Low-temperature Crystallization of Anodized TiO$_2$ Nanotubes at Solid/Gas Interface and their Photoelectrochemical Properties

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TiO$_2$ nanotubular arrays formed by electrochemical anodization have attracted significant attention for photoelectrochemical applications that utilize solar energy. However, the as-anodized TiO$_2$ nanotubes are amorphous, and need to be crystallized by high-temperature thermal annealing. Herein, we describe a low-temperature hydrothermal solid–gas route to crystallize TiO$_2$ nanotubes. In this process, the as-anodized TiO$_2$ hydroxoh nanotubes are dehydrated to yield anatase phase via solid–gas interface reaction in an autoclave at a temperature of less than 180 °C. The solid–gas interface reaction alleviates the collapse of as-anodized TiO$_2$ nanotubes during hydrothermal process efficiently. Compared with the common thermal annealing at the same temperature but at atmospheric pressure, the hydrothermal route improves the photocurrent density of TiO$_2$ nanotubes by ~10 times in KOH electrolyte. The duration of the hydrothermal reaction has a substantial effect on the photoelectrochemical properties of TiO$_2$ nanotubes, which is ascribed to the synergetic effect between the crystallization and structural evolution. Electron donors can further suppress the charge recombination in the low-temperature crystallized TiO$_2$ nanotubes and boost the photocurrent density by ~120%.

![Graph showing photocurrent density vs. potential](image-url)