Modulating Carrier Kinetics in BiVO4 Photoanodes through Molecular Co4O4 Cubane Layers

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In this work, Co4O4 cubane molecular catalysts were successfully immobilized on BiVO4 photoanodes, significantly enhancing their photoelectrochemical water oxidation performance. Optimization of the cubane layer thickness at 10-12 bilayers led to a substantial improvement in photocurrents and a remarkable cathodic shift in the onset potential, with stable performance maintained for over 20 hours. Detailed analyses employing advanced photoelectrochemical techniques elucidated the intricate charge carrier dynamics at the semiconductor-electrolyte interface (SEI), where the cubane layer acts as (i) passivation layer at lower potentials, minimizing surface recombination, and (ii) hole scavenger at higher potentials, mediating charge transfer at the SEI. Further surface-sensitive characterizations confirmed the stability of the Co4O4 layer. This research not only deepens our understanding of charge carrier behavior in molecular-modified photoanodes but also offers a promising approach for stable and efficient integration of molecular catalysts into photoelectrodes, paving the way for advanced materials in renewable energy applications.

Authors’ comments:
“This study highlights the dynamic role of molecular catalysts immobilized on photoanodes for efficient solar fuel generation. Our insights into charge carrier behaviour shed new light on water oxidation processes.”

Design, Synthesis and Biological Evaluation of Simplified Analogues of the Major Corn Strigolactones, Zealactone and Zeapyranolactone

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Strigolactones are vital plant hormones influencing growth and development, making them central to crop productivity. Harnessing strigolactone technology holds great promise for sustainable agriculture. In particular, corn, a major staple, has unique strigolactones (zealactone and zeapyranolactone) in its root exudates. Recent work achieved the first complete synthesis of zealactone and examined its effects on corn. This study outlines the creation and evaluation of simplified analogues of these corn-derived strigolactones. This research investigates their performance in soil, an essential aspect for practical use in agriculture, and their biological activities. These newly designed compounds have the potential to lead the development of synthetic strigolactones, fostering more sustainable crop production. Ultimately, this work contributes to advancing agricultural technology by offering innovative solutions for enhancing crop yield and resilience in a modern and sustainable context.

Authors’ comments:
“Zealactone displays very promising biological activities for corn growth stimulation. However, the search for improved analogues and the understanding of the structural features required for high biological performance were of crucial importance. We identified simplified corn strigolactones analogues retaining high potential for application to sustainable agriculture.”
Selective Oxidative Dehydrogenation of Ethane and Propane Over Copper-Containing Mordenite: Insights into Reaction Mechanism and Product Protection

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Copper(ii)-containing mordenite (CuMOR) effectively activates C1-C3 alkanes, but the reactivity differs significantly for ethane, propane, and methane. Ethane and propane interaction with CuMOR produces ethylene and propylene with high selectivity. Conversely, methane primarily yields methanol and dimethyl ether. The reaction mechanism investigation uses in situ FTIR, MAS NMR spectroscopies, and time-resolved Cu K-edge X-ray absorption spectroscopy, revealing distinct pathways for each alkane. For ethane and propane, oxidative dehydrogenation occurs, forming stable π-complexes with CuI sites upon CuII-oxo species reduction. These complexes shield olefins from further oxidation or oligomerization. In contrast, methane activation involves oxidative hydroxylation, resulting in surface-bound methoxy species on the zeolite framework. These findings represent a significant advance in converting alkanes into valuable products and pave the way for selective olefin synthesis, marking a major step towards transforming alkanes into essential commodities.

Authors’ comments:
“In addition to well-established oxidation of methane, we discover a novel direction of potential application of copper-exchanged zeolites leading straight to monomers for plastics production.”

Fingerprinting of Chlorinated Paraffins and their Transformation Products in Plastic Consumer Products

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Chlorinated paraffins (CPs) with diverse carbon and chlorine homologues, are used in high volumes for applications like flame-retardants, plasticizers, and coolants. Short-chain CPs (SCCPs) are subject to strict regulation due to their environmental persistence, bioaccumulation and toxicity. Furthermore, CPs can transform into unsaturated compounds, including chlorinated mono-, di-, and tri-olefins. These transformations occur at different stages of CP processing, yielding unique carbon and chlorine homologue distributions. The authors of this study developed a CP-fingerprinting method to distinguish CP-containing samples, allowing for source identification and reducing environmental and human hazards. CP-containing plastics were analysed using reverse-phase liquid-chromatography coupled with a high-resolution mass spectrometer. An R-based routine was applied to efficiently process the data, identifying 340 CP and transformation product homologues, forming specific fingerprints based on carbon and chlorine numbers and saturation levels. These fingerprints were compared to those obtained using an alternative GC-ECNI-Orbi-trap-MS method.

Authors’ comments:
“Mass spectra of CPs and their transformation products contain several tens of thousands of ions, ~50 ions per mass unit. We have developed new tools based on high resolution MS and automated data processing to identify individual CP-homologues in this universe of ions and deduce characteristic fingerprints.”