Sequential synthesis of a 2D metal-covalent organic framework

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On-surface synthesis (OSS) is emerging as a powerful bottom-up strategy for the fabrication of atomically precise organic nanoarchitectures. It has demonstrated remarkable success in the synthesis of a plethora of graphene nanoribbons (GNRs) [1], a few 2D covalent organic framework (COF) structures [2,3], and even more seldom 2D metal covalent organic frameworks (MCOF) [4]. The 2D nanoarchitectures can be obtained either by following a direct 2D synthetic approach, or a sequential approach that involves the generation of 1D components that subsequently couple giving rise to 2D nanostructures. This is the case of nanoporous graphene (NPG) structures that can be obtained by the lateral fusion of GNRs [5,6,7].

Here we extend the sequential strategy to synthesize 2D MCOF by the metalation of the pores of an NPG that acts as the COF matrix. The whole sequence consists of i) polymerization of precursor monomers by Ullmann coupling; ii) formation of GNRs by cyclodehydrogenation of the polymers; iii) formation of NPG by dehydrogenative coupling of GNRs; and iv) metalation of the NPG pores by dehydrogenative coordination of Au adatoms that originate from the underlying Au(111) surface. High-resolution scanning tunneling microscopy provides direct atomic-scale visualization of the incorporated Au atoms, providing insight into the structural and electronic properties.

We discuss the opportunities and limitations of this strategy, including pore selectivity, metal stabilization, and the impact of single-atom incorporation on the electronic structure of the graphene framework. The resulting multifunctional nanoarchitectures establish a versatile platform for graphene-based devices, with potential applications in single-atom catalysis (e.g., CO oxidation and CO_2 reduction) and chemical sensing.

References

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