Ti-Nb Oxide Nanotube Arrays with Cathodic Engineering for Photoelectrochemical Water Treatment and Molecular Hydrogen Production

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Significance and Relevance

This study comprehensively investigated the cathodization engineering on the TiO_2 nanotube array (TNA), Nb_2O_5 nanotube array (NNA), and Nb-doped TNA (Nb-TNA) for photoelectrochemical (PEC) water treatment with simultaneous energy storage into H_2. The (self-)doping mechanism depending on the cathodization conditions was tackled with thorough material characterizations. The blue-TNA, black-NNA, and Nb-TNA marked advantages under UV-, visible light-, and solar-irradiation, respectively. The results of this work would broaden the practical applicability of Ti/Nb based PEC catalysts for environmental and energy storage purposes.

Preferred and 2nd choice for the topic: Water treatment / Photocatalysis and photoelectrocatalytic approaches, solar energy utilization
Preferred presentation: Oral only

Introduction and Motivations

Amid the growing attention to the water pollution caused by recalcitrant organic micropollutants and concomitant demands on (industrial) wastewater reuse, photoelectrochemical (PEC) water treatment has been noticed as a feasible advanced oxidation process with minimal usage of chemicals with H_2 generation. Cathodization of TiO_2 nanotube array (TNA) in ambient conditions has been widely deployed to enhance the PEC) activities. Self-dopants (Ti^{3+}, intercalated H, and oxygen vacancy) or heteroatom dopants could tune the band structure, light absorbance, electrical conductivity, capacitance, and charge transfer characteristics among others. This study systematically evaluated the effects of variable cathodization conditions, including current density/duration, pH/buffering intensity of electrolyte, and sequence of annealing. This study stepped further for engineering of Nb_2O_5 nanotube array (NNA) and Nb-doped TNA (Nb-TNA) via analogous cathodization doping. The PEC activity for aqueous pollutants degradation and photocurrent generation (for H_2 generation on cathode) were comparatively evaluated. The doping mechanism was disentangled by thorough characterization based on X-ray diffraction, X-ray photoelectron/absorption spectroscopy, electron spin resonance (ESR) spectroscopy, and secondary ion mass spectroscopy.

Results and Discussion

The self-doping of anatase TNA brought about blue colored TNA, whereas the same sequence for amorphous TNA gave degenerately doped black TNA. The self-dopants were exclusively located on surface for blue TNA to improve the PEC activity for water oxidation, whereas they penetrated into bulk structure for black TNA with quasi-permanent lattice distortion to lose the PEC activity. The passed charge was more effective than the current density, whose level could be optimized by an in-situ monitoring of photocurrent. The pH and buffering intensity of electrolyte switched the levels of self-dopants on surface, owing to the doping mechanism of reductive Ti dissolution and proton intercalation. The maximal photocurrent and incident photon to current efficiency were noted in a phosphate buffer with circum-neutral pH. The cathodically modified NNA into a Black-NNA also revealed ample oxygen vacancies to elevate donor density and electrical conductivity. The band-edge shift and narrowed band gap (3.0 eV to 2.6 eV) brought about a visible light response activity of the Black-NNA. A current switching mode could overcome the chemical instability of the self-dopants under the anodic environment to elongate the lifetime. Thus, under a visible light irradiation, total amount of model aqueous pollutants degradation (under the current switching) on Black-NNTs was

39% higher than Blue-TNA. Moreover, cathodization of TNA in the presence of Nb cations effectively allowed atomic dispersion of hetero-atoms via substitutional doping. The Nb-TNA marked the supreme solar PEC activity (photocurrent), hydroxyl radical generation (as confirmed by scavenging tests, ESR, and model aqueous pollutants degradation) among the catalysts under interrogation.

Consequently, relatively simple electrochemically self-doping was confirmed to be a viable way for the engineering of TNA, NNA, and hybrids to be utilized for PEC water treatment. The hydroxyl (OH) radical by water oxidation on the PEC catalysts could be utilized for degradation of non-biodegradable organic compound (poly-acrylic acid, aromatic micropollutants among others) for water reuse. In addition, the OH radical driven chlorine evolution reaction can mediate breakpoint chlorination of aqueous ammonia as a pollutant. Simultaneous conversion of solar energy into molecular hydrogen can be a sustainable approach towards water-energy nexus. The results of this study would broaden the usage of TiO_x and NbO_x nanomaterials by engineering the physico-chemical properties depending on variable energy input and application scenarios.

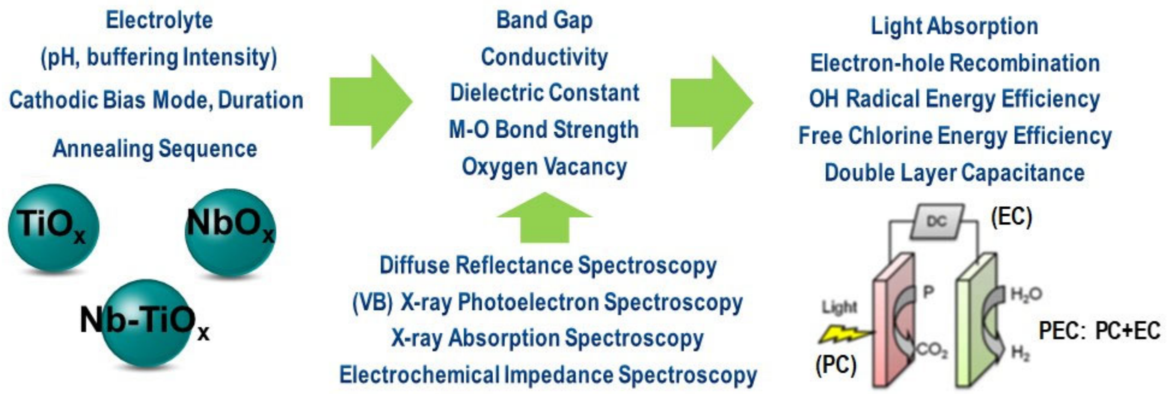

Figure 1. Outline of the research scope