

# Nanostructured Photovoltaics Using Porous Alumina Templates as Structure-Directing Agents

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## Abstract

Nanostructured architectures for use in type II heterojunction photovoltaic devices are explored in this report. Porous aluminum oxide (PAO) templates were employed as structure-directing agents in the electrochemical synthesis of cadmium selenide (CdSe) nanorod arrays. Arrays fabricated using a cyclic voltammetry (CV) method were subjected to photoelectrochemical measurements to determine the effect of rod dimensions on device performance. Additionally, an alternating current (AC) electrolysis method for CdSe deposition was developed and optimized.

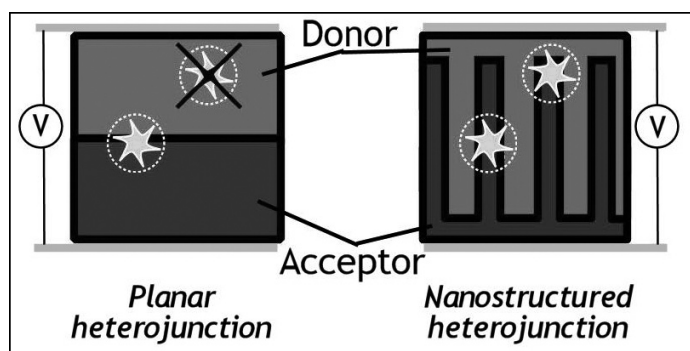


Figure 1: Solar cell schematic. Stars represent photoexcitation; X denotes exciton recombination.

## Introduction

Separation of electrostatically bound charge-carrier pairs in photovoltaics is crucial to proper device function. Following photoexcitation in a solar cell, an exciton (electron-hole pair) can only diffuse a finite distance before recombination occurs. Semiconductor nanorod arrays provide a highly ordered device architecture in which an exciton can reach the donor-acceptor heterojunction prior to recombination. This strategy (Figure 1) could produce highly efficient photovoltaics.

Free-standing semiconductor nanorod arrays can be fabricated using PAO templates [1]. CdSe, due to its high electron mobility and wide (1.77 eV) bandgap, was an attractive material for this study. It has been studied in photoelectrochemical cells, which provide a means to analyze photocurrent generation in nanorod arrays with varying dimensions [2,3]. The liquid electrolyte junction eliminates problems associated with poor interface morphology found in solid bulk heterojunctions. However, since photovoltaic device operation requires a transparent electrode,

usually indium tin oxide (ITO), we also sought a synthetic method that would create nanorod arrays with a surface onto which ITO could be affixed. The known CV method deposits nanorods onto a conductive substrate, but requires acidic solution which etches ITO [4]. This led us to AC electrolysis, which plates material directly onto a thin insulating layer of alumina in the pores of the template and provides a semiconductor film at the base of the rods [5].

## Experimental Procedure

**Photoelectrochemistry:** PAO templates were prepared according to literature methods and were anodized with either sulfuric acid (45 nm pore width) or oxalic acid (60 nm pore width) [1]. Nanorod arrays were fabricated using the PAO templates and a known CV method, and characterized using x-ray photoelectron spectroscopy (XPS) [4]. The arrays were annealed for 30 minutes at 400°C under argon to increase crystal grain size. The gold backing was then attached to copper wire and the assembly was coated in epoxy, leaving the wire tip and CdSe nanorods exposed. Etching in 5 M NaOH for 3 hours removed the alumina template. The photoelectrochemical cell used a 0.2 M solution of NaOH, Na<sub>2</sub>S and S as the electrolyte and a Pt mesh counterelectrode. All measurements were taken under argon.

**AC Electrolysis:** PAO templates were anodized in oxalic acid; some were also subjected to a 15 minute pore-widening soak in H<sub>3</sub>PO<sub>4</sub>. A solution of 0.01M CdCl<sub>2</sub> in DMSO was heated to 180°C under argon. Se was then added to saturation. The PAO template and a graphite rod were submerged in this solution and used as electrodes as an AC potential was applied. CdSe nanorod growth on the template was then characterized by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX).

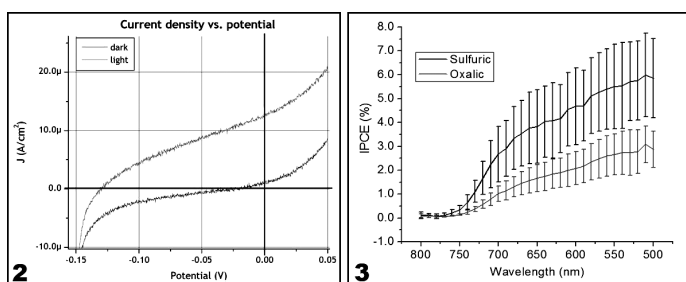


Figure 2, left: Representative  $J$ - $V$  curve for photoelectrochemical cells.

Figure 3, right: Efficiency of nanorods produced using sulfuric vs. oxalic acid anodization.

## Results

XPS measurements for the nanorods produced using the CV method revealed an average 45:55 Cd:Se stoichiometry. (Any deviation from 1:1 stoichiometry indicates point defects within the lattice, which may act as charge-carrier traps.) The nanorod arrays displayed some photoresponse in photoelectrochemical device assemblies (Figure 2), but the low short-circuit current density ( $12.5 \mu\text{A}/\text{cm}^2$ ) indicated that optimization is necessary. The open-circuit potential (vs. Pt counterelectrode) was measured at 0.13 V. Figure 3 illustrates the efficiency (expressed as incident photons converted to electrons, or IPCE) of the sulfuric and oxalic acid-anodized templates. Sulfuric acid-anodized PAO templates produced more efficient nanorods than did oxalic acid-anodized templates. The absorption onset near 700 nm corresponds to the CdSe bandgap. The electrolyte solution absorbed strongly below 500 nm, precluding any efficiency measurements in that range.

The AC electrolysis method for nanorod array fabrication was explored using PAO templates with 200 nm average pore depth. This length of nanorods, in addition to uniform, 100 to 200 nm CdSe films, is expected to allow effective photovoltaic device fabrication. The nanorods were deposited by applying 30 V AC to a PAO template for 30 minutes. Alternatively, a pore-widened PAO template produced nanorod arrays with the appro-

priate CdSe film thickness with application of 45 V AC for 15 minutes. EDX analysis indicated a Cd:Se stoichiometry of 61:39. Decreasing the concentration of the  $\text{CdCl}_2$  solution may bring the stoichiometry to the desired 1:1 ratio.

## Future Work

The device fabrication process for CdSe arrays in photoelectrochemical cells requires optimization. Additionally, efficiency measurements of flat thin films of CdSe would allow a comparison to be drawn between thin film and nanorod performance.

The arrays produced using AC electrolysis are attached to thin films of CdSe, which may provide a useful surface onto which an ITO electrode may be sputtered. Once ITO is applied, the PAO template can be etched away, and a donor material and back electrode can be added to the photovoltaic assembly. Fabrication of proof-of-concept devices is underway.

## Acknowledgments

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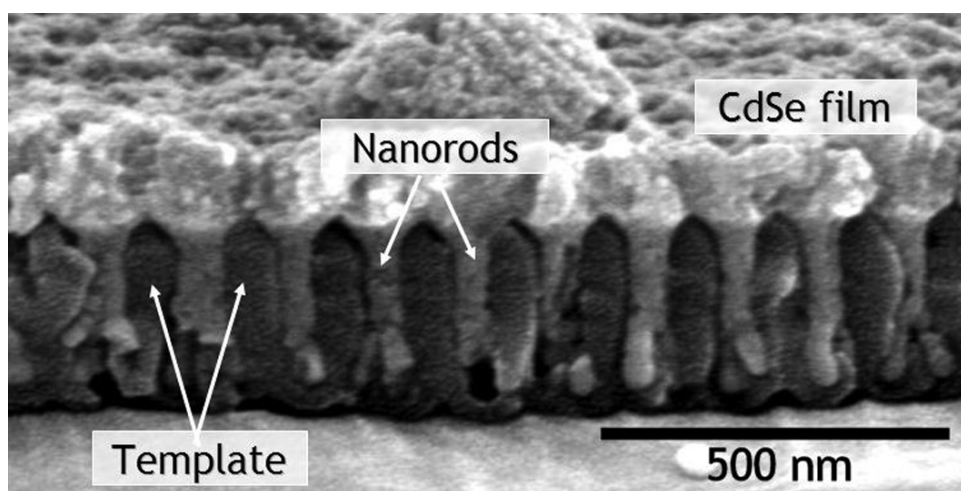


Figure 4: SEM micrograph of nanorod array produced using AC method.