

# Effect of Acid Etching upon ZnO Anodes in Dye Sensitized Solar Cells

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Solar cells must accomplish two basic tasks to generate current: absorb incident photons and conduct excited electrons to the circuit. Traditional solar cells made of silicon accomplish these with a single, expensive material. Dye sensitized solar cells (DSSC) are an alternative using separately optimized materials for each task. In short, a dye absorbs the photons and injects them into a semiconductor substrate which ferries the electrons into the circuit. An electrolyte containing a redox couple completes the circuit by reducing the oxidized dye. The best performing DSSCs contain a TiO<sub>2</sub> nanoparticle (NP) anode sensitized by a ruthenium dye commercially known as N719; these have reached 12% efficiency.

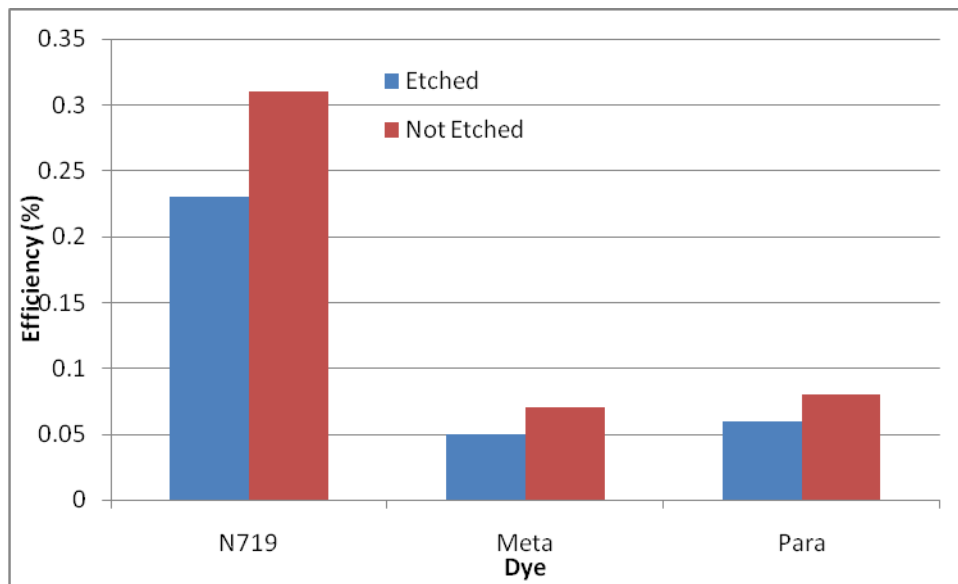
One route for improving efficiency is extending dye absorbance into the red or infrared. This would allow for the capture of the greater percentage of the energy of the solar spectrum. Porphyrins are a highly functionalizable class of molecules which show incredible absorption cross sections. Porphyrin dimers and trimers have red shifted absorption spectra. However, they exhibit poor surface coverage on nanoparticles due to their large size. Nanomorphologies such as tubes (NT), rods, or disks would be more suited for large porphyrins; however, there is little literature on the production of these morphologies with TiO<sub>2</sub>. One promising alternative material is ZnO due to its similar band edge energies and wide variety of obtainable nanostructures.

ZnO DSSCs have yet to perform as well as TiO<sub>2</sub> due in part to the inferior surface electronics of ZnO. The Van Ryswyk lab focuses on looking for methods of improving ZnO as well as understanding the chemistry of these improvements. The recent focus has been on acid treatment of cells.

It has been observed that acidic dyes perform better on ZnO NT. However, the mechanism was unclear. It was believed that the acid could etch the surface and reveal a certain crystal face which dye absorbed to better, that the protons could intercalate into the ZnO and help with charge balance during electron injection, or that the protons accumulate on the surface and so aid in the separation of charge.

Through previous work in this lab, it was found that the performance of some dyes could be improved by pre-etching the ZnO NT with acid. To test the hypotheses of proton buildup and intercalation, other cells were treated with a hindered base after acid etching to remove all excess protons. The same improvement was observed for these cells. Thus, it was shown that acidic dyes perform better because they etch the NT.

The work this summer focused on determining the effect of acid etching upon ZnO NP. Although this morphology is not ideal for porphyrin dimers and trimers, it is an easily producible system which could provide a cheap way of studying porphyrin dyes before moving to the more limited NT anodes. A similar acid etching effect was not observed for any of the four dyes studied. This begged the question of whether the acid etching effect was due to the NT morphology or the chemical process of creating the tubes (atomic layer deposition or ALD). This was elucidated by laying down a thin ZnO layer with ALD on TiO<sub>2</sub> NP. As seen in Figure 1, acid etching of these anodes showed no effect either. This suggests that it is the NT morphology and not the ALD chemistry which produces the acid etching effect.



**Figure 1 shows the efficiency of the cells constructed of TiO<sub>2</sub> NP with a ZnO layer prepared by ALD. The dyes used were N719 (a ruthenium dye), and two porphyrin dyes with meta and para carboxylic acid linking groups.**