Reaction kinetics and interplay of two different surface states on hematite photoanodes for water oxidation

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The design of efficient photoanodes for water oxidation is highly dependent on the understanding of the function of their surface states. Hitherto, only one surface state with higher oxidative energy (S1) has been interpreted as reaction intermediate. In this work, a second surface state with lower oxidative energy (S2) is also recognised as reaction intermediate. The dynamic interplay of both surface states has been identified by kinetic analyses. Furthermore, the density and distribution of the two surface states is herein described to be highly dependent on several parameters as the illumination intensity, electrolyte pH, applied potential, etc. These insights are a new step to enhance the complex performance of photoelectrochemical devices through better understanding.

Authors’ comments:
“We shed new light on the dynamic nature of surface states as reaction intermediates on hematite photoanodes for water oxidation.”

Merging shuttle reactions and paired electrolysis for reversible vicinal dihalogenations

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Vicinal dibromides and dichlorides are crucial commodity chemicals used as polymers, pest control agents, flame retardants, and pharmaceuticals. They also serve as important synthetic intermediates because of the carbon–halogen bonds’ innate reactivity. Traditional methods to access such species often rely on toxic and corrosive Cl₂ and Br₂. Additionally, the high environmental stability and toxicity of some once widely used polyhalides, e.g. the insecticide Lindane, calls for a sustainable remediation approach. Electrochemically assisted shuttle reactions (e-shuttle) now provide an easy and scalable interconversion of vicinal dihalides and alkenes. This reaction can be used to synthesize useful dihalogenated molecules from easy-to-handle dihalide donors (e.g. 1,2-dichloroethane and 1,2-dibromoethane), and to sustainably recycle waste materials through retro-dihalogenation while producing value-added products.

Authors’ comments:
“This interdisciplinary e-shuttle approach, which merges shuttle chemistry and electrochemistry, opens a new and exciting field of research in organic chemistry. The power of this reversible process is best highlighted by the remediation of the end-of-life pollutant Lindane through the concomitant synthesis of valuable halogenated chemicals.”

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A reprogrammable mechanical metamaterial with stable memory

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Metamaterials are artificial materials engineered to have exotic properties. In this case, the authors have developed a new metamaterial to achieve mechanical re-programmability. Formed by a repetition of identical but independent units called m-bits, the metamaterial can be ‘programmed’ using electromagnetic coils into two states (ON and OFF, depending on the position of the magnetic cap). The state of the metamaterial defines its elastic response towards mechanical compression. The authors show that the programmed state (memory) is non-volatile or that the deformation is elastic. Furthermore, they prove that the combination of more than one m-bit to create a planar array structure allows, depending on the programmed state of each m-bit, to tune the mechanical properties of the whole surface, opening the door to a new generation of metamaterials capable of altering their properties on demand.

Authors’ comments:
“We are the first to create a ‘material’ whose mechanical properties can be remotely programmed on-demand. This idea may prove useful in many applications and provides countless future research directions.”

Cycloparaphenylene- Phenalenyl Radical and Its Dimeric Double Nanohoop

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Open-shell nanographenes characterized by delocalized spin density are synthetic targets of fundamental interest to chemists for their amphoteric redox properties, magnetism and conductivity, and potential applications in spintronics and quantum computing. In this work, the authors report the first example of a neutral spin-delocalized carbon-nanoring radical, achieved by integration of the open-shell phenalenyl unit into cycloparaphenylene (CPP). The resulting structural geometry is reminiscent of a diamond ring, with a pseudo-perpendicular arrangement of the radial and the planar π-surface. The phenylene rings attached directly to the phenalenyl unit give rise to a steric effect that governs a highly selective dimerization pathway, yielding a giant double nanohoop. This work provides the basis for future investigation of spin-delocalization through a radially π-conjugated backbone, which can be applied to understand through-space interactions in multi-spin and host–guest CPP systems.

Authors’ comments:
“We conceptualize carbon nanorings as a new structural platform to control spin-delocalization via interplay of steric and electronic effects and turn the ‘decomposition’ pathway of phenalenyl into a useful synthetic tool towards new nanocarbon architectures.”