Nanostructured TiO$_2$ Microrods with 3D Nanovoids for Green Photocatalysis - PEC Water Splitting

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Titanium dioxide (TiO$_2$) has been studied for several decades due to its versatility for a diverse range of applications. TiO$_2$ is robust, thermally stable, non-toxic, as well as inexpensive. One-dimensional (1D) TiO$_2$ nanostructures have attracted attention because of their unique optical and electronic properties. The first study of photoelectrochemical (PEC) water splitting on TiO$_2$ was reported in 1972 by Fujishima and Honda [1] showed that TiO$_2$ photoanode exhibits outstanding PEC properties, which may be utilized for the conversion of solar energy into chemical energy. It was known that TiO$_2$ could not be used in the visible light region and could only split water under UV light irradiation. The large band gap (3.0 – 3.2 eV) is the reason why TiO$_2$ is transparent across the entire visible spectral range. The efficient photocatalysts which could produce electron–hole pairs under VIS light irradiation should be developed because VIS light occupied 43% of sunlight.

Novel nanostructures with dense-stacked nanocavities inside 1DTiO$_2$ have been prepared, which present excellent photocatalytic and PEC properties. Recently was observed [2] that the photocatalytic activity of 1D-bicrystalline nanoribbons with alternate structure of TiO$_2$(B) and anatase under visible light irradiation was due to the formation of nanocavities inside the TiO$_2$ nanocrystals. The research revealed that TiO$_2$(B) with nanocavities exhibited a narrow band gap and improved its absorbance coefficient in the UV region. An enhanced optical absorption induced by dense nanovoids inside titania nanorods was also reported by Han et al. [3]. The molar absorption coefficient of TiO$_2$ nanorods with nanovoids was found to be about 25% higher than that of TiO$_2$ without nanovoids.

Our group has recently reported an environmental friendly, smart and unexpensive preparation method for the synthesis of 1DTiO$_2$ microrods (MRs) in aqueous media starting with hydrated titanyl sulfate crystals (TiOSO$_4$.2H$_2$O). The method is based on the extraction of sulfate ions from the TiOSO$_4$ crystals and their replacement with hydroxyl groups in aqueous ammonia solution leaving the Ti–O framework intact [4] (Fig. 1a-d). Heat treatment process (from 500 to 950 °C) causes the evaporation of nanoconfined water which hollowing out empty spaces inside the 1DTiO$_2$ MRs. The self-assembled nanovoids along certain crystallographic directions of anatase NCs were confirmed by STEM and EELS study (Fig. 1e-g). The nanovoids with size ranging from 5 to 78 nm in both, length and width, and depth of about 9 nm (Fig. 1e) are responsible for the possibilities of applying 1DTiO$_2$ in the photoelectrochemistry as a stable working electrodes. We are concerned with the nanovoid phenomenon as governed by the evaporation of ice (water) and found that the as-created dense 3D nanovoids...
enhanced significantly the electrochemical properties of TiO\textsubscript{2}, thereby providing a new approach to increase the reactivity of 1D TiO\textsubscript{2} MRs for use in the PEC cell for water splitting (Fig. 1h). The incorporation of Ag, Au or Cu nanoscale particles could make a promising future for 1D TiO\textsubscript{2} MRs to be applied in the PEC systems.

References:

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![Figure 1](image-url). HRTEM observation of 1D TiO\textsubscript{2} MRs (a) BF image (b) Z-contrast image of nanovoids by HAADF (c-d) anatase crystals along the [111] direction (e) Z-contrast image of single nanovoid with the position of the EELS spectra indicating the depth of the nanocavity 9 nm (f) HRTEM observation of single nanovoid (g) EELS analysis confirming TiO\textsubscript{2} (h) voltammetry in dark and under light irradiation.