

Leveraging reactions and electrodeposition to fabricate photoanodes for oxygen production

Semiconductor materials like silicon convert solar energy to electricity. A related, highly relevant scientific and technological challenge is to produce useful chemicals by using sunlight. Photoelectrodes are a possible avenue to realize this conversion. In a recent *Nature Communications* article (<https://doi.org/10.1038/s41467-021-24229-y>), Edward Yu and collaborators from The University of Texas at Austin and State Key Laboratory of ASIC and System, China, propose a fabrication route that is both cheap and scalable to manufacture photoanodes for the oxygen evolution reaction. A photoanode is one of the two electrodes required for conversion of sunlight and water to hydrogen gas.

In simple terms, photoelectrodes use semiconductors to convert sunlight into electrons and holes that subsequently drive electrochemical reaction(s) generating a desired chemical product. The

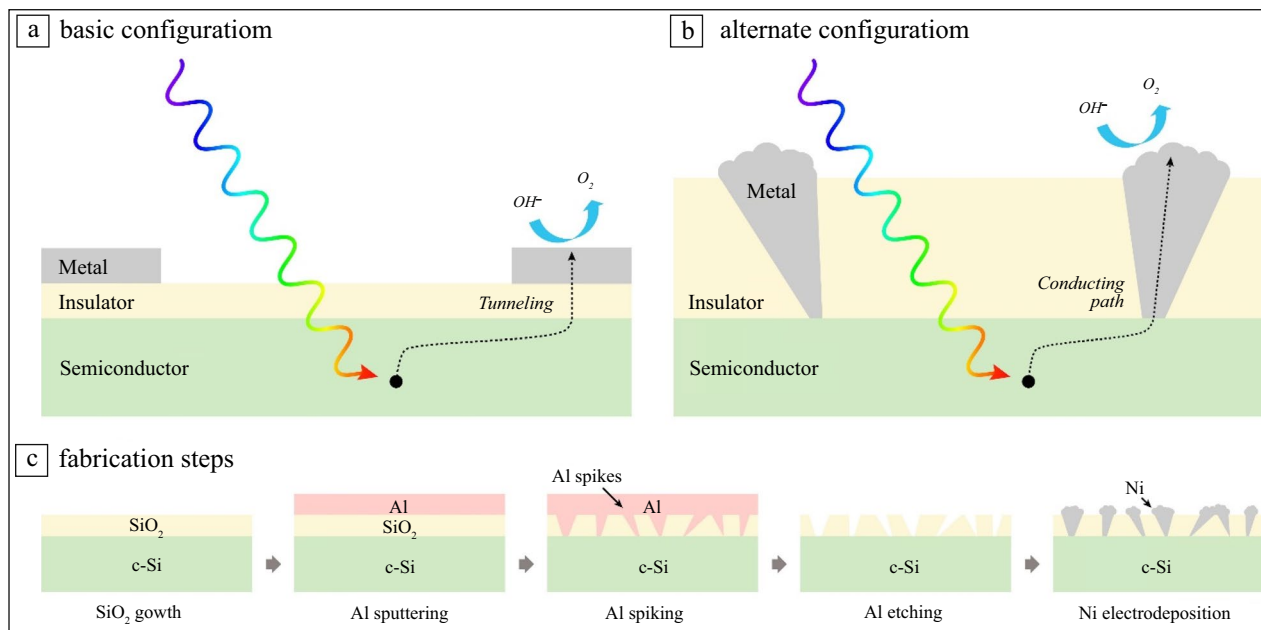
first conversion is very similar to solar cells, while the second step is common to electrochemical systems like batteries. However, when both steps are to be carried out in a single device, materials selection and fabrication processes, particularly at scale, can be challenging.

In this work, the research team examined photoanodes for producing oxygen from a solution containing OH^- ions (1 M KOH, pH 14). The basic configuration for such a photoanode is shown in **Figure a**. The semiconductor material absorbs light and generates electrons but degrades over time if it directly contacts the ionic solution. Hence, a transparent insulating material is coated on the semiconductor to prevent such degradation. Ordinarily, this layer needs to be thin enough that carriers can travel through it by tunneling to reach the ions and drive electrochemical reactions, but thick enough to protect against semiconductor degradation.

Given the conflicting requirements, one of these functions is sacrificed if the photoanodes are prepared in this configuration, which limits their usefulness. Instead, an alternate configuration has

been demonstrated, as shown in **Figure b**, which creates separate metallic paths for carrier conduction. In this configuration, the insulator layer can be made thicker without negatively affecting carrier conduction. This alternate configuration provides more flexibility and superior performance but is difficult to fabricate by traditional means given the intricate arrangement of insulator windows and conductor pathways on the semiconductor substrate. Both the configurations are metal–insulator–semiconductor (MIS) structures and the key to their usefulness is the specific arrangement of the three material phases.

Unlike more expensive fabrication processes that might involve lithographic patterning, this latest study explores a different scheme—see **Figure c**—combining thin-film and electrochemical reactions to fabricate the configuration in **Figure b**. Starting with a silicon substrate, an insulating SiO_2 layer is formed by thermal oxidation. Next aluminum is sputter-coated and the entire system is heated to a high enough temperature where aluminum reacts



Photoelectrodes are metal–insulator–semiconductor structures where each material phase serves a specific function. By modifying the arrangement of these phases, constraints of basic configuration (a) can be relaxed; (b) shows such an alternative configuration. Often it is difficult to fabricate more complex arrangements—(b) is more complex than (a)—but in this study, the researchers have demonstrated (c) a simple fabrication route by combining chemical and electrochemical reactions. Credit: Soonil Lee and Edward Yu.



with the SiO₂ layer and creates spikes (a thermally activated reaction that is well known in the semiconductor industry). By systematically varying the temperature and time, the aluminum spikes are controlled to reach the silicon surface. Subsequently, the aluminum is etched away to create the void structure within which nickel contacts are electrodeposited (nickel is an electrocatalyst for the oxygen evolution reaction, which is the intended function of this photoanode). The electrodeposition voltage and time are adjusted to grow nickel to fill the voids and create islands on the surface of the remaining SiO₂ layer as shown in **Figure c**. These processing conditions are carefully selected to make sure enough electron

conduction paths are available per unit area as well as the nickel islands allow enough of the open SiO₂ surface to be available for light to pass through and reach the silicon substrate. Each of these steps is cheaper and scalable compared to the existing fabrication route, for example, lithography.

According to Frank Osterloh from the University of California, Davis (not involved in this study), the new approach is complementary to previously reported fabrication routes that used atomic layer deposited (ALD) titanium dioxide as a protection layer. Potentially, this new approach may allow cost savings over slow ALD methods, and improved stability resulting from the thicker silicon dioxide passivation layer, especially if

the corrosive potassium hydroxide electrolyte can be replaced with a less basic alternative.

Yu alluded to the remaining challenges for this particular electrode and repurposing this technique for other photoelectrodes. The performance of this electrode for oxygen generation is limited by the use of nickel given its moderate catalytic activity, and the research group is on the lookout for a better candidate to replace nickel. Being able to identify a metal that is cheap, exhibits high catalytic activity, and is suitable for the electrodeposition step in **Figure c** is the key to leveraging the proposed fabrication route for other photoelectrodes.

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