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Introduction

Hybrid or multifunctional nanoparticles constructed from more than one metallic phase have attracted interest to an increasing degree because of their unique catalytic, optical, electric, and magnetic properties, which differ from those of individual monometallic metals.^{1–17} Core–shell, phase-separated, and alloy type nanoparticles are typical hybrid and multifunctional nanoparticles. Core–shell nanoparticles of two types exist.⁵ One type is the most common concentric spherical nanoparticles, where a spherical core particle is covered by a shell of a different metal. The other type is polygonal core–shell particles prepared *via* heterogeneous, epitaxial growth of polyhedral shells over polyhedral core seeds having well-defined facets. In general, a strong correla-

Synthesis of Au@Ag@Cu trimetallic nanocrystals using three-step reduction[†]

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Au@Ag@Cu trimetallic nanocrystals were prepared using a three-step reduction method. In the first step, decahedral Au core seeds were prepared by reducing HAuCl₄·4H₂O in diethylene glycol (DEG) under oilbath heating in the presence of polyvinylpyrrolidone (PVP) as a polymer surfactant. In the second step, Ag shells were overgrown on these Au seeds in N,N-dimethylformamide (DMF) in the presence of PVP under oil-bath heating to prepare decahedral Au@Ag nanocrystals. In the third step, Cu shells were overgrown further on Au@Ag core-shell nanocrystals in ethylene glycol (EG) in the presence of PVP under oil-bath heating. The resultant crystal shapes were characterized using transmission electron microscopic (TEM), TEM-energy dispersed X-ray spectroscopic (EDS), and X-ray diffraction (XRD) measurements. Results show that Cu shells of two kinds are grown over Au@Ag core seeds: a phase-separated major Cu component attached to one or two side edges of decahedral Au@Ag cores, and a minor Cu component that appears as thin Cu shells over decahedral Au@Ag cores. Partial reservation of pentagonal shape and appearance of Moiré patterns in Au@Aq@Cu particles suggest that epitaxial growth occurs on some parts of the Au@Aq cores despite a large lattice mismatch between Ag and Cu (11.5%). The growth mechanism of Au@Ag@Cu nanocrystals was discussed in terms of lattice mismatch, decahedral particle defects, and the favorable shape of metallic shells. Optical properties of Au@Ag@Cu nanocrystals were determined by measuring extinction spectra.

> tion exists between core and shell shapes, enabling shapeselective preparation of desired morphologies of core-shell particles. Among various parameters that affect the epitaxial growth of core-shell nanoparticles, the lattice mismatch between core and shell metals has been regarded as an important factor. Fan *et al.*⁸ pointed out, based on systematic investigation of the growth of four typical novel metals (Au, Ag, Pd, and Pt), that the lattice mismatch must be less than about 5% for the epitaxial growth of core-shell nanocrystals.

> Compared with extensive studies of the syntheses of hybrid nanoparticles of novel metals, little work has been conducted to examine the preparation of nanoparticles involving transition metals. Among many multimetallic nanoparticles involving Cu metal, Ag-Cu and Au-Cu bimetallic and Au-Ag-Cu trimetallic systems have received great attention because of their high electron conductivity and application to lead free paste.18-22 We recently synthesized spherical Ag@Cu and Cu@Ag core-shell and phase-separated Ag-Cu particles using a one-step or two-step polyol method.¹⁹ When a Cu salt was reduced in the presence of spherical Ag seeds, concentric Ag@Cu core-shell particles are not formed. Instead, Ag-Cu phase-separated particles are prepared, which implies that the stability of the shapes of products (core-shell or phaseseparated type) affects the final shape of products. In the Au-Ag-Cu trimetallic system, we prepared spherical AuAgCu

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alloy core–Cu shells, denoted as AuAgCu@Cu, and AuAgCu alloy particles by co-reduction of Au, Ag, and Cu salts. 22

Epitaxial growth of core-shell particles having Cu shells has been studied for Au@Cu and Pd@Cu nanocrystals.20,23 Because the respective lattice constants of Au, Ag, Pd, and Cu are 0.4080, 0.4086, 0.3891, and 0.3615 nm, large lattice mismatches occur in Au-Cu (11.4%), Ag-Cu (11.5%), and Pd-Cu (7.1%) systems. According to the rule of lattice mismatch by Fan et al. described above,8 epitaxial growth of Cu shells over Au, Ag, and Pd cores is difficult because of the large lattice mismatches of more than 5%. However, our results obtained using polygonal Au@Cu nanocrystals demonstrated that the epitaxial growth of Cu layers over Au cores is possible, although the growth rate depends strongly on the positions of Au cores, e.g., flat planes or sharp corners, and that epitaxial growth rate on sharp corners is generally slower than that on flat planes.²⁰ Very recently, Jin et al.²³ reported that the epitaxial growth of Pd@Cu is also possible over cubic Pd crystal.

Although spherical Ag@Cu core-shell particles have been prepared,^{18,19} no study of the epitaxial growth of Cu shells over Ag polygonal surfaces has been reported. Moreover, no study of the preparation of Au-Ag-Cu trimetallic particles using polygonal Au@Ag seeds has been reported in the literature. In this study, we attempt to prepare Au@Ag@Cu trimetallic nanocrystals using decahedral Au@Ag particles as seeds. Three main purposes, answers to important questions in this field, were the goals of our study. What shape of products, core-shell or phase-separated particles, is produced when decahedral Au@Ag particles are used as seeds? Is epitaxial growth of Cu layers over Ag intermediate layers possible, and do defects of cores such as twin planes affect the crystal growth of Cu shells? What kind of change occurs in surface plasmon resonance (SPR) band by the formation of the Cu component? Based on TEM, TEM-EDS, XRD, and ultravioletvisible-near infrared (UV-Vis-NIR) data, information related to the above three points was obtained.

In this study, new Au–Ag–Cu trimetallic particles, which consist of decahedral Au@Ag cores covered by both phase-separated and core–shell types of Cu components, are prepared through reduction of Cu²⁺. For clarity, we designate these Au–Ag–Cu trimetallic particles having two components in a particle as Au@Ag@Cu for this study. The growth mechanism of Au@Ag@Cu nanoparticles is discussed in terms of lattice mismatch, defects of decahedral particles, and shape stability between core–shell and phase-separated types of nanoparticles.

Experimental

For use in this study, $HAuCl_4 \cdot 4H_2O$ (>99.0%), $AgNO_3$ (>99.8%), $Cu(OAc)_2 \cdot H_2O$ (>99.0%), ethylene glycol (EG: >99.5%), diethylene glycol (DEG: >99.5%), tetraethylene glycol (TEG: >99.0%), and C_2H_5OH (>99.5%) were purchased from Kishida Chemical Co. Ltd. The PVP powder (average

molecular weight M_W = 55 and 1300 k in terms of monomer units) was purchased from Sigma-Aldrich as a polymer surfactant. In addition, Ar (>99.9995%) gas was obtained from Taiyo Nippon Sanso Corp.

Au@Ag@Cu core-shell nanocrystals were prepared using a three-step reduction method. Decahedral Au@Ag seeds were prepared using the same method as that reported previously.¹⁷ As the first step, DEG was used as both reductant and solvent for the preparation of decahedral Au core seeds.^{17,24} In the process, 2 g of PVP (M_W = 55 k) solution was dissolved in 25 mL DEG and heated to 230 °C in the oil bath. Then 20 mg of HAuCl₄·4H₂O in 2 mL DEG was added to the above solution and heated at 230 °C for 10 min. The respective final concentrations of HAuCl₄·4H₂O and PVP in DEG were 1.8 and 670 mM. After cooling the Au seed solutions described above to room temperature in a water bath, the Au seeds were separated by centrifuging the colloidal solution from C₂H₅OH solution three times at 15 000 rpm for 60 min and from DMF solution once at 15 000 rpm for 60 min. Then they were redispersed in a 5 mL DMF solution to prepare the Au seed solution.

For the overgrowth of Ag shell on decahedral Au cores in the second step, DMF was used as a reductant and solvent. DMF solution (14 mL) containing 536 mM of PVP (M_W = 1300 k) was preheated at 140 °C for 30 min, and decahedral Au seeds in 1 mL DMF solution were added to the solution described above. Then, 15 mL of AgNO₃-DMF solution was injected dropwise to the solution using a syringe pump at an injection rate of 0.3 mL min⁻¹. The final concentrations of Au and Ag atoms used for Au@Ag nanoparticles and PVP were, respectively, 1, 3, and 250 mM. After all reagents were introduced to the solution, the solution was heated in an oil bath for 3 h.

Cu shells over Au@Ag seeds were prepared using a similar method to that used for the preparation of Au@Cu nanocrystals.²⁰ In the third step, 17 mL EG solution containing 4.24 mM of Cu(OAc)₂·H₂O and 249 mM of PVP ($M_W = 55$ k) was prepared and Ar gas was bubbled at a flow rate of 150 mL min⁻¹ for 10 min at room temperature. This solution was heated to 175 °C under bubbling Ar gas. Subsequently, Au@Ag seeds in 3 mL EG solution with Au and Ag atomic concentrations of 4 and 12 mM, respectively, were added to the solution described above. The final concentrations of Au, Ag, and Cu atoms used for Au@Ag@Cu particles and PVP in 20 mL EG solution were, respectively, 0.6, 1.8, 3.6, and 211 mM. After all reagents were introduced to the solution, the solution was heated at 175 °C in the oil-bath under bubbling Ar gas for 5–20 min.

Au@Ag@Cu products were obtained from C_2H_5OH solution by centrifuging the colloidal solution at 15 000 rpm for 30 min three times to remove remaining PVP and all by-products in the supernatant. The precipitates were collected and then redispersed in deionized water. For TEM and TEM–EDS observations at an accelerating voltage of 200 kV (JEM-2100F; JEOL), samples were prepared by dropping colloidal solutions of the products onto Au grids. XRD patterns of the samples obtained after the third step were measured (SmartLab with Cu K α radiation operating at 45 kV and 200 mA; Rigaku Corp.). Extinction spectra of the product solutions were measured using a spectrometer (UV-3600; Shimadzu Corp.) in the UV-Vis-NIR region.

Results and discussion

Preparation of decahedral Au@Ag nanocrystals under oil-bath heating

Fig. 1a-1d show TEM and TEM-EDS images of Au@Ag nanocrystals prepared through the two-step reduction method in DEG and DMF under oil-bath heating. The TEM-EDS data clarify that decahedral Au cores are covered by the same decahedral Ag shells, as presented in Fig. 1e, indicating that only {111} facets of decahedral Ag shells are produced from the Au seed-AgNO₃-PVP(1300 k)-DMF solution at 140 °C. The average size and the number density of decahedral particles were estimated by measuring more than 100 particles. The definition of the size of decahedral nanocrystal is presented in Fig. 1e. After 20 min heating, decahedral Au@Ag nanocrystals with average size of 134 ± 15 nm were prepared using decahedral Au seeds with average size of 82 \pm 15 nm. Results show that the thickness of Ag shells was ≈ 25 nm. The number density of decahedral particles was 85%. In addition to decahedral particles, small amounts of icosahedral particles and triangular plate were obtained (15%).



Fig. 1 (a) TEM and (b)–(d) TEM–EDS data of decahedral Au@Ag nanocrystal prepared under oil-bath heating at an [Au] : [Ag] atomic ratio of 1 : 3.



Fig. 2 (a) TEM, (b)–(e) TEM–EDS data of decahedral Au@Ag@Cu nanocrystal prepared under oil-bath heating for 5 min at an [Au] : [Ag] : [Cu] atomic ratio of 1 : 3 : 6 and (f) line analyses along the line in panel (e).

Preparation of Au@Ag@Cu nanocrystals under oil-bath heating

Fig. 2a–2f show a TEM image, TEM–EDS data of Au, Ag, and Cu components, and line analysis data along the red line in Fig. 2e. The TEM image (Fig. 2a) implies that decahedral structures observed in Au@Ag nanocrystals were not preserved well and irregular shapes of particles are produced after Cu shell formation. Expanded TEM images of typical decahedral



Fig. 3 Expanded TEM images of Au@Ag@Cu nanoparticles prepared using the three-step reduction method.

Au@Ag@Cu are shown in Fig. 3a-3d. Although some Cu shells have partial memory of decahedral Ag particles because of the presence of twin plane and irregular pentagonal structures, Cu shells having well-defined pentagonal edges were not grown. All Au@Ag@Cu particles have phase-separated type of Cu component on Au@Ag cores (see red arrows in Fig. 3). Based on the line analysis data, the Au and Ag components give symmetric distributions because of uniform coverage of Ag shells (red and green lines in Fig. 2f), whereas the Cu component gives an asymmetric distribution (blue line in Fig. 2f). The Cu distribution has two parts in many particles: formation of phase-separated quasi-spherical particles on the side edge of decahedral Au@Ag nanocrystals, and thin uniform coverage of Cu shells over the decahedral particles. For some particles, the phase-separated part is not so readily apparent in Fig. 2e, mainly because phase-separated part is located along a perpendicular direction of the TEM-image plane (compare Fig. 2d with 2e).

To examine the time evolution of Au@Ag@Cu particles, products were sampled after oil-bath heating for 5, 10, and 20 min. Fig. 4a–4c show TEM and TEM–EDS data of Au@Ag@Cu nanocrystals prepared under oil-bath heating for each time. Only slight shape changes occur in the Au@Ag@Cu particles in the reaction time range of 5–20 min. The Au : Ag : Cu atomic ratios of total Au@Ag@Cu nanocrystals were 15 \pm 2 : 44 \pm 4 : 41 \pm 4, which were fundamentally independent of

the heating time in the 5–20 min range. These results imply that all Au and Ag reagents were reduced in the first and second steps, whereas about half of Cu^{2+} reagent was reduced in the third step after oil-bath heating for 5 min. The rest was not reduced even after further heating for 5–15 min in our present experimental condition.

XRD pattern of Au@Ag@Cu particles

XRD patterns were measured for the sample obtained after 20 min heating (Fig. 5). Prominent diffraction peaks were indexed to the {111}, {200}, {220}, {311}, and {222} planes of Au and Ag components with fcc structure (PDF 00-004-0784, PDF 01-087-0720), and the {111}, {200}, and {220} planes of Cu component (PDF 00-004-0836). Because the lattice constants of Au (0.4080 nm) and Ag (0.4086 nm) are similar, their peaks heavily overlap one another. Therefore, it was difficult to separate Au and Ag peaks. Based on XRD patterns, it was concluded that the crystal structures are similar to those of face-centered cubic (fcc) crystals of Au, Ag, and Cu. No amorphous crystals are formed. No peaks of Cu₂O and CuO were observed, indicating that oxidation of the Cu component is negligible.

UV-Vis-NIR spectra of decahedral Au@Ag@Cu nanocrystals

The UV-Vis-NIR spectra of decahedral Au@Ag core and Au@Ag@Cu particles prepared under oil-bath heating for 5–20 min were measured to characterize their optical properties



Fig. 4 Au@Ag@Cu nanocrystals prepared by the three-step reduction method. Heating times in the third step were (a) 5 min, (b) 10 min and (c) 20 min.



Fig. 5 XRD pattern of Au@Ag@Cu nanocrystals prepared using the three-step reduction method.

(Fig. 6a). The SPR band of decahedral Au@Ag nanocrystals prepared under oil-bath heating shows a broad peak in the 320–900 nm regions with a strong peak at \approx 540 nm and weak shoulder peaks at \approx 350 and \approx 400 nm. Peak maxima of the dominant longitudinal mode of decahedral Ag particles varies from 455 to 570 nm with increasing in size from 35 to 120 nm.²⁵ The observed SPR band of decahedral Au@Ag particles is broader than that of decahedral Ag particles because of changes that occur in the dielectric constant of decahedral Ag



Fig. 6 UV-Vis-NIR spectra of (a) Au@Ag and Au@Ag@Cu and (b) Cu nanoparticles.

shells through interaction with the decahedral Au core component.

After addition of Cu(OAc)₂·H₂O to decahedral Au@Ag nanocrystal solution and heating at 175 °C for 5 min, the SPR band becomes weak and broad with a weak peak at ≈ 600 nm. For comparison, Fig. 6b shows the SPR band of pure Cu particles obtained from Cu(OAc)₂·H₂O-PVP-EG solution under MW heating for 15 min at 365 W. The SPR band of Cu nanoparticles with average diameter of 71 ± 14 nm (Fig. S1, ESI†) appears in the 500–1000 nm region with a sharp peak at ≈ 600 nm. Therefore, the weak peak at ≈ 600 nm can be ascribed to the Cu component of Au@Ag@Cu nanoparticles, although the Cu component becomes broad because of changes in the dielectric constant of Cu shells through interaction with the decahedral Au@Ag core component.

No significant change in the UV-Vis-NIR spectra was observed under oil-bath heating for 5–20 min, indicating that reduction of Cu was completed within 5 min and indicating that the crystal shape of products was unchanged between 5 and 20 min. This observation was consistent with the TEM and TEM–EDS data, which show that crystal structures were nearly the same within 5–20 min. The peak positions of decahedral Au@Ag particles and pure Cu particles are observed, respectively, at \approx 540 and \approx 600 nm. The observed peak position is close to that of pure Cu particles, indicating that the SPR band reflects the outermost Cu component dominantly.

Crystal structures and growth mechanisms of Au@Ag@Cu nanocrystals using decahedral Au@Ag seeds

We examined the synthesis and crystal shape of Au@Ag@Cu trimetallic nanocrystals using decahedral Au@Ag seeds.



Fig. 7 TEM, TEM–EDS and crystal structures of (a) Au@Ag@Cu and (b) Au@Cu decahedral-like particles prepared in liquid phase. Data for Au@Cu were obtained from ref. 20.

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Fig. 7a shows a TEM-EDS image and the crystal structure of Au@Ag@Cu nanocrystals. For comparison, Fig. 7b shows a TEM image and the crystal structure of decahedral-like Au@Cu nanocrystal prepared using a two-step reduction method in EG.²⁰ Based on our previous studies of epitaxial growth of Au@M (M = Ag, Pd, Cu, Ni) particles in EG, Ag shells having {100} facets are produced selectively for Au@Ag, whereas Au@M (M = Pd, Cu, Ni) produced Pd, Cu, and Ni shells having {111} facets.^{9,17,20,26} In the case of Au@Ag@Cu, pentagonal shapes of Au@Ag cores are partially reserved in some particles (e.g., Fig. 3a and 3b), indicating that epitaxial-like growth takes place during Cu shell formation. In some Au@Ag@Cu particles, epitaxial growth occurs partially on the flat surface of Au@Ag particles, as evidenced by Moiré patterns appearing on the {111} facets of Au@Ag cores, as shown by blue circles in Fig. 3a and 3b. These results led us to conclude that epitaxial growth of Cu shells on Au@Ag cores partially occurs and that favorable facets of outmost Cu shells in decahedral Au@Ag@Cu nanocrystals are {111}, as in the cases of Au@M (M = Pd, Cu, Ni).

Lattice mismatch between the core and shell is regarded as an important factor for the epitaxial growth of core-shell nanocrystals. In general, epitaxial growth becomes difficult with increasing lattice mismatch because of increased stress in the interfaces. For Au@Ag and Au@Pd with small lattice mismatches of 0.2 and 4.6%, respectively, decahedral coreshell nanocrystals having well-defined facets were formed.9,17 On the other hand, the epitaxial growth rate of decahedral Cu shells having a large lattice mismatch of 11.4% depends strongly on the Au core position (Fig. 7b).²⁰ The Cu shells are grown epitaxially over Au cores on the flat {111} facets because a Moiré pattern appears on the {111} facets (red circle in Fig. 7b). However, the growth rate on the corner is so slow that a flower-like Cu shell is formed over the Au core. Because a large mismatch exists in Au@Cu, Cu shells show some distortion. Such a distortion of Cu shell layers suppresses the epitaxial growth rate of the Cu shell, especially on the corners.

A decahedron can be regarded as the assembly of five singlecrystal tetrahedral units sharing a common edge. Because the theoretical angle between two {111} planes of a tetrahedron is 70.53°, five tetrahedra joined with {111} twin planes will leave a gap of 7.35°, as portrayed in Fig. 7b.^{2,10} Although no cavities attributable to such defects are observed in the products, decahedral Au@Ag particles have some defects and distortion in their crystals, especially in corners, which suppress epitaxial growth of Cu shells especially over corners. Such defects and distortion constitute reasons explaining why epitaxial growth of perfect shapes of shells having sharp corners and edges is difficult for Au@Cu.

For Au@Ag@Cu, lattice mismatch between Ag and Cu is also large (11.5%). Therefore, epitaxial growth of the outermost Cu shells is observed only in small parts of decahedral Cu shells. Decahedral Au@Ag@Cu nanocrystals having well-defined facets were not grown under the present experimental conditions. For Au@Cu, the distribution of the Cu component on the corner was small. On the other hand, it is rather larger than that of edges in some Au@Ag@Cu particles (*e.g.*, Fig. 3a3d) because it becomes a growth point of the phase-separated type of Cu component, as discussed below.

According to results of our systematic study of the synthesis of Ag-Cu bimetallic nanoparticles, 19,21,22 Ag@Cu and Cu@Ag core-shell, Ag-Cu phase-separated, and AgCu alloy nanoparticles were prepared, depending on the experimental conditions. When spherical Ag seeds with average diameters of 21 +3 nm were prepared and then Cu(OAc)₂·H₂O were added and heated at 195 °C under oil-bath and MW irradiation, Ag-Cu phase-separated particles with average diameters of 29 \pm 6 nm were formed via melt of Ag seeds (see Fig. S2, ESI[†]).¹⁹ No Ag@Cu core shell particles were formed. We have also studied preparation of AgCu bimetallic nanoparticles using a mixture of AgNO₃ and Cu(OAc)₂·H₂O in EG solution.²² After heating the reagent solution at 175 °C for 17.5-27 min, AgCu alloy core Cu shell particles, denoted as AgCu@Cu, were prepared. After further heating for 10 min, their shapes were changed to phase-separated type particles, which were composed of AgCu alloy component and Cu component. Judged on the basis of these facts, phase-separated particles are more stable than core-shell ones in Ag-Cu bimetallic system in the temperatures of 175-195 °C.

Similar phase-separated spherical Cu parts appeared in Au@Ag@Cu particles as a major Cu component in this study. Therefore, another reason why thick Cu shells are not formed over decahedral Au@Ag cores is that the thermochemically favorable structure is not core-shell type particles but phase-separated type particles, when Cu²⁺ was added to the Au@Ag core particles (Fig. 7a). The Au@Ag cores are covered by thin Cu shells. Phase-separated Cu components are combined with the major decahedral Au@Ag cores by corners or edges of particles, which implies that corners and edges are active sites for the further growth of the phase-separated component (Fig. 3). Therefore, the distribution of Cu components over some corners of decahedral Au@Ag@Cu nanoparticles is much larger than that of Au@Cu nanoparticles.

We found here that decahedral Au@Ag particles are covered by thin Cu shells in Au@Ag@Cu nanoparticles. When Ag–Cu phase-separated particles are prepared using the two-step reduction method with spherical Cu particles as seeds, quasispherical phase-separated Ag–Cu particles are produced where no thin Cu shells are formed over Ag seeds (see Fig. S2, ESI†). This result arises from the absence of well-defined facets in spherical Ag seeds, so that epitaxial growth cannot take place. On the other hand, decahedral Au@Ag particles consist of well-defined {111} facets, so that epitaxial layered growth of Cu shells over intermediate Ag layers is possible. In such a case, crystal growth over polygonal cores occurs even though phaseseparated particles are more favorable than core–shell particles. Consequently, two components appear in decahedral Au@Ag@Cu nanoparticles.

Conclusion

Au@Ag@Cu trimetallic core-shell nanocrystals were prepared using three-step reduction with decahedral Au@Ag core as seeds. Crystal structures of products were characterized using TEM, TEM-EDS, and XRD. Results show two Cu components in Au@Ag@Cu nanocrystals. A major component was phaseseparated type spherical Cu component attached to one or two side edges of decahedral Au@Ag cores. The other was a minor Cu component: thin Cu shells on decahedral Au@Ag cores. For some Au@Ag@Cu nanocrystals, the pentagonal shape was partially preserved and Moiré patterns were observed. It was therefore concluded that epitaxial growth occurs over some parts of decahedral Au@Ag cores. Results show that the product shape of core-shell nanocrystals depends not only on lattice mismatch and on the core particle shape, but also on a favorable crystal shape of product particle (core-shell or phase-separated type). Optical properties of Au@Ag@Cu nanocrystals dominantly reflect the outermost Cu component. This report is the first describing that a phase-separate component is produced over polygonal core particles. These data provide new information related to the preparation of hybrid nanoparticles involving Cu using polygonal Au@Ag cores.

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