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## II.K.8 Electrochemical Construction of High Performance, Low Cost Polycrystalline Photoelectrodes for Solar Hydrogen Production

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property relationships. Therefore, in order to develop commercially viable PECs there is an urgent need to develop a practical synthetic method that possesses sophisticated interfacial engineering skills.

### Abstract, Progress Report and Future Directions

Our efforts resulted in various new synthetic methodologies that enabled us to tailor the interfacial structures of semiconducting films and crystals. We also observed many intriguing shape-dependent properties, which clearly demonstrate the importance of shape control for maximizing photoelectrochemical properties. Our main research focuses are briefly described below.

### Objectives

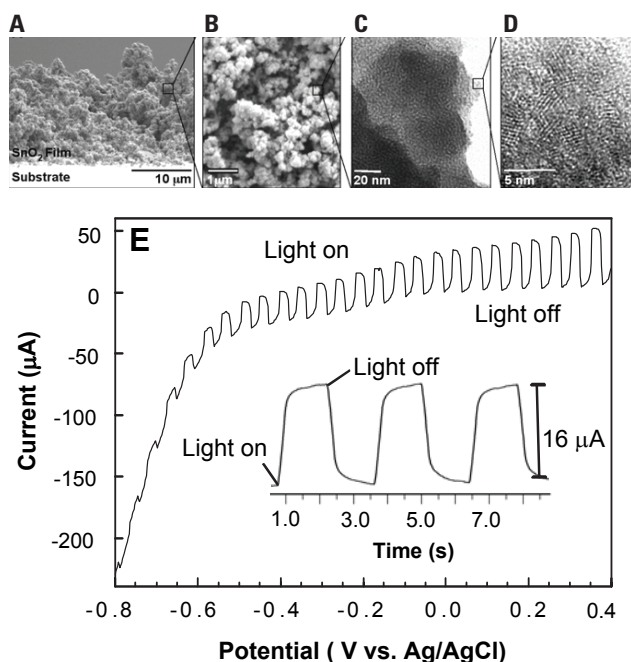
Considering the high manufacturing cost of single crystal-based devices, future commercially viable photoelectrochemical cells (PECs) will be built based on polycrystalline photoelectrodes. In order to satisfy various thermodynamic and kinetic requirements for efficient photoelectrolysis of water, combining multiple components in a precisely designed architecture is necessary. Achieving this goal requires a synthetic ability that can freely and methodically control polycrystalline architectures of photoelectrodes. The major goal of this research project is to gain such ability through compositionally versatile electrodeposition methods. This allows for assembling various multijunction, multicomponent photoelectrodes with optimum junction structures that can maximize desired photoelectrochemical properties and stabilities.

### Technical Barriers

When photoelectrochemical devices are built based on polycrystalline electrodes that are commercially more viable than single crystal electrodes, particle shapes, sizes, orientations, and interconnections can significantly affect the chemical and physical factors that define the energetics and kinetics of the electrodes. Therefore, precisely controlling micro- and nano-scale morphologies of photoelectrodes and understanding their effects on functional properties are critical for producing highly efficient and cost effective photoelectrode materials. However, synthetic methods previously used to produce polycrystalline photoelectrodes have limited control over the systematic manipulation of morphological features. This has restricted the construction of highly efficient photoelectrodes using the solid understanding of morphology-photoelectrochemical

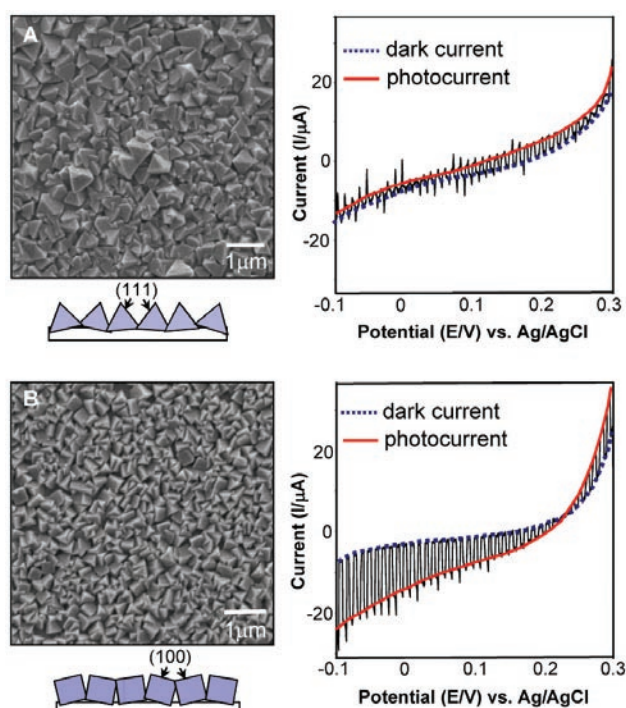
**Electrochemical Construction of Mesoporous Electrodes** Incorporating mesoporous structures into inorganic electrodes can generate an enhanced surface area per unit volume and significantly improve the kinetics and mass transport at the interfaces of electrodes. We have developed a new electrochemical method to produce various inorganic films containing uniformly organized mesoporous structures. Our method is based on creating interfacial amphiphilic layers on the working electrode by surface forces and using them as surface templates to electrodeposit inorganic mesoporous films. This method is quite different from and complementary to conventional sol-gel based dip-coating methods where amphiphilic assembly is evaporation-induced and the inorganic wall construction is achieved by the sol-gel process. As a result, this interfacial electrochemical surfactant templating method significantly enhances our ability to assemble various inorganic mesoporous electrodes (e.g. material type, mesostructure type, pore orientation against the substrate) that cannot be produced by previous means. The resulting mesoporous electrodes contain uniform pore sizes and pore connectivities, which allows us to investigate the effect of nanostructural details on photoelectrochemical properties (Figure 1).

**Regulation of Individual Particle Shapes in Polycrystalline Electrodes** The shapes of individual crystals that compose polycrystalline electrodes dictate interfacial atomic arrangements and can significantly affect interfacial organic-inorganic interactions (e.g. dye adsorption), interfacial charge transfer processes, catalytic properties and stabilities of electrodes. Therefore, gaining the ability to uniformly regulate the shape and connectivity of each crystal in polycrystalline electrodes is crucial for identifying optimum interfacial structures that can maximize desired



**FIGURE 1.** A-B) SEM images show the side and top view of mesoporous SnO<sub>2</sub> films; C) TEM shows worm-like mesopores; D) HR-TEM showing the nanocrystalline feature of the mesoporous wall; E) Potential-dependent photocurrent measurement. The inset shows a short-circuit photocurrent with a chopped irradiation.

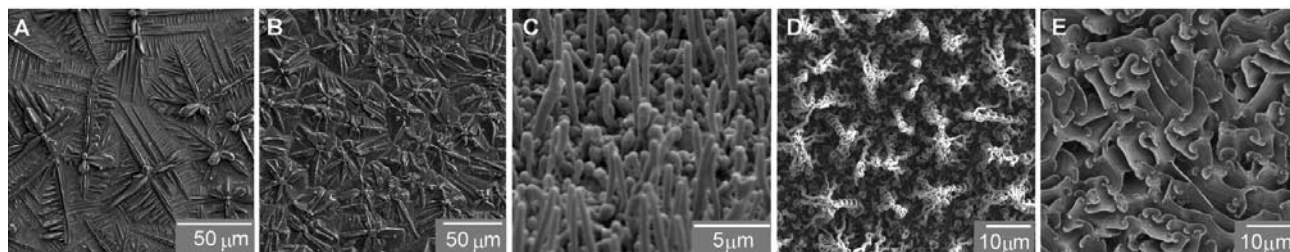
photoelectrochemical properties. Earlier efforts toward controlling crystal shape and branching have been limited to simply stabilizing a few certain shapes instead of providing a general methodology to systematically evolve shapes. Our research specifically focuses on establishing synthetic strategies/conditions that can methodically control habit formation and branching growth processes of inorganic crystals. Homogeneous habit control enables us to study any dependence of physical and chemical properties on different crystallographic planes (e.g. {100} vs. {111} planes) while controlled branching growth provides means to expose highly reactive surfaces at the interfaces (Figure 2). We also investigate formation of dendritic and fibrous architectures in inorganic electrodes. As crystals in dendrites and fibers form physically continuous



**FIGURE 2.** Polycrystalline Cu<sub>2</sub>O electrodes with only (A) (111) and (B) (100) planes exposed at the interfaces. Photoelectrochemical properties of these electrodes measured with chopped light are also shown.

networks by nature, regulating the details of dendritic growth (e.g. particle sizes, shapes, and degree of branching) allows us to achieve enhanced surface areas while decreasing the rate of charge recombination due to grain boundary problems (Figure 3).

**Tuning Band Gaps and Doping Types of Semiconducting Electrodes** In addition to gaining higher degrees of freedom in controlling morphological features, our research project simultaneously focuses on tuning doping types, compositions, and band positions of semiconducting electrodes. For example, we can now produce Cu<sub>2</sub>O as both p-type and n-type electrodes and increase its bandgap energy ( $E_g$ ) up to 2.6 eV. Bulk Cu<sub>2</sub>O ( $E_g = 1.9$  eV - 2.2 eV) cannot photoelectrolyze water to H<sub>2</sub> and O<sub>2</sub> without applying an external bias



**FIGURE 3.** A-B) SEM images of Dendritic Cu<sub>2</sub>O films with varying nucleation densities and degrees of branching. C-E) SEM images of Sn/SnO<sub>2</sub> electrodes with varying growth morphologies.

due to the proximity of its valence band to the oxidation potential of water, leaving little overpotential for the production of O<sub>2</sub>. However, the Cu<sub>2</sub>O electrode with E<sub>g</sub> = 2.6 eV can photoelectrolyze water without applying an external bias due to its lowered valence band position.

Based on our ability to tailor the morphology, composition, and band structure of individual inorganic components, we are now building a variety of multicomponent, multijunction photoelectrodes that can enhance photon absorption and interfacial charge transfer processes while diminishing charge recombination and photocorrosion. Considering that the overall efficiency of the multicomponent photoelectrodes depends not only on the material-types combined, but also on their junction areas/structures, our synthetic ability will create a multitude of opportunities to assemble and investigate multijunction photoelectrodes.

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