

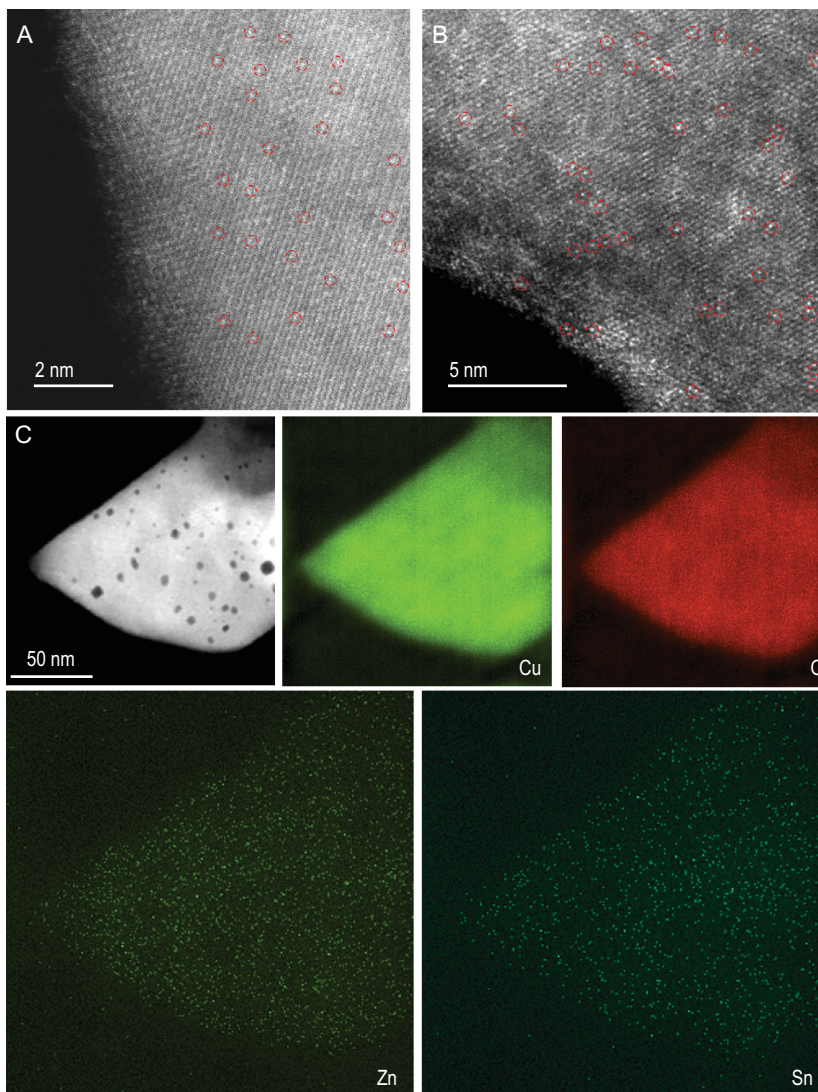
## Dual single-site catalyst promoter boosts catalytic performance

Bin Liu

Single-atom catalysts (SACs) have received great research interest because of their maximum atom-utilization efficiency and unique catalytic properties [1–5]. However, most of the reported SACs only focus on single-site active components, with rare reports studying catalyst promoters in their single-site forms [6–8]. Because promoters are essential components in many industrial catalysts, the exploration of the single-site promoters should be of great significance in catalysis, both in fundamental and application research. Similar to SACs, these single-site promoters have structural simplicity and homogeneity, and the synergistic effect on the catalytic reaction should be unique yet clarified.

Very recently, Ligen Wang and Limin Wang at the General Research Institute for Nonferrous Metal (GRINM), and Yongjun Ji and Fabing Su at the Institute of Process Engineering, Chinese Academy of Sciences, reported a new catalyst consisting of atomically dispersed Sn and Zn co-promoters on the CuO surface. As demonstrated, this catalyst exhibited a greatly enhanced promoting effect in the industrially important Rochow reaction for dimethyldichlorosilane synthesis.

The authors employed a facile hydrothermal method to synthesize  $\text{Sn}_1/\text{CuO}$  with abundant surface Cu vacancies. These cation vacancy defects generated by incorporating single-site Sn could be further utilized to anchor single-site Zn. Direct experimental results proved the successful loading of the two single-site promoters on the CuO surface (Fig. 1). X-ray photoelectron



**Figure 1.** (A) Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) image of  $\text{Sn}_1/\text{CuO}$ , (B) AC HAADF-STEM and (C) HAADF-STEM images as well as the corresponding energy-dispersive X-ray mappings of  $\text{Zn}_1\text{-Sn}_1/\text{CuO}$ . The bright dots marked with the red circles in images A and B indicate the single atom. The figure was obtained with permission from Ref. [8].

spectroscopy (XPS) measurements gave direct evidence that there existed strong interactions between single-site Sn and Zn promoters in this  $Zn_1-Sn_1/CuO$  catalyst, leading to a significant increase of the electron density on the Cu atoms in CuO. Density functional theory (DFT) calculations show that on the Sn-doped CuO(110) surface, the formation energy of Cu vacancy is 0.78 eV lower than that on the clean CuO(110), indicating that it is easier to form Cu vacancies in the Sn-doped surface. The calculation results also support that Zn prefers to fill in the nearby Cu vacancies caused by Sn doping to form Sn-Zn pairs.

Compared with conventional catalysts with promoters in the form of nanoparticles, this novel catalyst exhibits much higher activity, selectivity and stability in the synthesis of dimethyldichlorosilane via the industrially important Rochow reaction. The enhanced catalytic performance is attributed to the generated cooperative electronic interaction of single-site Sn and Zn with the CuO support, which further promotes the adsorption of reactant molecules. The authors demonstrated the obvious advantages of the single-site promoters, not only helping to elucidate

their real promotion mechanism in the catalytic reaction, but also opening up a new path to optimize catalyst performance. On one hand, the single-site promoters can maximize the catalytic interfaces between the promoter and the catalyst; on the other hand, the specific coordination between the single-site promoters and the catalyst can generate unique electronic properties, thereby promoting the catalytic reaction.

As two or more types of promoters are often used in one industrial catalyst, this work will stimulate research in single-site promoters in catalyst design and thus provide better understanding of the synergistic effect among various promoters. In a certain distance range, the multiple single-site promoters will have strong electronic interactions with the catalyst, which can optimize the electronic structure of the catalyst and thus change its surface adsorption properties. Therefore, it is believed that optimizing the distance between metal atoms is the key to achieving synergy of multiple single-site promoters. Moreover, as the catalyst support is the bridge of electronic interaction, the synergy is expected to be further optimized by adjusting the local microstructure of the catalyst support.

**Conflict of interest statement.** None declared.

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## MATERIALS SCIENCE

# Discovery of 2D van der Waals layered $MoSi_2N_4$ family

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Two-dimensional (2D) materials have attracted increasing interest since the first isolation of graphene from graphite in 2004 [1] and subsequent exfoliation of other 2D crystals from a variety of layered, van der Waals (vdW), materials [2]. For such crystals, atoms within each layer are connected by strong chemical bonds, while the adjacent layers are stacked with weak vdW forces. Therefore monolayers can be exfoliated from the three-dimensional (3D) layered crystals, also called the parent materials. So far, dozens of such 2D vdW materials have been

synthesized, such as graphene, *h*-BN, transition metal dichalcogenides and phosphorene [2–4]. The discovery of such 2D vdW materials has led to the observation of numerous exciting physical phenomena and exotic properties and already resulted in a number of intriguing applications. Furthermore, such 2D materials enable creation of a very broad class of artificial materials, vdW heterostructures, by layer-by-layer stacking in a designed sequence [3,4]. However, the structure of 2D vdW materials is essentially limited for those exfoliated

from the parent materials. Synthesizing 2D vdW materials without known 3D layered parents would provide a huge opportunity for engineering materials with new attributes and functionality.

Of all known 3D materials, the majority are non-layered, including metals, transition metal carbides/nitrides (TMC/TMN), metal dichalcogenides, metal oxides, III-V semiconductors and organic-inorganic perovskites. Different from the vdW materials, the atoms in non-layered materials are connected by strong chemical bonding in 3D