Hierarchical self-assembly of atomically precise nanoclusters

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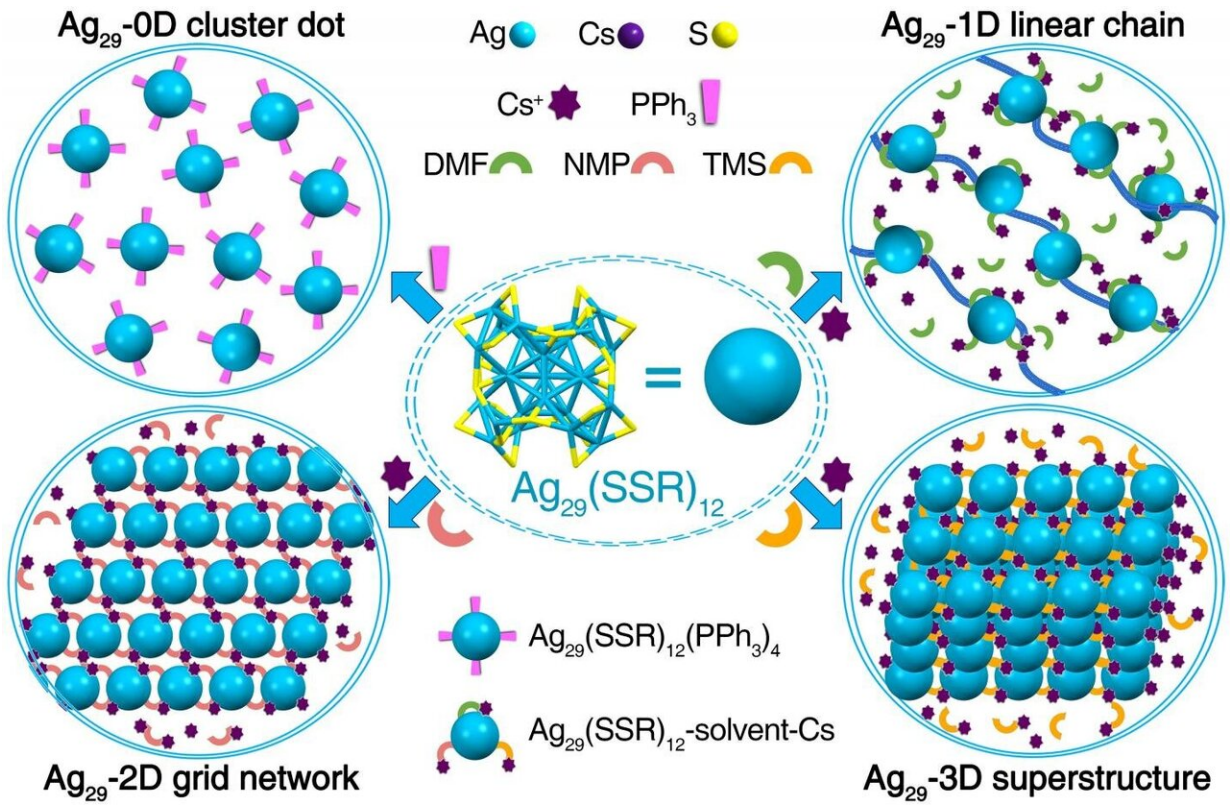

Scheme illustration of the 1-D-3-D assemblies of $Ag_{29(}SSR)_{12}$ nano-building blocks including Ag_{29}-0-D cluster dots in the presence of $_{PPh3}$, Ag_{29}-1-D linear chains (1-D array) in the presence of Cs^+ and DMF, Ag_{29}-2-D grid networks (2-D array) in the presence of Cs^+ and NMP and Ag_{29}-3-D superstructures (3-D array) in the presence of Cs^+ and TMS. Credit: Science China Press

Metal nanoclusters are an emerging class of modular nanomaterials owing to their atomically precise structures, fascinating properties, and potential applications. The subject of cluster-based supramolecular assembly represents one of the most dynamic areas and has emerged recently as a new "growth point" in nanocluster science. Such assemblies originate in different types of inter-cluster interactions such as chemical bonding, hydrogen bonding, electrostatic, van der Waals, π-π and C-H-π interactions.

On one hand, these cluster-based aggregates typically display enhanced performance (e.g., stability and fluorescence) relative to their constituent cluster building blocks, owing to the synergy from the cluster-linker-cluster assembly system. On the other hand, the precise structures of nanoclusters allow for the atomic-level understanding of inter-cluster interaction modes, and such knowledge further guides us to controllably constitute hierarchically assembled cluster-based nanomaterials. However, up to the present, the controllable assembly of cluster nano-building blocks in different arrays remains challenging.

In a new paper published in the *National Science Review*, scientists at Anhui University (China) and Nanjing University (China) reported the hierarchical self-assembly of atomically precise nanoclusters. On the basis of the Ag_{29} $(SSR)_{12}$ cluster nano-building framework (where SSR is 1,3-benzene dithiol), Professor Manzhou Zhu and his coworkers selectively constructed cluster-based 1-D linear chains, 2-D grid networks, and 3-D superstructures in the presence of different solvent-conjoined Cs^+ cations. Crystal structures of these cluster-based assemblies have been successfully determined. The hierarchical self-assembly of these Ag_{29} $(SSR)_{12}$ nano-building blocks has not only been observed in their crystalline state, but also in their amorphous state, with the help of the aberration-corrected HAADF-STEM (high angle annular dark field scanning transmission electron microscope).

"Such Ag_{29}-based assemblies manifest distinguishable optical absorptions and emissions in both solutions and crystallized films; such differences originate from their different surface structures and crystalline packing modes," they state, "Furthermore, the surface areas of these cluster-based assemblies are evaluated, the maximum value of which occurs when the cluster nano-building blocks are assembled into 2-D arrays. The 2-D-array assembly endows the best gas storage capability of these cluster-based frameworks."

"This work presents an exciting example of the hierarchical assembly of atomically precise nanoclusters by simply controlling the adsorbed molecules on the cluster surface," they add, "and we believe that this work will shed light on more future works touching upon the supramolecular chemistry of metal nanoclusters."

More information: Xiao Wei et al, Hierarchical structural complexity in atomically precise nanocluster frameworks, *National Science Review* (2020). DOI: 10.1093/nsr/nwaa077

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