



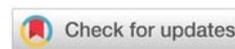
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***Corresponding author:** PD Dr. Engelbert Redel, KIT Faculty for Chemistry and Biochemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, Tel: +49 721 6190 9518; E-mail: engelbert.redel@partner.kit.edu

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Research Article

Tandem architectures for artificial thylakoid membranes

Engelbert Redel*

KIT Faculty for Chemistry and Biochemistry, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

Abstract

In this concept paper, new layered materials, such as multilayer hybrid systems, are described. These materials can be implemented into novel biomimetic devices, which can act as artificial photosystems or as "artificial thylakoid membranes" e.g. for the splitting of water. The architecture can be based on active nanoparticles or small catalytic clusters which can be synthesized from robust, inexpensive, and abundant material precursors. These multi-layered architectures can act as "artificial thylakoid membranes", which can mimic the photosynthetic apparatus on the nanoscale. The development of "artificial thylakoid membranes" and tandem devices promises a strong impact and benefits for the field of artificial photosynthesis and the development of artificial leaves.

Abbreviations

NPs: Nanoparticles; MOF: Metal-Organic Framework, S: Separator Layer; LH: Light Harnessing Layer; PSI/PSII: Photosystem I & II; CVD: Chemical Vapor Deposition; ALD: Atomic Layer Deposition; VB: Valence Band; CB: Conduction Band.

Introduction

One noble aim of mankind is to develop artificial photosynthesis on the nanoscale, which can mimic the complex process of natural photosynthesis [1].

In the process of natural photosynthesis, sunlight energy is absorbed through "antenna" chlorophyll molecules [2] e.g. LCHs I+II, which are embedded in the multi-layered cell membranes, referred to as thylakoid membrane stacks, where, the photo-generated excitons are transferred and efficiently charge separated to the reaction chlorophyll pigment centres with very high Quantum Efficiencies (QEs) [3]. This light-driven reaction requires the cooperation of two different, membrane-bound photochemical assemblies, referred to as photo-systems

PSI and PSII [3]. At the nanoscale photosynthesis occurs in the 1D periodic stacked nano-layered thylakoid stacks, with high surface areas and distinct layer/membrane thicknesses ≈ 10 nm - 12 nm. The thylakoid membrane stacks are also favourable for high-efficiency light harvesting processes occurring in natural leaves [4].

In general, the term "tandem architecture" [5] describes a catalytic materials configuration in which multiple catalytic reactions e.g. the splitting of water can take place in a sequential manner, within one single device or architecture. This includes the arrangement, of different catalytic layers, porous thin film architectures, or photocatalytic membrane architectures in a 1D fashion [6]. Within this arrangement one reaction can act from a starting material layer e.g. oxidation process for the subsequent reduction process. This approach enables the effective transformation of initial substrates into desired products by integrating multiple catalytic steps within a multilayer tandem architecture, promoting enhanced efficiency in the overall process [7].

In the last years, there is a growing interest in "tandem catalytic architectures" due to their ability to enhance reaction

efficiency, selectivity, and atom economy [8]. The integration of multiple redox reactions in a catalytic tandem sequence offers the advantage of minimizing or eliminating undesired side reactions without additional purification steps [9].

Materials and methods

Especially for photocatalytic application [10], SC (Semiconductors) with a cubane-type core-unit can mimic the oxidation process for $[\text{CaMn}_4\text{O}_5]$ clusters in PSI as well as the reduction chain process for $[\text{Fe}_4\text{S}_4]$ core clusters in PSII that are part of the Z-Scheme [3,4]. Especially spinel nanoscale materials $\text{M}_1\text{M}_2\text{X}_4$; $(\text{M}_1)_3\text{X}_4$ (e.g. composed out of $\text{M}_1/\text{M}_2 = \text{Fe, Cu, Ni, Co, Ru, Pt, Rh}$ and $\text{X} = \text{O, S, Se}$), which inherently possess a $[(\text{M}_2)_4\text{X}_4]$ or $[(\text{M}_1)_4\text{X}_4]$ with a catalytic cubane-core unit. Therefore, the development of new synthetic pathways to novel cubane-type $[\text{M}_4\text{X}_4]$ with $\text{M} = \text{Fe, Ni, Cu}$; $\text{X} = \text{O, S, Se}$ nano-cluster materials has already been facilitated for the synthesis of a variety of new homo-nuclear and hetero-nuclear cubane-type $[\text{M}_4\text{S}_4]$ cluster-materials [11]. They can contain a number of different metals (e.g. $\text{M}_1 = \text{Fe, Cu, and Ni}$) e.g. from the first row of transition metals, but they are not limited to these metals and instead can include other catalytic metals (e.g. Ir, Rh, Pt) from the second- and third-row of transition metals [12]. These cubane-core catalytic units can mimic the reduction process e.g. in $[\text{NiFe}]$ hydrogenases and have been identified to show a significant O_2 tolerance under ambient conditions. $[\text{Fe}_4\text{S}_4]$ core clusters materials have already been reported as "Building Blocks for Solar Fuel Catalysis" [13] (Figure 1).

Moreover, E. Redel, et al. and co-workers have reported a general route to the synthesis of photocatalytic active metal-oxide NPs; for the purpose of constructing multi-layered porous metal oxide thin films [14,15]. Such synthesis routes are starting from bare metal powder particles (e.g. micrometer-scale metal powders are available for W, Mo, Ni, Co, Fe, In, Sn, Sb, Zn, and Mg with purity 99.5 to 99.95%) followed by an oxidative etch process yielding different metal-oxide dispersions [14,15]. The use of metal powders instead of e.g. expensive sol-gel precursors offers an elegant, inexpensive, robust, and universal green synthesis route to produce a broad variety of tailored metal oxide compositions, which furthermore allows the 'one-pot' multi-gram synthesis of stable 0-D metal oxide NP with diameters in the range of 3 nm – 5 nm [14,15].

Novel hierarchical tandem-based photocatalytic architectures can be created by the combination of different bottom-up and top-down deposition and/or growth techniques [16], e.g. through sol-gel spin-coating [16], anodic oxidation, sputtering, CVD [16] as well as LPE (Liquid Phase Epitaxy) [17] and sALD (solution based Atomic Layer Deposition) [18]. First examples of such tandem hybrid materials, e.g. MOF/ITO have been already published by E. Redel, et al. and co-workers [19]. Various redox-active metal oxide and chalcogenide nanomaterials with catalytic cubane-core cluster-units $[(\text{M}_2)_4\text{X}_4]$ or $[(\text{M}_1)_4\text{X}_4]$ can be chemically synthesized in solution and then spin-coated onto a porous thin film, Figure 2.

The LH-MOF or S-MOF layer will be grown on top of the first deposited metal oxide or chalcogenide porous catalytic layer. The second catalytic layer will be deposited e.g. by sputtering or spin-coating on top of the LH layer or S layer. Development of these tandem hybrid materials will utilize

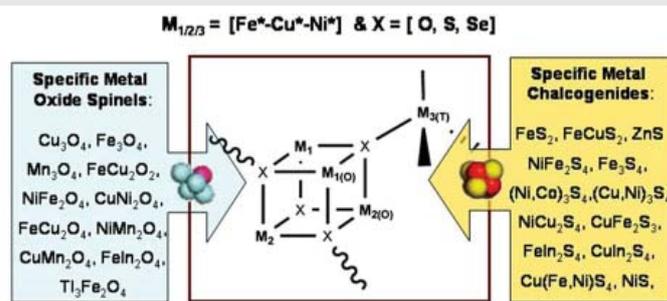


Figure 1: Materials composition with a cubane-type core-unit with the focus on new spinel $\text{M}_1\text{M}_2\text{X}_4$; $(\text{M}_1)_3\text{X}_4$ compositions.

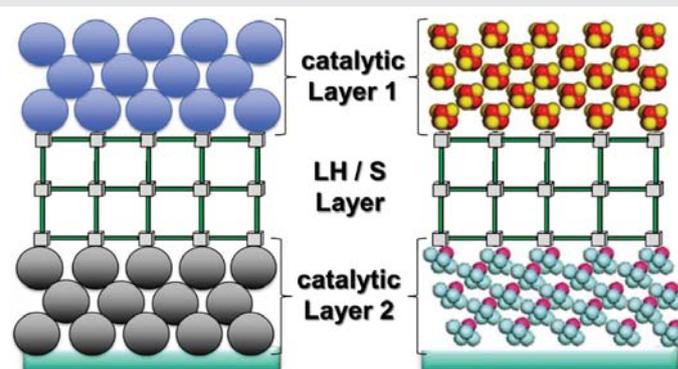


Figure 2: Schematic picture of tandem-based multilayer assemblies composed with an LH-Layer or S-Layer as well as catalytic active NPs and small clusters (from Figure 1) as the catalytic Layers 1 & 2 forming a three-component tandem hybrid material.

band-gap engineered layered components, with tuneable absorption properties in the visible range as highly-active photoactive materials architectures. The porous catalytic layers 1 and 2 between an LH-Layer or a Separator (S) Layer, Figure 2 will also allow gas and water penetration through the porous MOF structure and will utilize the catalytic active surface of the porous layer, e.g. for water splitting.

The LH or S layers can be made up of a huge variability of MOFs (up to now more than 70.000 different MOF types have been reported [20,21] resulting in an enormous flexibility in tuning the MOF properties with regard to a desired and distinct function [22]. Metal-Organic Frameworks (MOFs) are porous and crystalline Coordination Network Compounds (CNCs) consisting of inorganic metal (or metal/oxo) clusters connected by organic linkers [23–25]. Due to their crystalline, highly ordered, and porous structure, this class of solids exhibits a number of exciting properties. The size of the pores within MOFs has been shown to be very adjustable, and pore diameters up to 10 nm [26] have recently been realized, yielding highly porous materials with exceptionally low densities.

In recent years, a number of methods have been developed to deposit MOFs on solid substrates. These deposition processes include spraying, painting, dipping into suspensions, spin-coating as well as electrochemical methods and have been reported to yield rigid MOF thin films [27].

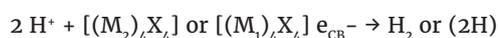
Results and discussion

Optically transparent and porous 1D multi-layered thin films will be then fabricated by either using catalytic active

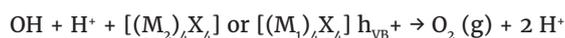
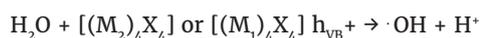
nanoparticles porous thin films (layer 1 and 2) with optimized film-thicknesses in the range of the respective exciton diffusion-length scale or Bohr exciton radius of NPs; of the two employed SC-materials or the MOF separating thin film. These multi-layered architectures can act as an “artificial thylakoid membrane” comprising ultra-small NPs and/or active clusters as layered catalytic layers separated by the S or LH MOF layer. The absorption properties of the multi-layered materials can be either tuned by the MOF material in particular through the LH or the Separator (S) MOF layer as well as by the absorption properties of the deposited SC materials in tandem hybrid materials (Figures 1,2). Whereby with both approaches, the multi-layered tandem architectures will be able to harness efficiently different parts of the solar spectrum.

The multi-layered device, Figure 3 conceived as an “artificial thylakoid membrane” or as a MOF-based hybrid material will be designed with custom-tailored electronic Band-Gap (Eg) Energy levels (CB = Conduction Band and VB = Valence Band), which are suitably aligned to enable sunlight powered electron-hole generation and charge carrier separation between the layers. The hybrid materials can be sandwiched between top- and bottom conductive electrodes (e.g. Au, ITO) while applying an external BIAS. The generated electron-hole pairs (e^-/h^+) will be separated at the interface of the multi-layered material in the separated catalytic layers 1 and 2 within the artificial thylakoid membrane architecture. The generated and efficiently separated charge carriers in the distinct layers can be used for the reduction or oxidation process of water splitting:

Reduction (electron-rich layer 1)



Oxidation (hole-rich layer 2)



The MOF layer can act as a Separator layer (S) or LH layer, between the separated redox-active porous catalytic layers e.g. for the oxidation as well as the reduction process, including a proton H^+ conductive transport layer, enabling the splitting of water in such a biomimetic device concept, Figure 3.

To further evaluate the efficiency of proton H^+ transport over the S/LH Layer additional conductivity measurements as well as gas-permeability tests can be applied for the generated H_2 and O_2 as separated products from the tandem MOF-based hybrid-system architectures.

The overall idea described here, is to develop hybrid-based “artificial thylakoid membranes”, which can mimic the photosynthetic apparatus on the nanoscale in a multi-layered tandem architecture. Basic insight into the working principle and function of these artificial hybrid-based thylakoid membranes and devices promises important contributions to the field of artificial photosynthesis.

Conclusion

In this concept paper new hierarchical materials, like multilayered tandem hybrid-system are described. These materials and devices can be implemented into novel bio-mimetic devices, which can act as “artificial thylakoid membranes” or as “artificial photosystems” e.g. for water splitting. These multilayered architectures are based on active NPs or small active clusters with a cubane-type core unit that can mimic the oxidation as well as the reduction process. It is quite appealing to design and fabricates hybrid materials at the nanometre precision scale with thin film thicknesses of the exciton diffusion lengths of the catalytic active components. These novel “artificial thylakoid membranes” and devices could mimic the photosynthetic apparatus and are able to harness sunlight on the nanoscale within a multi-layered architecture. The basic insight of the working principle of “artificial thylakoid membranes” and devices promises strong impact and benefits for the field of artificial photosynthesis and for the development of artificial leaves.

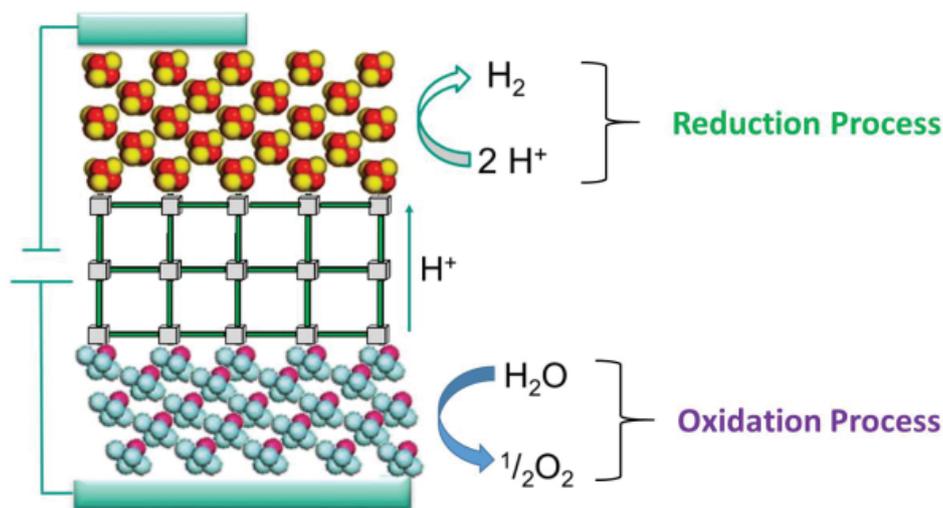


Figure 3: Device concept example of a Tandem based multilayer assemblies e.g. for H_2O splitting under an external BIAS.

References

- Ciamician G. THE PHOTOCHEMISTRY OF THE FUTURE. *Science*. 1912 Sep 27;36(926):385-94. doi: 10.1126/science.36.926.385. PMID: 17836492.
- Mandal R, Dutta G. From photosynthesis to biosensing: Chlorophyll proves to be a versatile molecule, *Sensors International*, 2020; 1: 100058.
- Collings AF, Critchley C. *Artificial Photosynthesis*, Wiley-VCH, Germany. 2005;13-35.
- Zhou H, Guo J, Li P, Fan T, Zhang D, Ye J. Leaf-architected 3D hierarchical artificial photosynthetic system of perovskite titanates towards CO₂ photoreduction into hydrocarbon fuels. *Sci Rep*. 2013;3:1667. doi: 10.1038/srep01667. PMID: 23588925; PMCID: PMC3627189.
- Cho HJ, Xu B. Enabling Selective Tandem Reactions via Catalyst Architecture Engineering, *Trends in Chemistry* 2020; 2: 929-941.
- Akter T, Pan H, Barile CJ. Tandem Electrocatalytic CO₂ Reduction inside a Membrane with Enhanced Selectivity for Ethylene, *J. Phys. Chem. C* 2022; 126: 10045-10052.
- Bazyar H, Moultois OA, Lammertink RGH. A review on nature-inspired gating membranes: From concept to design and applications. *J Chem Phys*. 2022 Oct 14;157(14):144704. doi: 10.1063/5.0105641. PMID: 36243535.
- Wasilke JC, Obrey SJ, Baker RT, Bazan GC. Concurrent tandem catalysis. *Chem Rev*. 2005 Mar;105(3):1001-20. doi: 10.1021/cr020018n. PMID: 15755083.
- Fogg DE, dos Santos EN. Tandem catalysis: A taxonomy and illustrative review, *Coordination Chemistry Reviews* 2004; 248: 2365-2379.
- Melchionna M, Fornasiero P. Updates on the Roadmap for Photocatalysis, *ACS Catal*. 2020; 10: 5493-5501.
- Seino H, Hidai. Catalytic functions of cubane-type M₄S₄ clusters. *Chem. Sci.*, 2011; 2: 847-857.
- Henderson RA. Mechanistic studies on synthetic Fe-S-based clusters and their relevance to the action of nitrogenases. *Chem Rev*. 2005 Jun;105(6):2365-437. doi: 10.1021/cr030706m. PMID: 15941217.
- Cox N. and Lubitz W. in *Chemical Energy Storage* (R. Schlögel, Editor) 2013 Walter de Gruyter GmbH, Chapter 3.4,199-224 (and references therein).
- Redel E, Petrov S, Dag O, Moir J, Huai C, Mirtchev P, Ozin GA. Green nanochemistry: metal oxide nanoparticles and porous thin films from bare metal powders. *Small*. 2012 Jan 9;8(1):68-72. doi: 10.1002/smll.201101596. Epub 2011 Nov 18. PMID: 22095912.
- Redel E, Huai C, Dag Ö, Petrov S, O'Brien PG, Helander MG, Mlynarski J, Ozin GA. From bare metal powders to colloidal stable TCO dispersions and transparent nanoporous conducting metal oxide thin films. *Small*. 2012 Dec 21;8(24):3806-9. doi: 10.1002/smll.201200864. Epub 2012 Oct 4. PMID: 23034953.
- Ozin GA, Arsenault AC, Cademartiri L. *Nanochemistry – A Chemical Approach to Nanomaterials*, The Royal Society of Chemistry 2009; 1-785.
- Mahi FT, Nakajima K. Liquid Phase Epitaxy, *Encyclopedia of Materials: Science and Technology*. 2001; 4588-4596.
- Barr MKS, Nadiri S, Chen DH, Weidler PG, Bochmann S, Baumgart H, Bachmann J, Redel E. Solution Atomic Layer Deposition of Smooth, Continuous, Crystalline Metal-Organic Framework Thin Films. *Chem Mater*. 2022 Nov 22;34(22):9836-9843. doi: 10.1021/acs.chemmater.2c01102. Epub 2022 Nov 2. PMID: 36439317; PMCID: PMC9686130.
- Liu JX, Redel E, Walheim S, Wang ZB, Oberst V. Monolithic High Performance Surface Anchored Metal-Organic Framework Bragg Reflector for Optical Sensing, *Chem. Mat*. 2015; 27: 1991-1996.
- Tranchemontagne DJ, Mendoza-Cortés JL, O'Keeffe M, Yaghi OM. Secondary building units, nets and bonding in the chemistry of metal-organic frameworks. *Chem Soc Rev*. 2009 May;38(5):1257-83. doi: 10.1039/b817735j. Epub 2009 Mar 31. PMID: 19384437.
- Zhou HC, Long JR, Yaghi OM. Introduction to metal-organic frameworks. *Chem Rev*. 2012 Feb 8;112(2):673-4. doi: 10.1021/cr300014x. Epub 2012 Jan 26. PMID: 22280456.
- Gangu KK, Maddila S, Jonnalagadda SB. The pioneering role of metal-organic framework-5 in ever-growing contemporary applications - a review. *RSC Adv*. 2022 May 12;12(22):14282-14298. doi: 10.1039/d2ra01505f. PMID: 35702657; PMCID: PMC9097495.
- Li H, Eddaoudi M, O'Keeffe M, Yaghi OM. Design and synthesis of an exceptionally stable and highly porous metal-organic framework, *Nature* 1999; 402: 276-279.
- Yaghi OM, Li GM, Li HL. Selective binding and removal of guests in a microporous metal-organic framework, *Nature* 1995; 378:703-706.
- Férey G, Serre C. Large breathing effects in three-dimensional porous hybrid matter: facts, analyses, rules and consequences. *Chem Soc Rev*. 2009 May;38(5):1380-99. doi: 10.1039/b804302g. Epub 2009 Feb 26. PMID: 19384443.
- Deng H, Grunder S, Cordova KE, Valente C, Furukawa H, Hmadeh M, Gándara F, Whalley AC, Liu Z, Asahina S, Kazumori H, O'Keeffe M, Terasaki O, Stoddart JF, Yaghi OM. Large-pore apertures in a series of metal-organic frameworks. *Science*. 2012 May 25;336(6084):1018-23. doi: 10.1126/science.1220131. PMID: 22628651.
- Zhang Y, Chang CH. Metal-Organic Framework Thin Films: Fabrication, Modification, and Patterning, *Processes* 2020; 8: 377. doi:10.3390/pr8030377.

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