Noble metal nanomaterials have been the subject of extensive research interest owing to their unique properties associated with various promising applications. In the past two decades, tremendous effort has been devoted to fine-tuning the size, shape, dimension and chemical composition of noble metal nanocrystals, as these are vital parameters affecting their properties [1]. Recent experimental studies have revealed that the crystal phase of noble metal nanocrystals can also significantly affect their physicochemical properties and applications [2]. Therefore, besides the well-established strategies in size, shape, dimension and composition control based on kinetic and/or thermodynamic studies, the rise of crystal-phase-controlled synthesis of noble metal nanocrystals will open up new opportunities to further modulate their physicochemical properties, thus shedding new light on their potential applications. However, the crystal-phase-controlled synthesis of noble metal nanocrystals still remains underdeveloped and challenging, because noble metals tend to crystallize into their thermodynamically stable phases due to the strong metallic interactions between atoms [2]. The traditional methods to obtain some novel crystal phases in noble metal nanocrystals are physical deposition and post-synthesis phase transformation [3]. However, physical deposition has a limited choice of materials and it usually produces supported thin films, which have very limited applications compared with free-standing colloidal nanomaterials. As for phase transformation, it is usually realized under extreme conditions, such as high pressure and high temperature, which may induce the aggregation/degradation of noble metal nanostructures, thus causing negative effects on their corresponding properties and applications. In comparison, wet-chemical synthesis methods can produce a large variety of colloidal nanomaterials with good uniformity and tunability; the adoption of these methods is thus highly desirable in the preparation of noble metal nanocrystals with unusual crystal phases [3].

Zhang’s group at Nanyang Technological University have recently done some pioneering research work and made some important progress in the crystal-phase-controlled synthesis of novel noble nanomaterials by wet-chemical methods, including Au nanosheets with hexagonal close-packed (hcp) phase, Au nanoribbons with 4H structure and bi/tri-metallic nanocomposites based on hcp Au nanosheets and 4H Au nanoribbons [2,4]. In the latest review, they summarized the synthesis methods and unique characteristics of the noble metals with novel crystal phases, e.g. Au, Ag, Ru and Rh. Meanwhile, various factors in the wet-chemical syntheses were discussed in detail, including size effect, surface configuration, template effect, growth kinetics, surface/internal stress, and epitaxial strain [3]. Recently, in order to investigate the effects of crystal phase on the nucleation and seeded growth in the preparation of novel heterometallic nanomaterials, thus exploring their crystal-phase-dependent properties and applications, Zhang’s group conducted systemic studies and reported a new strategy for the synthesis of binary and ternary hybrid noble metal nanostructures [5]. They used pre-synthesized crystal-phase-heterostructured 4H/fcc (face-centered cubic) Au nanowires (NWs) as seeds to epitaxially grow Ru nanorods (NRs) (Figs 1 and 2a–d). Statistical data show that these NRs can only grow on the 4H phase (ca. 83.3%) and fcc-twin boundary (ca. 16.7%) in 4H/fcc Au NWs, indicating that the 4H structure and fcc twins could serve as preferential nucleation sites for the hetero-epitaxial growth of the second metal. Moreover, in the synthesized bimetallic NWs, the Ru NRs with highly active 4H or fcc-twin structures could serve as nucleation sites for the further growth of a third metal, such as Rh or Pt, thus forming Au–Ru–Rh (Fig. 2e–h) and Au–Ru–Pt hybrid NWs. As a proof-of-concept application, the obtained Au–Ru NWs are used as electrocatalysts for the hydrogen evolution reaction (HER) in alkaline media, exhibiting superior electrocatalytic activity compared to Pt/C, Ru/C and most of the reported electrocatalysts. These findings demonstrate the significant advances in crystal-phase engineering in the rational design and controlled synthesis of novel heterometallic nanomaterials, which may result in much improved properties.

Figure 1. Schematic illustration of the synthesis of a Au–Ru NW. After the 4H/fcc Au NW is synthesized, it is used as a seed for the crystal-phase-based epitaxial growth of Ru NRs. The black dashed line labels the fcc-twin boundary. The partial enlarged sectional view illustrates the epitaxial growth of Ru NR on the Au NW. The growth direction of Ru NRs on the Au NW is [1100]Au. Reprinted with permission from Ref. [5].
Figure 2. a: Transmission electron microscopy (TEM) image of synthesized Au–Ru NWs. b: High-angle annular dark-field scanning TEM (HAADF–STEM) image of a Au–Ru NW. b1 and b2: Fast Fourier transformation (FFT) images taken from the two green dashed squares (areas b1 and b2) in b. c: Integrated pixel intensities of Au (taken from the red solid rectangle in b) and Ru (taken from the green solid rectangle in area b1 in b) along the arrow directions ([0004]_{4H} directions), which are perpendicular to the (0004)_{4H} facets. d: Scanning TEM (STEM) elemental mapping of a Au–Ru NW. e: TEM image of synthesized Au–Ru–Rh NWs. f: HAADF–STEM image of a Au–Ru–Rh NW. f1 and f2: FFT images taken from the corresponding two dashed squares (areas f1 and f2) in f. g: Integrated pixel intensities of Au (taken from the red solid rectangle in area f2) and Rh (taken from the yellow solid rectangle in area f1) along the arrow directions ([0004]_{4H} directions), which are perpendicular to the (0004)_{4H} facets. h: STEM elemental mapping of the Au–Ru–Rh NW. Reprinted with permission from Ref. [5].

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