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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 ($TiOSO_4.2H_2O$). 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_2, thereby providing a new approach to increase the reactivity of $1DTiO_2$ 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 $1DTiO_2$ MRs to be applied in the PEC systems.

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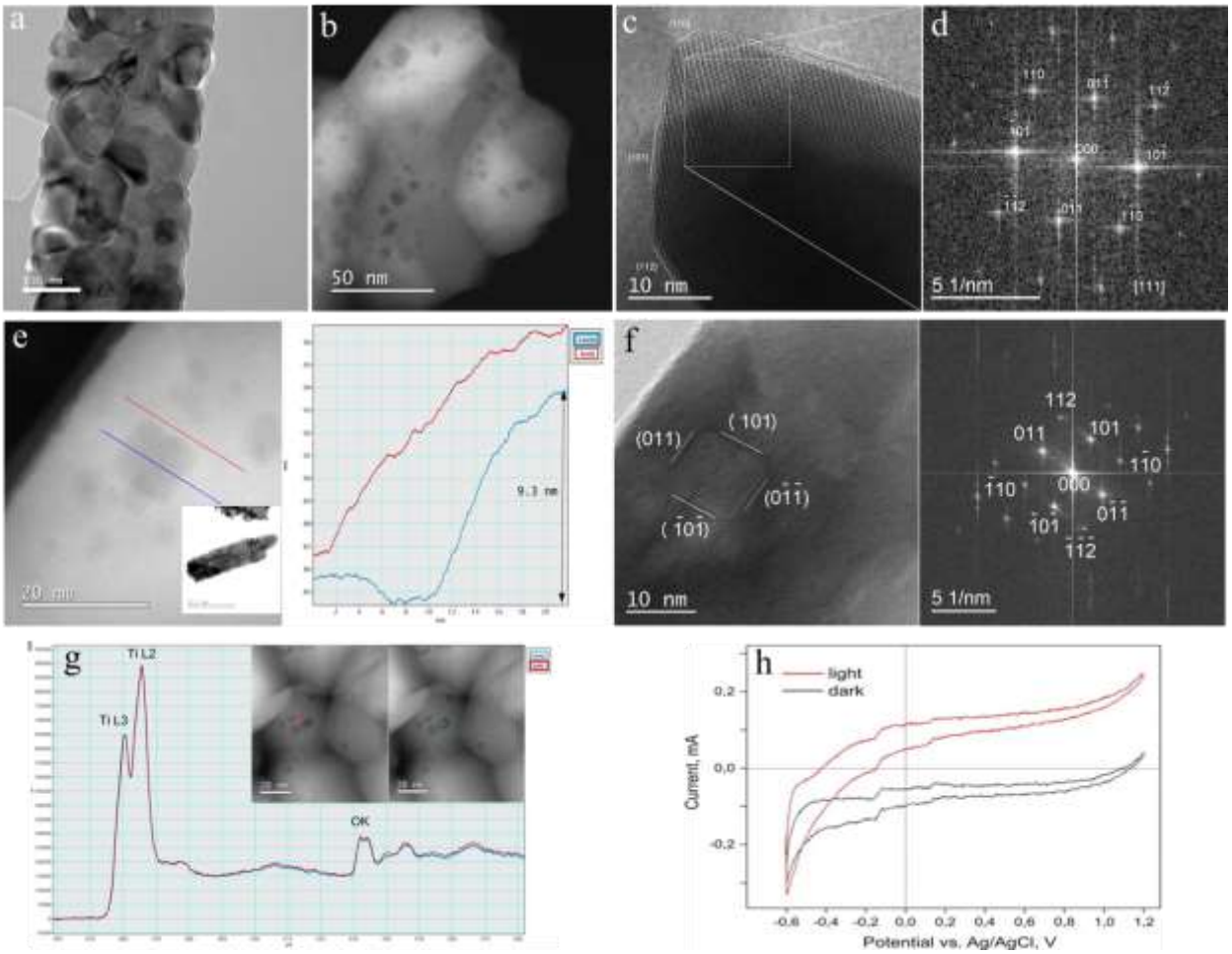

Figure 1. HRTEM observation of $1DTiO_2$ MRs (a) BF image (b) Z-contrast image of nanovoids by HAADF (c-d) anatase crystals along the [111] direction (e) Z-contrast image of single nanovoid with the position of the EELS spectra indicating the depth of the nanocavity 9 nm (f) HRTEM observation of single nanovoid (g) EELS analysis confirming TiO_2 (h) voltammetry in dark and under light irradiation.

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