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Advanced silicon photoelectrodes for water splitting devices: design, preparation and functional characterization by photo-electrochemistry and high-energy X-ray spectroscopy

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Akademisk avhandling

som med vederbörligt tillstånd av Rektor vid Umeå universitet för avläggande av filosofie doktorsexamen framläggs till offentligt försvar i KBE301 (Lilla hörsalen), byggnad KBC-huset, torsdag den 13 December, kl. 10:00. Avhandlingen kommer att försvaras på engelska.

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### **Abstract**

For the last century, mankind has been hugely dependent on fossil fuels to meet its energy needs. Harnessing energy from fossil fuels led to the emission of greenhouse gases. Greenhouse gases such as CO<sub>2</sub> are a major contributor to global warming. Since the last decade, the global annual average temperature has increased by almost 1 °C, while the annual average temperature of Europe has increased by almost 1.7 °C. It is high time to find an alternative source of energy. Such an energy source must be renewable, sustainable, robust and free of greenhouse gases. Our earth has a non-stop supply of solar energy and water in oceans, harvesting energies from such resources will not only be clean but also inexpensive. Solar fuels such as H<sub>2</sub> generated from sunlight and seawater using earth-abundant materials are expected to be a crucial component of a next generation renewable energy mix.

My PhD research was thus focused on the use of solar energy to split water into molecular hydrogen and oxygen, a process that is referred to as 'artificial photosynthesis'. This can be achieved with the help of semiconductor photocatalysts. As most of the earth crust has a high abundance of silicon (Si), I prepared my semiconductor photoelectrodes using Si. However, Si tends to degrade in an aqueous environment. Thus, my PhD research comprises the synthesis of microstructured Si photoelectrodes and their protection with a TiO<sub>2</sub> inter layer followed by functionalization with various earth abundant co-catalysts. The study on the synthesis, morphology and elemental characterization of the photoelectrodes was carried out under the supervision of Prof. Dr. Johannes Messinger at the Chemistry Department of Umeå University. Deep insight on the electronic and atomic structure of the functionalized Si photoelectrodes was obtained by careful experiments at the European Synchrotron Radiation Facility (ESRF) under the supervision of Dr. Pieter Glatzel. I investigated the electronic and geometric structural properties of my photocatalysts using inner shell electron spectroscopy, which is also referred to as 'X-ray spectroscopy'. Thus, my PhD thesis falls under the broad title of "Artificial Photosynthesis and X-Ray Spectroscopy".

With the motivation of developing a bias free photoelectrochemical device for overall water splitting, I first developed cost effective earth abundant photocathodes. The experimental data and detailed analysis of the photocathodes are presented in Paper I. The best photocathode obtained in Paper I (p-Si/TiO<sub>2</sub>/NiO<sub>x</sub>) was then coupled with a well-studied FTO/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode in parallel-illumination mode. The two most significant information obtained in Paper II were: 1) p-Si/TiO<sub>2</sub>/NiO<sub>x</sub> outcompetes Pt as a counter electrode and 2) a space charge region in the pristine hematite can be enhanced using p-Si/TiO<sub>2</sub>/NiO<sub>x</sub> as photocathode without bias or using any dopant. The proof of concept device studied in Paper II was further optimized in Paper III by replacing the FTO substrate with the n-Si MW to obtain n-Si MW/TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode. A record high photocurrent density of 5.6 mA/cm<sup>2</sup> was achieved for the undoped hematite photoanode. I also found out that the TiO<sub>2</sub> inter layer plays a crucial role in enhancing the overall device performance. The role of TiO<sub>2</sub> was thus further studied using valence to core X-ray emission spectroscopy, which opened a new avenue for identifying and investigating the prime components in such devices. Paper I to III discuss the role of TiO<sub>2</sub> and of the co-catalysts towards solar water splitting and thus the only material left to study was the Si substrate. For paper IV, a detailed analysis on Si substrate was performed. The electronic structural changes on Si L<sub>II, III</sub> edge was studied using X-ray Raman spectroscopy. The X-ray spectroscopic studies presented in papers I to III were performed at the ID-26 beamline at ESRF, while the X-ray Raman Spectroscopy presented in Paper IV was performed at the ID-20 beamline at ESRF. The data presented in Paper IV is preliminary and needs to be processed and analyzed further.

### **Keywords**

Photoelectrochemical cell, photoelectrodes, solar-water splitting, artificial photosynthesis, X-ray absorption and emission spectroscopy

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