Investigation of PEC performance of molybdenum (Mo)-doped bismuth vanadate

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Photoelectrochemical (PEC) water splitting, generation of strong oxidants and organic pollutant degradation driven by visible light have attracted worldwide attention as promising applications of solar energy. Photocatalytic semiconductor materials absorb sunlight and can convert solar energy into chemical energy by water splitting into hydrogen and oxygen using photogenerated charge carriers [1]. Depending on photoanode used in the system and composition of solution, strong oxidants, such as perchlorite and persulphate, can be produced by the same way. Bismuth vanadate ($BiVO_4$), with a monoclinic crystalline structure, is recognized as a promising photoanode due to its low cost, high optical absorption coefficient (10^4 – 10^5 cm^{-1} at 350–520 nm), well-suited band structure and favorable flat band potential (< 200 mV) positive to hydrogen evolution reaction [2]. Despite its excellent properties, however, $BiVO_4$ intrinsically suffers from poor charge carriers mobility for the oxygen and other species evolution reaction. To date, several strategies have been used to overcome these obstacles such as doping of small amount of transition metals (e. g.,molybdenum and tungsten) into crystalline structure of $BiVO_4$ is a simple and effective strategy for PEC performance improvement [2].
In this work sol-gel approach and dip-coating technique was applied to synthesize Mo-doped bismuth vanadate and not doped $BiVO_4$ coatings to compare how doping influence electrochemical properties, kinetics and photoelectrochemical activity of coatings. Molybdenum (Mo) is a transition metal with half-filled orbital electronic configuration having six free electrons in its outer layer of electron structure. After addition of Mo to $BiVO_4$, Mo can replace with V, creating more free electron and donor concentration in electron-deficient structure of $BiVO_4$. Substitution of V^{5+} site by Mo^{6+} atom can strengthen the n-type characteristics of $BiVO_4$, increase the electric conductivity and consequently improve the PEC performance by supplying additional free electrons[1]. Composition and morphology of the coatings were analyzed using XRD and SEM techniques. Photoelectrochemical activity of Mo-doped $BiVO_4$ films was investigated by cyclic voltammetry in three electrode cell in 0.5 M Na_2SO4 solution in the dark and under illumination. Faradaic efficiency of generated hypochlorite species were evaluated by chronoamperometry measurement in two electrode cell in 0.5M NaCl solution.

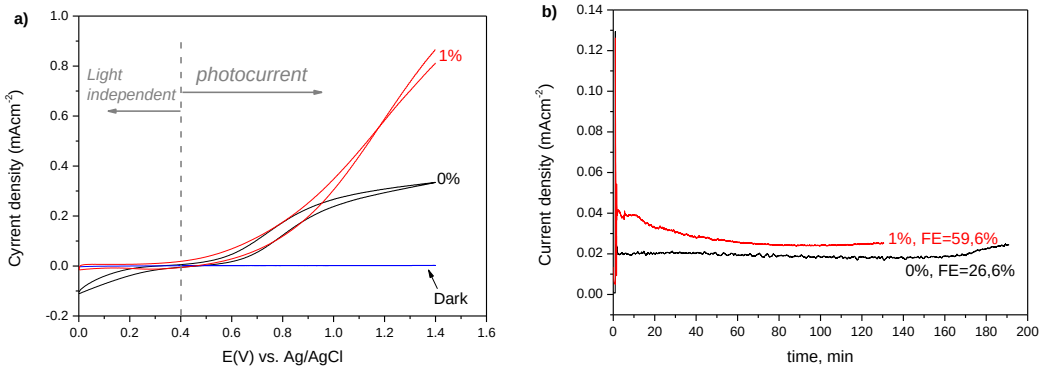

Fig. 1. a) Cyclic voltammograms in 0.5 M Na_2SO_4 solution (potential scan rate 50 mV/s) and b) chronoamperograms in 0.5M NaCl at U_{cell}=1.4V of not doped $BiVO_4$ and 1% Mo-doped $BiVO_4$ electrodes; intensity of illumination ~ 100 $mWcm^{-2}$

It was found that doping with 1% of Mo has significant influence to photoelectrochemical performace of coatings (Fig.1 a). Photocurrent of Mo-doped sample was reached 3 times higher (0.86$mAcm^{-2}$) in comparison with not doped coating. Chronoamperometry measurements showed that Faradaic efficiency (FE) of production of hypochlorite species was reached 59.6% of doped sample, however FE of not doped sample was 26.6%. Mott-Schottky and electrochemical impedance spectroscopy (EIS) will be applied for further investigations of kinetics and electrochemical properties of synthesized coatings.
Refernces:

[1] M. Tayebi, Improved photoelectrochemical performance of molybdenum (Mo) -doped monoclinic bismuth vanadate with increasing donor concentration, Catal. Today., **328** 35–42 (2019).
[2] M. Tayebi, Solar Energy Materials and Solar Cells The e ff ect of silver doping on photoelectrochemical (PEC) properties of bismuth vanadate for hydrogen production, Sol. Energy Mater. Sol. Cells. **200** 109943 (2019).