

Optimizing Catalyst Loading and Location within Nanostructured Si Photoelectrodes

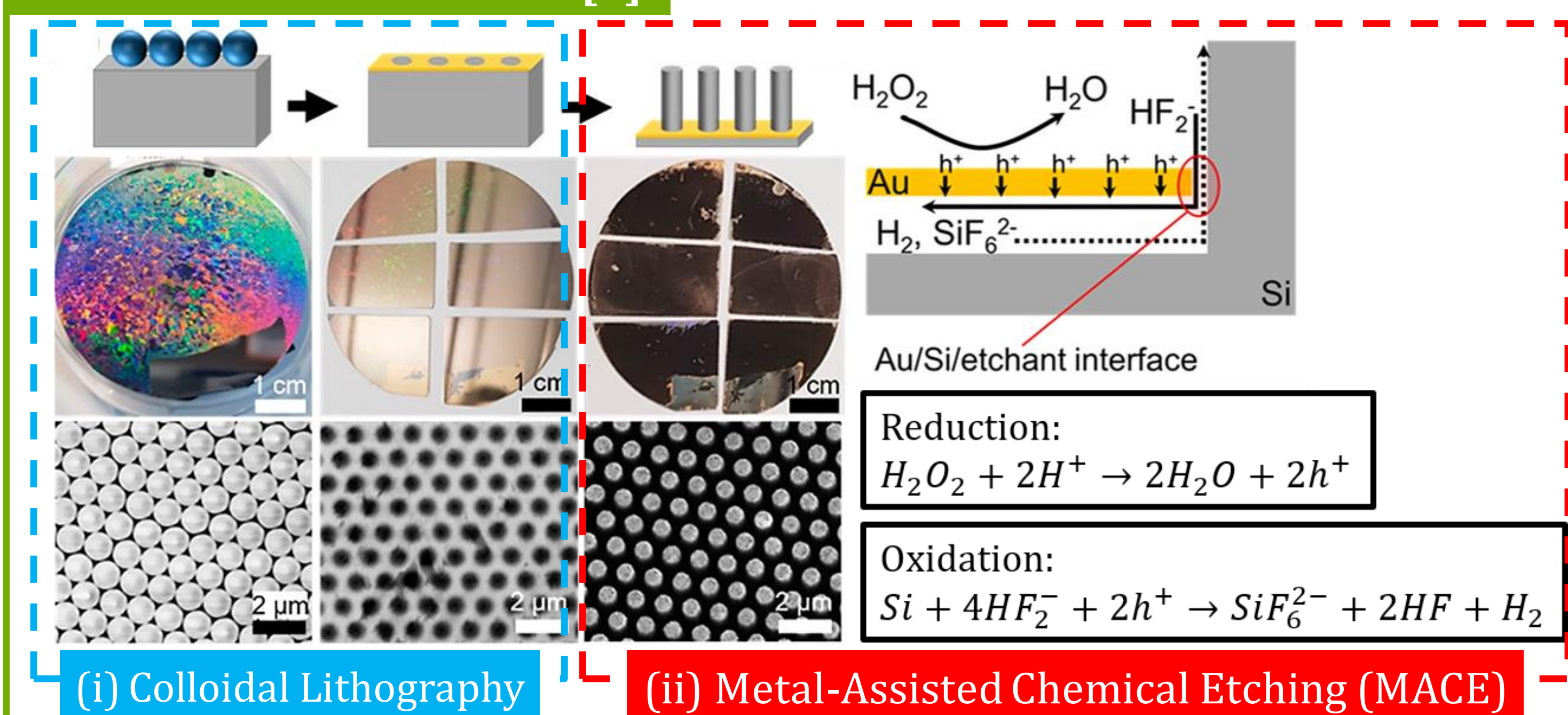
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Introduction and Motivation

The production of alternative clean fuels such as H₂ or conversion of CO₂ into chemical building blocks are considered as promising strategies towards coping with global warming. Photocatalysis utilizing solar energy has shown great promise to secure these goals in an environmentally-friendly manner. Heterogeneous photocatalysts are usually composed of nanostructured metal/semiconductor hybrids, where the metal acts as the catalyst and the semiconductor acts as the light absorber. In that regard, vertically aligned Si nanowires (VA-SiNWs) are capable of accommodating high catalyst loadings thanks to their high surface area, while their one-dimensional morphology provides the opportunity to decouple charge separation and light absorption. Moreover, by controlling geometrical factors such as diameter and pitch size, their optical properties can be easily tuned. To this day charge recombination, incomplete light absorption and limited mass transfer to the catalyst still limit conversion efficiencies. A few studies have shown that these issues could be mitigated by optimizing catalyst loading and location within Si nanowire arrays. This doctoral project will investigate how these factors can be optimized to improve electrocatalytic and photoelectrocatalytic activity of SiNWs/Metal hybrids in the context of solar water splitting.

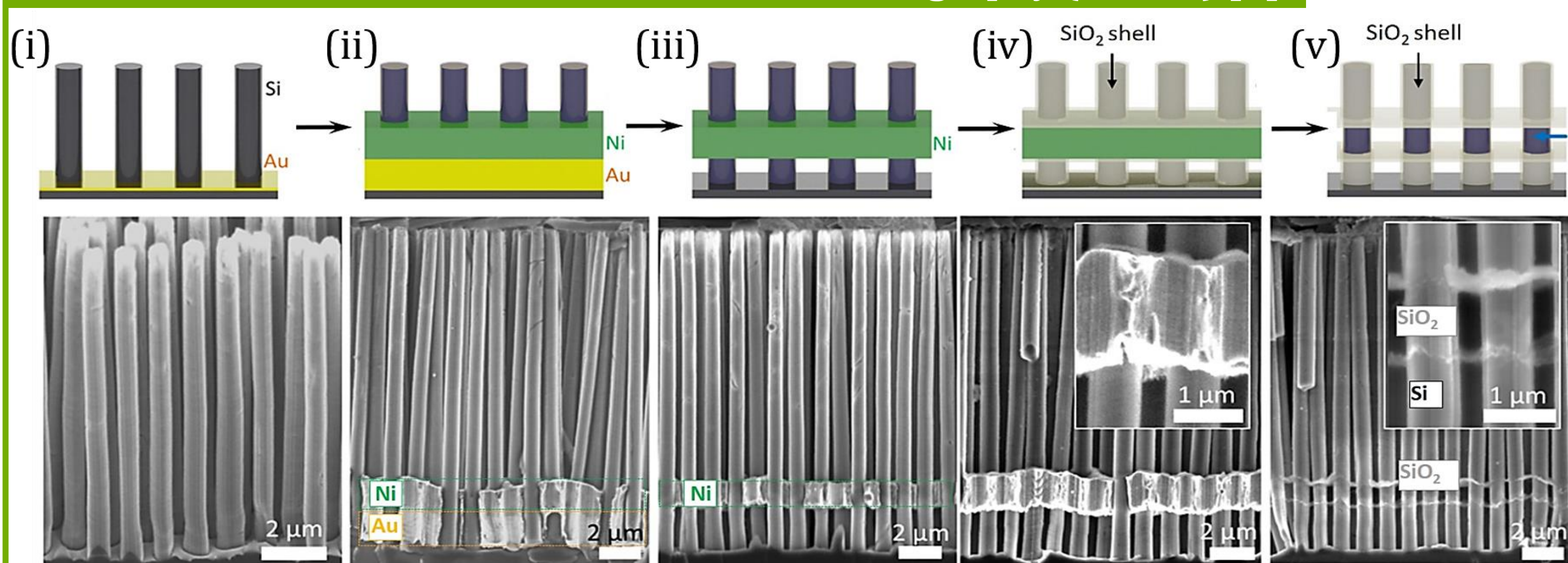
Materials and Method

1- Fabrication of VA-SiNWs [1]



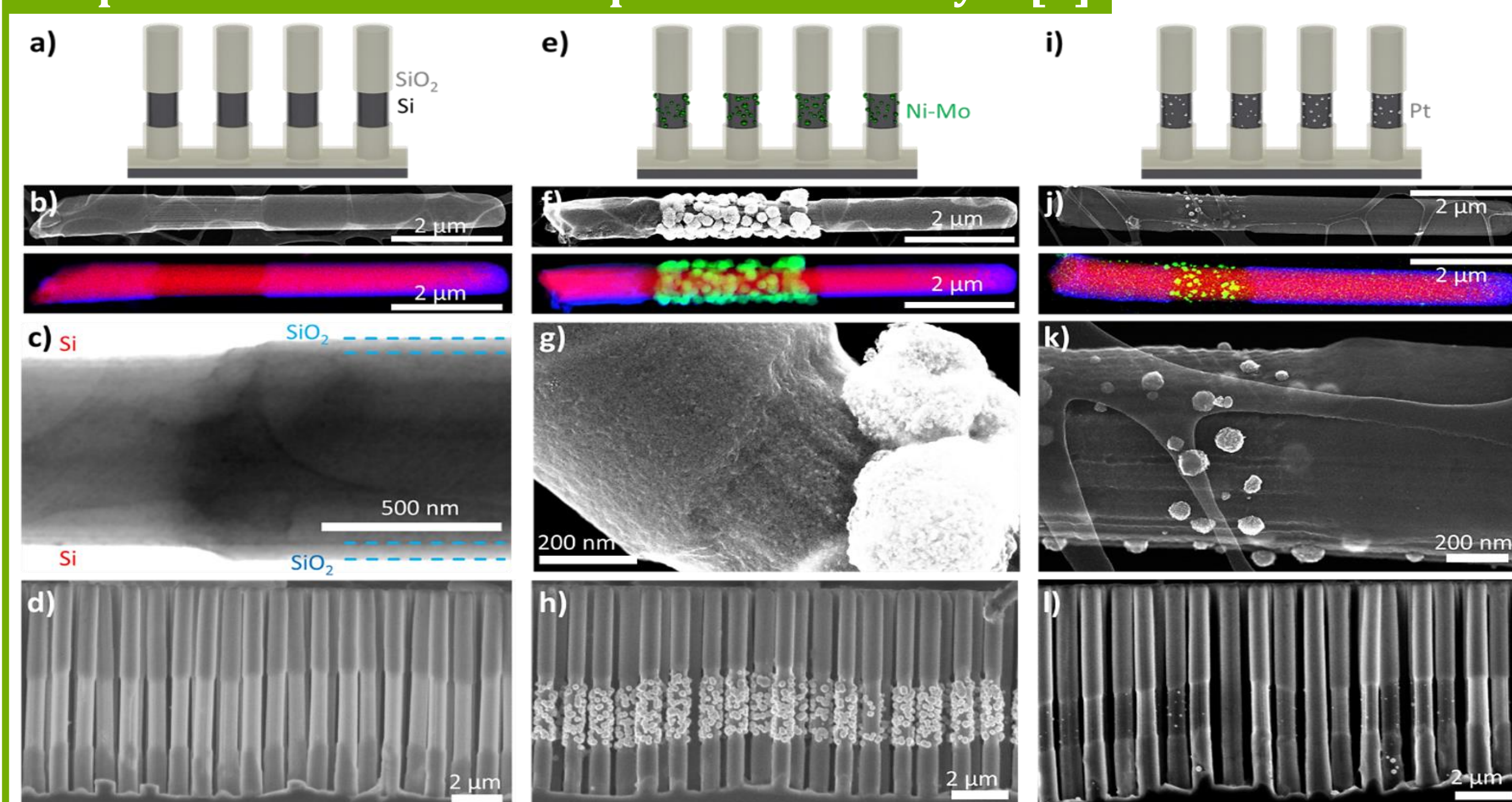
- A gold nanomesh is patterned on the surface of silicon wafer via colloidal lithography.
- The gold film etches into the substrate to fabricate silicon nanowire arrays (MACE).

2- Three-Dimensional Electrochemical Axial Lithography (3DEAL) [2]

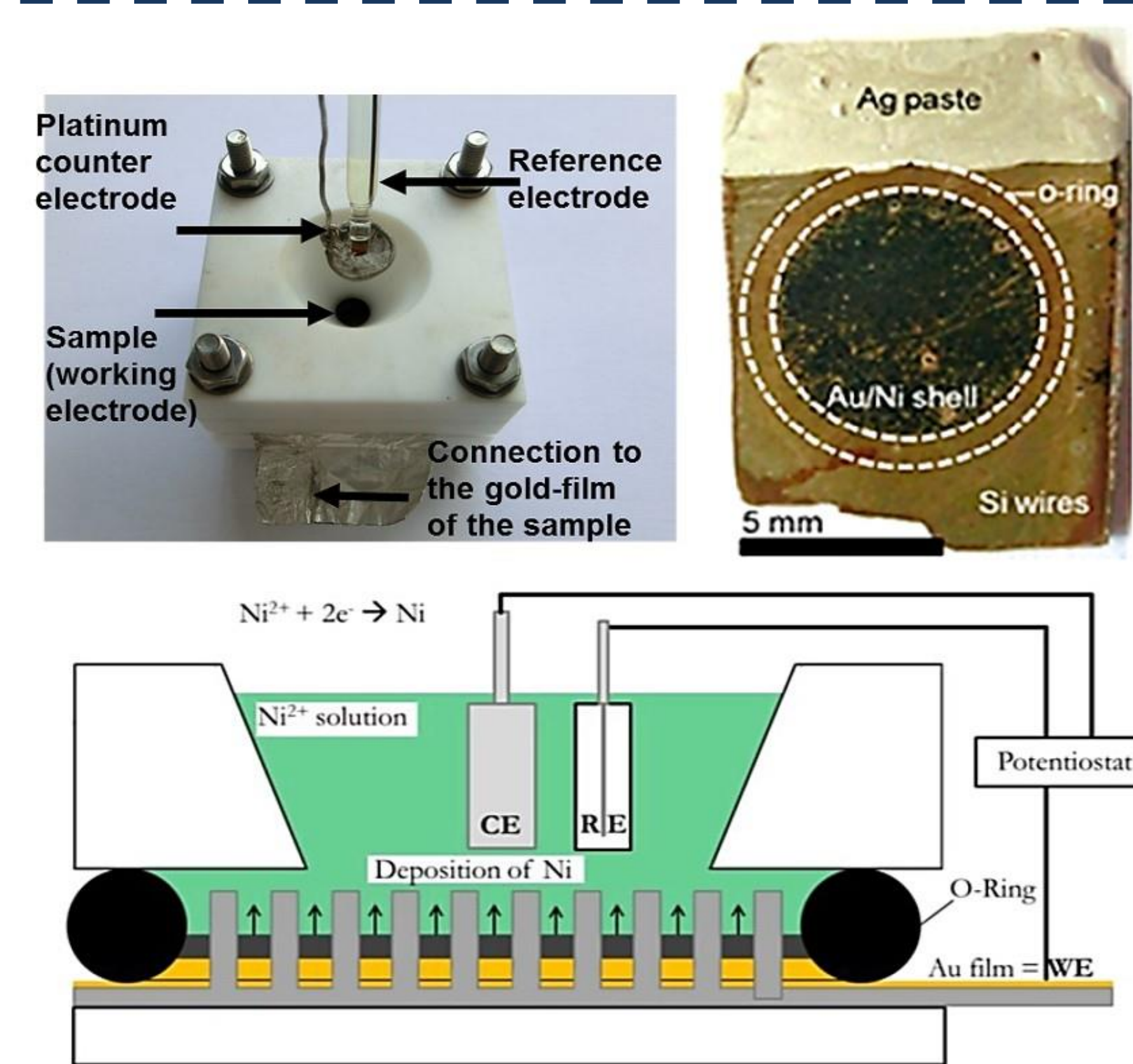


- VA-SiNWs array after MACE and deposition of a sub-5 nm conformal SiO₂ shell.
- Planar electrodeposited gold and nickel films that are embedded within the VA-SiNWs.
- Selective etching of gold with an aqueous KI/I₂ solution.
- Deposition of a conformal SiO₂ thick film. The inset shows higher magnification.
- Selective etching of nickel yields VA-SiNWs arrays patterned with continuous thick SiO₂ shells. The area in between is passivated with a sub-5 nm SiO₂ layer (shown in blue) that can be etched at a later stage via KOH. Spatioselective electrodeposition of metal particles can now be realized at these defined locations.

3- Spatioselective electrodeposition of catalyst [3]



Spatioselective metal deposition characterized via SEM, STEM, TEM, and EDX analysis. (a-d) Nanowires patterned with SiO₂. (e-h) Nanowire arrays patterned with SiO₂ and Ni-Mo. (i-l) Nanowire arrays patterned with SiO₂ and Pt.



Experimental setup for the successive electrodeposition of metals utilized in the steps 2 and 3.

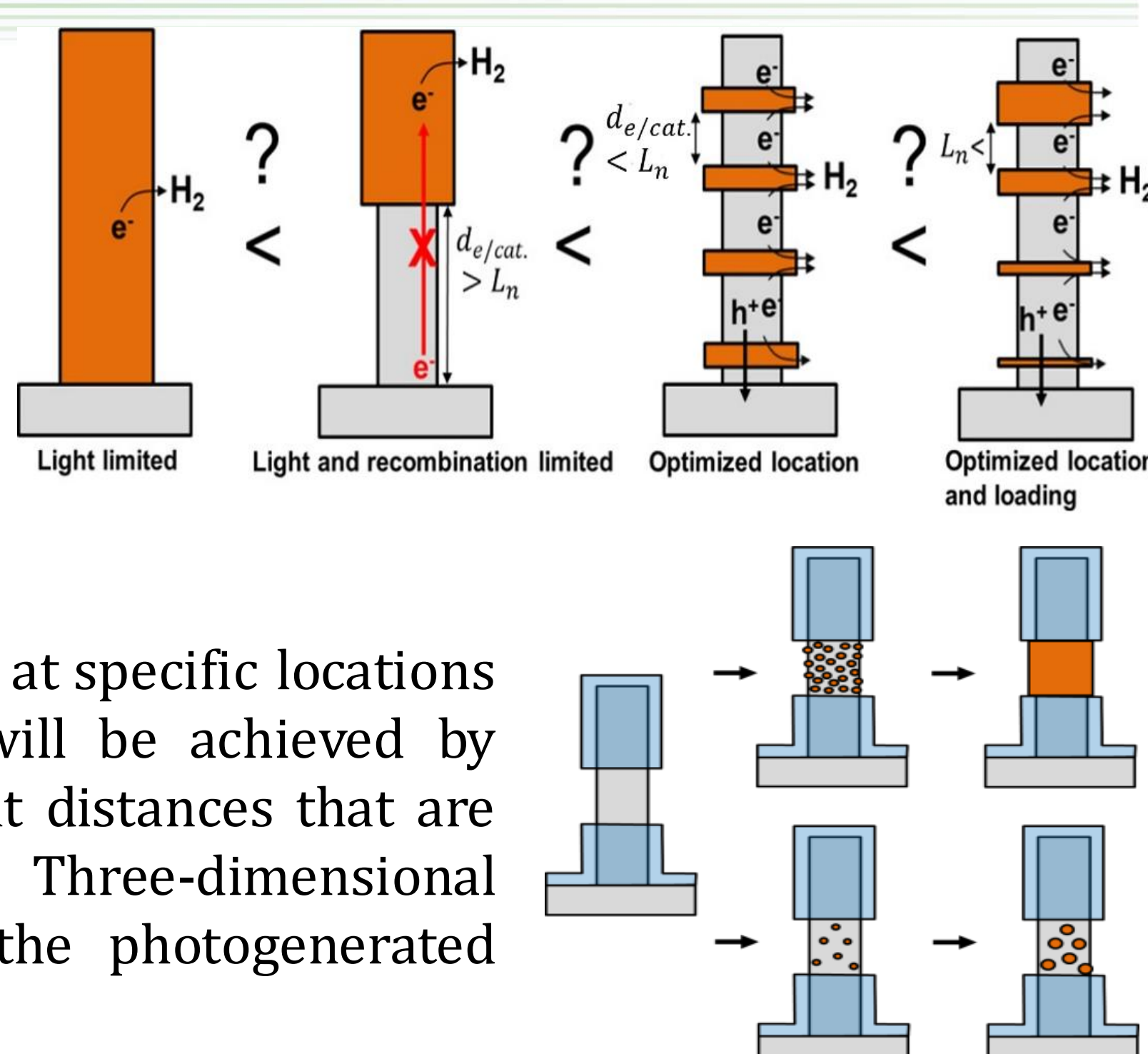
Aims and Approach

Aims:

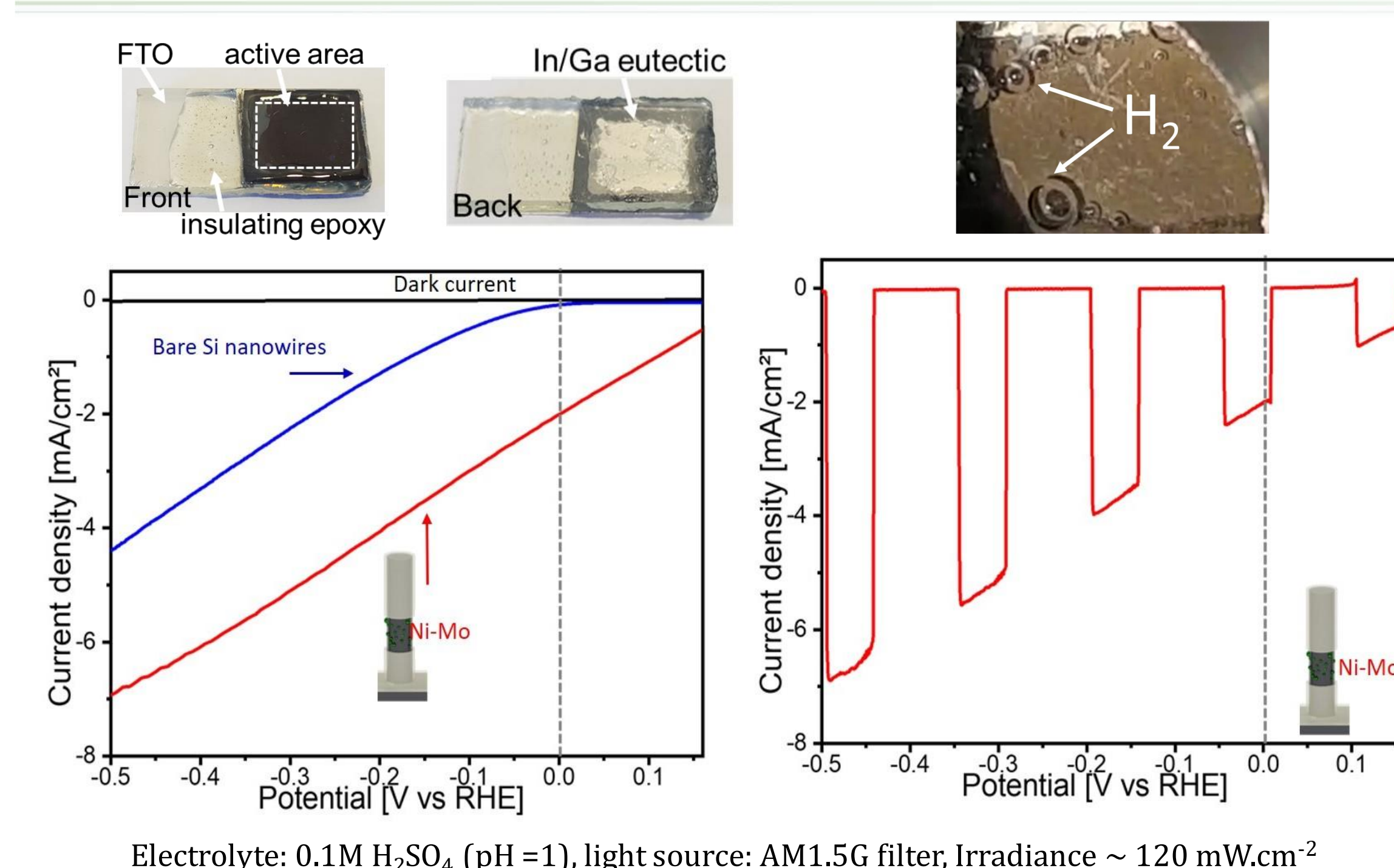
- Control of metal catalyst density and morphology
- Control of metal catalyst loading and location
- Map (photo-)electrochemical activity along the SiNWs

Approach:

Various metal catalyst rings will be deposited using 3DEAL at specific locations along the nanowires. Optimization of catalyst loading will be achieved by depositing the catalyst periodically along the nanowires at distances that are shorter than the minority carrier diffusion length (L_n). Three-dimensional electromagnetic simulations will be used to estimate the photogenerated electron flux as a function of location within the nanowires.



Preliminary Photoelectrochemical Tests [3]



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