Scalable Si-Based Metal-Insulator-Semiconductor Photoanodes for Water Oxidation Fabricated Using Nanosphere Lithography and Thin Film Reaction

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Photoelectrochemical (PEC) water splitting is a promising approach for converting solar energy into storable hydrogen, offering a sustainable alternative to fossil-based hydrogen production. PEC cells rely on semiconductor materials to absorb sunlight and generate mobile charge carriers that drive the hydrogen and oxygen evolution reactions. Si-based photoelectrodes are especially attractive due to their optimal bandgap, high charge mobility, long diffusion lengths, and cost-effective, scalable manufacturing process. To improve the stability of Si-based PEC cells, metal-insulator-semiconductor (MIS) structures have emerged as a promising approach [1]. MIS photoanodes integrate ultrathin insulating layers that protect the Si surface while maintaining charge transfer efficiency. The thickness of the insulator is critical: ultrathin layers facilitate effective charge tunneling, whereas thicker layers enhance long-term stability in corrosive environments.

In our previous work, we demonstrated that localized conduction paths formed via an Al/SiO_2 thin-film reaction enable low-resistance charge extraction through thick insulating layers, while also providing excellent stability and scalability to full-wafer photoanodes [2]. However, the performance of such photoelectrodes can be limited by nonuniformity in thin-film reaction behavior. We have now demonstrated a method for creating more controllable and uniform localized conduction paths on the photoanode by employing nanosphere lithography (NSL), a low-cost and highly scalable patterning technique. NSL is used to create a patterned mask for Al deposition that enables the density and locations of Al/SiO_2 thin-film reactions and consequently metal catalysts to be precisely controlled, leading to improvements in both photocurrent density and onset voltage. Moreover, a technique we have recently developed for extremely rapid large-area nanosphere monolayer formation [3] makes this patterning approach easily scalable to fabrication of full-wafer photoanodes and therefore, highly promising for large-scale PEC applications.

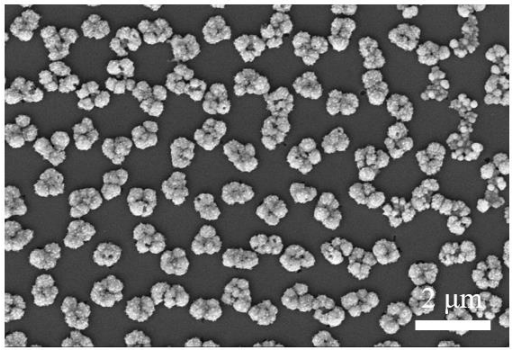

Fig 1. SEM image of patterned photoanode

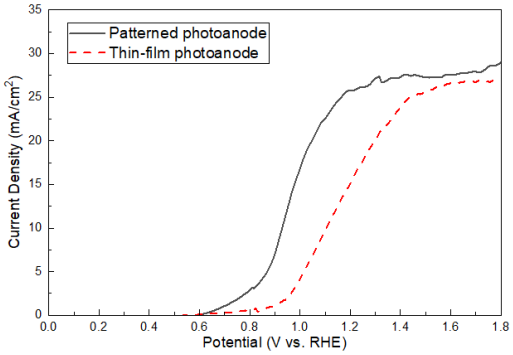

Fig 2. LSV curve for patterned and thin-film photoanode

[1] M. J. Kenney, M. Gong, Y. Li, J. Z. Wu, J. Feng, M. Lanza, H. Dai, Science, 342, 6160, 836-840, (2013)
[2] S. Lee, S. Wu, E. T. Yu, ACS Appl. Energy Mater. 2024, 7, 8, 3253–3262
[3] G. Cossio, R. Barbosa, B. Korgel, E. T. Yu, Adv. Mater. 2309775 (2023)

Supplementary Pages

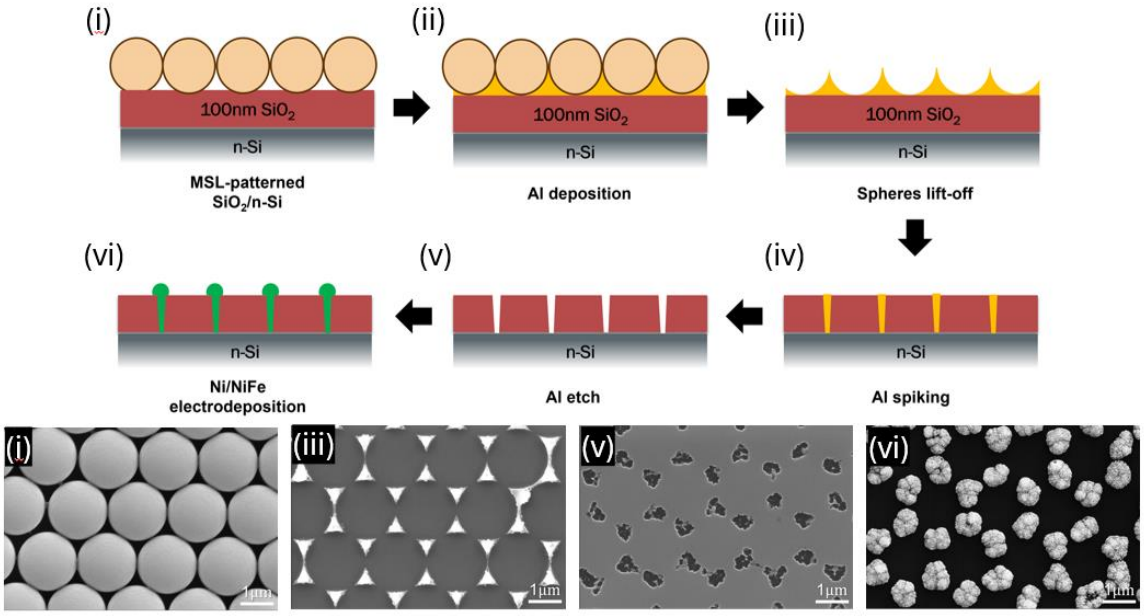

Figure 3. Process flow and SEM images of fabrication of patterned photoanode

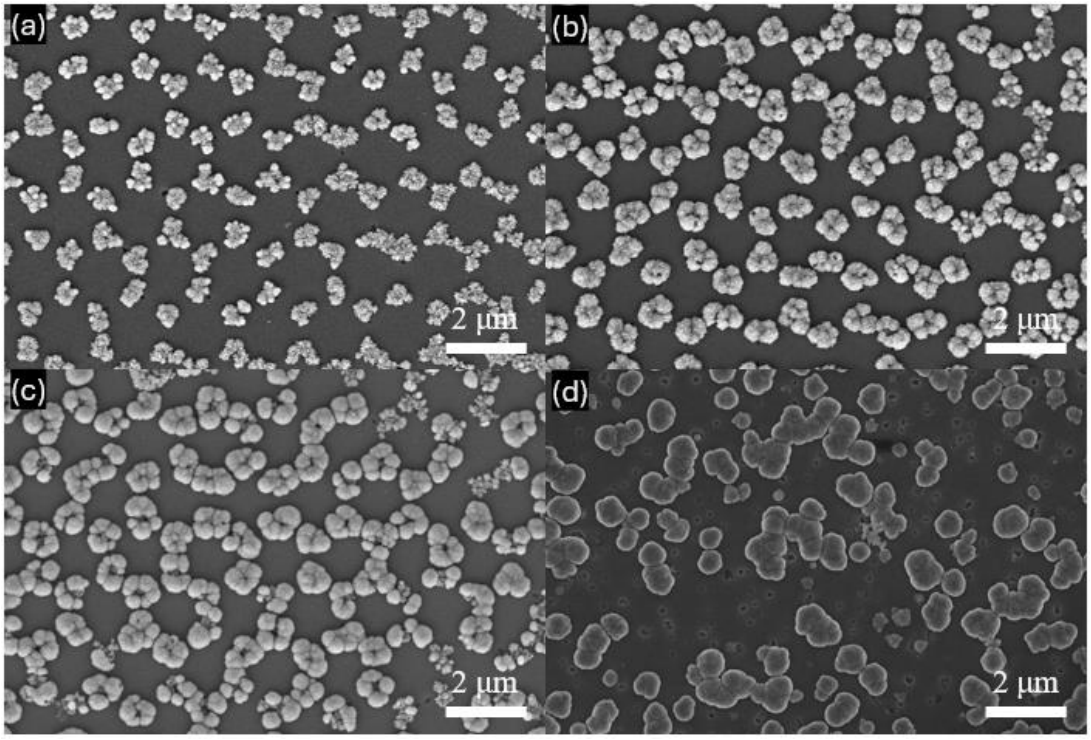

Figure 4. SEM images of patterned photoanode with different Ni electrodeposition time (at the same voltage of 3.5 V) (a) 10 minutes (b) 15 minutes (c) 20 minutes (d) Unpatterned photoanode (electrodeposition at 3.5 V for 15 minutes)