Development of a versatile TEM specimen holder for the characterization of photocatalytic materials

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Background

Photocatalysts are of fundamental interest for sustainable energy research [1]. By means of transmission electron microscopy (TEM), it is possible to obtain insight into their structure, composition and reactivity. Such insight can then be used for their further optimization [2]. Here, we combine conventional TEM analysis on photocatalysts with several in situ TEM techniques including environmental TEM (ETEM), in situ photo activation and localized surface plasmon resonance (LSPR) spectroscopy [3-4].

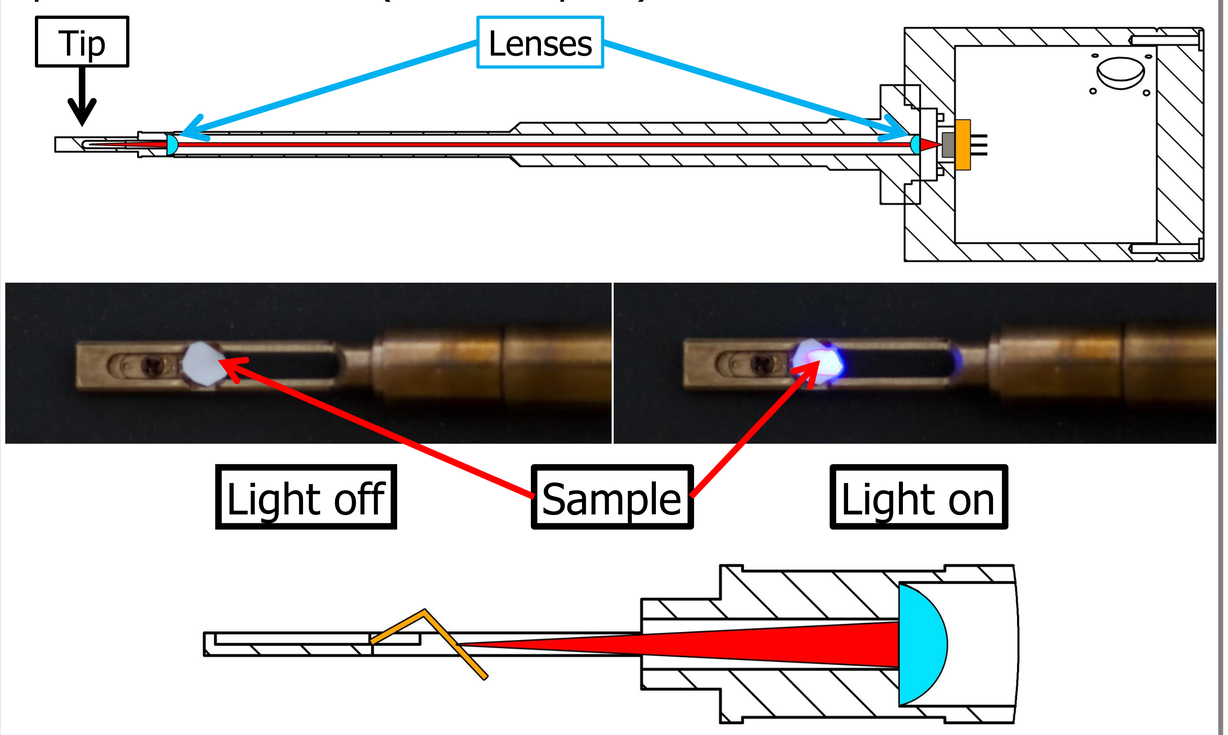
This project is part of the CAtalysis for Sustainable Energy (CASE) initiative and involves characterization of catalysts using methods available at DTU Center for electron nanoscopy (Cen).

Design

Two versions of a new specimen holder capable of shining light onto samples inside the TEM have been developed.

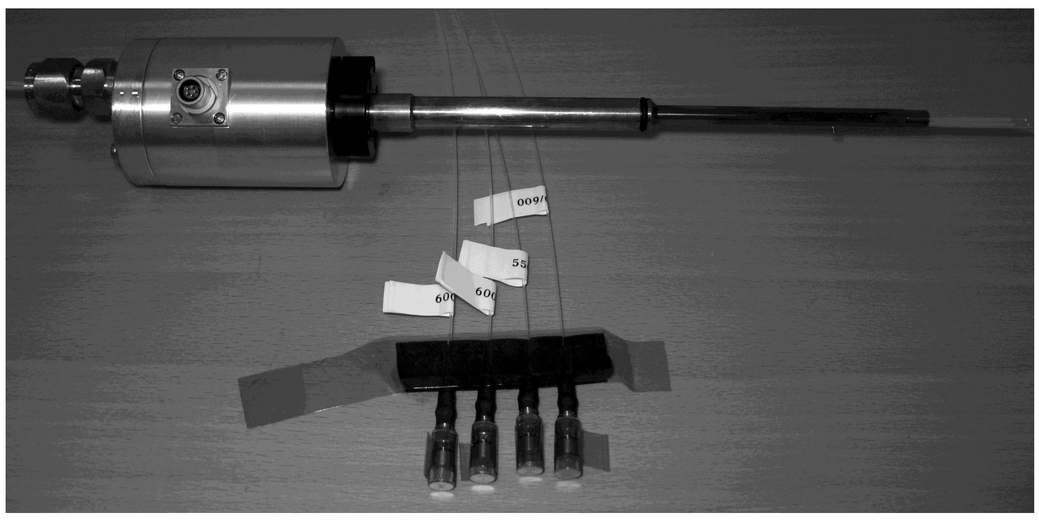
Lensed model

The holder is implemented with a laser diode and a lens system to guide and focus light onto the sample surface with maximum power transmission (no fiber optics).



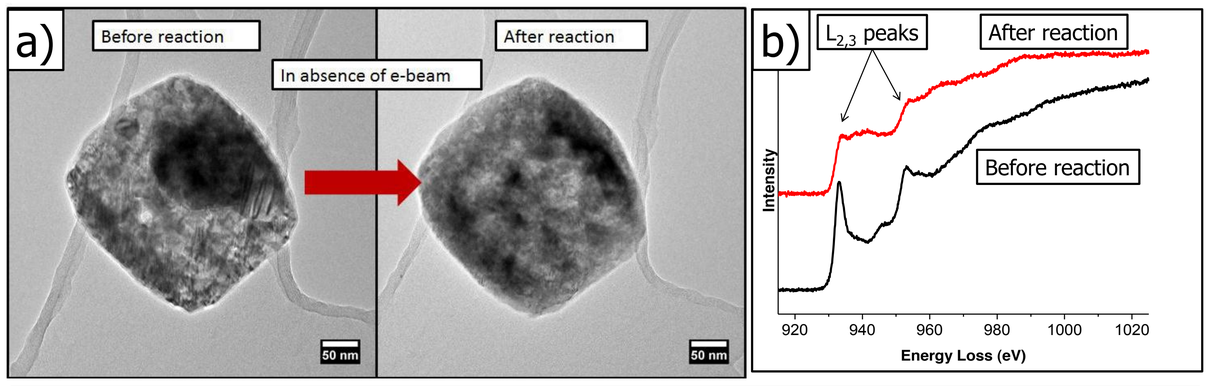
Multiprobe model

- 5 fiber optic feedthroughs.
- Simultaneous illumination by up to five different light sources.
- Light sources and combinations can be changed during microscope operation.
- An additional optical fiber provides the ability to collect light emitted from the sample and to perform spectroscopic analysis in real time.
- 5 electrical connections.



In situ Cu_2O nanocubes photoreduction

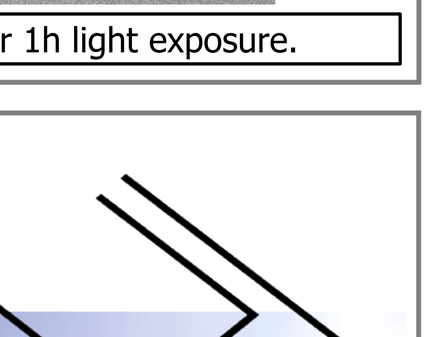
- Cu_2O is a photocatalyst for water splitting under visible light illumination.
- It undergoes photodegradation in an aqueous environment.
- The electron beam was blanked before exposing the sample to 5mbar H_2O and light and unblanked for investigation after high vacuum was restored.
- EELS: $L_{2,3}$ edges («white lines») reflect the chemical state of Cu.

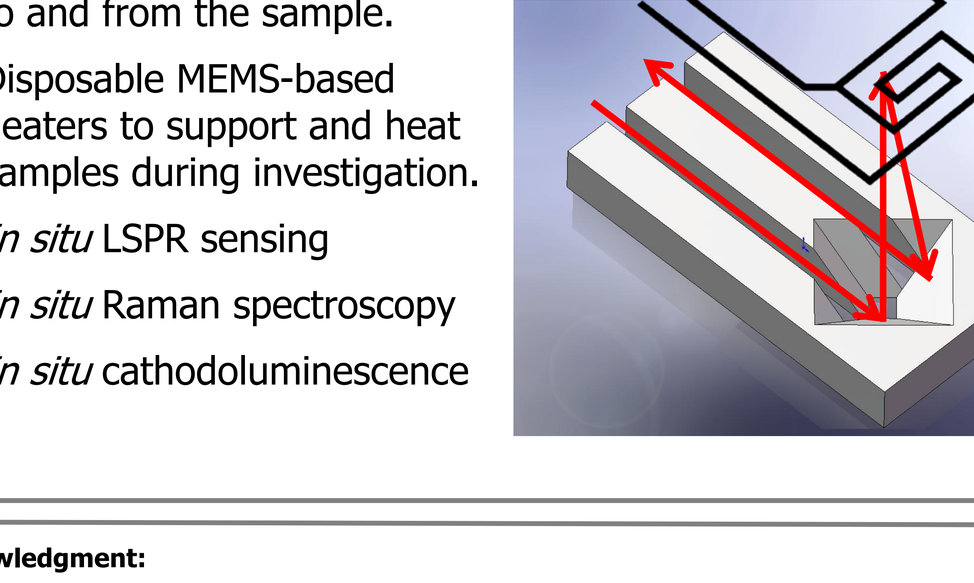


Degradation of Cu_2O nanocubes in H_2O (5 mbar) under visible light illumination (405 nm) for 1 hour. (a) Cu_2O Nanocube before and after reaction and (b) Relative EELS signal of the same cube. The nanocube was reduced to metallic copper after reaction.

In situ Pt nanoparticle photodeposition

- $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ powder substrate.
- Powder coated with Pt precursor (H_2PtCl_6).
- H_2O vapor atmosphere @ 10 mbar.
- 405 nm laser light = 3 eV.





Pt photodeposition on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ after 1h light exposure.

Work in progress

- Implemented silicon mirror chip to direct the light beam to and from the sample.
- Disposable MEMS-based heaters to support and heat samples during investigation.
- *In situ* LSPR sensing
- *In situ* Raman spectroscopy
- *In situ* cathodoluminescence

References
[1] J. M. Herrmann, Top. Catal. **34** (2005), p. 49-65.
[2] M. Tsujimoto, S. Moriguchi, et al., J. Electron Microsc. **48** (1999), p. 361-366.
[3] C. Langhammer, E. M. Larsson, B. Kasemo, I. Zorić, Nano Letters **10** (2010), p. 3529-3538
[4] E. M. Larsson, C. Langhammer, I. Zorić, B. Kasemo, Science **326** (2009), p. 1091-1094.

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