

GENERATION OF REACTIVE CHLORINE SPECIES ON HIGHLY POROUS THICK WO₃ PHOTOANODE

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Photoelectrochemical (PEC) generation of reactive chlorine species (RCS) has been attracting increasing attention recently because it can be coupled with H₂ production in light-assisted splitting of aqueous chloride solutions. Tungsten (VI) oxide has been intensively studied as photoanode material due to its highly tunable composition, chemical stability, relatively narrow band gap of 2.6-2.7 eV, which allows absorbing of ~ 12% of solar light, and good charge carrier transport properties (hole diffusion length is ~150 nm). Photoelectrochemical (PEC) generation of reactive chlorine species (RCS) In this study, porous WO₃ films were formed on fluorine-doped tin oxide (FTO) substrates by low temperature chemical bath deposition (CBD) and tested for PEC chloride oxidation [1-3].

WO₃ photoanode was prepared using facile chemical bath deposition method in HCl acid medium. Cleaned FTO substrates were immersed into the solution and the deposition was allowed to proceed for two hours. The films were annealed at 400°C. The same procedure was repeated four times to obtain layers with increasing thickness. The coatings were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM)(Fig.1). Photoelectrochemical behavior was investigated by cyclic voltammetry (CV) (Fig.2), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).

SEM analysis revealed that WO₃ coatings are composed of clusters of randomly oriented nanosheets. With first coating procedure, only about 420nm thickness of WO₃ nanostructured film was obtained (Fig. 1.a). After four chemical bath deposition cycles, several micrometres thick porous WO₃ layers were formed (Fig.1.b-d). Cyclic voltammograms (CV) of different layers of WO₃ photoanodes were measured in 0.5M H₂SO₄ and 0.5 M NaCl under light to evaluate the PEC performance of the film and production of RCS respectively. Photocurrent density of CBD-deposited WO₃ films was found to be increasing with the increasing layer thickness. Speciation of photoelectrochemically formed RCS in the solution was analyzed by iodometric titration. Almost 100% efficiency of PEC formation of RCS has been observed.

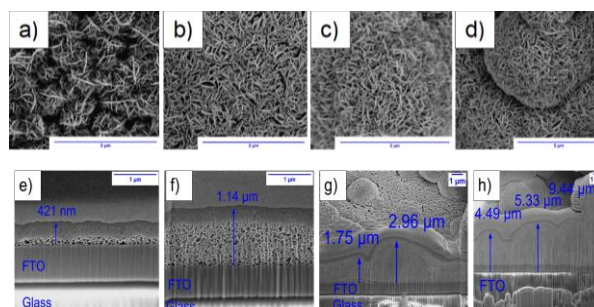


Fig. 1. Top-view (a – d) and crosssectional (e-h) SEM images of a), e) one-layer, b), f) two-layered, c), g) three-layered, d), h) four-layered

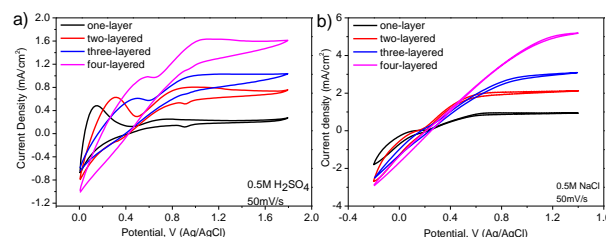


Fig. 2. Cyclic voltammograms of one, two, three and four-layered WO₃ coatings in a) 0.5 M H₂SO₄ and b) 0.5 M NaCl, potential scan rate 50 mV s⁻¹, illumination intensity ~ 100 mW cm⁻².

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References

1. X. Li, M. Kan, T. Wang, Z. Qin, T. Zhang, X. Qian, and Y. Zhao, Y. Appl. Catal. B Environ. **296** 120387 (2021).
2. A.G. Breuhaus-Alvarez, Q. Cheek, J. Cooper, S. Maldonado, and B.M. Bartlett, Phys. Chem. C. **125** 8543 (2021).
3. S. Iguchi, Y. Miseki and K. Sayama, Sustain. Energy Fuels. **2** 155(2018).