DS 16: Focus Session: 2D Transition Metal Carbides, Nitrides and Carbonitrides III (joint session DS/MM/O)

Properties: Catalysis & electrochemistry; physical properties

Time: Thursday 15:00–17:30 Location: A 053

Invited Talk DS 16.1 Thu 15:00 A 053

Heterogeneous catalysis with MXenes: the role of the surface passivating groups and the structural defects — •Alexey Fedorov — Department of Mechanical and Process Engineering, ETH Zürich, CH-8092 Zürich, Switzerland

Mo2CTx, two-dimensional (2D) molybdenum carbide of the MXene family (Tx are passivating surface groups), contains only surface Mo sites and is therefore a convenient model catalyst for structure-activity studies. For instance, the catalytic activity of Mo2CTx in Fischer-Tropsch (FT) synthesis increases when a Tx coverage is minimized, the latter achieved via reductive defunctionalization of Tx groups under H2. However, high temperature H2 treatment of Mo2CTx removes also ca. one third of the carbidic lattice carbon, yielding a 2D-Mo2C1-x material that is an active methanation catalyst. The removal of Tx species is also possible in the FT conditions (i.e., in the presence of CO), and this gives 2D-Mo2C without detectable carbon vacancies and Tx groups. 2D-Mo2C material, in contrast to 2D-Mo2C1-x, converts CO to diesel range alkanes. Other examples considered include dry reforming of methane, (reverse) water gas shift as well as electrocatalytic reactions (HER, NO3RR) of Mo2CTx:M, i.e., a material with dopant sites (M = Co, Fe) replacing Mo sites in the lattice of Mo2CTx.

DS 16.2 Thu 15:30 A 053

Pt-doped Ti3C2Tx and Mo2Ti2C3Tx MXenes for catalytic hydrogenation — •Yilong Yan[1], Franck Morfin[1], Stéphane Célérier[2], and Laurent Piccolo[1] — [1]IRCELYON, CNRS & Université Lyon 1, 69626 Villeurbanne, France — [2]IC2MP, CNRS & Université de Poitiers, 86073 Poitiers, France

Transition metal carbides can act as efficient metal-like catalysts or catalyst supports, and MXenes offer renewed possibilities to anchor metal atoms and promote catalytic performances. Herein, we report on the elaboration of Pt/MXene single-atom catalysts and their performance in CO2 and alkadiene hydrogenation reactions.

Anchoring of single Pt atoms is favorable at the surface of Ti3C2Tx and Mo2Ti2C3Tx MXenes. According to in situ XAS and XPS, Pt cations partially reduce upon thermal treatment at 400 °C in H2 flow, while forming bonds with surface M atoms of the MXene. This includes the probable location of Pt atoms at M vacancies or Pt-M substitution, consistently with STEM. In addition, XAS, XRD and TPR reveal MXene restructuring together with desorption of chemical intercalants and terminal groups.

While Ti3C2Tx is inactive, Mo2Ti2C3TX exhibits significant catalytic activity for both reactions. The addition of single Pt atoms on Ti3C2Tx leads to unusually high selectivity to 2-butene from butadiene hydrogenation [Mater. Today Catal. 2023, 2, 100010]. For CO2 hydrogenation, Pt/Ti3C2Tx shows a high Pt-molar activity and almost 100% selectivity to CO; Pt/Mo2Ti2C3TX is even more active, while methane and methanol are formed as minority products.

DS 16.3 Thu 15:45 A 053

Cobalt based MXene composites for the Oxygen Evolution Reaction — •Michelle Browne — Young Investigator Group Electrocatalysis: Synthesis to Devices, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, Berlin 14109, Germany

In the Electrocatalysis: Synthesis to Devices Group at HZB, our research is focused on combining MXenes and metal oxides to create the next generation Oxygen Evolution Reaction (OER) catalysts. Metal oxides are known to be active for the OER but lack high conductivity. On the other hand, MXenes are highly conductive but oxidise readily under several conditions due to its termination sites and don't contain OER active sites. To overcome these issues, we employ several strategies in our group to combine these two materials to make one material which is OER active and high conductive. Furthermore, by blocking the MXene termination sites with a metal oxide, this may lead to less oxidation of the MXenes structure. This presentation will focus on the development of Co-based MXene materials for the OER through various fabrication methods and combining Co with other metal oxide materials (e.g. CoCu and CoRu). The OER performance of the MXene/metal oxides composites compared to their parent materials will be discussed. We will also evaluate the various strategies to one another and how the initial activity and stability of the composite materials are affected.

15 min. break

Invited Talk DS 16.4 Thu 16:15 A 053

Ultrafast Photoexcitations in 2D MXenes — •Lyubov Titova — Worcester Polytechnic Institute, Worcester, MA, USA

MXenes are 2D transition metal carbides and nitrides with electronic properties that can be tuned by their chemistry and structure. Metallic-like conductivity, flexibility, high optical damage threshold and ease of processing owing to their hydrophilicity, make MXenes candidates for a host of electronic and optical applications. We use ultrafast optical and THz spectroscopic techniques to investigate the nature and behavior of photoexcitations in MXenes of different chemistries. We show that electronic and optical properties of MXenes can be engineered by choices of the transition metals and their order as well as by controlling the intercalants in the interlayer gaps. Furthermore, we demonstrate that MXenes with high free carrier density show promise as polarizers and tunable electromagnetic interference shields in the THz range.

DS 16.5 Thu 16:45 A 053

UV-to-IR Broadband Ellipsometry Characterization of Spray-Coated MXenes — •Andreas Furchner[1], Tetiana Hryhorchuk[2], Yury Gogotsi[2], and Tristan Petit[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — [2]Drexel University (Nanomaterials Institute), Philadelphia, USA

The chemical composition of MXenes determines whether they exhibit metal-, semi-metal- or semiconductor-like properties, which is important knowledge regarding optoelectronic applications. We employ broadband ellipsometry to characterize the optical and structural properties of spray-coated MXene layers of different chemical composition on silicon and glass substrates. Measuring from the deep-UV (200 nm) to the mid-infrared (25 μm) provides simultaneous access to the electronic and free-charge-carrier properties of the MXenes, as well as to their vibrational fingerprints. Furthermore, ellipsometry enables the quantification of layer thicknesses, roughnesses and film inhomogeneities. The results are corroborated by Vis microscopy and atomic-force-microscopy (AFM) measurements. The authors acknowledge support from the Federal Ministry of Education and Research in the framework of the project Catlab (03EW0015A/B) and funding from the U.S. National Science Foundation (Grant Number CHE-2318105, M-STAR CCI).

DS 16.6 Thu 17:00 A 053

2D to 3D weak localization dimensional crossover in $Ti_3C_2T_x$ MXene induced by thickness and defect engineering — •Sophia Tangui[1], Simon Hurand[1], Lola Loupias[2], Stéphane Célérier[2], Ayoub Benmoumen[1,3], Philippe Moreau[3], Marie-Laure David[1], and Vincent Mauchamp[1] — [1]Université de Poitiers, ISAE-ENSMA, CNRS, PPRIME, Poitiers France — [2]Université de Poitiers, CNRS, IC2MP, Poitiers, France — [3]Nantes Université, CNRS, IMN, Nantes, France

Due to their hydrophilic properties and very good metallic electrical behavior, MXenes are promising materials for numerous applications, including transparent conductive thin films. Therefore, there is a need to unravel the transport mechanism involved in MXene multilayers. Although weak localization (WL) has been proposed as the dominating low-temperature transport mechanism in thin films, there have been however few attempts to model quantitatively temperature and magnetic field dependent resistivity measurements.

In this talk, we will focus on the dimensionality of the low-temperature transport mechanisms in spin coated thin films elaborated with the most-studied and metallic $Ti_3C_2T_x$ MXene. The influence of the thin film thickness on one hand and of defects introduced by ion

irradiation at different fluences on the other hand is studied by low temperature and magnetic field dependant resistivity measurements. The data are analyzed in the framework of both 2D and 3D models : we will demonstrate a non-trivial evolution between the two behaviors and discuss the validity of both models.

DS 16.7 Thu 17:15 A 053

Non-Covalent Functionalized Schottky Interface at Ti3C2Tx/c-Si Van der Waals Heterojunction — •Eloi Ros Costals, Sergio Giraldo, Marcel Placidi, Cristobal Voz, Joaquim Puigdollers, Edgardo Saucedo, Zacharie Jehl Li Kao, and Kunal Tiwari — Electronics Engineering Department, Polytechnic University of Catalunya (UPC), Barcelona Spain

Synergistic interaction between 2D materials and organic molecules presents an additional dimension for tuning their intrinsic properties. Herein, we aim to finely tune the work function of 2D Ti3C2Tx MXene by introducing ultrathin interlayers of organic dipoles (O.D.) with a defined dipole moment value. Interface engineering is achieved through the inclusion of poly(ethylene)amine (PEI 0.1%) and third generation poly(amido-)amine (PAMAM G3), between the Ti3C2TX and c-Si. Charge transport properties of the fabricated Schottky diodes with a structure of c-Si/O.D./Ti3C2TX were evaluated through systematic analysis of the I-V and C-V characteristics. Our investigations reveal that diodes featuring O.D. as interlayers exhibit substantially reduced reverse saturation current density (J0) and enhanced built-in potential (Vbi). We also report a significant reduction in the work function value of Ti3C2Tx from 5.8 eV to 4.2 eV for Ti3C2Tx/PEI 0.1% and 3.3 eV for Ti3C2Tx/PAMAM-G3 heterostructures. On the basis of inferences drawn from photoemission spectroscopy we ascribe this to formation of oriented interfacial dipoles at the Ti3C2Tx/O.D. interface. Our study introduces an innovative approach for precisely controlling the work function of Ti3C2Tx through the incorporation of O.D.