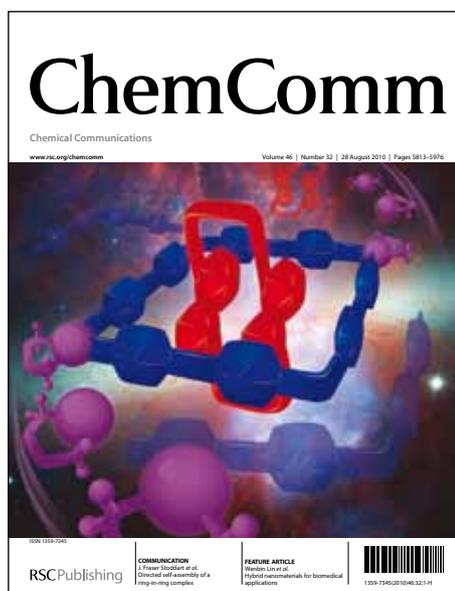


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# Multiply-Twinned Intermetallic AuCu Pentagonal Nanorods<sup>†</sup>

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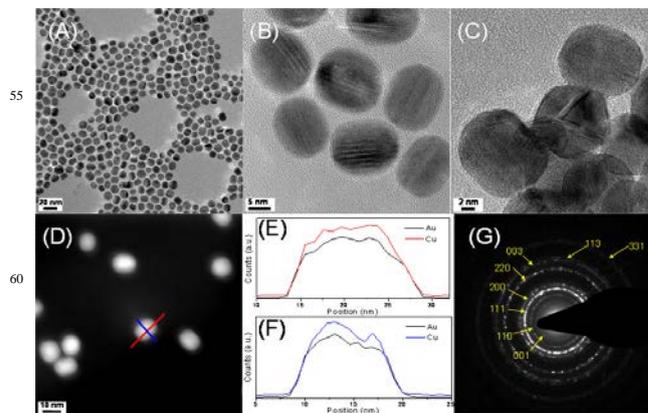
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Monodispersed intermetallic AuCu pentagonal nanorods with controlled size and composition have been developed by a seed-mediated growth route. The AuCu/C nanomaterial catalyzed the coupling reaction of sulfonamide with benzyl alcohol in good to excellent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

Nanorods with shape anisotropy have received much interest due to their promising applications in electronics,<sup>1,2</sup> biomedicine,<sup>3,4</sup> chemical sensing, imaging,<sup>5</sup> and catalysis.<sup>6-8</sup> Among different types of nanorods, the pentagonal nanorod possesses unique morphology, which has many interesting composition- and shape-dependent properties, such as excellent stability and high catalytic activity.<sup>9-11</sup> Their enhanced catalytic performance is attributed to the higher activity of the surface atoms on the twins of multiply-twinned particles (MTPs).<sup>12-14</sup> Pentagonal nanorods of one or two metals have been successfully developed in the past decade.<sup>15</sup> 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.<sup>16,17</sup> Those 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.<sup>18</sup>

Bimetallic AuCu nanoparticles with tunable sizes and compositions offer a broader control over properties than single metallic nanoparticles.<sup>19-21</sup> Spherical intermetallic AuCu multiply-twinned nanoparticles have been successfully synthesized by a seed-based diffusion route.<sup>20</sup> However, shape-controlled growth of AuCu nanoparticles appeared to be very difficult due to complications in the solution phase and the tendency of self-purification, which have been rarely reported in the literature.<sup>22,23</sup> Liu and Walker have reported monodispersed Au-Cu nanocubes with controllable sizes and compositions.<sup>19</sup> 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.<sup>24-26</sup>

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 Cu precursor (shown in Scheme S1). The simultaneous alloying of Au and Cu resulted in the growth of the



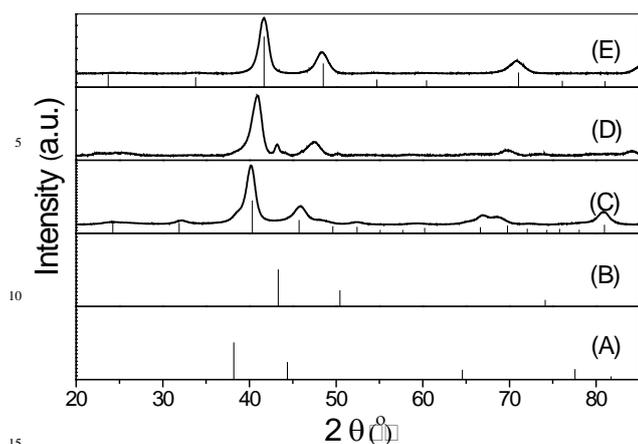
**Fig. 1** (A) TEM, (B, C) HRTEM, and (D) HAADF-STEM images of AuCu pentagonal nanorods. Cu and Au elemental profiles along the (E) red and (F) blue lines, respectively, across the AuCu nanorod shown in (D). (G) SAED pattern of the AuCu nanorods.

of the AuCu nanorods in 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  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  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  $\sim 20^\circ\text{C}/\text{min}$ , and then 60 mg of  $\text{Cu}(\text{acac})_2$  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 (ESI Fig. S1A). The multiply-twinned decahedral structure of the nanoparticles was confirmed by the high-resolution TEM (HRTEM) image (ESI Fig. S1B). These Au decahedra were then used as seeds for the formation of AuCu nanorods.

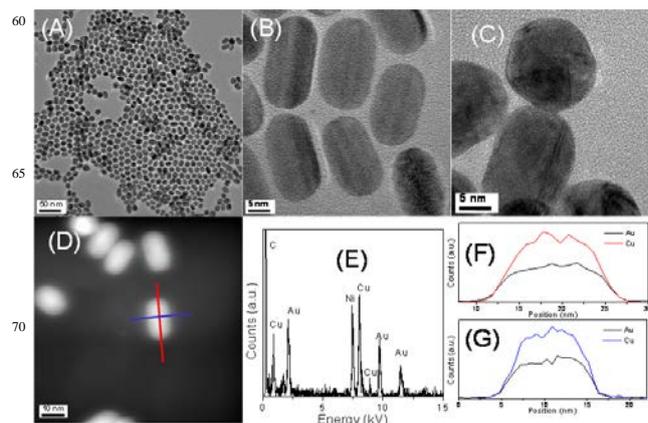
When a Au/Cu atomic ratio of 1:1 was used (denoted as AuCu), the synthesized nanoparticles were nearly uniform pentagonal nanorods with an average size of  $\sim 15$  nm in length and  $\sim 12$  nm in diameter (shown in Fig. 1A). HRTEM image in Fig. 1B revealed that the synthesized nanoparticles



**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 AuCu<sub>2</sub> pentagonal nanorods. (E) XRD pattern of AuCu<sub>3</sub> pentagonal nanorods, and XRD reference lines of AuCu<sub>3</sub> (JCPDS 35-1357).

were predominantly multiply-twinned with a pentagonal nanorod morphology. The ends of the nanorods still kept 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 Figs. 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.<sup>20,27</sup> 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 (ESI Fig. S2A), 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 (ESI Fig. S3). 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 (ESI Fig. S4). In contrast, significant red shift of the Cu nanoparticles solution (ESI Fig. S4) 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 (ESI Fig. S6B), while the two ends of the AuCu nanorods have the same faces of {110} and {111} (ESI Fig. S6C) as the decahedral Au seeds (ESI Fig. S6A). 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,



**Fig. 3** (A) TEM, (B, C) HRTEM, and (D) HAADF-STEM images of AuCu<sub>2</sub> pentagonal nanorods. (E) EDX spectrum of a single AuCu<sub>2</sub> nanorod specified in (D). Cu and Au elemental profiles along the (F) red and (G) blue lines, respectively, across the AuCu<sub>2</sub> nanorod shown in (D).

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). Cu could grow along the {111} and {110} faces (ESI Fig. S6C) with oleylamine blocking the high-energy {100} surface (ESI Fig. S6D). The anisotropic growth mechanism for AuCu pentagonal nanorods was consistent with that of AuAg nanorods, whereby the nanorods were directly grown from well-defined multiply-twinned decahedral Au particles.<sup>8,9,18</sup> However, the growth of the AuCu pentagonal nanorods involved the formation of 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 AuCu<sub>2</sub> were obtained with a uniform length of ~ 19 nm, and a similar diameter of ~ 12 nm as the AuCu nanorods (Fig. 3A). Although the length of the nanorods increased from ~ 15 nm to ~ 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 (ESI Figs. S6B and C). Figs. 3F and G confirmed that the AuCu<sub>2</sub> nanorods have a uniform Au and Cu profile across the entire particle. The powder XRD pattern of AuCu<sub>2</sub> 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 AuCu<sub>3</sub> 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 AuCu<sub>2</sub> nanorods solution remained stable after one month (ESI Fig. S4). By further decreasing the ratio of Au:Cu to 1:3, pentagonal nanorods termed AuCu<sub>3</sub> were obtained with a greater length (~ 24 nm) and a similar diameter of ~ 12 nm (ESI Fig. S7). These nanorods showed a XRD pattern that corresponded to the AuCu<sub>3</sub> 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,<sup>20</sup> spherical multiply-twinned AuCu nanoparticles with a monodispersed size distribution (~ 14 nm) were obtained under the otherwise similar synthesis conditions as the AuCu pentagonal nanorods (ESI Fig. S8). 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 HAADF-STEM image (ESI Fig. S9(C)). The HRTEM images (ESI Fig. S9(B)) 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 hydrogen-borrowing 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<sup>28,29</sup> with *p*-toluenesulfonamide and benzyl alcohol as the model substrates. Using a catalyst loading of 1 mol% Cu and 20 mol% K<sub>2</sub>CO<sub>3</sub> as the base, the coupling reaction proceeded smoothly at 120°C under air, and the desired product was obtained in 88% isolated yield after 15 h (ESI Table S1, Entry 1). Very little or no product was formed in the absence of the base or the catalyst (see ESI Table S1, Entries 2–4). This heterogeneous catalyst was successfully recycled 4 times without a reduction in the catalytic activity (ESI Table S2). The average particle size of the AuCu nanorods increased to 17–20 nm after the coupling reaction according to TEM images (ESI Fig. S10). The AuCu/C catalyst was also active for the alkylation of different types of substituted sulfonamides and alcohols (see ESI Table S3). Good to excellent yields (71–98%) were obtained for substituted benzyl alcohols or sulfonamides with either electron-donating or electron-withdrawing substituent 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, 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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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental protocols, synthesis scheme, TEM and HRTEM images of Au, Cu, AuCu<sub>3</sub>, and Au@Cu nanoparticles, XPS spectra, ultraviolet-visible (UV-Vis) spectra and coupling reactions of AuCu nanorods.

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## Graphical abstract

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