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A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Clustering of catalytic nanocompartments for enhancing an extracellular non-native cascade reaction

Viviana Maffeis, Andrea Belluati, Ioana Craciun, Dalin Wu, Samantha Novak, Cora-Ann Schoenenberger, Cornelia G. Palivan,* *Chem. Sci.* **2021**, *12*, 12274-12285, https://doi.org/10.1039/D1SC04267J
University of Basel, NCCR-Molecular Systems Engineering, Basel

Bioinspired catalytic nanocompartments (CNCs) have been designed with the aim of increasing the efficiency of enzymatic cascade reactions. Indeed, the CNCs effectively protect the enzymes from the environmental conditions and allow for a distance control of the reaction spaces. Clusters of CNCs were generated using nanometric polymer vesicles (polymersomes), which conferred stability to the architecture and offered modularity to the system by tuning the polymersomes properties. The clusterization was promoted through the DNA hybridization of complementary ssDNA available on the surface of the polymersomes. A model cascade reaction has been successfully established combining the activity of glucose oxidase (GOX), lactoperoxidase (LPO) and amyloglucosidase (AMG). This work confirms the potentiality of CNC clusters in biocatalysis, therapeutics and other biomedical applications.

Authors' comments:
"We engineered artificial nano-compartments to expand the cell's metabolic repertoire with a unique exogenous pathway. Our strategy is based on a robust decoration of cell membranes with complex 'artificial organelles', which endow cells with non-native extracellular functions."

Direct Amidation of Esters by Ball Milling

William I. Nicholson, Fabien Barreteau, Jamie A. Leitch, Riley Payne, Ian Priestley, Edouard Godineau, Claudio Battilocchio,* Duncan L. Browne,* *Angew. Chem. Int. Ed.* **2021**, *60*, 21868-21874, https://doi.org/10.1002/anie.202106412
Syngenta Crop Protection AG, Syngenta Ltd.; University College London; Cardiff University

Due to the predominance of the amide bond in nature, as well as in biologically active and fine chemical products, the development of methods for the formation of this motif remains a topic of ongoing interest. The use of common coupling reagents, such as EDC or HATU, often leads to the generation of stoichiometric quantities of toxic waste by-products, illustrating the need to develop greener and more sustainable alternatives to achieve coupling. Here, using ball milling methodology, Browne *et al*. report an elegant and generally-applicable procedure for amide bond formation – using the respective ester, amine, and a substoichiometric amount of KOtBu, the authors successfully accessed a large library of 78 amides, including various APIs and agrochemicals, at gram-scale, and all in the absence of a reaction solvent. This sustainable, mild, and efficient amidation procedure highlights the potential of this technology in an industrial setting.

Authors' comments:
"Mechanochemistry offers great opportunities to deliver more sustainable solutions for chemical processes – we are thrilled with the demonstration of solvent-free access to amides. We believe this is an enabling technology that industry needs to explore more regularly with the aid of academia."

Prepared by Lucia Robustini, Valentina Marchini, Lauriane Pillet, David Lim, and Francesca Paradisi*

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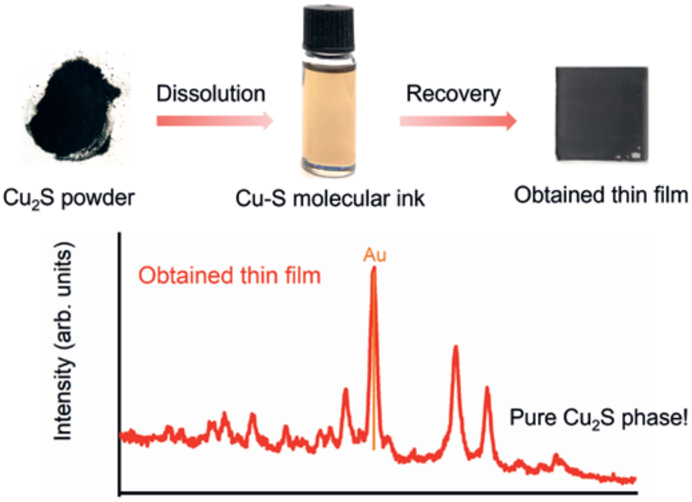
Thiol-Amine-Based Solution Processing of Cu_2S Thin Films for Photoelectrochemical Water Splitting

Xi Zhang,* Wooseok Yang, Wenzhe Niu, Pardis Adams, Sebastian Siol, Zhenbin Wang, S. David Tilley,* *Chem. Sus. Chem.* **2021**, *14(18),* 3967-3974, https://doi.org/10.1002/cssc.202101347
University of Zürich

In this work, the authors obtained the first thiol-amine-based ink deposition strategy to prepare phase-pure Cu_2S thin film with modest photoelectrochemical performance, using a simple, cost-effective, and high-throughput approach. The Cu_2S thin film can be prepared by dissolution and recovery of commercial Cu_2S powder with thiol-amine-based solution. At the end of the process, this photocathode delivered a photocurrent density of 2.5 mA cm^{-2} at –0.3 V_{RHE}, an onset potential of 0.42 V_{RHE}, and an extended stability over 12 h under simulated sunlight illumination. The remarkable stability of the Cu_2S photocathode is promising for stable solar-driven hydrogen fuel production based on affordable Cu_2S which makes this strategy scalable and low-cost.

Authors' comments:
"Cu_2S is notorious for being difficult to make it phase pure. In this study, we developed a simple solution-based approach to fabricate phase pure Cu_2S thin films."



Computational Study of Benzosultam Formation through Gold(I)-Catalyzed Ammoniumation/Nucleophilic Substitution Reaction

Romain Pertschi, Adiran de Aguirre, Patrick Pale, Aurélien Blanc,* Amalia I. Poblador Bahamonde,* *Helv. Chim. Acta* **2021**, *104*, e2100133. *https://doi.org/10.1002/hlca.202100133*
University of Geneva

Thanks to its strong π-Lewis acidity, the gold(I) cation activates alkynes towards nucleophilic addition allowing the synthesis of complex azacycles. Recently the authors studied gold(I)-catalysed ammoniumation of (2-alkynyl)phenylsulfonyl azetidines to reach benzosultams. The postulated mechanism proceeds through a nucleophilic addition of the nitrogen on the alkyne leading to a vinyl-ammonium-gold(I) intermediate further reacting with a protic nucleophile by ring opening of the azetidine. Herein, the authors performed density functional theory (DFT) calculations confirming the mechanism by showing clear evidence of the involvement of this intermediate. Interestingly, with terminal alkynes, the monogold activation pathway was found to be in competition with a digold inactivating process. Overall, these studies facilitate the design and the optimization of new gold(I)-catalysed ammoniumations reactions.

Authors' comments:
"Undoubtedly our work highlights that gold catalysis associate with DFT calculations could lead to a powerful tool to reach molecular diversity through the divergent synthesis control."