Heterostructured Intermetallic Janus System with Atomic Precision

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Resolving Janus nanoclusters with atomic precision paves the way for future preparation and application of heterostructured intermetallic Janus systems.

Janus nanoarchitectures, an emerging class of nanostructures, named after the Roman god with two faces, are a fascinating class of nanomaterials with promising applications in various areas, including catalysis, optical imaging, and so on. Although matter with structural and chemical homogeneity tends to display high stability owing to the low entropy, its heterogeneous counterpart is also attractive because of the high reactivity arising therefrom. To date, several bimetallic Janus nanocrystals have been fabricated; however, the atomic-level investigation of their structure−property correlations remains highly challenging due to two intrinsic characteristics: ununiform sizes and imprecise surface chemistry. In this issue of ACS Central Science, Shuang-Quan Zang and co-workers have structurally resolved Janus nanoarchitectures at the atomic level and mapped out their interfacial linkages and the synergistic effect.

In this work, four Janus nanoclusters, including racemate Au₈Cu₄, R/S-Au₈Cu₄ enantiomers, and racemate Au₃Cd₁, costabilized by thiol and phosphine ligands, were controllably synthesized and structurally determined, serving as research templates to resolve fundamental issues of asymmetric bimetallic Janus nanocrystals. Structurally, these four alloy nanoclusters perfectly reflected the two-face characterization of Janus architectures (Figure 1a−e): the gold sides are stabilized by phosphine ligands (i.e., PPh₃, BINAP, and DPPM), whereas the transition metal copper/cadmium sides are anchored by thiol ligands (i.e., MNT). In addition, the six achiral PPh₃ ligands in racemate Au₈Cu₄ could be substituted by diphosphine BINAP ligands, and the postmodified synthesized R/S-Au₈Cu₄ nanocluster enantiomers exhibited obvious chiroptical properties. By analyzing the density functional theory calculation results of the Au₈Cu₄ nanocluster, the authors demonstrated that the Au−Cu interaction may play a critical role in forming the Janus nanocluster, and the lattice adaptability from the protecting thiol/phosphine ligands induced asymmetric growth. In addition, the dipolar distribution of Au/Cu bicomponents in Au₈Cu₄ led to a maximum dipole moment up to 45 D (Figure 1f,g), which further drove the self-assembly of Au₈Cu₄ nanocluster molecules into one-dimensional nanowires (Figure 1h,i).

Through the continuous accumulation of synthetic experience and advances in analytical methods, metal nanoclusters can now easily be tailored to desired composition and morphology. The concept of alloying has been extensively exploited in dictating the geometric/electronic structures.

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and customizing the chemical/physical properties of metal nanoclusters. In most alloying cases, the active alloying sites tend to have more equal distributions in metallic skeletons of metal nanoclusters (Figure 2a). For example, the incorporated Ag heteroatoms prefer to occupy the icosahedral kernel surface with a uniform pattern in \( \text{Ag}_{x}\text{Au}_{25-x}(\text{SR})_{18} \), \( \text{Au}_{x}\text{Ag}_{25-x}(\text{SR})_{5}(\text{PPh}_3)_{10}\text{Cl}_2 \) and \( \text{Au}_{x}\text{Ag}_{25-x}(\text{SR})_{18}(\text{PPh}_3)_4 \) nanoclusters. (b) Structural and chemical heterogeneity in several Janus nanoclusters with high reactivity, such as \( \text{Au}_{3}\text{Cd}_1 \) nanoclusters. Reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.

The equal distribution of heterometals in these commonly researched alloy nanoclusters is reasonable because the structural and chemical homogeneity should reduce the entropy value of a cluster system and produce an alloy nanocluster with high stability. Such a tendency is in line with the expressions of “life feeds on negative entropy” and “survival of the fittest”.7,8

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**Figure 1.** (a) Scheme illustration of the bimetallic Janus structures of the obtained nanoclusters. (b, c) Structures of the racemate \( \text{Au}_{x}\text{Cu}_{4} \) and \( \text{Au}_{x}\text{Cd}_1 \) nanoclusters. (d, e) Structures of R/S-\( \text{Au}_{x}\text{Cu}_{4} \) enantiomers. Color legends: orange sphere, Au; turquoise sphere, Cu; indigo sphere, Cd; pink sphere, P; yellow sphere, S; blue sphere, N; green sphere, Cl; gray sphere, C. Hydrogen atoms are omitted for clarity. (f, g) Directions and values of the dipole moment of \( \text{Au}_{x}\text{Cu}_{4} \) nanoclusters. Reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.

**Figure 2.** (a) Structural and chemical homogeneity in several alloy nanoclusters with high stability, such as \( \text{Ag}_{x}\text{Au}_{25-x}(\text{SR})_{18} \), \( \text{Ag}_{x}\text{Au}_{25-x}(\text{SR})_{5}(\text{PPh}_3)_{10}\text{Cl}_2 \) and \( \text{Au}_{x}\text{Ag}_{25-x}(\text{SR})_{18}(\text{PPh}_3)_4 \) nanoclusters. (b) Structural and chemical heterogeneity in several Janus nanoclusters with high reactivity, such as \( \text{Au}_{3}\text{Cu}_4 \) and \( \text{Au}_{3}\text{Cd}_1 \) nanoclusters. Reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.
Janus nanoclusters, on the other hand, exhibit structural and chemical heterogeneity. The asymmetrical structures endow these Janus nanoclusters with distinctively chemical-physical properties owing to the emerging large dipole moments, in addition to the synergistic effect between different metal components. In addition, the high reactivity of Janus nanomaterials originating from their dynamically unfavorable characterization makes them well-suited as optical devices or nanocatalysts. In this work, the Janus Au₈Cu₄ nanoclusters displayed high surface energy and were self-assembled into cluster-based nanowires with the driving force of their inherent bipolar phase and intercluster dipole interactions. In addition, the photocurrent response properties of such Janus nanoclusters were excellent, manifesting good photogenerated electron/hole pair generation and separation efficiencies.

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However, the bottom-up synthesis of Janus nanoclusters remains highly challenging since they are dynamically unfavorable and require a delicate interplay balance between entropy and enthalpy. Shuang-Quan Zang and co-workers prepared such Janus nanoclusters by using mixed ligands with different metallic affinities and electronegativities of the substituents. We envision that such a controllable method (i.e., mixed ligands stabilizing noble/transition metals) will allow for the efficient fabrication of more atomically precise Janus nanostructures in the near future.

In summary, the four reported Au–Cu or Au–Cd Janus nanoclusters reported by Shuang-Quan Zang and co-workers resolved several fundamental issues at the atomic level, including the interfacial linkages and the synergistic effects in Janus nanoarchitectures. The new findings provide atomic-level clues for understanding the heterogeneous architectures of Janus nanomaterials. In addition, such new findings will hopefully pave the way for the future fabrication of heterostructured intermetallic Janus systems for several downstream applications in optics and catalysis.

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