

# $\text{Cu}_x\text{O-gCN-TiO}_2\text{-Au}$ ( $x=1,2$ ) photocatalysts for hydrogen generation by a hybrid liquid-vapor phase strategy



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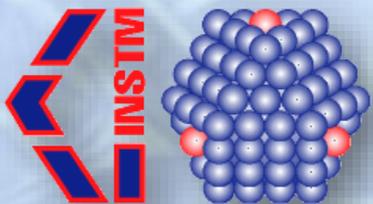
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<https://wwwdisc.chimica.unipd.it/multi-functional-material-group/>

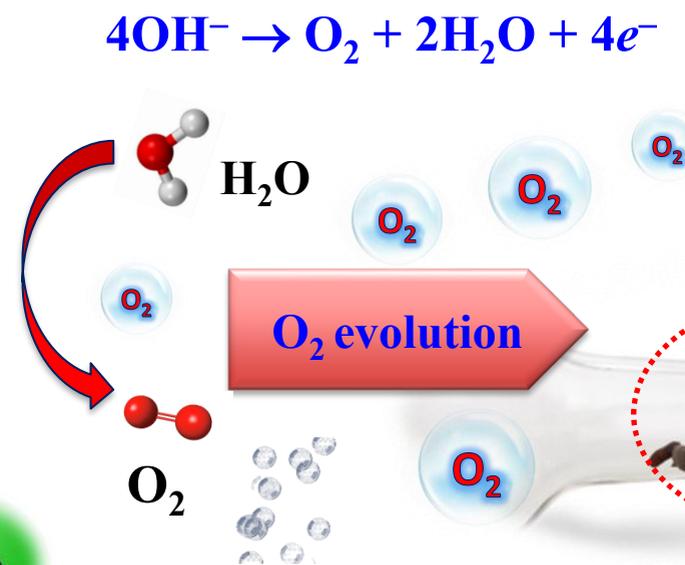
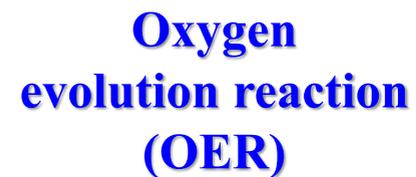
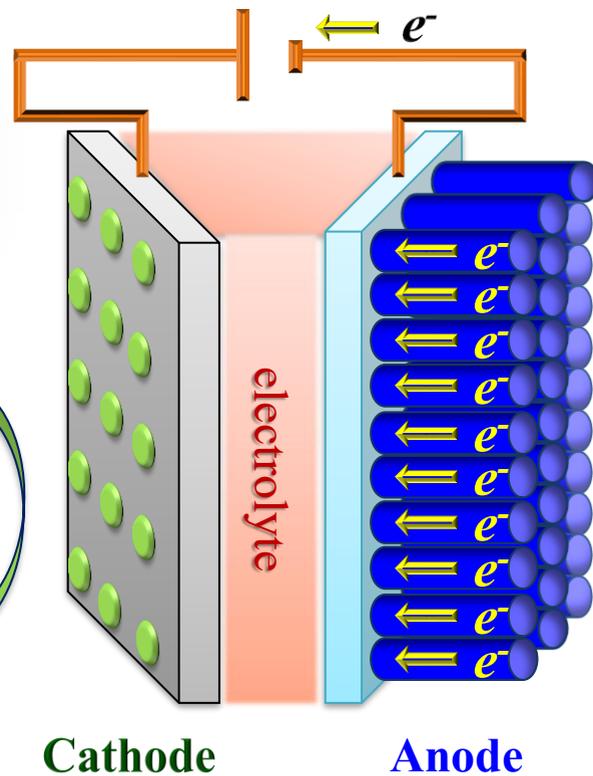
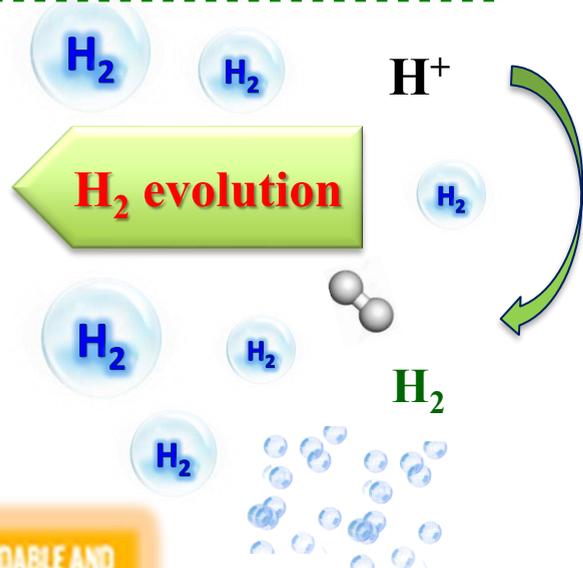
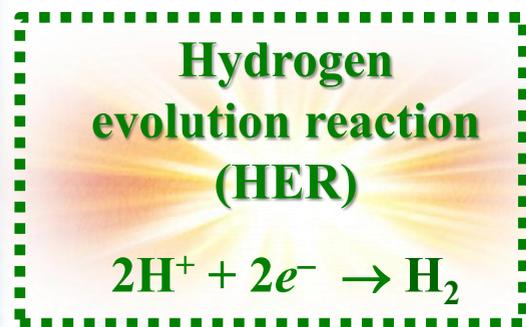


**X Workshop Italiano  
Sol-Gel**

**Padova, 15-16.09.2025**



# Sunlight-driven water splitting to *green hydrogen*



the bottleneck of water splitting...



7 AFFORDABLE AND CLEAN ENERGY



Development of eco-friendly, cheap, durable and efficient catalysts

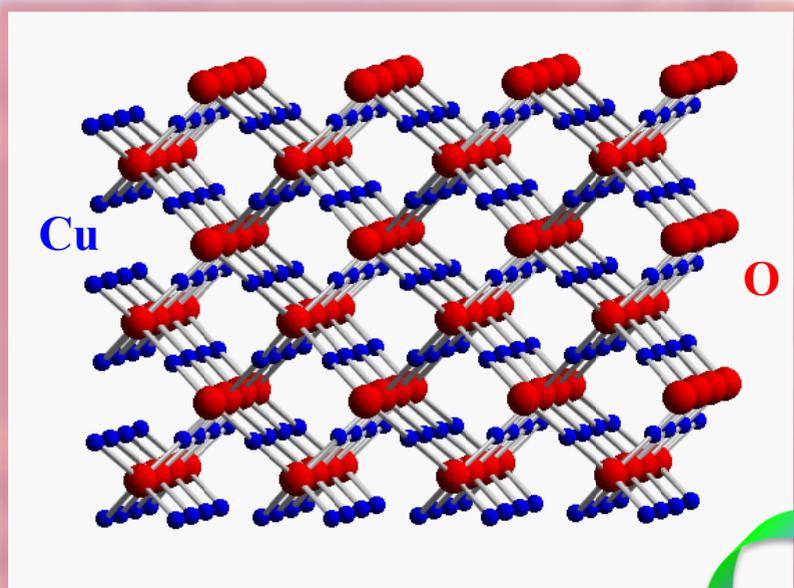
High surface-area nanosystems with tailored properties!

13 CLIMATE ACTION



D. Barreca *et al.*, "Metal oxide electrodes for photo-activated water splitting", in *Multifunctional Photocatalytic Materials for Energy*, edited by Z. Lin, M. Ye, M. Wang, Elsevier, 2018; *CrystEngComm* 2023, 25, 3968

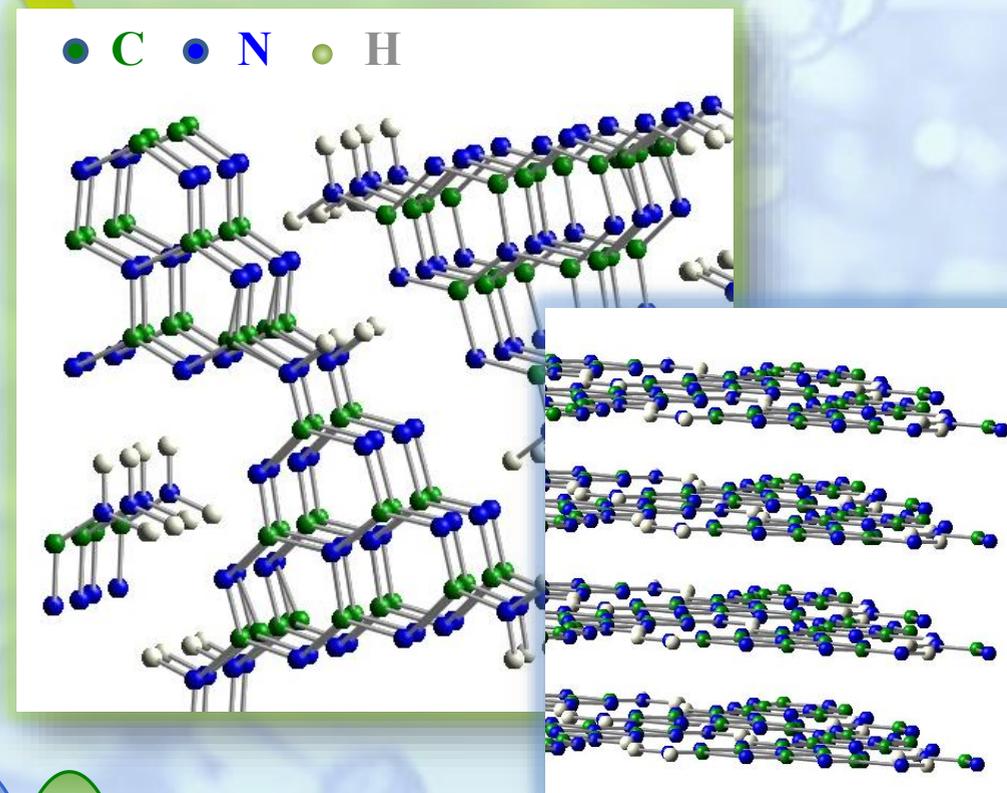
$\text{Cu}_2\text{O}$  (cuprite);  $E_G \approx 2.1 \text{ eV}$



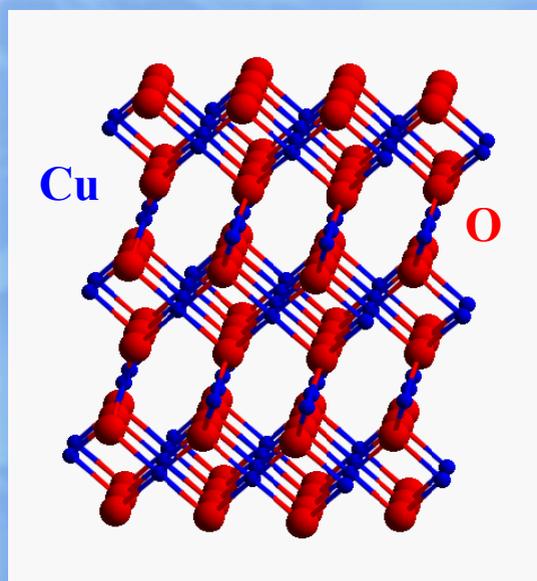
**Multi-component functional nanoarchitectures**

- gCN/ $\text{Cu}_x\text{O}$  nanoheterojunctions
- Introduction of  $\text{TiO}_2$
- Functionalization with Au NPs

Graphitic carbon nitride (gCN)

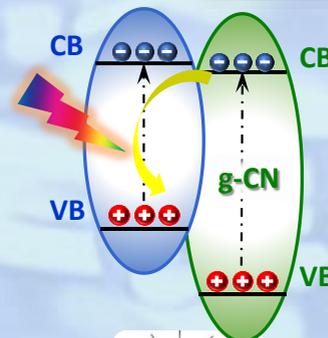


$\text{CuO}$  (tenorite);  $E_G \approx 1.5 \text{ eV}$



- ☺ Non-toxicity
- ☺ Inexpensive
- ☺ Naturally abundant
- ☺ Efficient sunlight harvesting

- ☹  $e^-/h^+$  transfer kinetics
- ☹ Photocorrosion

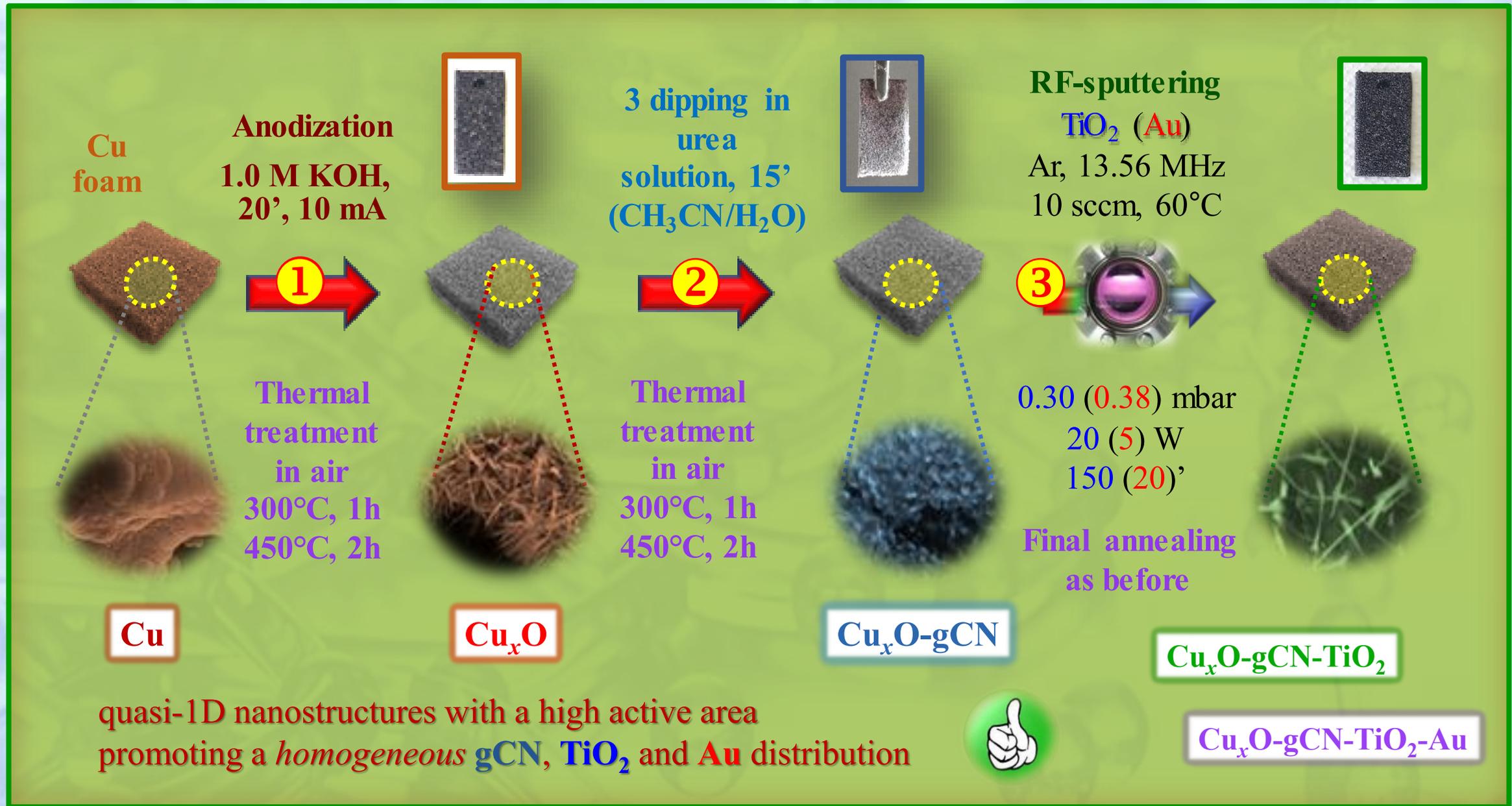


- ☺ Cost-effectiveness
- ☺ Eco-friendly
- ☺ Tuneable electronic structure
- ☺ Attractive photoactivity
- ☺ Favorable  $E_G$  ( $\approx 2.7 \text{ eV}$ )

# A multi-step hybrid fabrication route...

D. Barreca *et al.*, *RSC Adv.* 2024, 14, 7221

What's the plan?



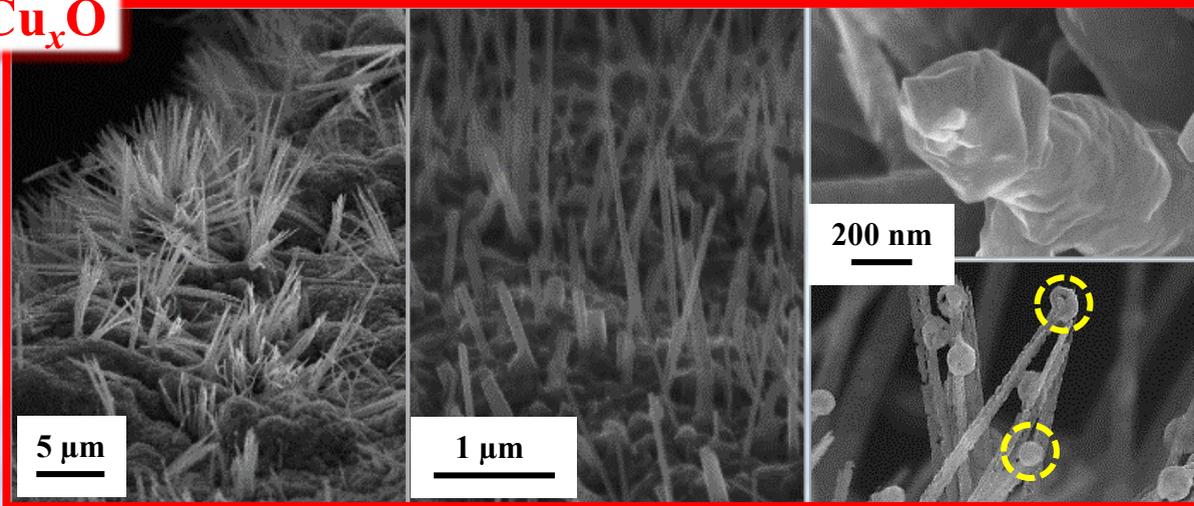
↑↑ mechanical stability than electrocatalysts obtained by immobilization on substrates of ink/pastes with binders

Intimate contact of the single components & efficient dispersion of Au NPs

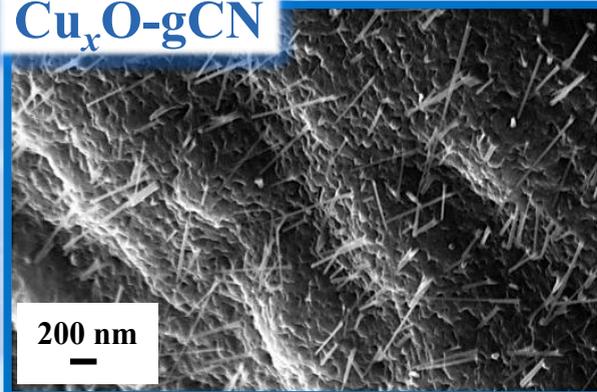
# FE-SEM

✓ High-area arrays of  $\text{Cu}_x\text{O}$  nanowires ( $L/d \approx 33$ ) with spheres on their tips

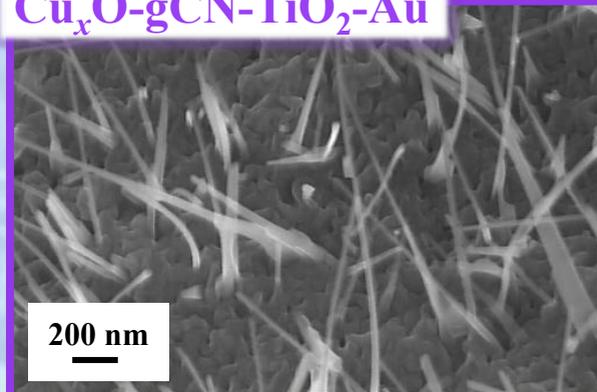
$\text{Cu}_x\text{O}$



$\text{Cu}_x\text{O-gCN}$



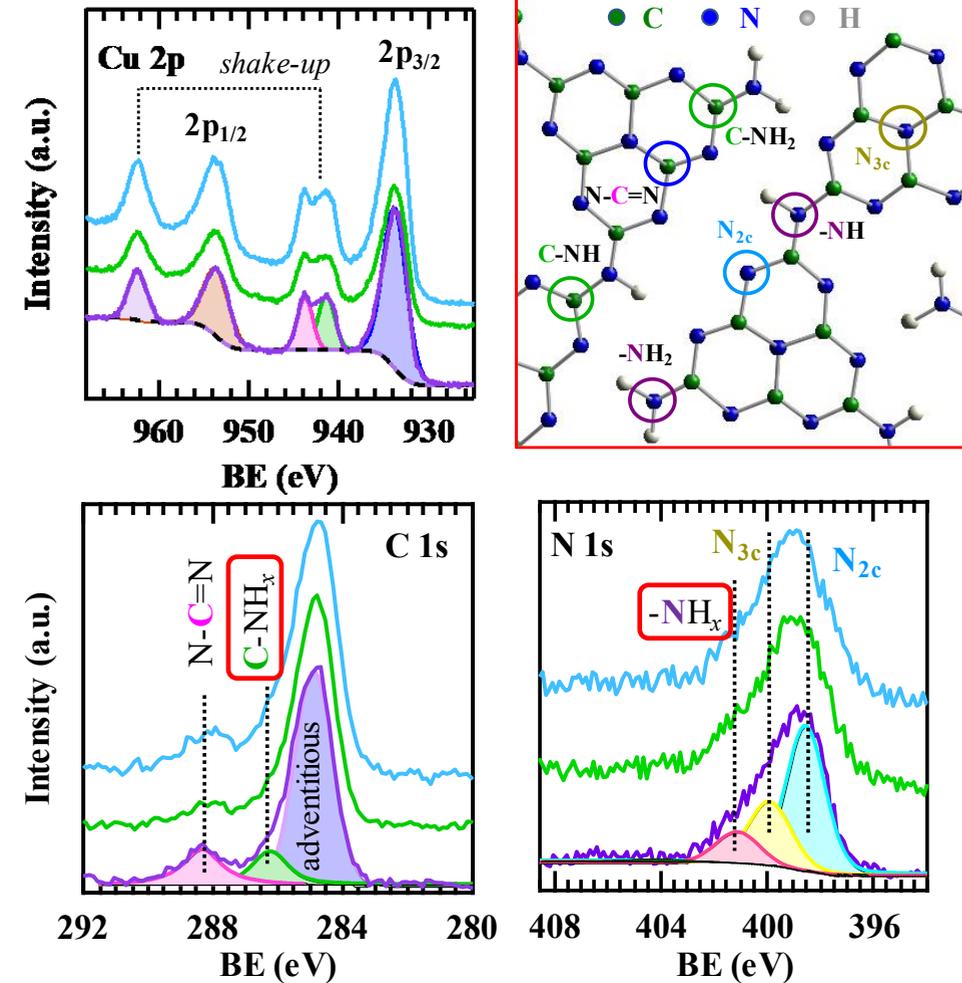
$\text{Cu}_x\text{O-gCN-TiO}_2\text{-Au}$



- ✓ Porous gCN overlayer
- ✓  $\Rightarrow$  partial coverage and embedding of  $\text{Cu}_x\text{O}$  nanowires into gCN, even after  $\text{TiO}_2$  and Au introduction
- ✓ Porosity of the starting Cu foam & RF-Sputtering infiltration
- $\Rightarrow$  intimate intermixing of the system components

# XPS

$\text{Cu}_x\text{O-gCN}$   $\text{Cu}_x\text{O-gCN-TiO}_2$   $\text{Cu}_x\text{O-gCN-TiO}_2\text{-Au}$



D. Barreca  
et al.,  
RSC Adv.  
2024, 14, 7221

No Ti  
and Au  
peaks  
(where  
are  $\text{TiO}_2$   
and  
Au...?)



✓ **CuO on the surface**

$$\text{BE}(\text{Cu } 2p_{3/2}) \approx 933.8 \text{ eV}; \alpha = \text{BE}(\text{Cu } 2p_{3/2}) + \text{KE}(\text{Cu LMM}) = 1851.4 \text{ eV}$$

✓ Typical gCN signals with **uncondensed amino-groups**

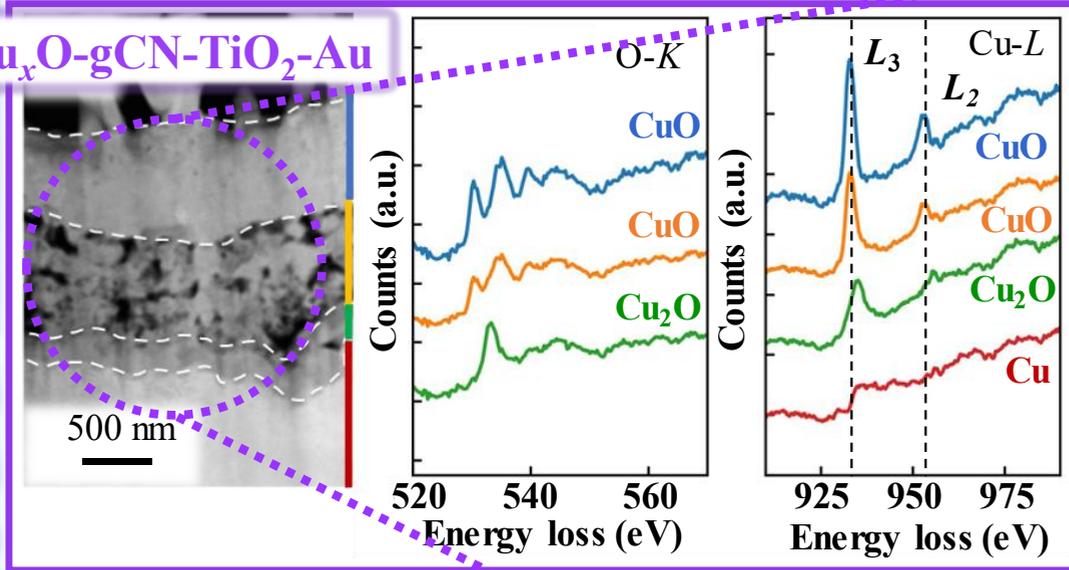
**defects increasing photoactivity**

✓ Chemisorbed -OH groups and direct gCN-CuO bonding



# TEM, EELS, EDXS

## Cu<sub>x</sub>O-gCN-TiO<sub>2</sub>-Au



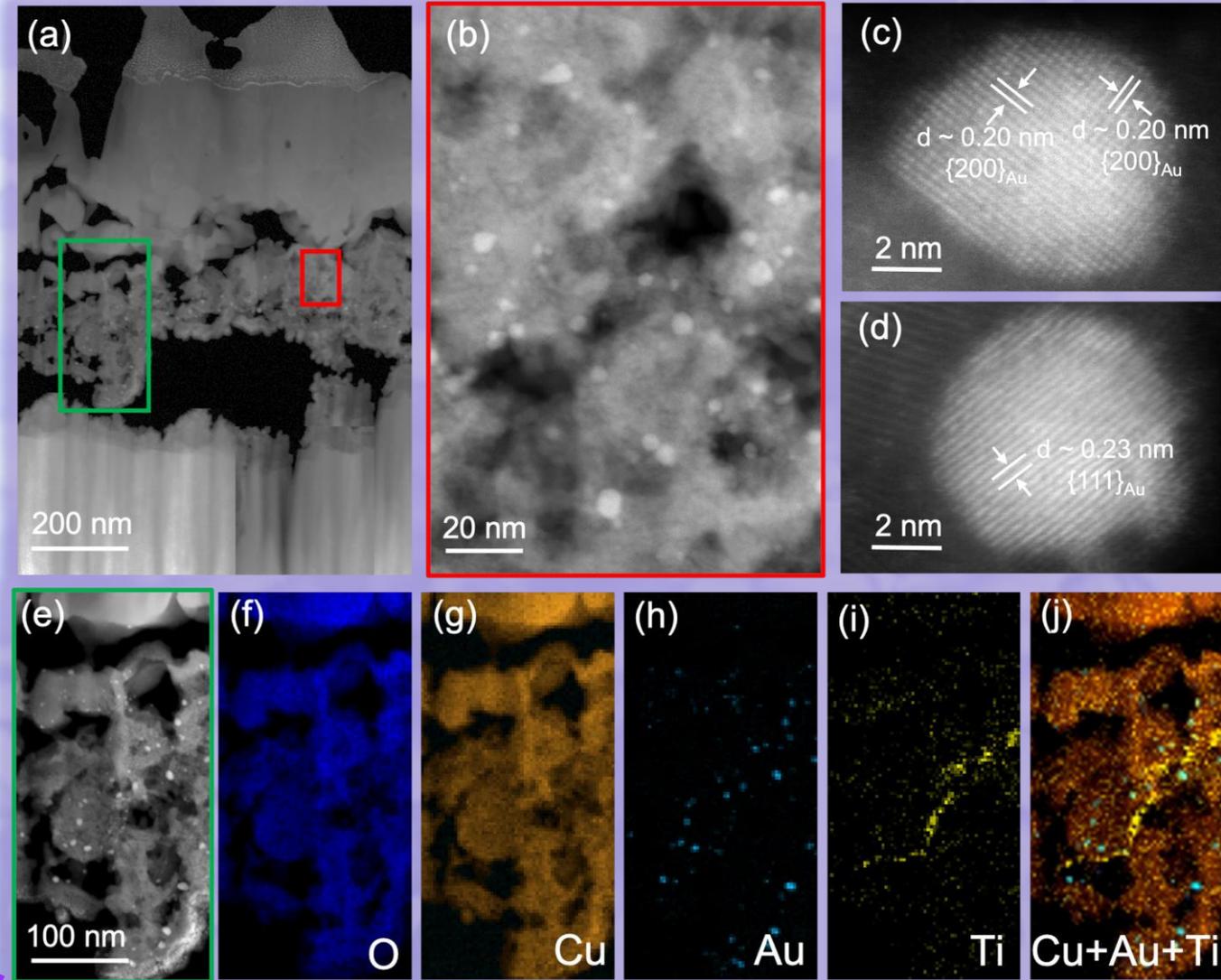
Variations in local chemical bonding

- Stacked structure over the Cu foam substrate
- Top two layers → CuO; next to the substrate → Cu<sub>2</sub>O

- Au NPs (2÷10 nm) dispersed in Cu<sub>x</sub>O
- TiO<sub>2</sub> concentrated in strip-shaped domains in close vicinity to Au NPs
- amorphous gCN
- close contact between material components



D. Barreca  
et al.,  
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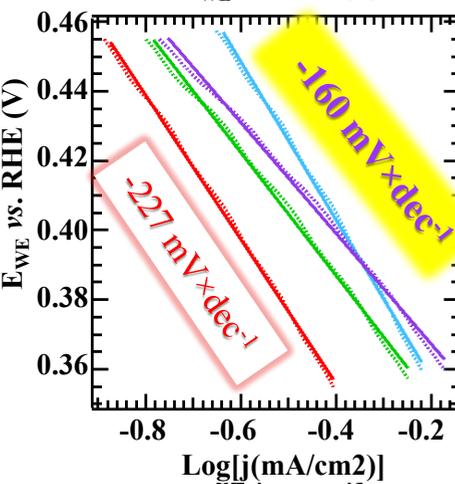
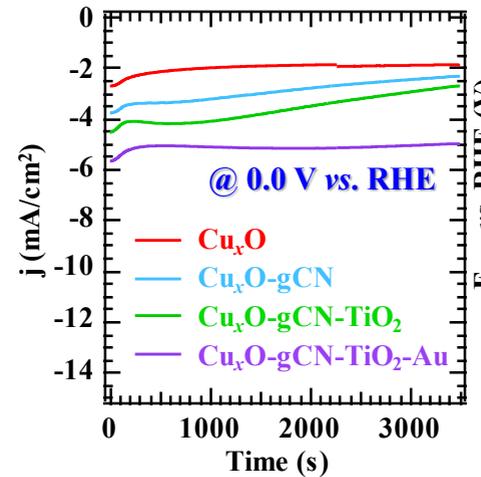
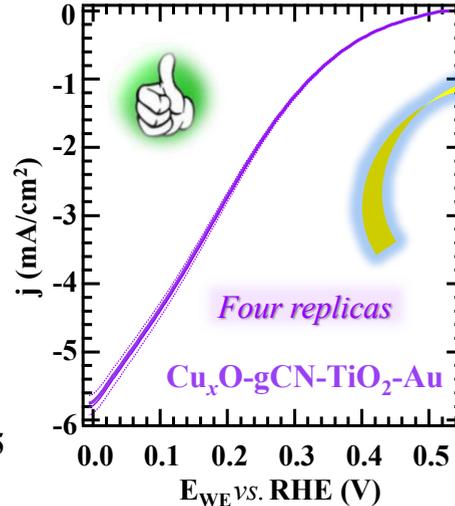
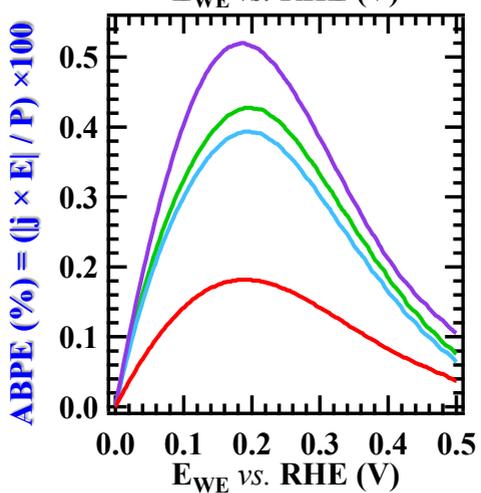
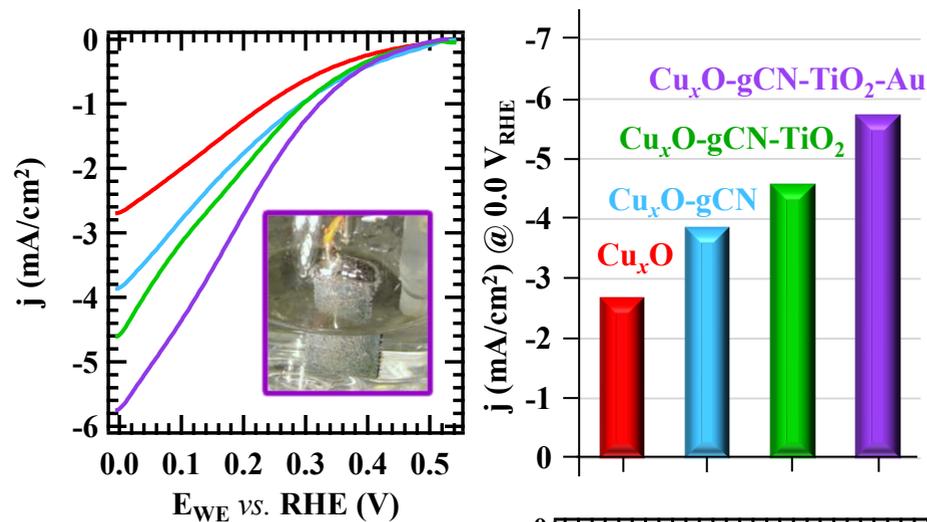


(b) micrograph of the area marked by the red box in (a). (c,d) Atomic resolution images of Au NPs, with indexing of gold lattice fringes and interplanar distances. Lattice fringes below Au NP in (d) are from TiO<sub>2</sub>. (e) Image of the area marked by the green box in (a), and EDXS elemental maps of O (f), Cu (g), Au (h), Ti (i), and overlaid image (j).



# Photo-assisted HER in alkaline water

0.5 M KHCO<sub>3</sub> (pH = 8.5); white light LED source, 100 mW×cm<sup>-2</sup>



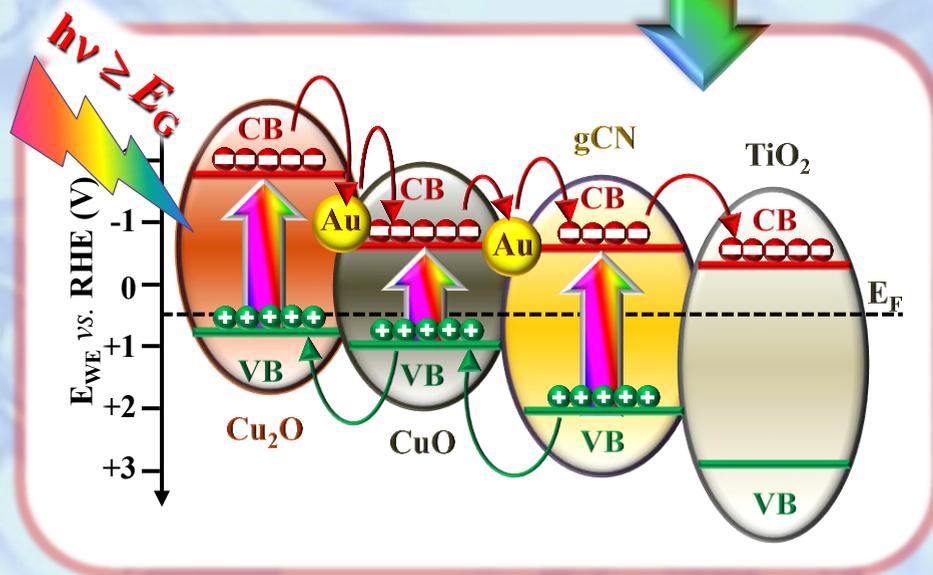
☛ Photocurrent & ABPE ↑ upon **Cu<sub>x</sub>O** functionalization

☛ **Cu<sub>x</sub>O < Cu<sub>x</sub>O-gCN < Cu<sub>x</sub>O-gCN-TiO<sub>2</sub> < Cu<sub>x</sub>O-gCN-TiO<sub>2</sub>-Au**

☛ good service life & ↓ Δj vs. time

☛ **High reproducibility**

☛ Performances *compare favorably* with previous Cu<sub>x</sub>O-based oxides



junction formation

- ☛ Cu<sub>2</sub>O protection
- ☛ ↓ e<sup>-</sup>/h<sup>+</sup> recombination
- ☛ **Cu<sub>x</sub>O-gCN-TiO<sub>2</sub>-Au: the best electrocatalyst** ⇒ ↓ Tafel slope

- ☛ photoexcitation of **Cu<sub>2</sub>O**, **CuO**, and **gCN**
- ☛ **h<sup>+</sup> confinement** in Cu<sub>2</sub>O VB & **cascade-e<sup>-</sup> transfer** into the CBs of the other constituents up to the electrolyte interface
- ☛ **Au NPs**: e<sup>-</sup> sinks with *improvement of the electrical contact*
- ☛ **TiO<sub>2</sub>**: protective action against photocorrosion & ↑ charge injection into the electrolyte

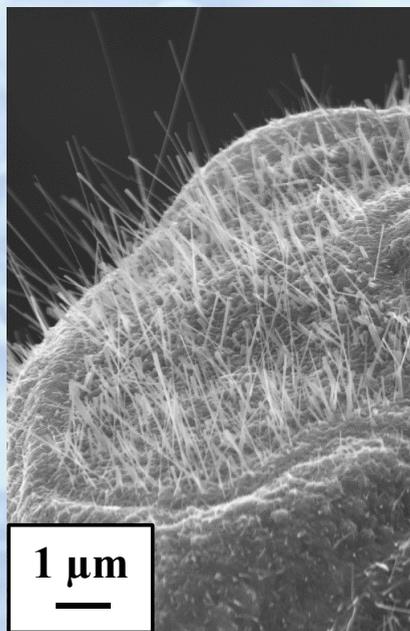
# Post-operando analyses

after storage under ambient conditions for 6 months, during which each specimen was subjected to photoelectrochemical tests every 90 days → high repeatability



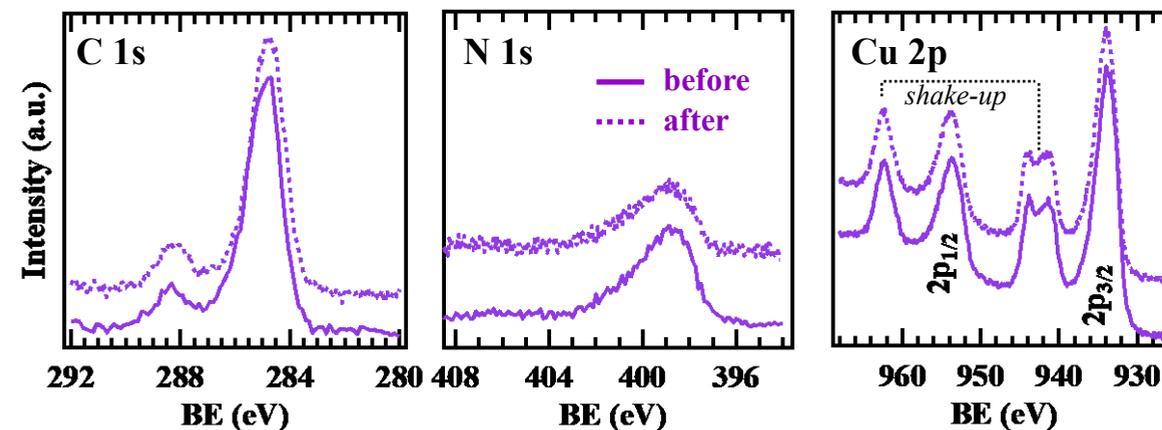
FE-SEM

$\text{Cu}_x\text{O-gCN-TiO}_2\text{-Au}$

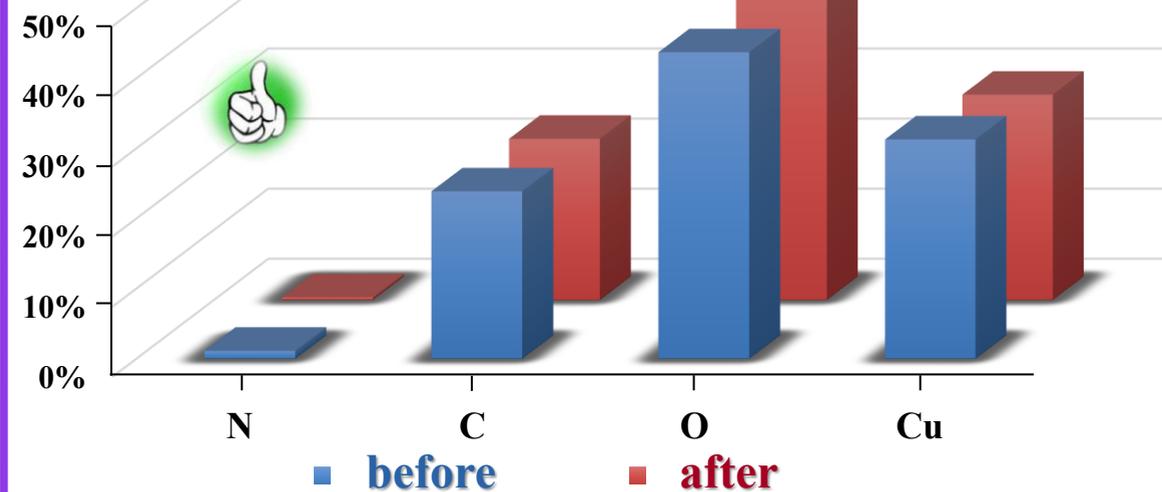


D. Barreca *et al.*,  
*RSC Adv.* 2024, 14, 7221

XPS

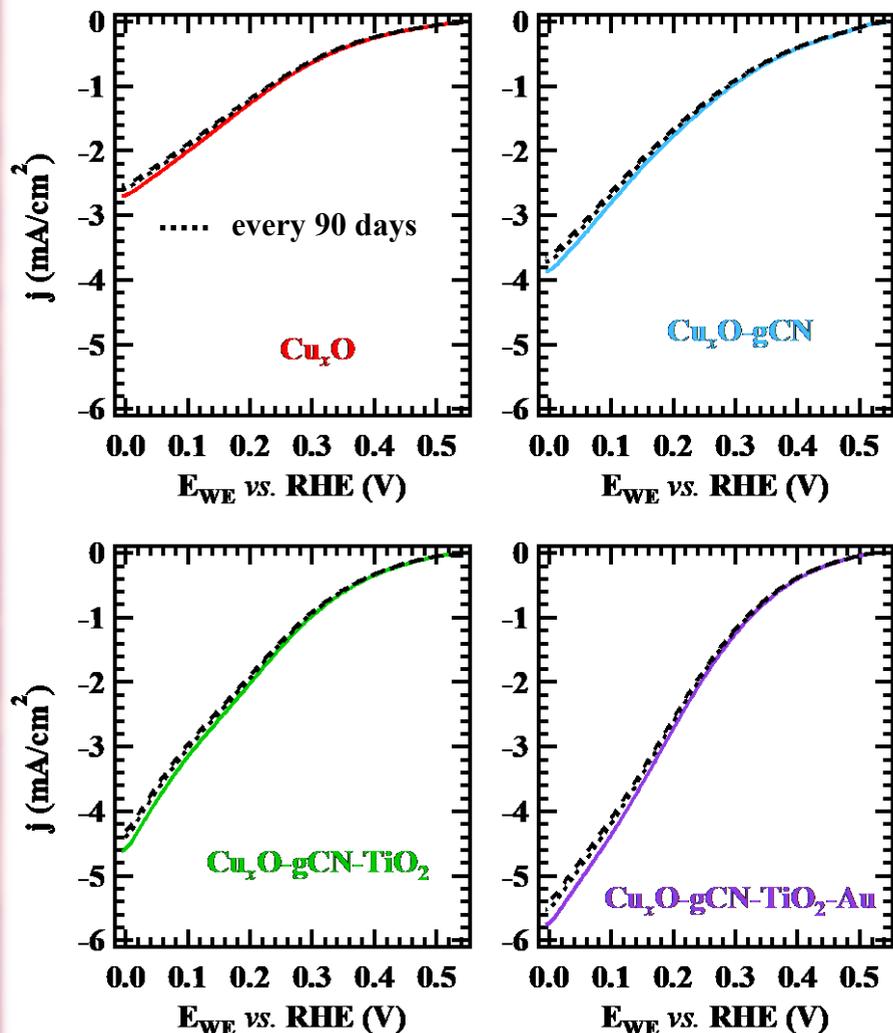


$\text{Cu}_x\text{O-gCN-TiO}_2\text{-Au}$

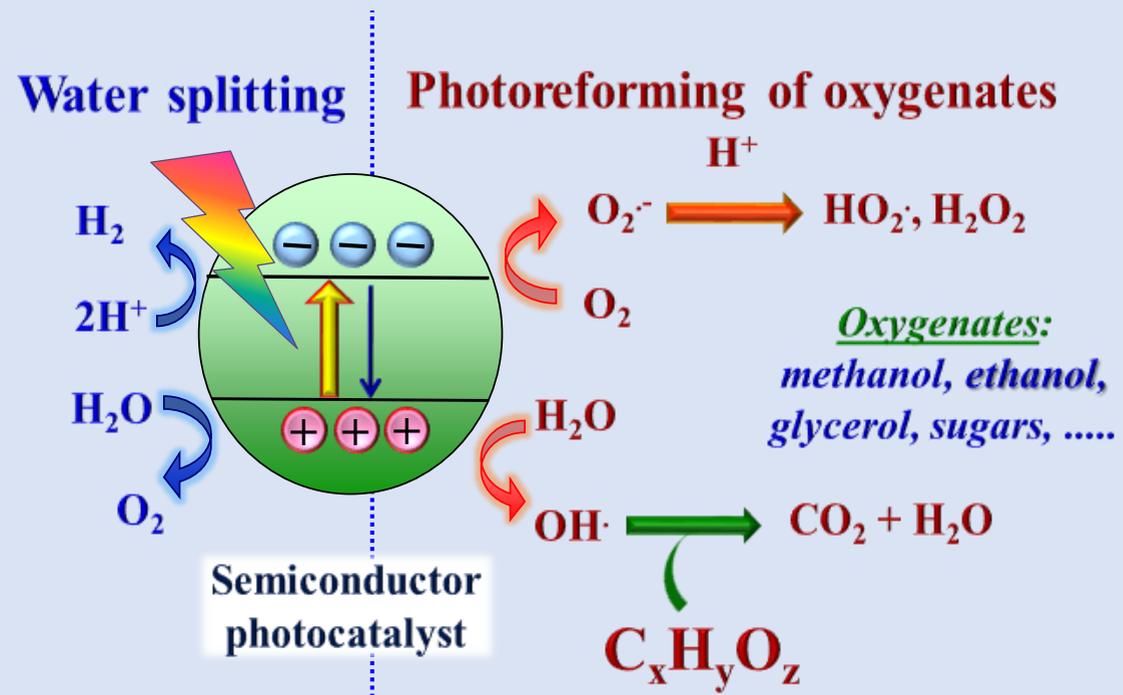
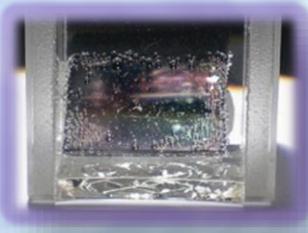


Very good operational stability!

No significant alteration/degradation upon prolonged operation



# Photo-assisted H<sub>2</sub> production



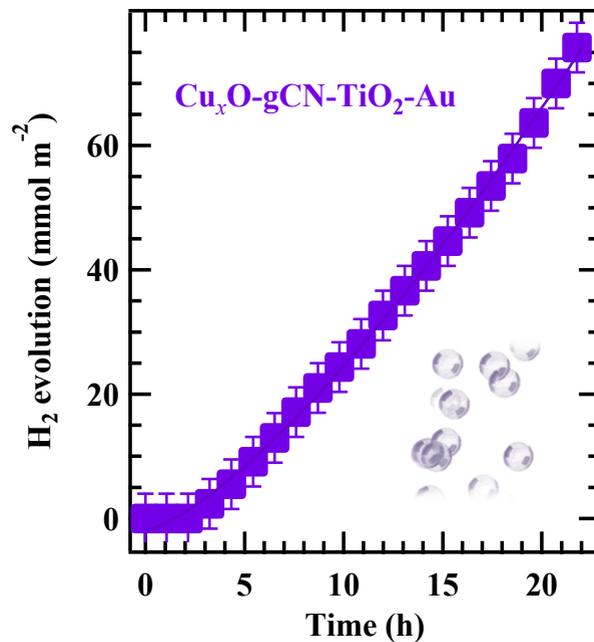
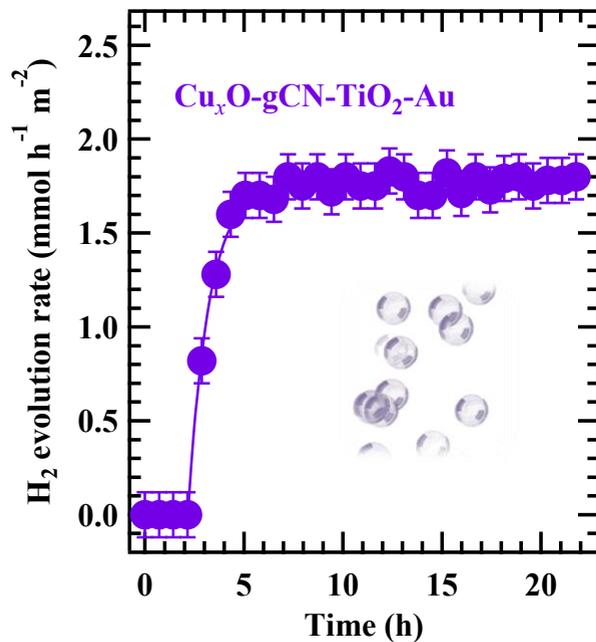
Photoreforming of H<sub>2</sub>O/CH<sub>3</sub>CH<sub>2</sub>OH (1:1) solutions

**Simulated solar radiation**

150 W Xe lamp

**no applied bias**, 25°C

D. Barreca *et al.*,  
*Eur. J. Inorg. Chem.* 2011, 4309;  
*Adv. Funct. Mater.* 2011, **21**, 2611



**Bias-free H<sub>2</sub> evolution performances of Cu<sub>x</sub>O-gCN-TiO<sub>2</sub>-Au were higher than those afforded by various homologous photocatalysts reported so far :**

- i) Cu<sub>2</sub>O-TiO<sub>2</sub>; ii) gCN-TiO<sub>2</sub>;
- iii) gCN-Cu<sub>2</sub>O; iv) gCN-CuO;
- v) gCN-CuO-TiO<sub>2</sub>; vi) gCN-Cu<sub>2</sub>O-TiO<sub>2</sub>;
- vii) gCN-TiO<sub>2</sub>-Au; viii) gCN-TiO<sub>2</sub>-Pt.



## ... in conclusion

- ✓ Supported **green nanoarchitectures** ( $\text{Cu}_x\text{O-gCN-TiO}_2\text{-Au}$ ) on Cu foam substrates by a scalable and modular **hybrid liquid/vapor phase route** (*Cu anodization, liquid-phase gCN introduction, RF-Sputtering of  $\text{TiO}_2$  and Au*) & **final annealing in air**
- ✓ **High-area, multi-component systems** with an *intimate constituent contact* ⇒ **multiple junctions**
- ✓ Synergistical **chemical & electronic interplay** ⇒ **remarkable HER activity** ( $\approx -5.7 \text{ mA/cm}^2$  at 0.0 V vs. RHE) **and very good stability**
- ✓ Many degrees of freedom to **tailor photoactivity & service life**

↑↑↑ **photo-electrocatalyst performances**

... **perspectives & open challenges**

- ✓ Implementation of **tailored nanoheterostructures** for *clean energy production* from **seawater** and **natural wastes**
- ✓ Optimization of material performances for bias-free photocatalytic  $\text{H}_2$  evolution
- ✓ **Tests for a possible real-world utilization under different conditions**
- ✓ Performance mastering of **(photo)electrocatalysts for  $\text{H}_2\text{O}$  purification**



KEYS TO SUCCESS



$\text{H}_2$