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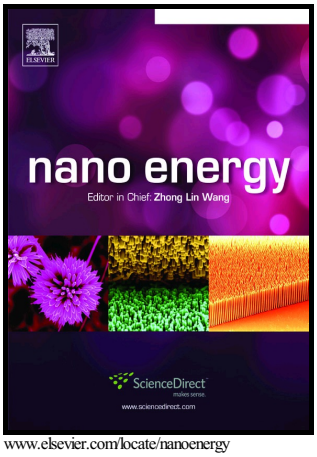

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Solar water splitting on porous-alumina-assisted TiO_2-doped WO_x nanorod photoanodes: paradoxes and challenges

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Abstract

Arrays of self-organized WO_3-based semiconductor nanorods are prepared from a thin W layer, W/Ti bilayer (tungsten-on-titanium), and W-10at.%Ti alloy layer via the porous-anodic-alumina (PAA)-assisted anodization at various conditions to address the radius/length ratio of ~13/130 and ~70/700 nm (respectively 'small' and 'big' nanorods). Doping the WO_3 nanorods with TiO_2 was achieved, for the first time, simply by anodizing the W/Ti and W-10at.%Ti layers through the alumina nanopores. The post-anodizing treatments combined PAA dissolution with annealing in air and vacuum at 500–550 °C to alter the film composition, crystal structure, and electrical properties. The air-annealed big nanorods comprising monoclinic and triclinic WO_3 crystal phases reveal their superior performance in photoelectrochemical (PEC) water splitting, showing a low onset potential (0.5 V_{RHE}) and a competitive value of photocurrent (15.5 $mA \cdot cm^{-2}$) in 0.1 $mol \cdot dm^{-3}$ Na_2SO_4 solution (pH 5.0) under chopped illumination at a single wavelength of 405 nm, 1 $W \cdot cm^{-2}$, with no sign of photocorrosion. Paradoxically, the presence of monoclinic $WO_{2.9}$ phase in the vacuum-annealed nanorods worsens the PEC behavior and stimulates the peroxo-assisted dissolution. Unexpectedly, electrochemically doping both the WO_3 and $WO_{2.9}$ big nanorods with TiO_2 causes the photocurrent to decrease dramatically. An advanced approach developed for modeling charge transport processes in the PAA-assisted WO_x nanorods predicts a 7-fold further rise in the solar current should the big nanorods grow longer (1.5 μm) and wider (300 nm) to absorb a bigger portion of light and support a thicker depletion layer, without, however, getting fully depleted, which is the case of the small nanorods.

Keywords: anodizing, porous anodic alumina, tungsten oxide, titanium oxide, nanorods, photoelectrochemical water splitting