

Solar Water Splitting by Transition Metal Oxide – Silicon Photoanodes Prepared under Cathodic Electrochemical Conditions

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Photo-assisted water splitting represents a pivotal strategy for realization of the hydrogen economy of the future. In the search for appropriate anode materials, transition metal oxides have already proved sufficiently high electrocatalytic activity to reduce the required overall energy, ranging between about 1.5 and 2.0 eV, to split water into hydrogen and oxygen [1-3]. While light-induced evolution of hydrogen with highest efficiency (> 10%) is currently achieved by semiconductor-based photocathodes [4, 5], oxygen evolving photoanodes of comparable efficiency are still to be developed. A transfer of the heterostructure concept, comprising electrocatalytic films on photoactive semiconductor substrates – as realized for hydrogen evolving photocathodes – is impeded by the corresponding decomposition energy levels in aqueous solutions. Stability of a catalyst/semiconductor heterostructure is therefore a key factor in photoanode design.

Here, we demonstrate a metal-organic electrochemical approach by which several amorphous transition metal oxides were formed on conductive substrates under cathodic conditions. The dark catalytic activity, assessed in alkaline electrolytes after deposition on FTO substrates, proved oxygen evolution with overpotentials in the range between 250 and 350 mV in dependence on the metal used. With n-type silicon as substrate, metal oxide-semiconductor photoanodes were realized, and overpotentials could be reduced by about 150 mV due to the photoactivity of the silicon support (see Fig. 1). Pretreatment of the silicon surface by nanoscopic metal deposits allowed for further lowering of overpotentials (by 150 – 200 mV): in a three-electrode analysis with Ag/AgCl reference electrode, oxygen was evolved in 0.1M NaOH, pH13, directly at the water oxidation potential with current densities up to 1 mAcm⁻²; these results could be confirmed by corresponding two-electrode measurements at a potential difference of 1.23V between working and Pt-counter electrode. The stability of the photoanodes was investigated upon initial operation (~ 1 hour). Particularly in the potentiostatic mode, no degradation of the heterostructures was observed despite susceptibility of the substrate to photoinduced decomposition. Flat band potentials were calculated from impedance spectroscopy measurements and showed dependence on the conditioning steps of the oxide-silicon interface prior to metal oxide formation. Gaseous reaction products were analyzed by differential electrochemical mass spectroscopy (DEMS) confirming thereby light-induced evolution of oxygen at potentials at and below the redox potential.

The complex formation mechanisms, resulting in metal oxide films on semiconductor substrates under cathodic electrochemical conditions, will be discussed and a model for the main reaction route will be proposed.

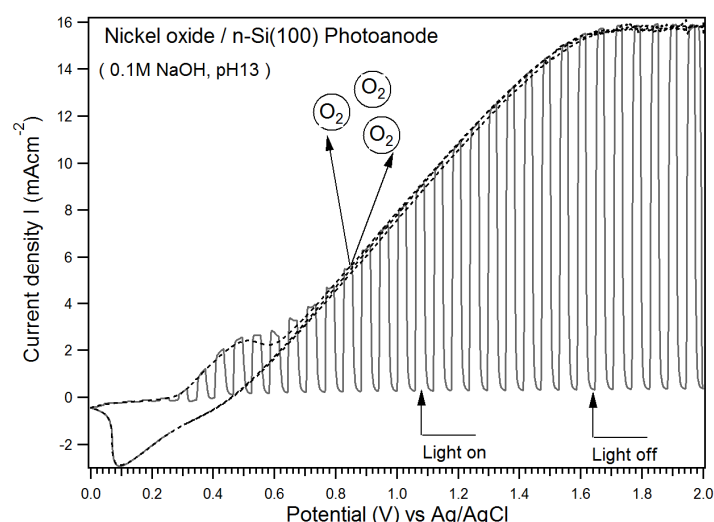


Fig. 1: Photo- and dark current behavior of an n-Si(100) substrate covered by an amorphous film of nickel oxide. The dashed curve shows the heterostructure upon operation under continuous illumination (~ 100 mWcm⁻²). The solid curve results from intermittent illumination demonstrating thereby the low dark current activity of the electrode. Evolution of oxygen was confirmed by mass spectrometric O₂-detection by DEMS. Scan rate 20mV/s. Electrolyte 0.1M NaOH, pH13.

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