



HAL
open science

Thermally assisted photocatalytic hydrogen production and CO₂ methanation in aqueous solutions over magnetic nitinol

Sergey I. Nikitenko, Sara El Hakim, Xavier Le Goff, Tony Chave

► **To cite this version:**

Sergey I. Nikitenko, Sara El Hakim, Xavier Le Goff, Tony Chave. Thermally assisted photocatalytic hydrogen production and CO₂ methanation in aqueous solutions over magnetic nitinol. SPEA12 - 12th European Conference on Solar Chemistry and Photocatalysis: Energy and Environmental Applications, Jun 2024, Belfast, United Kingdom. hal-04706138

HAL Id: hal-04706138

<https://hal.science/hal-04706138v1>

Submitted on 23 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The logo for SPEA12, where the letters 'S', 'P', 'E', and 'A' are filled with images of a person, a globe, and a plant respectively, and '12' is in grey. A red arrow points to the right from the left edge of the slide.

SPEA12



Thermally assisted photocatalytic hydrogen production and CO₂ methanation in aqueous solutions over magnetic nitinol

Sergey I. Nikitenko, Sara El Hakim, Xavier Le Goff, Tony Chave

ICSM, Univ. Montpellier, CEA, CNRS, ENSCM, Marcoule, France

E-mail: serguei.nikitenko@cea.fr

www.icsm.fr





Nitinol as photothermal catalyst?

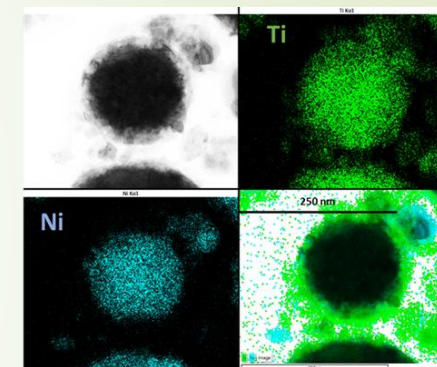
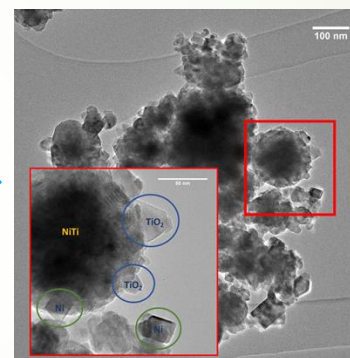
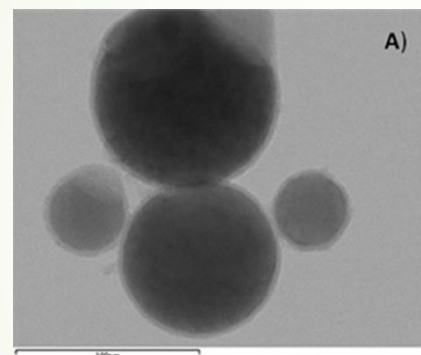
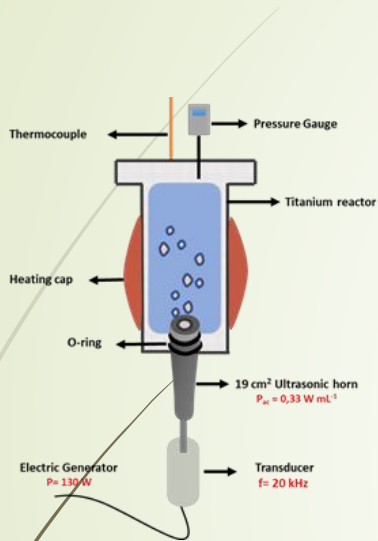
Nitinol, NiTi, is a famous shape-memory alloy widely used in medicine, aerospace industry, instrumentation etc.

But what about catalysis with NiTi?



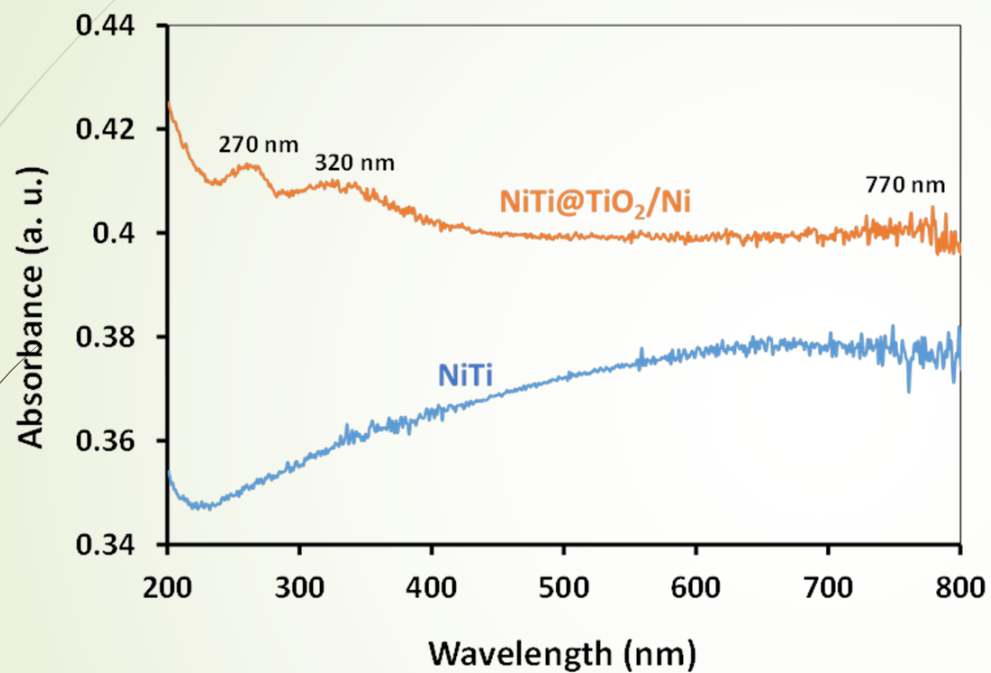
Preparation of NiTi@TiO₂/Ni catalyst

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



SHT treatment leads to the appearance of metallic Ni and anatase TiO₂ NPs at the surface of pristine NiTi indicating **non-congruent oxidation** of NiTi in hydrothermal water

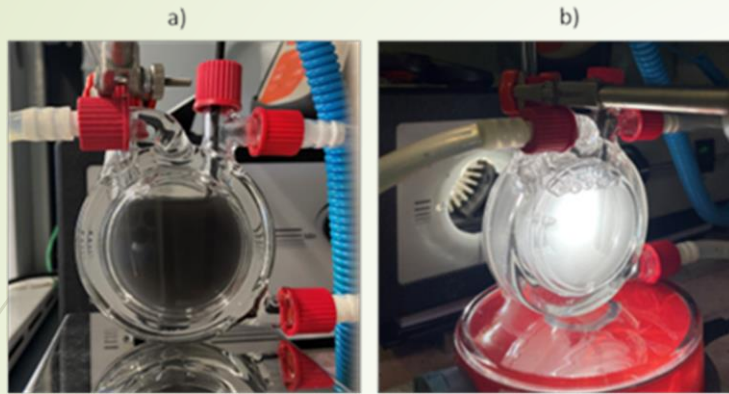
Optical and magnetic properties of NiTi@TiO₂/Ni NPs



UV/vis/NIR absorption spectra of NiTi and NiTi@TiO₂/Ni NPs suspended in water

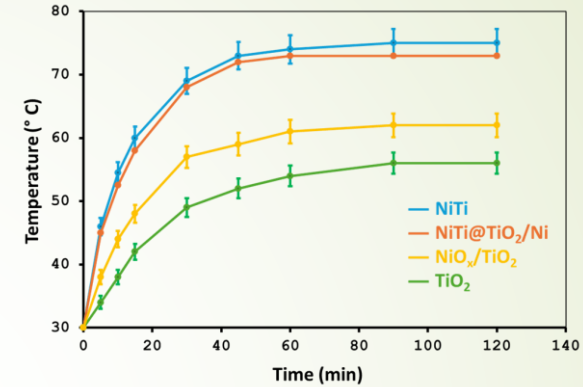
Poster P16 " Synthesis of magnetic nitinol and its application for light-to-heat conversion and photothermal glycerol reforming "

Light-to-heat conversion



Photocatalytic cell before (a) and during (b) illumination with xenon lamp

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



Temperature evolution with time under Xe lamp exposure for the aqueous suspensions of NPs

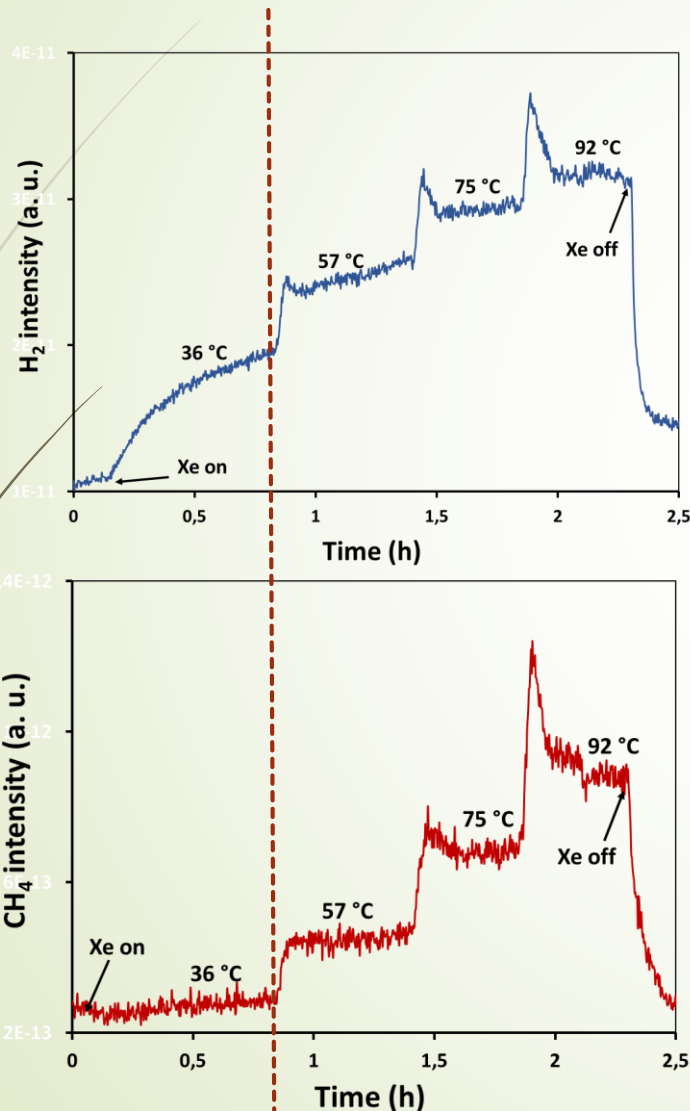
Product	T° C
NiTi	174
NiTi@TiO ₂ /Ni	172
TiO ₂ P25	103



Temperature of NiTi, NiTi@TiO₂/Ni, and TiO₂ pellets under Xe lamp exposure on air. Image of irradiated pellet taken with thermal camera

Strong self-heating effect is determined by NiTi metallic core rather than by TiO₂/Ni shell

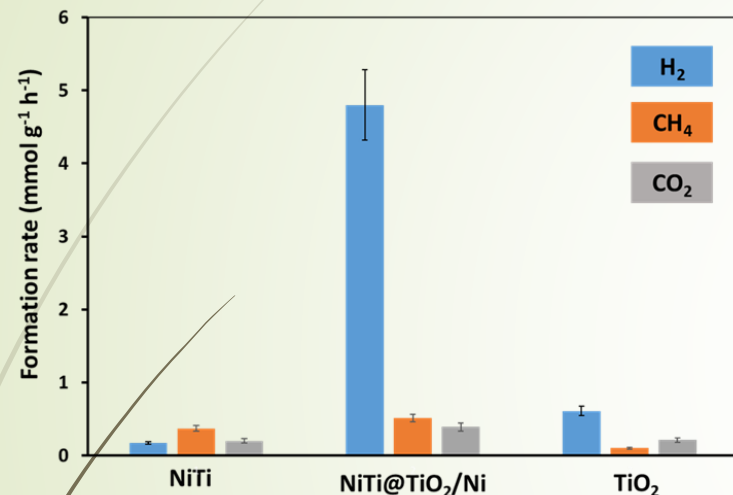
Photocatalytic glycerol reforming under assisted heating



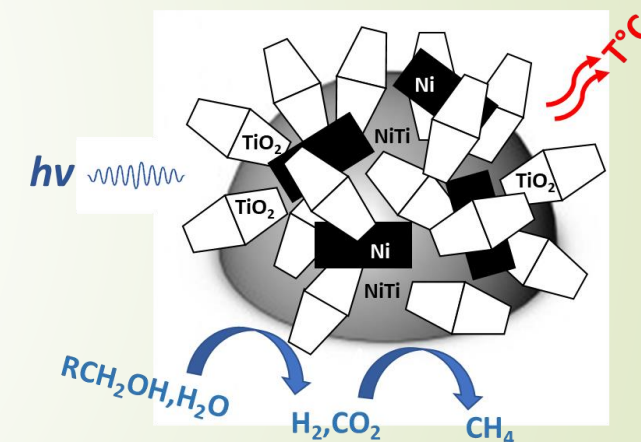
Major gaseous products: $[H_2] \gg [CH_4] > [CO_2]$
 Minor products ($T > 70 \text{ }^\circ\text{C}$): CO and C_2H_2

- ✓ Photocatalytic activity of NiTi@TiO₂/Ni is much higher than for NiTi
- ✓ Under dark conditions there is no products even at 92 °C
- ✓ Kinetics of photocatalytic process is largely enhanced by heating
- ✓ Methane is formed at higher temperature compared hydrogen
- ✓ Ridge-shaped profile is associated with methane formation

Suggested mechanism



Product	E_a , kJ mol ⁻¹
H ₂	19±2
CO ₂	16±2
CH ₄	59±6



Two stage thermally assisted photocatalytic mechanism:

- ✓ Reforming of glycerol leading to the formation of H₂ and CO₂
- ✓ CO₂ methanation at the second stage

Poster **P16** " Synthesis of magnetic nitinol and its application for light-to-heat conversion and photothermal glycerol reforming "

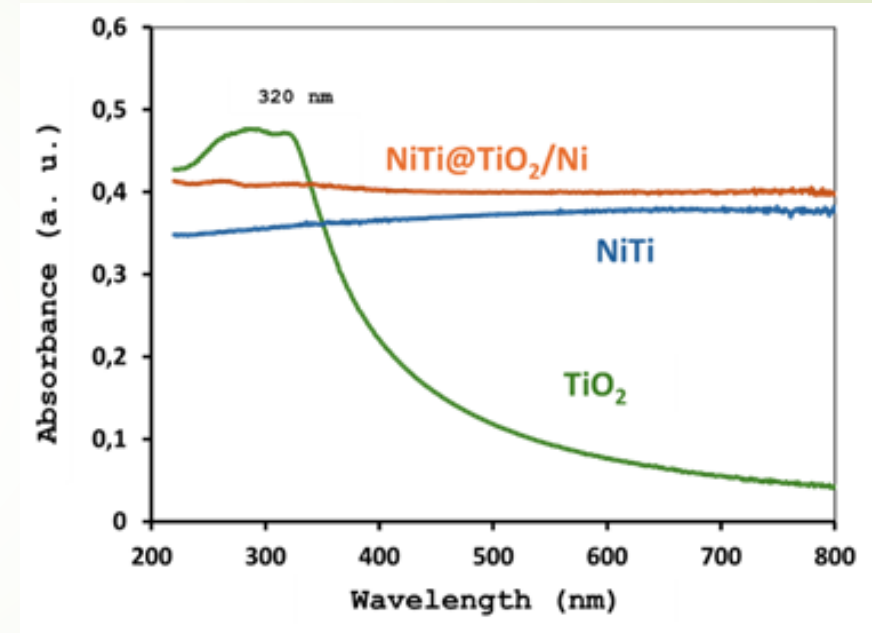
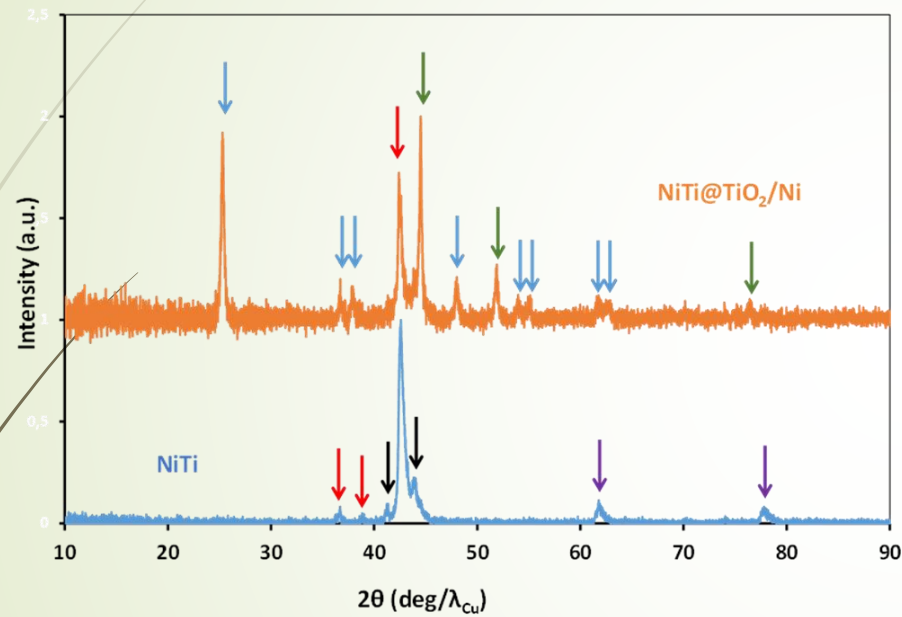
Acknowledgements

The authors gratefully acknowledge Dr. Valérie Flaud for XPS analysis and Dr. Corine Reibel for magnetic measurements.

This work was partially supported by French SPLEEN ECOCHEM PEPR program.



Supporting Information



Supporting Information

Species	BE (eV)	Atomic % (± 5 %)	
		NiTi	NiTi @TiO ₂ /Ni
O 1s A	529.76	38.0	36.1
O 1s B	531.08	18.0	15.6
O 1s C	532.21	7.7	12.4
O 1s D	533.34	3.6	4.0
Ti ⁰ 2p	454.01	1.2	0
TiO 2p	455.15	0.8	0
Ti _x O _y 2p	456.23	1.0	0
Ti ₂ O ₃ 2p	457.21	0.7	0
TiO ₂ 2p	458.35	21.8	17.5
Ni ⁰ 2p	852.0	2.5	3.2
NiO 2p	861.20	5.6	11.2

Supporting Information

