

Oxygen evolution at vertically aligned core-shell iron-iron oxide nanowire arrays

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The oxygen reduction and oxygen evolution reactions are required for a number of technological processes. They have and continue to receive significant attention in the context of renewable energy, energy storage and electromobility. These electrochemical processes are demanding as four electrons are transferred to or from one small molecule. Large research efforts are underway to find catalysts with improved kinetics for the oxygen reduction reaction and selectivity towards the four electron route. Microelectrochemical detection schemes are suitable to detect dissolved intermediates such as hydrogen peroxide (H_2O_2) or superoxide anions ($\text{O}_2^{\bullet-}$) that may be formed during oxygen reduction at enzymes(1) or at noble metal catalysts(2, 3) as well as in oxygen evolution reactions.(4) The possibility to detect such intermediates has been exploited to generate reactivity maps using scanning electrochemical microscopy.(1)

With a 2.1 eV band gap, hematite is an interesting anode material for the photoelectrochemical generation of oxygen. As with most semiconducting photocatalytic materials the challenge is to prevent the recombination of the holes and electrons. This can be achieved by controlling the thickness of the oxide to promote the electron capture by the underlying current collector. Another challenge is to maximise photon harvest. To promote the capture of photons and electrons whilst preventing the recombination of the charge carriers nanostructured electrodes were prepared as a dense arrays of iron-iron oxide core-shell nanowires (Figure 1)

The nanostructures were produced via electrodeposition through a nanoporous Al_2O_3 template.(5) The electrodeposition yielded wires of uniform length adjusted to the absorption length. Controlled electrochemical and thermal oxidation were used for producing the core-shell nanorod structure. This allowed to fine-tune the thickness of the oxide film. The anode materials were structurally characterised by SEM, TEM, X-ray diffraction,

voltammetry, electrochemical impedance spectroscopy and scanning electrochemical microscopy (SECM). The preparation on a highly conductive metallic support lent mechanical strength to the array that would allow their easy incorporation into modules.

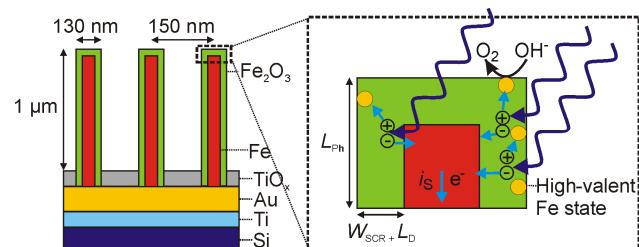


Figure 1. Schematic representation of the aligned core-shell nanowire structure allowing decoupling of charge carrier diffusion length and absorption length.

Tip-substrate voltammograms were obtained by sweeping the sample potential and recording the tip current for the amperometric detection of oxygen with the tip located a few micrometres above the sample (Figure 2). To improve the tip sensitivity and thus accurately determine the onset potential for oxygen evolution, the tips were modified with a circa 1 micrometre-thick film of nanostructured Pt prepared by electrodeposition within a lyotropic liquid template.(6) Experiments were performed with and without illumination to assess the photocatalytic activity of the films. Experiments were also carried out with flat samples devoid of nanowires for comparison.

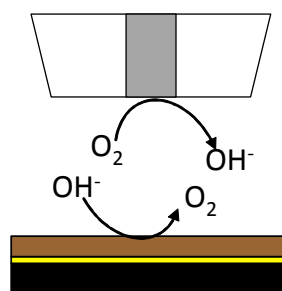


Figure 2. Schematic of the recording tip-substrate voltammograms with an SECM apparatus.

This tip current allows a direct detection of the onset of O_2 evolution as compared to other parasitic currents that may flow at the sample (other oxygen-containing products, photocorrosion).

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