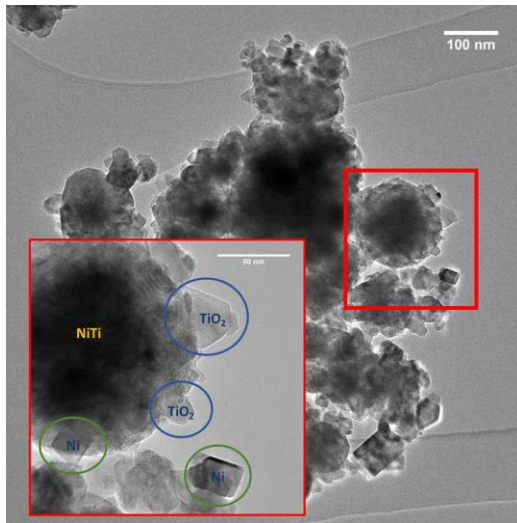
## Rietveld refinement of the PXRD data

Sample	mol % ( $\pm 10\%$ )				
	NiTi cubic	NiTi monoclinic	Ni <sub>3</sub> Ti	Ni	TiO <sub>2</sub>
NiTi	91	5	4	–	–
NiTi@TiO <sub>2</sub> /Ni	31	–	<1	35	34



The SHT treatment leads to the appearance of metallic Ni and anatase TiO<sub>2</sub> indicating non-congruent oxidation of nitinol in hydrothermal water

# HRTEM/EDX images of NiTi@TiO<sub>2</sub>/Ni NPs

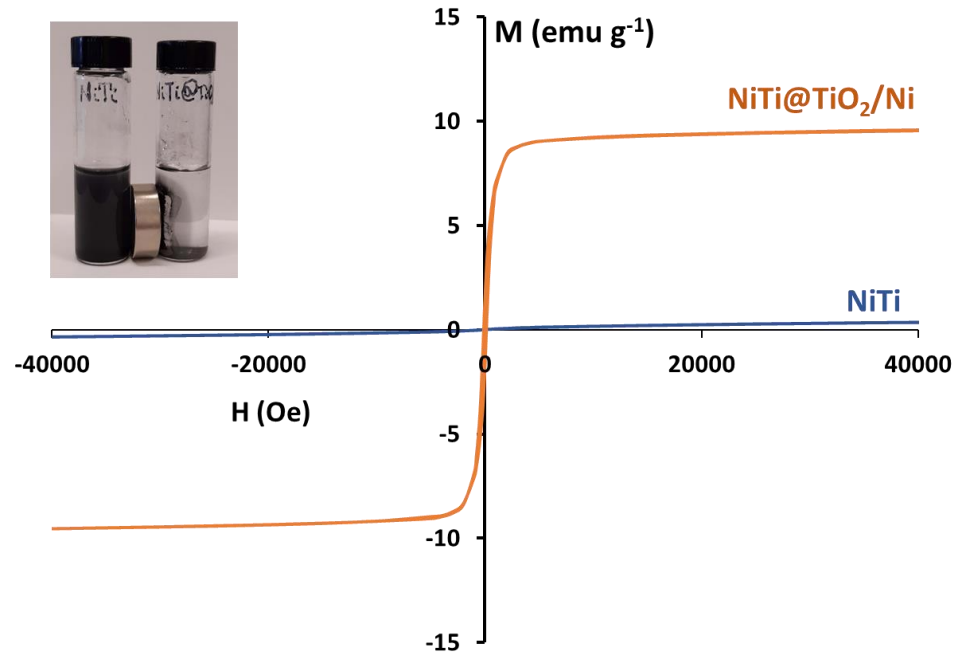


Ultra-micro tomographic image/EDX mapping of NiTi@TiO<sub>2</sub>/Ni NPs, Ni (blue) and Ti (green)

Ni NPs ( $\approx 20$  nm) are attached onto TiO<sub>2</sub> shell forming core-shell-satellite structure

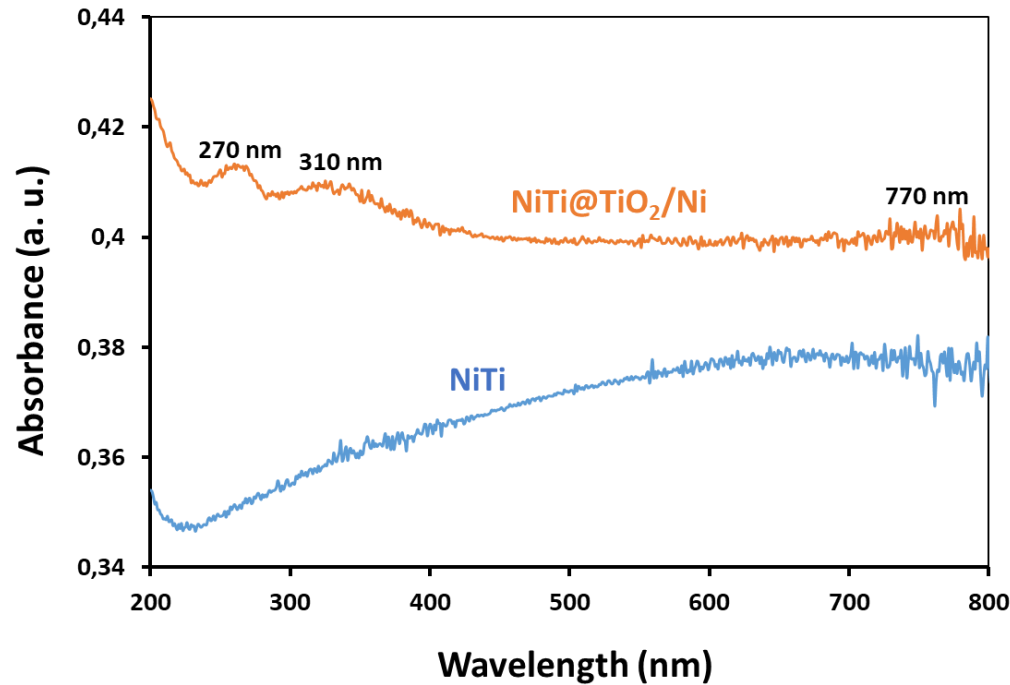


# Magnetic properties



*Magnetization curves for NiTi and NiTi@TiO<sub>2</sub>/Ni NPs measured at room temperature*

- Pristine NiTi NPs show very low magnetization
- NiTi@TiO<sub>2</sub>/Ni NPs are ferromagnetic ( $M_s = 9 \text{ emu}\cdot\text{g}^{-1}$ )



*UV/vis/NIR absorption spectra of NiTi and NiTi@TiO<sub>2</sub>/Ni NPs (100 ppm) in water (l = 1 cm)*

- ✓ NiTi: UV-NIR broad continuum of interband/intraband transitions
- ✓ NiTi@TiO<sub>2</sub>/Ni: peaks at 270 and 310 nm are ascribed to Ni SPR and TiO<sub>2</sub> bandgap



# Photothermal and photocatalytic experiments



✓ Solutions: 100 ppm of NiTi or NiTi@TiO<sub>2</sub>/Ni NPs dispersed in 1M Glycerol

## Experimental conditions:

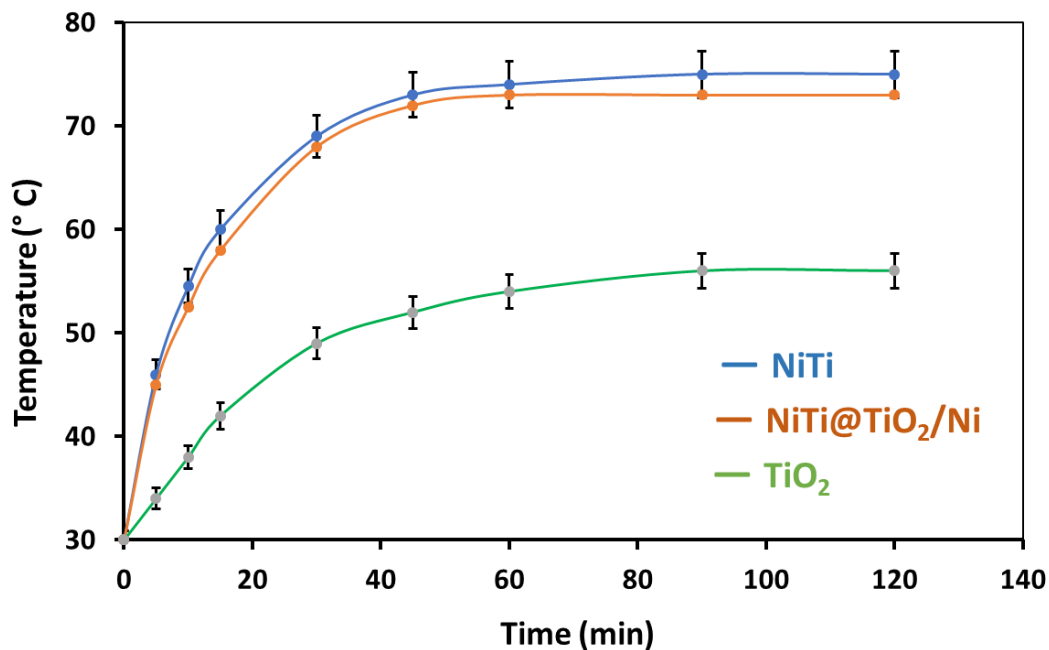
- Glass-made continuous Ar-flow thermostated cell  
T= 30-100°C
- V= 50 mL (l = 3 cm)
- Xe lamp:  
400-1100 nm: 8.9 W  
300-420 nm: 0.6 W
- Online mass spectrometric analysis of the outlet gases



# Light-to-heat conversion



100 ppm of NPs  
Xe lamp:  
400-1100 nm: 8.9 W  
300-420 nm: 0.6 W

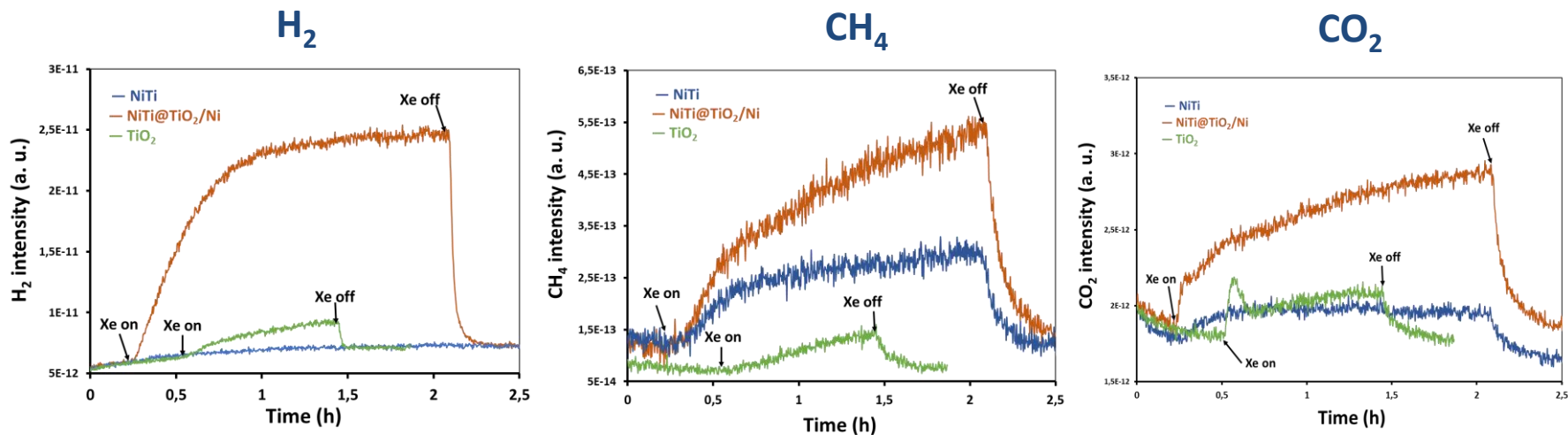


✓ NiTi and NiTi@TiO<sub>2</sub>/Ni NPs show strong and very similar heat generation capacity under light exposure indicating that self-heating is determined by the metallic core

# Photocatalysis under self-heating

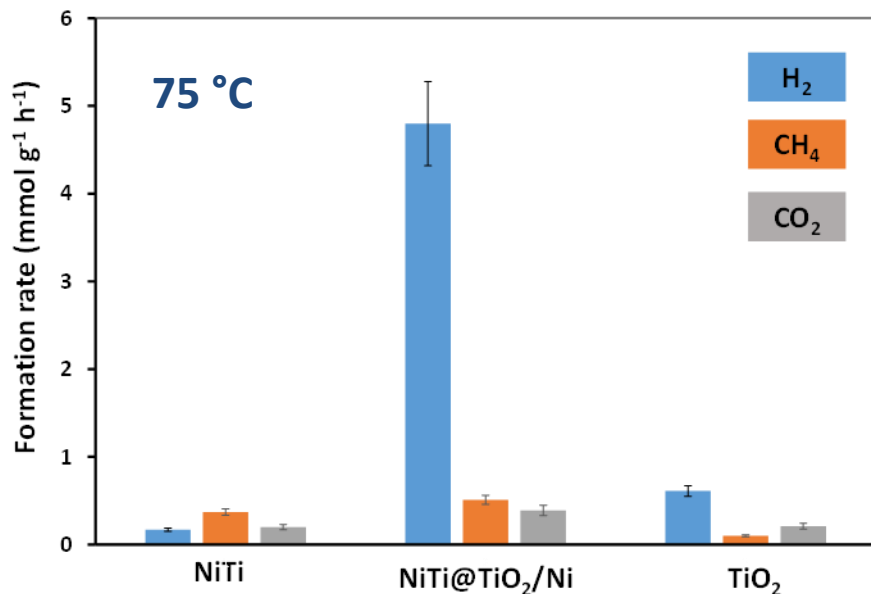


100 ppm of catalyst, 1M Glyc, Xe lamp, steady-state temperature 75 °C



- Upon light exposure the concentration of H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> gradually increases with temperature rise reaching a steady state value simultaneously with that of temperature
- Heating at 75 °C under dark conditions does not lead to gaseous products formation indicating the photonic origin of the process
- **CO is not formed**

# Photocatalysis under self-heating



Product	$E_a$ , kJ mol <sup>-1</sup>
H <sub>2</sub>	19±2
CO <sub>2</sub>	16±2
CH <sub>4</sub>	59±6

At 30-90 °C kinetics follows Arrhenius law

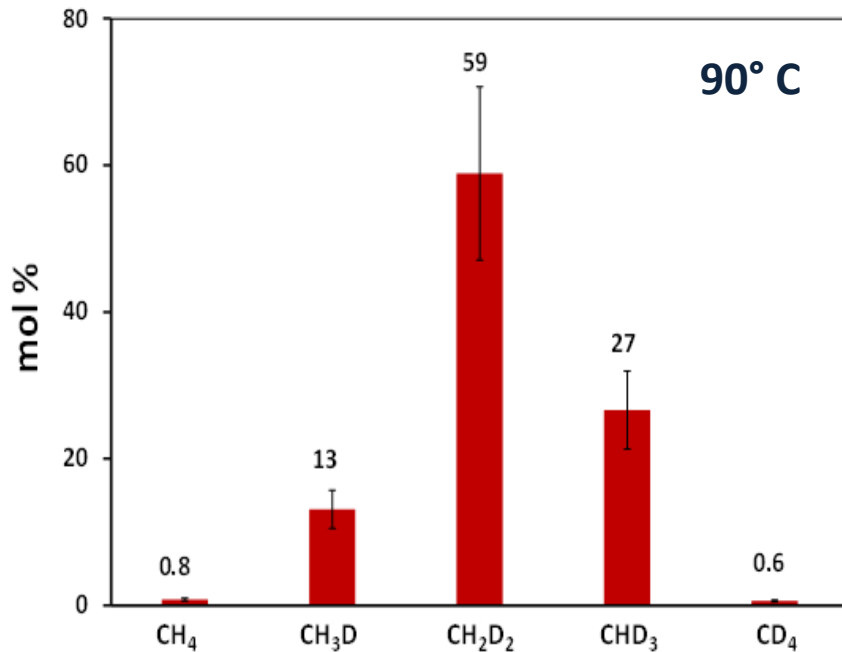
- Global photocatalytic activity:  
NiTi@TiO<sub>2</sub>/Ni >> NiTi ≈ TiO<sub>2</sub>

- .....
- NiTi@TiO<sub>2</sub>/Ni: [H<sub>2</sub>] >> [CH<sub>4</sub>] > [CO<sub>2</sub>]
  - NiTi : [CH<sub>4</sub>] > [H<sub>2</sub>] ≈ [CO<sub>2</sub>]
  - TiO<sub>2</sub> : [H<sub>2</sub>] > [CO<sub>2</sub>] > [CH<sub>4</sub>]

$$E_a(\text{CH}_4) > E_a(\text{H}_2) \approx E_a(\text{CO}_2)$$

- First step: formation of H<sub>2</sub> and CO<sub>2</sub>
- Second step: CO<sub>2</sub> methanation

# H/D KIE in CH<sub>4</sub> formation

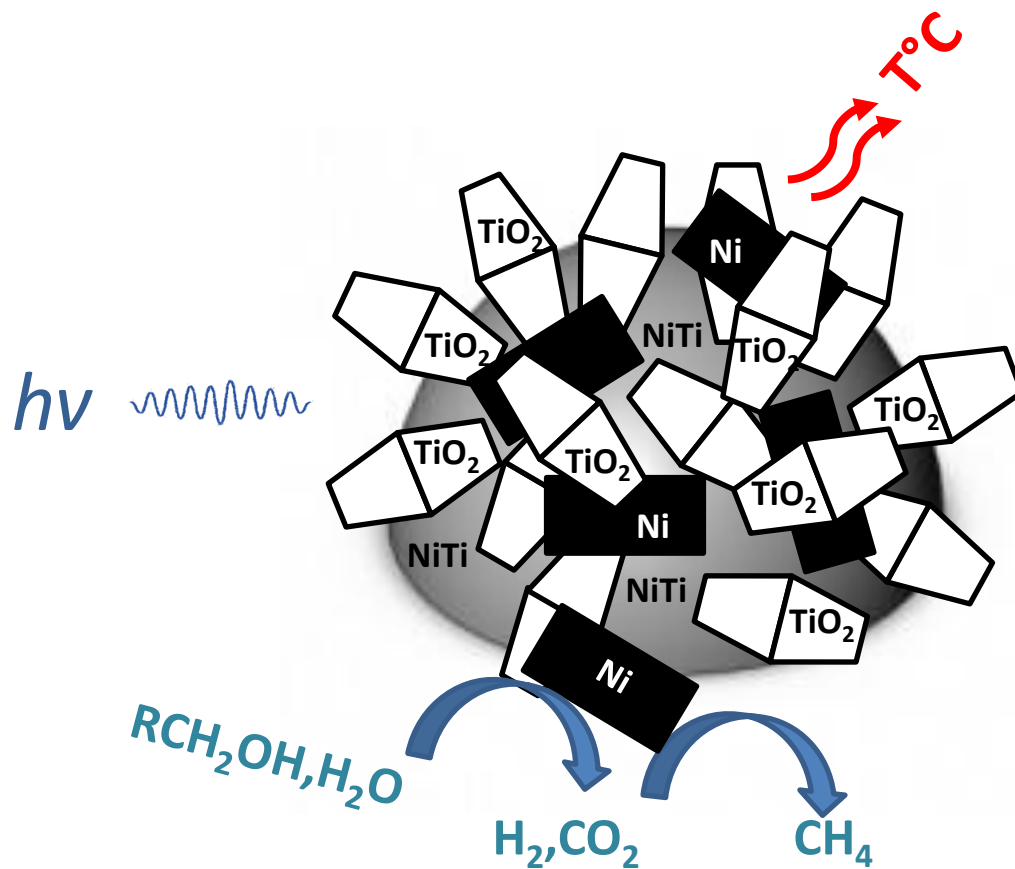


Equimolar H<sub>2</sub>O/D<sub>2</sub>O mixture:



- 5 isotopic species CH<sub>x</sub>D<sub>y</sub>, with domination of CH<sub>2</sub>D<sub>2</sub>
- H/D ratio in released methane is close to HDO in agreement with light-driven CO<sub>2</sub> methanation mechanism

# Suggested overall mechanism





# Concluding remarks



- ✓ **“Magnetic nitinol” exhibits unique set of properties: strong capability of heat generation under light irradiation, good magnetization, remarkable thermally assisted photocatalytic activity, and high stability**
- ✓ **Noncongruent surface oxidation of nanoalloys paves the way to the preparation of new generation of catalysts with advanced photothermal properties**

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**Thank you!**