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Multiply-twinned intermetallic AuCu pentagonal

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Monodispersed intermetallic AuCu pentagonal nanorods with controlled size and composition have been developed by a seed-mediated growth route. The AuCu/C nanomaterial catalyzed the coupling reaction of sulfonamide with benzyl alcohol in good to excellent yields.

Nanorods with shape anisotropy have received much attention due to their promising applications in electronics,^{1,2} biomedicine,^{3,4} chemical sensing, imaging,⁵ and catalysis.⁶⁻⁸ Among different types of nanorods, the pentagonal nanorods possess a unique morphology, which have many interesting composition- and shapedependent properties, such as excellent stability and high catalytic activity.9-11 Their enhanced catalytic performance is attributed to the higher activity of the surface atoms on the twins of multiply-twinned particles (MTPs).¹²⁻¹⁴ Pentagonal nanorods of one or two metals have been successfully developed in the past decade.¹⁵ Murphy and co-workers prepared a high yield of Au pentagonal nanorods in aqueous solution by a seed-mediated growth method from multiply-twinned decahedral Au nanoparticles, and postulated a general mechanism for the pentagonal nanorod growth.^{16,17} These Au pentagonal nanorods showed improved plasmonic properties. For bimetallic pentagonal nanorods, Song and co-workers have developed Ag-Au-Ag heterometallic nanorods through directed anisotropic growth from gold decahedrons.18

Bimetallic AuCu nanoparticles with tunable sizes and compositions offer a broader control over properties than single metallic nanoparticles.^{19–21} Spherical intermetallic AuCu multiply-twinned nanoparticles have been successfully synthesized by a seed-based diffusion route.²⁰ However, shape-controlled growth of AuCu nanoparticles has been rarely reported in the literature.^{22,23} It appeared to be very difficult due to complications in the solution phase and the tendency of self-purification. Liu and Walker have reported monodispersed Au–Cu nanocubes with controllable sizes and compositions.¹⁹ To the best of our knowledge, the synthesis of AuCu pentagonal nanorods has remained a great challenge because of the distinct reduction rates and the lattice mismatch of the different components, which would be quite different from the reported Au and Au–Ag pentagonal nanorods with similar lattice parameters.^{24–26}

Herein, for the first time, we report a facile approach to synthesize monodispersed AuCu pentagonal nanorods with controlled sizes and compositions by elongating the multiply-twinned Au decahedrons in the oleylamine solution containing the Cu precursor (shown in Scheme S1, ESI†). The simultaneous alloying of Au and Cu resulted in the growth of the AuCu nanorods. We also evaluated the catalytic activity of the AuCu nanorods in a carbon–nitrogen (C–N) coupling reaction. Our heterogeneous catalysts exhibit high catalytic activity towards the C–N coupling reaction with excellent recyclability.

For a typical synthesis of multiply-twinned intermetallic AuCu pentagonal nanorods, a simple one-pot reaction was first employed to synthesize Au decahedral nanoparticles, which were subsequently used as seeds for the formation of AuCu pentagonal nanorods. Briefly, a solution of 93 mg of HAuCl₄·3H₂O in 10 mL of oleylamine was heated at 110 °C for 4 h under nitrogen flow with rapid magnetic stirring. To prepare AuCu pentagonal nanorods, the above Au colloidal solution was heated to 280 °C at a rate of ~ 20 °C min⁻¹, and then 60 mg of Cu(acac)₂ was added quickly. The mixture was kept at 280 °C for 1 h under nitrogen flow with magnetic stirring. The as-prepared colloidal solution was then cooled to room temperature, and the nanoparticles were precipitated, washed with methanol and re-dispersed in non-polar organic solvents (*e.g.* toluene, hexane and chloroform).

The transmission electron microscopy (TEM) image shows that the as-prepared Au nanoparticles have an average diameter of 10.0 \pm 0.8 nm (Fig. S1A, ESI[†]). The multiply-twinned decahedral structure of the nanoparticles was confirmed by the high-resolution TEM (HRTEM) image (Fig. S1B, ESI[†]). These Au decahedra were then used as seeds for the formation of AuCu nanorods.

When a Au/Cu atomic ratio of 1:1 was used (denoted as AuCu), the synthesized nanoparticles were nearly uniform pentagonal nanorods with an average size of ~ 15 nm in length and ~ 12 nm in diameter (shown in Fig. 1A). The HRTEM image (Fig. 1B) revealed

Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos,

Singapore 138669, Singapore. E-mail: jyying@ibn.a-star.edu.sg; Fax: +65 6478-9020 † Electronic supplementary information (ESI) available: Experimental protocols; synthesis scheme; TEM and HRTEM images of Au, Cu, AuCu₃, and Au@Cu nanoparticles; XPS spectra; ultraviolet-visible (UV-Vis) spectra and coupling reactions of AuCu nanorods. See DOI: 10.1039/c3cc47254j



Fig. 1 (A) TEM, (B, C) HRTEM, and (D) HAADF-STEM images of AuCu pentagonal nanorods. Cu and Au elemental profiles along the (E) red and (F) blue lines, respectively, across the AuCu nanorod shown in (D). (G) SAED pattern of the AuCu nanorods.

that the synthesized nanoparticles were predominantly multiplytwinned with a pentagonal nanorod morphology. The ends of the nanorods still retained the same structure as the Au decahedral seeds as shown in Fig. 1C. An arbitrary single particle specified in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image is shown in Fig. 1D. Furthermore, as shown in Fig. 1E and F, the signals of Au and Cu were detected across the entire particle along its length and width, which confirmed that the nanoparticle was indeed composed of Au and Cu across the entire particle. The AuCu particles were obtained via the rapid interdiffusion of metal atoms as a result of the elevated temperature, and the large number of interfacial vacancy defects.^{20,27} The XRD pattern of the nanorods corresponded to the AuCu intermetallic phase (JCPDS 65-2798) (see Fig. 2C), which was confirmed by the selected area electron diffraction (SAED) pattern (Fig. 1G). The energy dispersive X-ray (EDX) spectroscopy analysis showed that the AuCu nanorods have a Au/Cu atomic ratio of 47:53 (Fig. S2A, ESI[†]), which was in close agreement with the precursor composition employed. Peak deconvolution of the Cu 2p X-ray photoelectron spectroscopy (XPS) confirmed the zero valence of Cu in the AuCu nanorods (Fig. S3, ESI[†]). The peak position of the surface plasmon resonance of the AuCu nanorods remained stable, and no color change was noted in the AuCu nanorods solution after one month (Fig. S4, ESI⁺). In contrast, a significant red shift of the Cu nanoparticles solution (Fig. S4, ESI⁺) was observed, with a color change from red to green. This illustrated the excellent stability of Cu in the AuCu nanorods.

TEM showed that the side surface of the AuCu pentagonal nanorods was the $\{100\}$ face and multiply twinned between faces (Fig. S6B, ESI[†]), while the two ends of the AuCu nanorods have the same $\{110\}$ and $\{111\}$ faces (Fig. S6C, ESI[†]) as the decahedral Au seeds (Fig. S6A, ESI[†]). This indicated that the intermetallic AuCu pentagonal nanorods were directly grown from well-defined multiply-twinned decahedral Au seeds by elongating the $\{100\}$ face. Oleylamine is required to form the AuCu pentagonal nanorods, presumably to stabilize the faces during anisotropic growth, where Cu deposition on Au decahedral seeds led to the formation of high-energy surfaces such as the $\{100\}$ faces (Fig. S6B, ESI[†]). Cu could



Fig. 2 XRD reference lines of (A) Au (JCPDS 65-2870) and (B) Cu (JCPDS 85-1326). (C) XRD pattern of AuCu pentagonal nanorods and XRD reference lines of AuCu (JCPDS 65-2798). (D) XRD pattern of AuCu₂ pentagonal nanorods. (E) XRD pattern of AuCu₃ pentagonal nanorods and XRD reference lines of AuCu₃ (JCPDS 35-1357).

grow along the {111} and {110} faces (Fig. S6C, ESI[†]) with oleyamine blocking the high-energy {100} surface (Fig. S6D, ESI[†]). The anisotropic growth mechanism for AuCu pentagonal nanorods was consistent with those of AuAg nanorods, whereby the nanorods were directly grown from well-defined multiply-twinned decahedral Au particles.^{8,9,18} However, the growth of the AuCu pentagonal nanorods involved the formation of the AuCu intermetallic phase. The growth mechanism was different from that reported for the heterometallic AuAg nanorods.

The length of the pentagonal nanorods was controlled by the amount of Au seeds at a fixed Cu precursor concentration during synthesis. For a Au/Cu atomic ratio of 1:2, pentagonal nanorods denoted as AuCu₂ were obtained with a uniform length of \sim 19 nm, and a similar diameter of \sim 12 nm as that of the AuCu nanorods (Fig. 3A). Although the length of the nanorods increased from \sim 15 nm to \sim 19 nm when the Au/Cu atomic ratio was increased from 1:1 to 1:2, the multiply-twinned {100} faces on the side and the {110} and {111} faces at the two ends of the nanorods remained unchanged (Fig. S6B and C, ESI†). Fig. 3F and G confirmed that the AuCu₂ nanorods have a uniform Au and Cu profile across the entire particle. The powder XRD pattern of AuCu₂ nanorods (Fig. 2D) appeared to consist of (i) a set of peaks that were intermediate of the AuCu intermetallic phase (JCPDS 65-2798) and the AuCu₃ intermetallic phase (JCPDS 35-1357), and (ii) a set of peaks associated with Cu (JCPDS 85-1326), suggesting the segregation of a separate Cu phase. The surface plasmon resonance of AuCu₂ nanorods solution remained stable after one month (Fig. S4, ESI†). By further decreasing the ratio of Au:Cu to 1:3, pentagonal nanorods termed AuCu3 were obtained with a greater length $(\sim 24 \text{ nm})$ and a similar diameter of $\sim 12 \text{ nm}$ (Fig. S7, ESI⁺). These nanorods showed an XRD pattern that corresponded to the AuCu₃ intermetallic phase (JCPDS 35-1357) (Fig. 2E).

In order to further understand the growth mechanism, we also studied the effect of the capping agent on the formation of AuCu nanoparticles. In a strong capping agent, such as oleic acid/tri-*n*-octylamine solution,²⁰ spherical multiply-twinned



Fig. 3 (A) TEM, (B, C) HRTEM, and (D) HAADF-STEM images of AuCu₂ pentagonal nanorods. (E) EDX spectrum of a single AuCu₂ nanorod specified in (D). Cu and Au elemental profiles along the (F) red and (G) blue lines, respectively, across the AuCu₂ nanorod shown in (D).

AuCu nanoparticles with a monodispersed size distribution ($\sim 14 \text{ nm}$) were obtained under the otherwise similar synthesis conditions as those for the AuCu pentagonal nanorods (Fig. S8, ESI†). The formation of spherical MTPs instead of pentagonal nanorods in the solution of strong capping agents could be due to unselective adsorption of the capping agents on the different seed faces.

Besides the capping agents, the synthesis temperature also played an important role in the anisotropic growth of the pentagonal nanorods. At a lower synthesis temperature of 180 °C, spherical core–shell Au@Cu nanoparticles were obtained with a Au/Cu atomic ratio of 1:1. The core–shell Au@Cu structure was confirmed by the EDX spectroscopy analysis of an arbitrary single particle marked in the HAADF-STEM image (Fig. S9(C), ESI†). The HRTEM image (Fig. S9(B), ESI†) revealed that the Au@Cu nanoparticles with diameters of ~12 nm were multiply twinned with a decahedral morphology.

The alkylation of amines with alcohols via the hydrogenborrowing strategy is an attractive synthetic methodology for the C-N bond formation as it is an atom economical and environmentally friendly process with water as the only reaction byproduct. AuCu nanorods were dispersed on a carbon support (AuCu/C), and examined as a catalyst for the amination of alcohols *via* the hydrogen-borrowing methodology^{28,29} with p-toluenesulfonamide and benzyl alcohol as the model substrates. Using a catalyst loading of 1 mol% Cu and 20 mol% K₂CO₃ as the base, the coupling reaction proceeded smoothly at 120 °C in air, and the desired product was obtained in 88% isolated yield after 15 h (Table S1, entry 1, ESI⁺). Very little or no product was formed in the absence of the base or the catalyst (see Table S1, entries 2-4, ESI[†]). This heterogeneous catalyst was successfully recycled 4 times without a reduction in the catalytic activity (Table S2, ESI[†]). The average particle size of the AuCu nanorods increased to 17-20 nm after the coupling reaction according to TEM images (Fig. S10, ESI[†]). The AuCu/ C catalyst was also active for the alkylation of different types of substituted sulfonamides and alcohols (see Table S3, ESI⁺).

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Good to excellent yields (71–98%) were obtained for substituted benzyl alcohols or sulfonamides with either electron-donating or electron-withdrawing substituents in the substrates.

In conclusion, monodispersed AuCu pentagonal nanorods with controlled size and composition were successfully synthesized by seed-mediated growth using oleylamine. AuCu pentagonal nanorods were grown from well-defined multiply-twinned Au decahedral seeds. With the growth of pentagonal nanorods, the intermetallic AuCu phase was formed. The length and composition of the AuCu pentagonal nanorods could be controlled by changing the amount of Au decahedral seeds at a fixed Cu precursor concentration. The strength of capping agents and synthesis temperature were key factors in the formation of AuCu pentagonal nanorods instead of spherical MTPs. AuCu nanorods demonstrated very good catalytic activity in C–N coupling reactions with *p*-toluenesulfonamide and benzyl alcohol as the model substrates at a fairly low reaction temperature.

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