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Synthesis and Characterization of Highly-Ordered Doped Titania Nanotubes for Solar Hydrogen Generation

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Since the discovery of the photoinduced decomposition of water on metal oxides by Fujishima and Honda [1] considerable attention has been paid to the generation of hydrogen using semiconductor materials utilizing sunlight. Titanium dioxide has proven to be one of the best candidates because of its relative high efficiency, stability, biological and environmental compatibility, and low cost. Pure titania, however, is insufficient for hydrogen production under visible light, due to its wide band gap, which is around 3.2 eV. This demands an excitation wavelength of 387 nm or less, requiring ultraviolet (UV) light as excitation source. This significantly limits the utilization of such material for hydrogen production via photolysis; as a result, extensive efforts have been expended to enhance the photoactivity of titania by shifting its band gap from UV to visible region of the light spectrum through the inclusion of a number of materials, including metal ions (iron [2] and platinum [3]), non-metals (carbon, nitrogen [4] and sulfur) and metal oxides such as copper oxide [5].

Highly ordered titania nanotubes (TNTs) were fabricated using an aqueous solution of ammonium fluoride and ethylene glycol, employing a simple electrochemical anodization technique. Anodization was carried out in a conventional two-electrode cell with titanium foil and graphite as working and counter electrodes, respectively. The influence of different parameters, including applied voltage, electrolyte concentration, anodization time, electrolyte temperature, and annealing temperature and time on electrical, morphological and photo-electrochemical properties of the prepared TNTs were investigated. A series of samples were also doped with nickel (Figure 1) using a pulse current technique with two different waveforms—rectangular and ramp-down—a duty cycle of 5% and current densities ranging from 200 to 1100 mA cm^{-2}. All sample were characterized by scanning electron microscopy, X-ray powder diffractometry, and UV-Vis spectroscopy (Figure 2). Structural investigation of the prepared samples confirmed the presence of anatase nanocrystalline TNTs after annealing in air and vacuum at 500 °C for several hours. The presence of nickel nanoparticles 5-20 nm in diameter was also confirmed. The efficiency of the photoanodes was found to increase as the amount of dopant increased to 3.0%. Further increase in dopant, however, resulted in a decrease in efficiency, possibly due to a higher rate of electron-hole recombination.

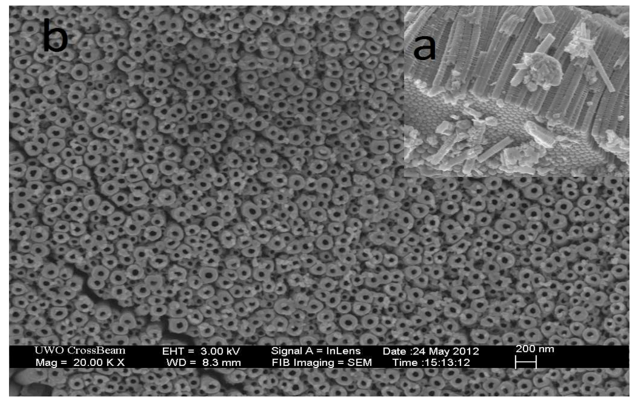

Figure 1 – Nickel-doped titania (a) bottom and (b) top views

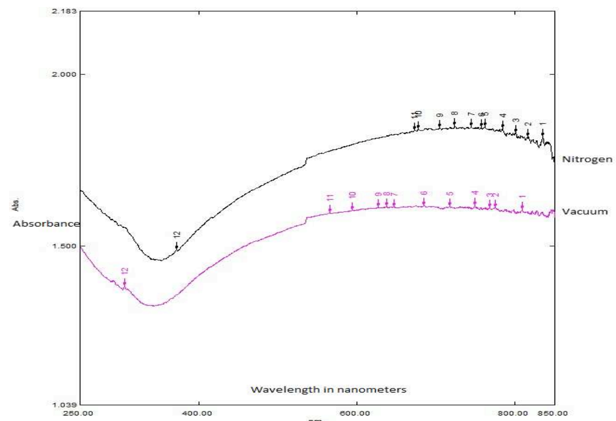

Figure 2 – Absorption spectra of pure and nickel-doped titania

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