A mix-and-match toolkit transforms simple nanoparticle synthons into complex derivatives

Complex heterostructured nanomaterials with precisely defined materials and interfaces are important for many applications. However, rationally incorporating such features into nanoparticles with rigorous morphology control remains a synthetic bottleneck, particularly for particles less than 100 nm in size. We define a modular divergent synthesis strategy that progressively transforms simple nanoparticle synthons into increasingly sophisticated products. Subsequent manipulation of these intraparticle frameworks yielded a library of 50+ distinct heterostructured metal sulﬁde derivatives, including particles that contain asymmetric, patchy, porous, and sculpted nanoarchitectures. This generalizable mix-and-match strategy provides predictable retrosynthetic pathways to complex nanoparticle features that are otherwise inaccessible.

Formation of an Intraparticle Framework
We begin with three different morphologies of Cu$_2$S: 0D spheres, 1D rods, and 2D plates. Under conditions that promote cation exchange with Zn$^{2+}$ and Cd$^{2+}$, we intentionally arrest these reactions prior to the complete replacement of the Cu$^{2+}$ cations, and observe the formation of new, embedded interfaces on multi-component ZnS–Cu$_2$S or CdS–Cu$_2$S nanostuctures that maintain the silhouette of the initial seed particle. Adjusting the reaction time tunes the extent of reaction, resulting in a library of particles with a tunable intraparticle framework of interfaces. The differing behavior of ZnS and CdS is attributed to the close relationship between the Cu$_2$S starting crystal structure and the wurtzite-type product phases, all of which contain a similar, hexagonal anion substructure.

Domain-Selective Exchanges Preserve Programmed Network of Interfaces
By using exchange conditions that selectively replace the remaining Cu$_2$S with Zn$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Mn$^{2+}$, or Ni$^{2+}$, we expand the library of integrated materials and accessible interfaces into our programmed frameworks to include ZnS, CdS, CoS, MnS, and NiS$_2$. In so doing, we replace all of the remaining Cu$_2$S on the particle, using this material as convenient, easily-synthesized synthons only to deﬁne the overall morphology of the structure.

Integration of Additional Synthetic Steps
The intraparticle frameworks produced in the first two steps of our process can be combined with a variety of existing nanosynthetic strategies, including orthogonal exchange reactions, selective deposition, and chemical etching. These steps allow integration of additional material components, as well as the ability to generate patchy, porous, and asymmetrically decorated architectures.

Crystallographic Regioselectivity Observed Through Multiple Sequential Exchange Reactions on Spheres and Rods
Using sequential, partial exchange reactions, we can produce distinct CdS–ZnS–Cu$_2$S nanosphere and nanorod isomers, among the most complex ever reported. As additional domains are added, the observed exchange behaviors of Zn$^{2+}$ and Cd$^{2+}$ are still governed by a tendency to form low-strain interfaces between domains. On nanorods, the crystallographic preferences can be temporarily supressed by the characteristic surface energy differences present in anisotropic structures, resulting in initial tip exchange for both cations.

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