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## **TiO<sub>2</sub> NANOTUBE ARRAYS DECORATED WITH Ir NANOPARTICLES FOR ENHANCED HYDROGEN EVOLUTION ELECTROCATALYSIS**

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Designing cost-effective hydrogen evolution reaction (HER) electrocatalysts containing highly active, but expensive platinum group metals (PGMs) is key to the commercialization of polymer electrolyte membrane water electrolysis systems for green hydrogen production. Our recent investigations have shown that efficient and durable HER composite cathodes can be prepared by spontaneous deposition of PGM nanoparticles on self-aligned titania nanotube (TNT) arrays formed by anodization [1]. In this synthesis route, anatase TNTs are first cathodically protonated (H-TNT), and then used as the reducing agent for PGM ions at room temperature. Herein, we employ the galvanic displacement strategy to decorate H-TNT arrays

with ultrafine Ir nanoparticles [2]. We demonstrate that transforming the top surface morphology of supporting TNT arrays from ordered open-top tubes to bundled nanowires (“nanograss”) is beneficial for exposing more Ir active centers during the HER operation. Consequently, applying very low concentrations of Ir(III) ions in the galvanic displacement step is sufficient to produce exceptionally active nanograss-modified Ir@TNT composites. An optimum Ir@TNT, possessing a low Ir loading of  $5.7 \mu\text{g}_{\text{Ir}} \text{ cm}^{-2}$ , requires overpotential of only  $-63 \text{ mV}$  to reach a current density of  $-100 \text{ mA cm}^{-2}$  and shows a stable long-term performance in a 1 M HClO<sub>4</sub> solution. Computational simulations suggest that the hydrogen-rich TiO<sub>2</sub> support not only strongly interacts with anchored Ir particles and weakens their H binding strength to a moderate level, but also actively provides hydrogen for rejuvenation of the Ir active sites at the Ir|H-TiO<sub>2</sub> interface, thereby significantly enhancing HER catalysis.

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## SYNTHESIS OF BISMUTH VANADATE PHOTOCATALYST WITH ENHANCED ADSORPTION PROPERTIES

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Efficiency of a semiconductor catalyst is directly correlated to its surface to which a reactant species is adsorbed. There are several ways to optimize the active surface, such as synthesis, processing or any aftertreatment of a photocatalytic material. Our research was focused on modifying the existing sonochemically assisted synthesis of bismuth vanadate.

Two optimization methods were used in order to increase specific surface of the photocatalyst and number of its active sites. The first method was to change concentration of reactants used in the synthesis to reduce agglomeration of bismuth vanadate. Sonochemically assisted synthesis was performed with three different concentrations of reactants to observe agglomeration tendency of the catalyst. The other method included the use of sodium dodecyl sulfate (SDS) as a surfactant in synthesis at highest concentration in order to hinder the particle growth.