



is the role of surface diffusion (*Energy Environ. Sci.*, doi:10.1039/C8EE01448E) that occurs concurrently with reaction and growth. Other exploratory opportunities are to scale up this mechanism to any current of interest and explore whether the

amorphous growth is a strict criterion for homogeneous deposition.

The research team is excited about examining the regimes of glassy electrochemical growth to enable anodes made of other metals. Given its correlation to small current

densities, (i.e., growth rate per unit area), one interesting possibility is to examine three-dimensional structures whose higher area-to-volume ratio can facilitate desired glassy growth for the same total current.

Aashutosh Mistry

Self-intercalation forms covalently bonded 2D transition-metal chalcogenide layers

A research team led by Kian Ping Loh and Stephen J. Pennycook of the National University of Singapore, as well as Xin Luo of Sun Yat-sen University, report a new class of metal chalcogenides in their article published in *Nature* (doi:10.1038/s41586-020-2241-9). These materials are transition-metal dichalcogenide bilayers sandwiching metal atoms covalently.

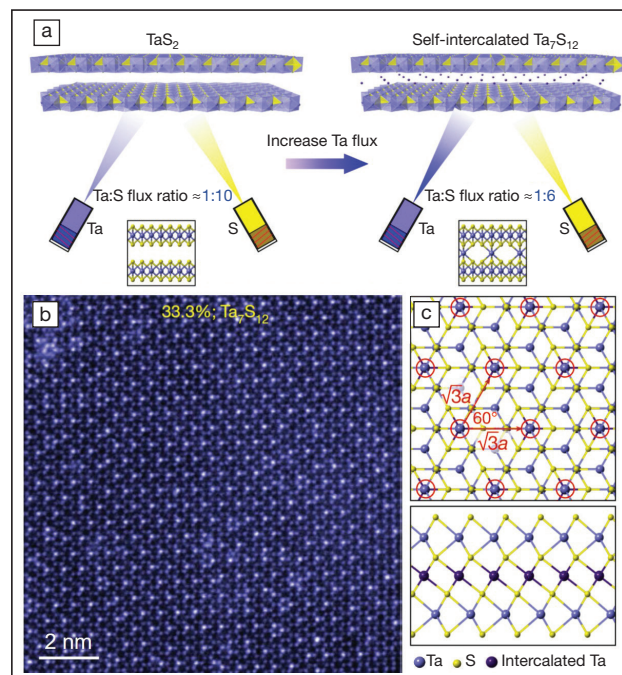
The layered structure of metal dichalcogenides enables the synthesis of novel materials. Typically, two-dimensional (2D) metal dichalcogenides are composed of nanosheets stacked together, in analogy to graphene. Adjacent layers are held together via weak van der Waals forces. The interlayer spaces can host guest species, including atoms and ions. Previous work focused primarily on introducing foreign ions or atoms within a single metal-chalcogenide layer, “but somehow, previous researchers missed considering the situation when the same metal atoms sit in between two layers,” says Xiaoxu Zhao, the lead author. The researchers decided to step into this unexplored area.

The research team modified the synthesis protocols involving molecular beam epitaxy (MBE) for synthesizing metal dichalcogenides. MBE is a gas-phase technique for growing highly uniform and crystalline thin films. The key to the synthesis of a new family of metal chalcogenides is to enhance the concentration of gaseous metal precursors intentionally. During the thin-film deposition, the additional metal atoms reside in the interstitial space between the as-formed metal dichalcogenide monolayers and formed covalent bonds with neighboring layers. For example,

increasing the Ta:S flux ratio from 1:10 (which formed conventional metal dichalcogenide, TaS_2) to 1:6 resulted in Ta-intercalated tantalum disulfide, Ta_7S_{12} . Changing the flux ratio was found to tune the stoichiometry to obtain other compounds, for example, Ta_9S_{16} and $\text{Ta}_{10}\text{S}_{16}$. Additionally, this strategy is also applicable to chemical vapor deposition, another common synthesis technique of metal dichalcogenides.

In some cases, the newly synthesized metal chalcogenides possess magnetic properties that their corresponding monolayer counterparts lack. The intercalated metal atoms located in the interstitial sites in the interlayer space can transfer electrons to the host layers, altering the electronic structure of the metal chalcogenides, rendering different magnetic behaviors. For instance, the newly synthesized Ta_7S_{12} is ferromagnetic, whereas its parental compound, TaS_2 , is non-ferromagnetic.

Babak Anasori of Indiana University–Purdue University Indianapolis believes that “adding covalent bonds between the flakes of transition-metal dichalcogenides will lead to new compounds with large available compositional space while keeping the thickness at ultrathin nanometer levels. This strategy might



Self-intercalation in TaS_2 crystals. (a) Scheme of the synthesis method, (b) atomic-resolution scanning electron microscopy–annular dark-field image, and (c) atomic model of Ta_7S_{12} . The bright dots in (b) and red circles in (c) highlight the location of intercalated Ta atoms. Credit: *Nature*.

[unveil] novel properties, including room-temperature, ambient-stable two-dimensional ferromagnets.” Anasori was not involved in this study.

Significantly, density functional theory predicts that besides Ta and S, transition metals of V, Cr, Mn, and Te, along with VI-A elements of S, Se, and Te, are feasible elements constituting the self-intercalated chalcogenides. Zhao says, “Owing to the versatility in the composition control, it is possible to tune, in one class of materials, properties that can vary from ferromagnetic to non-ferromagnetic and spin-frustrated Kagome lattices. This discovery presents a rich landscape of ultrathin three-dimensional materials that await the further discovery of new properties.”

Tianyu Liu