

Investigation on photocorrosion of TiO₂ during photoelectrochemistry process by electron microscopy together with operando ICP-MS

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Background incl. aims

With the growing environmental deterioration and ever-increasing energy demand, exploring a renewable and clean energy for human development has been regarded as a promising research subject. Hydrogen is one of the most desirable energy carriers. Fujishima and Honda discovered that hydrogen can be generated from water splitting on a TiO₂ photoelectrode under UV light illumination.[1] TiO₂ is considered to be stable since its redox potential has been calculated to be more positive/negative relative to the water oxidation/reduction potential. This means that photogenerated charge carriers would participate in driving the desired water splitting reactions rather than oxidizing or reducing semiconductor photoelectrodes.[2] Nevertheless, it is reported that there is degradation of performance and alterations in surface morphology of TiO₂ under UV light irradiation. Understanding the dynamic catalyst behaviour during electrochemical application plays a key role in developing improved catalysts.

Methods

We applied scanning electron microscopy (SEM), aberration-corrected transmission electron microscopy (TEM), X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy together with operando inductively coupled plasma mass spectrometry (ICP-MS) coupled with illuminated scanning flow cell to investigate photoelectrochemical (PEC) corrosion pathways of TiO₂ semiconductor photoelectrodes. TiO₂ nanotube array was utilized as our model system to conduct the quantitative study in understanding the effect of the PEC conditions on its photostability. PEC measurements were performed on a Reference600 potentiostat (Gamry) with a three-electrode PEC cell in 0.1 M of HClO₄ solution as the electrolyte. The electrolyte was pumped through the PEC cell into ICP-MS for time-resolved analysis of the amount of dissolved titanium ions.

Results

The XRD pattern indicates that all peaks agree well with the tetragonal rutile phase (SG, P4₂/mnm; JCPDS No. 21-1276) which is further confirmed by Raman spectrum. X-ray photoelectron spectroscopy (XPS) analysis was performed to study the chemical components and the states of Ti and O in the TiO₂ nanocomposites. The XPS spectra reveal that the dominant elements are Ti, O of the TiO₂ composites. The peaks located at about 458 and 464 eV are corresponding to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. SEM (Figure a, b) show that the prepared TiO₂ exhibits nanotube morphology with a thickness of 2.1 μm and an average diameter of 150 ± 20 nm. TiO₂ nanotube grows along with the direction [001] as demonstrated from TEM images (Figure c,d) and high-resolution TEM (HRTEM) image confirms that the surface is (110) facet. From operando ICP-MS setup (Figure f), we can measure the dissolution of TiO₂ during PEC process. Through this method, the operation parameters of PEC on photoelectrodes can be controlled to elucidate sufficiently by quantifying dissolved metal ions of photoelectrode surface in the electrolyte during the whole PEC process in real time.

Conclusions

In summary, our work demonstrates that electron microscopy characterization together with operando ICP-MS plays an important role in investigating the intrinsic mechanism of the improved PEC performance and photostability of TiO₂. The technique will be strongly needed in our future research and offers significant guidance in (photo)electrochemistry field.

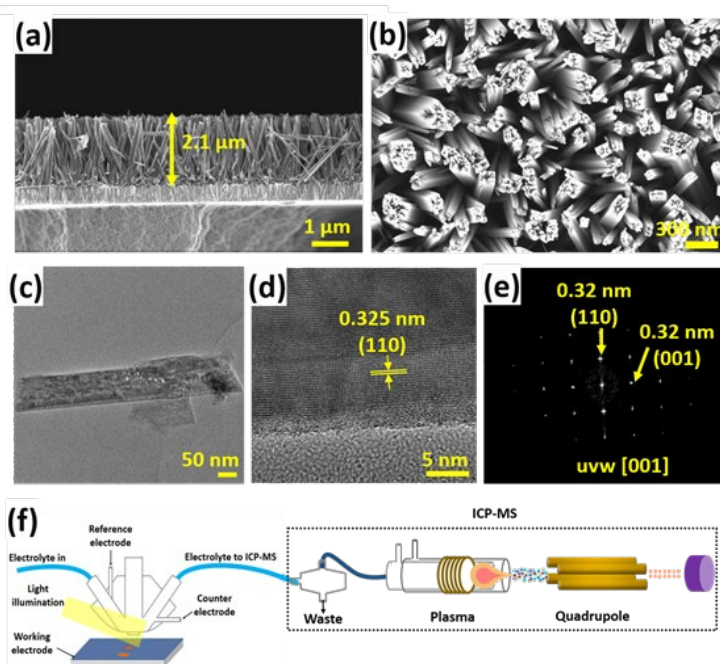
Keywords

TiO₂, electron microscopy, photocorrosion, photoelectrochemistry

Graphic

Figure 1. SEM images (a, b), TEM images (c, d), HRTEM image (e) and operando ICP-MS setup (f).

Graphic:



Keywords:

TiO₂, electron microscopy, photocorrosion, photoelectrochemistry

Reference:

- [1] Fujishima, A. and K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238(1972) 37-38.
- [2] S. Chen, L.-W. Wang, Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution, *Chemistry of Materials*, 24(2012) 3659-3666.