Identifying the local structure and oxidation state of photocatalytic water-splitting electrode materials

The Polish research company SajTOM Light Future is trying to find highly efficient and low-cost metal oxide semiconductor materials for use as photocathodes. They have conducted X-ray absorption spectroscopy on a few semiconductor materials at the synchrotron facility PETRA III at the DESY campus in Hamburg to observe the differences in the local structure and oxidation state before and after being used as a photocathode.

CHALLENGE

There are several ways of producing hydrogen, which is thought to be the fuel of the future. Not all means of producing hydrogen are truly green, as some emit CO_2 during the process. Splitting water into oxygen and hydrogen by electrolysis or photolysis does not emit CO_2 and is therefore a means of producing green hydrogen. In photolysis, the reaction energy is provided by light shining on a semiconductor photocathode. SajTOM is working to develop new, improved p-type semiconductor materials for splitting water, for example different copper metal oxides or copper oxide deposited on carbon nitride (CuO/ C_3N_4). Especially CuO/ C_3N_4 is a cheap, long-lasting and non-toxic resource, checking three boxes for the sustainable production of hydrogen.

While the new compounds displayed a higher cathodic current and higher hydrogen production rates in test runs, the reason for this is unknown. The local structure and oxidation states of the different materials used are unknown, as well as how these properties change after use. Identifying both the structure and the oxidations states will help to determine the elements and reaction mechanism involved.
X-ray absorption spectra can provide that information, but lab-based experiments often lack the radiation flux needed for a precise analysis. Synchrotron radiation facilities, like PETRA III at DESY in Hamburg, possesses the high brilliance needed.

METHOD

In total, 7 samples were examined by means of extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopy at the Applied X-ray Absorption beamline P65 at PETRA III. Measurements were conducted around 4 different K-edges, namely around the Cu, Ni, Zn and In K-edge. The samples used were different copper oxide electrode materials, i.e. CuInOx, CuNiOx, CuZnOx and CuO/ C3N4. Four samples were investigated in their powder form and three samples were thin copper oxide films on a glass substrate. For some samples, spectra were also recorded for fresh and used samples.

INSIGHTS AND SOLUTION

Scanning around the K-edges of an element allows the nearest neighbor of that element to be identified, the first valuable information in decoding the reaction mechanism and which atoms are included in the reaction. The EXAFS spectra were very similar for most samples, excluding the CuNiOx. While the other first peaks were located around 0.15 nm, indicating a small neighboring atom such as oxygen, the CuNiOx first peak was located at a higher value, identifying it as metallic copper.
The XANES identified the presence of copper (II) oxide for most semiconductors by comparison with copper oxide spectra in the literature. Also, the presence of other copper oxidation states could be ruled out. Interestingly for one of the other copper oxides, the copper is still in its metallic/non-oxidized state.
The CuO/ C_3N_4 spectra also delivered valuable information. The synchrotron radiation revealed that the local chemistry of the copper oxide species is undisturbed by carbon nitride. Moreover, the copper oxide is distributed in the form of nanoparticles over the carbon nitride and acts as a co-catalyst in photocatalytic reactions like the aforementioned water-splitting reaction.

BENEFITS

Synchrotron radiation is helping SajTOM to develop long-lasting and efficient semiconductor materials, suitable for the photocatalytic production of hydrogen. Identifying the oxidation state and local structure helped the researchers to understand the reactions that take place at the photocathode during the water-splitting reaction for several materials. With the knowledge gained, SajTom can concentrate on the most promising candidates, like CuO/ C_3N_4, and avoid unfruitful work on other materials. Subsequently SajTOM is ready to further improve photocathode materials for the green production of hydrogen, such as the promising, low-cost CuO/C_3N_4 composite.

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