**Titania Nanotube Supported Nanoscale Gold Photoanodes for Photoelectrochemical Hydrogen Production**

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**Introduction**

Photoelectrochemical cells (PEC) combine a photovoltaic device for light harvesting and an electrolyzer for water splitting into a single system. In its simplest form a PEC cell is composed of a photoanode for water oxidation and oxygen evolution, a cathode where hydrogen is evolved, and an electrolyte. A major obstacle for the widespread use of photoelectrochemical (PEC) cells is the poor photoanode performance. By some accounts, the rate of water oxidation has to be increased by more than an order of magnitude to keep pace with the production of electrons and holes [1]. In addition, recombination losses can limit performance. For example, when particulate catalysts are used in the photoanode only about 5% of the generated carriers are available for the reaction [2]. We explored two strategies for improving the photoanode performance: producing the photocatalyst in the form of nanotubes to improve collection efficiencies and depositing nanocrystalline gold onto the nanotubes to improve activity.

**Materials and Methods**

Highly ordered TiO$_2$ nanotube (TiNT) arrays were fabricated using an anodization process [3] (Figure 1.A). Gold nanoparticles were deposited onto the TiNTs using a deposition precipitation (DP) method [4]. The synthesis conditions (i.e pH, aging time, Au precursor concentration) were varied in an effort to manipulate the Au particle sizes and loading. Cyclic voltammetry was used to measure the total and Au electrochemical surface areas [5]. The performance of photoanodes was evaluated using a 3-electrode cell with a 1.0 M KOH electrolyte with a solar simulator (1.5 AM) and potentiostat. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and were used to characterize microstructural properties of the materials, and optical absorption measurements were used to determine their bandgaps.

**Results and Discussion**

 Longer nanotubes provided higher photocurrents compared to TiO$_2$ powders and short nanotubes. This was attributed to better separation of the charge carriers, as well as enhanced capture of the light. The deposition of Au nanoparticles resulted in a slight reduction of the bandgap of the TiO$_2$ (by ~0.15 eV); this has been attributed to the existence of impurity levels between the band edges of the oxide [6]. Incorporation of the gold nanoparticles also produced a significant improvement in the electrocatalytic properties. The photocurrent normalized by the Au electrochemical surface area increased significantly for particles smaller than ~5 nm (Figure 1. B). This behavior resembles trends for CO oxidation turnover frequencies [7]. Our observations suggest that either the active sites were not on the Au surfaces or the character of the active sites, including the turnover frequencies, varied with particle size. We note that there was no statistically significant correlation between the photocurrents and the perimeter length associated with the Au particles. We continue to characterize the Au/TiNT electrocatalysts using methods including in situ X-ray absorption spectroscopy in attempts to determine the location of the active sites.

**Significance**

Gold nanoparticles supported on TiNTs have been demonstrated to be effective photocatalysts for water oxidation to produce hydrogen. When combined with a high efficiency solar cell these materials hold promise for reaching the 10% energy efficiency target established by the Department of Energy. Nanostructured TiO$_2$ also finds applications in solar cells and batteries.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Scanning electron micrographs of TiO$_2$ nanotubes with a top view (inset) (A), and photoanode current densities (at 0.5 V) normalized by Au electrochemical surface area as a function of Au average particle sizes with TEM inset (B).

**References**