Doped and defective three phase Tio_2 Hetrojunctions for enhanced H2 generation by solar water splitting

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Hydrogen as a fuel from renewable energy resources has drawn immense attention recently. Among the various methods of H_2 production, sun light assisted water splitting using TiO2 catalyst is of high interest. The two major intrinsic issues with TiO_2 are high electron-hole pair recombination and absence of visible light absorption. An effective strategy to inhibit the charge recombination is generation of hetero-junctions formed by various TiO_2 phases. Among the various modifications adopted for making TiO_2 visible light active, nitrogen doping and native defect creation are the widely recognized ones. Hence smooth charge transfer pathways for effective charge separation wi th tuned band gap for visible light absorption, can be achieved by having large number of three phase heterojunctions modified with nitrogen doping and or native defects. The main drawback with doping is that the dopants have the high probability to act as recombination centres. Hence modification of titania to make it visible light active without external doping is appreciated. In this regard, band gap tuning of triphase TiO_2 with native defects is of interest. Although there are reports on H_2 generation using biphase TiO_2 , studies on facile methods for the synthesis of tunable TiO_2 hetrojunctions of pristine, nitrogen doped and native defects are still under progress. Herein, we report a novel synthesis method to prepare pristine, N-doped and oxygen deficient TiO_2 nanotubes having anatase -rutile, rutile-brookite, anatase-brookite and anatase -rutile-brookite heterojunctions by simple tuning of applied voltage in a novel electrochemical anodization technique, as well as their application in H_2 generation by water photolysis. The synthesized triphase TiO_2 nanotubes are found to be 1.6 times efficient than that of biphase nanotubes and 2.5 times that of single phase nanotubes. Similarly, the nitrogen doped anatase-rutile-brookite heterojunctions shows 7.5 times hydrogen generation efficiency than that of triphase TiO_2 nanotubes. The water splitting efficiency of triphase heterojunctions with native defects is found to be 16 times that of pristine triphase TiO_2 hetrojunctions. In addition, the charge transfer characteristics to determine the underlying physics behind the high efficiency of such systems will be presented. A band diagram is proposed for pristine and modified triphase hetrojunctions with the possible electron transfer pathway using synchrotron valence band edge analysis. It is found that the photoexcited charge transfer takes place from rutile to anatase to brookite in triphase TiO_2 nanotubes.

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