$NiTiO_3/TiO_2$ hybrid crystal for efficient overall water splitting

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The development of renewable energy is the crucial key to satisfying energy demand and decreasing CO_2 emissions. Due to its large energy density, sustainability, and environmental compatibility, hydrogen is considered a major next-generation energy source. In this aspect, electrochemical catalytic water splitting has gained attention because it is one of the most efficient ways to produce hydrogen. It consists of two half reactions at the cathode and anode: reductive hydrogen evolution (HER) and oxidative oxygen evolution (OER). However, to date, noble- metal based catalysts including Pt, Ru, Ir etc. with the greatest intrinsic activities are the benchmark catalysts for water splitting, but their real applications are significantly limited due to scarcity and high cost. At the same time, a truly efficient bifunctional catalyst that is comparable to the theoretical cell-voltage value of 1.23 V has still not been achieved due to the multistep proton-coupled electron-transfer processes as well as the sluggish OER kinetics. Thus it is essential to develop highly efficient electrocatalysts to reduce the overpotentials and boost the energy conversion efficiency.

Herein, an efficient electrocatalyst with bifunctional ability as well as effective photocatalytic properties was developed through a controlled crystal growth methods. $NiTiO_3/TiO_2$ hybrid composite crystal was synthesized by micro-pulling down method with an over eutectic point. As grown $NiTiO_3/TiO_2$ was annealed in H_2 atmosphere to introduce porosity at the crystal surface. Due to the presence of abundant interfaces and defects, $NiTiO_3/TiO_2$ exhibited efficient HER and OER property with low overpotential and fast reaction kinetics. The charge transfer resistance decreased significantly after annealing. At the same time, It was found the availability of electrochemically active voltametric site increased and formation of double layer at the electrode electrolyte interface was promoted after annealing. In addition, pseudocapacitive storage of electrolyte ions at the electrode surface also increased significantly after annealing. Annealing also created oxygen vacancy, which in turn reduced the overpotential and increased reaction kinetics. As a result, the annealed $NiTiO_3/TiO_2$ exhibited highly efficient overall water splitting with a very small overpotential of 80 mV (at 10 mA/cm^2 current density), and 120 mV (corresponding to 50 mA/cm^2 current density) for the HER and OER, respectively. $NiTiO_3/TiO_2$ also remain stable over thousand cycles. Thus, our work demonstrates a facile crystal growth strategy for the design of highly efficient, stable, and bifunctional catalysts for water splitting.