2-D ordered organic metal chalcogenides developed with widely tunable electronic band gaps

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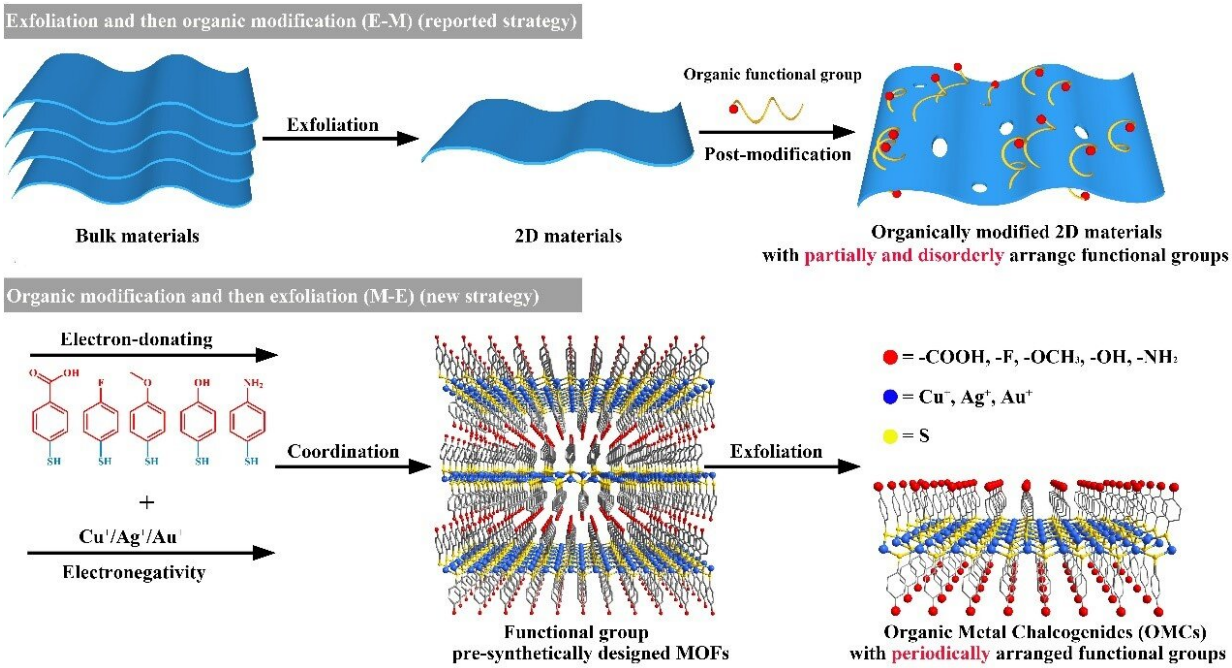

Schematic illustration of the research. Credit: Prof. XU's group

Two-dimensional (2-D) materials, which show excellent physical and chemical properties, have received unprecedented attention and become a research hotspot in scientific fields such as physics, chemistry and materials. Organic modification onto 2-D materials by covalently

bonding or physically adsorbing organic molecules can greatly regulate and optimize the properties of 2-D materials.
However, the organic modification methods reported so far are exfoliation first and then an organic modification (E-M) strategy, which usually possess some disadvantages such as less modification ratio, uncertain type, number and position of the functional groups, a tendency for defects and so on. Therefore, the development of functionalization of 2-D materials is greatly limited.

In a study published in *Nature Communications*, a research group led by Prof. Xu Gang from Fujian Institute of Research on the Structure of Matter (FJIRSM) of the Chinese Academy of Sciences developed a novel organic modification and then exfoliation (M-E) strategy to prepare 2-D organic metal chalcogenide (OMC) materials with tunable band gaps (0.83 eV) and electrical conductivities (9 orders of magnitude).

The researchers conveniently prepared the parent crystals with layered structures deriving OMCs by wet chemistry through the coordination between the metal ion and thiol ligand containing different uncoordinated para-substituted groups. They obtained OMCs by exfoliating their parent crystals into mono- or few-layer nanosheets.

Different from the 2-D materials modified by an E-M strategy, OMCs prepared by the M-E strategy are a series of homogeneous inorganic 2-D materials with periodically covalent bonding organic functional groups. This structure feature endows wide adjustments in the properties of OMCs by changing the metal centres and organic groups.

OMCs have unique 2-D graphene-like inorganic $\{Cu^{I}S\}\infty$, $\{Ag^{I}S\}\infty$ and $\{Au^{I}S\}\infty$ layer with sandwich modified functional group ($–NH_2$, –OH, $–OCH_3$, –F, or –COOH) which extends out from the inorganic layer. Hence, both surfaces of metal chalcogenide mono-layers are orderly and

fully covered by the predesigned functional groups.

Compared with the reported 2-D materials by an E-M strategy, OMC materials have the advantages of simple preparation, strong system expandability, functional group designable, and so on. OMCs have high thermal stability up to 300°C, and most OMCs also showed good chemical stability in pH ranging from 3 to 11 for >12 h.

In addition, the band gaps of OMCs can be high flexibility modulated by changing electronegativity of the metal ions or electron-donating ability of organic functional groups. The band gaps of OMCs are totally adjusted by 0.83 eV, which is the highest value reported to date achieved by all chemical methods.

The researchers calculated the thickness-dependent band structure of OMCs by density functional theory showing that OMCs are featured with nearly unchanged band gaps when decreasing layer number from bulk to single layer.

Besides, they found that the conductivity of OMCs can be modulated by changing the electronegativity of metal ions or electron-donating ability of organic functional groups. The conductivity of OMCs can be tuned over 9 orders of magnitude.

This study offers "organic modification first and then exfoliation (M-E) strategy" as an efficient approach for exploring new 2-D materials based on coordination self-assembly strategies.

More information: Yanzhou Li et al. Coordination assembly of 2D ordered organic metal chalcogenides with widely tunable electronic band gaps, *Nature Communications* (2020). DOI: 10.1038/s41467-019-14136-8

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