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Abstract: Intermetallic compounds and alloys are traditionally synthesized by heating mixtures of metal powders to high temperatures for long periods of time. A low-temperature solution-based alternative has been developed, and this strategy exploits the enhanced reactivity of nanoparticles and the nanometer diffusion distances afforded by binary nanocomposite precursors. Prereduced metal nanoparticles are combined in known ratios, and they form nanomodulated composites that rapidly transform into intermetallics and alloys upon heating at low temperatures. The approach is general in terms of accessible compositions, structures, and morphologies. Multiple compounds in the same binary system can be readily accessed; e.g., AuCu, AuCu₃, Au₃Cu, and the AuCu–II superlattice are all accessible in the Au–Cu system. This concept can be extended to other binary systems, including the intermetallics FePt, CoPt, CuPt, and Cu₃Pt and the alloys Ag–Pt, Au–Pd, and Ni–Pt. The ternary intermetallic Ag₉Pd₃S can also be rapidly synthesized at low temperatures from a nanocomposite precursor comprised of Ag₉S and Pd nanoparticles. Using this low-temperature solution-based approach, a variety of morphologically diverse nanomaterials are accessible: surface-confined thin films (planar and nonplanar supports), free-standing monoliths, nanomesh materials, inverse opals, and dense gram-scale nanocrystalline powders of intermetallic AuCu. Importantly, the multimetallic materials synthesized using this approach are functional, yielding a room-temperature Fe–Pt ferromagnet, a superconducting sample of Ag₉Pd₃S (T_c = 1.10 K), and a AuPd alloy that selectively catalyzes the formation of H₂O₂ from H₂ and O₂. Such flexibility in the synthesis and processing of functional intermetallic and alloy materials is unprecedented.

Introduction

Intermetallic compounds and alloys are among the most important solid-state materials in modern science and technology. They possess a surprisingly diverse range of physical properties, including ferromagnetism, superconductivity, shape-memory effects, catalytic activity, and hydrogen storage.

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Structural hardness,‡ and corrosion resistance,§ and thus find widespread use in many applications. As for all solid-state materials, the synthesis of these multimetallic compounds is crucial for controlling their performance in advanced applications. The possibility of integrating the well-established properties of intermetallic compounds with emerging nanotechnological applications has generated a renewed interest in controlling their synthesis. Controlling the nanostructure and morphology of multimetallic materials is particularly important, as these are the critical factors that limit their utility in future applications.

Metallurgy in a Beaker

Intermetallics and alloys are typically synthesized using traditional metallurgical techniques, which include powder reactions and arc melting. Both of these strategies require high-temperature heating (usually $>$1000 °C) and annealing for long periods of time (often days or weeks). While a few alternative approaches exist for controlling the nanostructure and morphology of multimetallic materials,\textsuperscript{13–16} low-temperature solution-based synthetic strategies do not exist. This is in contrast to many other classes of materials, where well-established solution routes are ubiquitous, e.g., sol–gel synthesis of oxides\textsuperscript{17} and spin coating of polymer and chalcogenide films.\textsuperscript{18}

We recently discovered that, under appropriate conditions, binary mixtures of weakly stabilized Au and Cu nanoparticles aggregate to form binary nanocomposites, which can thermally transform into intermetallic nanocrystals at low temperatures.\textsuperscript{19} Our subsequent work showed that this approach can be significantly expanded to include other bimetallic and trimetallic systems with a variety of compositions and accessible crystal structures. Furthermore, the synthetic process can be modified and scaled up to yield bulk and thin-film materials with controlled nanostructure and morphology. Accordingly, we describe here a generalized solution-based synthetic approach—“metallurgy in a beaker”—that uses metal nanoparticles as a robust toolkit for synthesizing morphologically diverse intermetallics and alloys. By using preformed nanoparticles of known metal ratios, multimetallic compounds of those ratios can be made by exploiting the nanoscale intermixing of the nanoparticles. This approach effectively separates the diffusion and nucleation steps, and eliminates solid–solid diffusion as the rate-limiting step in bulk-scale solid-state synthesis. Furthermore, the materials made by this method are functional, yielding properties that match or are superior to similar materials made by traditional routes. In this work, we establish the viability of this new synthetic paradigm for producing functional multimetallic solid-state materials with unprecedented synthetic flexibility.

Experimental Section

Synthesis of Binary and Ternary Intermetallics and Alloys. Au–Cu nanocomposites were synthesized in a manner similar to that of our previous report.\textsuperscript{10} Briefly, Cu(C$_2$H$_4$O$_2$)$_2$·H$_2$O (6.8 mg, 0.034 mmol; Alfa Aesar, 98.0–102.0%), HAuCl$_4$·3H$_2$O (13.3 mg, 0.036 mmol; Alfa Aesar, 99.99%), and poly(vinylpyrrolidone) (PVP; MW = 40000), 120 mg) were added to 25 mL of distilled, deionized water (NANOpure, 18.2 MΩ). (Note that water was the only solvent used in the synthesis of these materials.) After the mixture was stirred for at least 30 min under Ar, 25 mL of 0.01 M NaBH$_4$ (Alfa Aesar, 98%) was added to form a mixture of Au and Cu nanoparticles. After 3–6 h, the resulting nanocomposite was isolated in powder form by centrifugation (including several washing steps), and dried under ambient conditions. The powder was then annealed at 300 °C under flowing Ar. AuCu$_{50}$ was synthesized in the same way, using 10.1 mg (0.0505 mmol) and 6.1 mg (0.0168 mmol) of Cu(C$_2$H$_4$O$_2$)$_2$·H$_2$O and HAuCl$_4$·3H$_2$O, respectively. In some cases, poly(4-styrenesulfonic acid) sodium salt (PSS) (Alfa Aesar, MW = 70000) and poly(2-ethyl-2-oxazoline) (PEO) (Alfa Aesar, MW = 50000) were used instead of PVP. Other binary phases (Ag–Pt, Au–Pd, Co–Pt, Cu–Pt, Fe–Pt, Ni–Pt) were synthesized using similar molar ratios and the following metal salt precursors (obtained from Alfa Aesar): AgNO$_3$ (99.9+%), K$_2$PtCl$_6$ (40.11% Pt), PdCl$_2$ (99.9%), CoCl$_2$·6H$_2$O (98.0–102.0%), FeCl$_2$·4H$_2$O (99%), and NiCl$_2$·6H$_2$O (99+%). The ternary phase Ag–Pd–S was synthesized as follows: PVP-stabilized Ag,S nanoparticles were synthesized according to ref 20 using AgNO$_3$ and Na$_2$S·9H$_2$O (Alfa Aesar, 98.0–103.0%), washed, dried, and then added to a fresh aqueous solution of PVP-stabilized Pd nanoparticles synthesized according to ref 21. The final concentrations of Ag,S and Pd used to form the nanocomposite were 18 and 1 mg/mL, respectively. The resulting nanocomposite was isolated by centrifugation and annealed at 300 °C under Ar.

Synthesis of Morphologically Diverse Nanomaterials. Thin films were prepared by solution evaporation. A glass slide precleared in piranha solution (3:1 H$_2$SO$_4$·H$_2$O$_2$) was placed upright in a beaker containing the Au–Cu nanocomposite solution (recovered, washed, and redispersed to an approximate concentration of 5 mg/mL), which was allowed to evaporate in a fume hood. The resulting black Au–Cu nanocomposite film was converted to a film of intermetallic AuCu by annealing for 30 min at 300 °C in flowing Ar. To prepare free-standing films, the Au–Cu nanocomposite synthesis was scaled up by a factor of 20, and centrifuged in a round-bottom centrifuge tube to slowly precipitate the nanocomposite. Upon washing and drying, a free-standing nanocomposite was formed, and its surface features conformed to the surface of the centrifuge tube (showing microscale scratches). The free-standing Au–Cu nanocomposite was converted to intermetallic AuCu by annealing for 30 min at 300 °C in flowing Ar.

Nanostructured materials were synthesized by replicating against sacrificial templates. An inverse opal (colloidal crystal replica) was synthesized by infiltrating a colloidal crystal comprised of 1.0 μm polystyrene beads (prepared by centrifuging an aqueous suspension of polystyrene beads) with the Au–Cu nanocomposite, drying under ambient conditions, and then annealing to 350 °C under flowing Ar to remove the polystyrene beads and to crystallize the framework. A disordered porous nanomesh material was synthesized in a similar manner, using a disordered aggregate of polystyrene beads instead of a periodic colloidal crystal.

Characterization and Physical Property Measurements. Powder X-ray diffraction (XRD) data were collected on a Bruker GADDS three-circle X-ray diffractometer using Cu Kα radiation. Differential scanning calorimetry (DSC) data were collected on a TA Instruments Q600 SDT under an Ar purge. Elemental analysis (CHN) was performed by Atlantic Microlab (Norcross, GA). Inductively coupled plasma (ICP) elemental analysis results were obtained using a Perkin-Elmer DRCII ICP-MS. X-ray photoelectron spectroscopy (XPS) measurements were acquired on a Kratos Ultra Axis Hsi 165 XPS using an Al anode set at 15 mA and 15 kV. Samples were prepared by sonicating the nanoparticles in ethanol, dropping a dilute suspension on a clean Si wafer, and then drying. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns, and energy-dispersive X-ray analysis (EDS) were acquired using a JEOL JEM-2010 transmission electron microscope. Scanning electron microscopy (SEM) images were obtained at 15 kV using a JEOL JSM-6400 SEM. Optical microscope images were acquired on a Zeiss AxioSkop 2-MAT operating in reflection mode. Magnetic susceptibility and magnetization measure-
were reduced in solution by NaBH

ichiometric molar ratios of Au and Cu metal salt precursors

Results and Discussion

the superconducting transition of Ag

MPMS-XL. Magnetization vs applied field data were collected in the

temperature diffusion without the high-temperature melting step

nanocomposites into intermetallic AuCu and

C. The samples labeled “0 min” correspond

Stochiometric molar ratios of Au and Cu metal salt precursors

Au–Cu System: Synthesis and Characterization. Sto-

resolved XRD data for AuCu and AuCu

resolved XRD data for AuCu and AuCu

resolved XRD data for AuCu and AuCu

resolved XRD data for AuCu and AuCu

resolved XRD data for AuCu and AuCu

Figure 1. Powder XRD patterns showing the time-resolved transformation of (a) AuCu and (b) AuCu

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exists for controlling the carbon content by carefully choosing the polymer stabilizer and its decomposition properties.

XPS spectra for the AuCu and AuCu$_2$ samples show no evidence for impurities related to the chemical precursors. Specifically, no B, Na, or Cl was detected, and this was confirmed with ICP data. It is well-known that nanoparticle formation using borohydride reduction of metal salts can lead to boron and metal boride impurities. 23 However, prior studies of Au and Cu nanoparticles prepared by this route show no boron incorporation, 24 and our findings are consistent with this. Figure 2 shows XPS spectra for the Au 4f and Cu 2p core level regions of the AuCu nanocomposite precursor and the intermetallic AuCu product. The AuCu ratio, based on multiple XPS analyses, is 1:0.1:1 (e.g., AuCu$_{1.1}$), which is consistent with the EDS data. The spectra show features that are expected for zerovalent Au and Cu, along with some oxidized Cu. The Au 4f region of the AuCu nanocomposite precursor shows peaks matching those for metallic Au. Relative to those for pure Au metal, the peaks for the intermetallic AuCu product are shifted to higher binding energies by approximately 0.25 eV. Similar shifts have been observed previously for Au–Cu alloy nano-

Figure 2. XPS core level spectra for the (a) Au 4f and (b) Cu 2p regions of a 1:1 Au–Cu nanocomposite and the corresponding nanocrystalline intermetallic phase formed after heating of the nanocomposite to 300 °C for 30 min. The lines in (a) highlight the Au 4f peak shifts, which indicate the formation of an alloy phase.

Figure 3. DSC trace for binary Au–Cu nanocomposites with 1:1 and 1:3 stoichiometries, showing the formation of AuCu and AuCu$_2$, respectively. Positive output is exothermic.

The Cu 2p region of the nanocomposite precursor is complex, showing several overlapping peaks that match those expected for a mixture of metallic Cu and oxidized Cu. Deconvolution of the peaks (Supporting Information) yields a relative population of 68.8% Cu$^0$, 4.0% Cu$^{1+}$, and 27.2% Cu$^{2+}$. The Cu 2p region of the XPS spectrum for the intermetallic AuCu sample shows primarily metallic Cu. Analysis of AuCu$_3$ samples showed similar results. The presence of a large amount of Cu$^{2+}$ in the room-temperature nanocomposite sample is not unexpected, since postsynthesis sample handling was not performed in an air-free environment. The weakly stabilized copper nanoparticles that comprise the nanocomposite precursor are known to oxidize quickly under ambient conditions.

AuCu and AuCu$_3$ are model systems for order–disorder phase transitions in bulk materials, and the thermodynamics of their formation has been studied extensively for samples of homogenized Au–Cu alloys prepared by arc-melting and annealing. 25–29 DSC data for our AuCu and AuCu$_3$ nanocomposite samples, with inherent nanoscale intermixing of Au and Cu resulting from the spontaneous room-temperature aggregation of preduced metal nanoparticles, are shown in Figure 3. Our data appear similar to the data reported previously for bulk samples. The broad exotherms below 200 °C are attributed to interdiffusion of the Au and Cu. For the AuCu sample, exotherms centered near 250 and 280 °C have been observed previously and correspond to ordering of the AuCu solid solution into the intermetallic structure. 25 The broad endotherm centered near 415 °C results from the disordering of the intermetallic AuCu, as well as decomposition of the PVP at slightly higher temperatures. A previous calorimetric study of nanocrystalline AuCu films suggested that ordering and disordering transitions begin at grain boundaries due to enhanced mobility and the presence of vacancies, and that impurities do not influence the calorimetric data. 28 Our results are consistent with these observations.

are unique to the large AuCu-II superlattice. In addition to 

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(31) Villars, P., Calvert, L. D., Eds., Pearson’s Handbook of Crystallographic 

Data for Intermetallic Phases, 2nd ed.; ASM International: Materials Park, 


(32) Massalski, T. B., Ed., Binary Alloy Phase Diagrams; ASM International: 

Materials Park, OH, 1996.

**Figure 4.** (a) Powder XRD patterns for AuCu (synthesized at 240 °C) 

and CuAu (for comparison, since CuAu has a significantly smaller unit 

cell than AuCu). (b) structures of the four Au-Cu compounds accessed 

using nanocomposite precursors (based on crystallographic information in 

ref 31), and (c) powder XRD pattern for the AuCu-II superlattice 

formed by heating a PEO-stabilized Au–Cu nanocomposite to 360 °C. The asterisk 
in (c) represents an intermetallic AuCu impurity. The remaining peaks for 

the AuCu impurity overlap the fundamental peaks of the AuCu-II super-

lattice. The tick marks in (c) indicate the allowed reflections for the AuCu-

II superlattice.

DSC data for the AuCu3 sample are similar (Figure 3), although 

only one exotherm corresponding to the formation of ordered 

AuCu3 is observed. Again, this is consistent with literature 

reports.29 The disorder temperature is lower than for AuCu, and 

this is also consistent with previous calorimetry data,29 as well 
as the equilibrium phase diagram.

XRD data confirm the assignments of the thermodynamic 

transitions discussed above, including diffusion, nucleation of 

the ordered phases, and the order–disorder transition. However, 

using PVP as a surface stabilizer, we could not isolate the AuCu-

II superlattice, which is known to form in the Au–Cu system 

just before disordering occurs.30–32 We could, however, access 

AuCu-II using PEO. The AuCu-II superlattice is a long-period 

antiphase structure, which is shown in Figure 4b. Since it is 

orthorhombic and the lattice parameter for the c axis is approxi-

mately 10 times larger than that of tetragonal (LiCu2) 

AuCu, it can be clearly distinguished in the XRD pattern shown 
in Figure 4c. Specifically, the peaks near 30.5°, 33.5°, and 54.5° 

are unique to the large AuCu-II superlattice. In addition to 

**Table 1.** Summary of Binary Phase Formation

<table>
<thead>
<tr>
<th>nominal stoichiometry</th>
<th>apparent stoichiometry</th>
<th>crystalline XRD product</th>
<th>alloy temp range, °C</th>
<th>intermetallic temp range, °C</th>
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</thead>
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<tr>
<td>Ag2Pd     Au2Pd</td>
<td>fcc-type Au2Pd alloy</td>
<td>Na/A</td>
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<tr>
<td>AuCu-Cu   AuCu-Cu</td>
<td>AuCu-Cu-type AuCu-Cu</td>
<td>100–600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuCuCu    AuCu-Cu</td>
<td>AuCu-type AuCu-Cu</td>
<td>300–600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuCu-Pd   AuCu-Pd</td>
<td>AuCu-type AuCu-Pd</td>
<td>100–600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuCu-Pd   AuCu-Pd</td>
<td>AuCu-type AuCu-Pd</td>
<td>300–600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoPt      CoPt</td>
<td>CoPt-type CoPt</td>
<td>20–600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuPt      CuPt</td>
<td>CuPt-type CuPt</td>
<td>20–600</td>
<td></td>
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<tr>
<td>CuPt-Pd   CuPt-Pd</td>
<td>CuPt-type CuPt-Pd</td>
<td>20–600</td>
<td></td>
<td></td>
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<tr>
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<td>20–600</td>
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<td>NiPt-Pd   NiPt-Pd</td>
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<tr>
<td>NiPtNiPt  NiPtNiPt</td>
<td>NiPtNiPt-type NiPtNiPt</td>
<td>20–600</td>
<td></td>
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</tr>
</tbody>
</table>

* Estimated using Vegard’s law analysis. °C Temperature range over which 

alloy and intermetallic phases are observed experimentally.

**Figure 5.** Powder XRD patterns for intermetallic AuCu-type CoPt (600 °C), AuCu-type FePt (500 °C), AuCu-type CuPt (500 °C), and CuPt-type CuPt (400–600 °C) synthesized from the corresponding binary nanocomposite precursors. Intermetallic CuPt forms by 400 °C, and the peaks that appear in the XRD pattern for the sample heated to 600 °C confirm the rhombohedral structure.

forming the AuCu-II superlattice, Cu3Au-type AuCu can be 

formed by changing the ratios of the metal precursors (Figure 4a). These results for the AuCu system clearly show the 

versatility of the synthetic process with respect to the range of 

compositions and structures that are accessible.

**Extension to Other Binary Systems.** The concept of a 

nanoparticle toolkit for assembling binary composites that 

rapidly transform into alloys and intermetallics is general 

and can be extended to a variety of other binary late-transition-metal 

systems. The systems studied to date include Ag–Pt, Au–Cu, 

Au–Pd, Co–Pt, Cu–Pt, and Fe–Pt, and Ni–Pt, and these represent 

a variety of important materials with known magnetic, 
electronic, optical, and catalytic properties. Table 1 summarizes our 

results for these systems, highlighting the temperature ranges 

over which we observe the formation of alloys and intermetal-

lics. XPS and ICP analyses of the products indicate that only 

boron impurities (e.g., 2.0% B in Ni3Pt and 0.5% B in FePt), which is consistent with known 

boron incorporation in nanoparticles prepared using borohydride 

reduction.24 Figure 5 shows XRD data for representative binary 

phases, which include CoPt (tetragonal, AuCu-type), FePt 

(cubic, AuCu-type), CuPt (cubic, AuCu-type), and CuPt 

(rhombohedral, CuPt-type). All of these crystalline phases were
formed from nanocomposite precursors that were heated for only 30–60 min. The formation of rhombohedral CuPt is particularly interesting, since its distorted structure has a unique long-range ordering motif that differs from those of the Au–Cu alloys. The rhombohedral superstructure is formed within 30 min of heating at 400 °C, and becomes more crystalline at higher temperatures (Figure 5).

XRD data showing the formation of an Au–Pd alloy (Figure 6) are demonstrative of the low-temperature diffusion afforded by the nanocomposite synthetic route. At 20 °C, Au is crystalline, and Pd is amorphous. At 100 °C, the Pd crystallizes, and both Au and Pd can be seen in the XRD pattern. At 200 °C, Au and Pd are still present as separate phases, although a slight shift (approximately 1–2%) in the lattice constants for Au and Pd suggests that some interdiffusion is starting to occur. By 300 °C, a single phase is present, and the lattice constant is intermediate between those of Au and Pd. On the basis of Vegard’s law, the composition of this alloy is closer to AuPd than the nominal stoichiometry of AuPd. The difference in composition between the nominal stoichiometry and the actual composition of the product most likely results from incomplete aggregation of the nanoparticle precursors during the solid-state synthesis of the nanocomposite precursors.

Table 1 indicates differences between the nominal and actual stoichiometries for several of the binary systems studied. These values were derived using Vegard’s law, which allows us to estimate the composition of an alloy by comparing its lattice constant with those of the single-metal end members. The fact that we do not observe intermetallics in the Ag–Pt and Ni–Pt systems, where ordered intermetallic compounds are known, is likely because of the difference between the nominal and actual compositions, which places them in a different region of the phase diagram where the intermetallics are not stable.

**Extension to a Ternary System.** Ternary phases are generally more complex than binary compounds in terms of synthesis, structures, and properties. Forming a nanocomposite of binary and unary nanoparticles allows nanocomposites of ternary compositions to be accessed. These ternary nanocomposites can be thermally processed to form ternary intermetallic phases, in analogy to the binary compounds discussed earlier. This greatly expands the complexity of compositions and structures that are accessible using a nanoparticle toolkit for solid-state synthesis.

For proof-of-concept purposes, we chose the Ag–Pd–S system to demonstrate the formation of a ternary phase. Nanoalloys of Ag–S and Pd are easily synthesized according to literature methods and can serve as robust precursors to ternary Ag–Pd–S phases. Ag–S nanocrystals were synthesized, isolated by centrifugation, washed, and then added to a freshly prepared solution of PVP-stabilized Pd nanocrystals in a 1:3 ratio of Ag–S to Pd. The XRD patterns for powder samples of the Ag–S and Pd nanoparticles are shown in Figure 7, and the corresponding TEM micrographs and SAED patterns are shown in parts a and b of Figure 8, respectively. Both Ag–S and Pd nanocrystals are stable in solution, but when they are mixed together, a precipitate begins forming within minutes, and the resulting powder is easily isolated by centrifugation. The Ag–S and Pd nanoparticles were mixed in a 1:3 ratio, since stoichiometry (Ag:Pt) matches a known ternary phase that is superconducting at Tc = 1.13 K.

The XRD pattern for this Ag–S–Pd nanocomposite at room temperature is shown in Figure 7, and the corresponding TEM micrograph is shown in Figure 8c. The XRD pattern has broad peaks that match those expected for Ag–S and Pd, indicating that both of these phases are present in the nanocomposite. The peaks for Pd are shifted slightly to smaller angles in the Ag–S–Pd nanocomposite, suggesting that some low-temperature interdiffusion between Ag and Pd is occurring (since the lattice constant for Ag is larger than that for Pd). The TEM micrograph of the Ag–S–Pd nanocomposite in Figure 8c initially appears to be a large aggregate of many smaller nanoparticles. Upon closer inspection, however, two distinct regions are discernible—a core region that contains a hexagonal superlattice of nearly monodisperse 5 nm nanoparticles, and a surrounding region that

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(35) (a) Raub, V. E.; Wulffhorst, B.; Plate, W. Z. Metallkd. 1954, 45, 533–537.
contains a random network of irregularly shaped 5–20 nm nanoparticles. Comparison with the TEM micrographs for Ag$_2$S and Pd nanoparticles in parts a and b of Figure 8, respectively, suggests that the hexagonal superlattice in the Ag$_2$S–Pd nanocomposite contains Ag$_2$S nanoparticles, and the surrounding region is made up of Pd nanoparticles. The SAED pattern for the entire aggregate in Figure 8c is complex, and can be indexed to a mixture of Ag$_2$S and Pd. Likewise, EDS analysis of the entire region in Figure 8c confirms that Ag, Pd, and S are present with an approximate overall composition of Ag$_2$S–Pd$_3$S$_2$ (Supporting Information), and bulk ICP analysis indicates an average composition of Ag$_2$Pd$_3$S$_2$ (the sulfur content was not determined by ICP). These data, combined with the XRD data in Figure 7, confirm that the aggregate in Figure 8c is a composite of Ag$_2$S and Pd nanoparticles. While this nanocomposite is clearly much larger and less homogeneously mixed than the Au–Cu nanocomposites described earlier, the intermixing of Ag$_2$S and Pd is still homogeneous at the 50–200 nm scale, and this represents significantly better mixing than is attainable using traditional solid-state synthetic approaches. This nanoscale mixing, combined with the enhanced reactivity of nanoparticles relative to bulk powders, suggests that the Ag$_2$S–Pd nanocomposite may be easily converted into the ternary Ag$_2$Pd$_3$S$_2$ phase upon rapid low-temperature heating.

DSC data for the Ag$_2$S–Pd nanocomposite show a broad exotherm starting around 200 °C. Indeed, XRD data confirm that the nanocomposite begins converting to the ternary phase at this temperature. XRD patterns for the Ag$_2$S–Pd nanocomposite heated for 30 min at 300 and 500 °C are shown in Figure 7. Ag$_2$Pd$_3$S$_2$ adopts the b-Mn structure, which is distinct from any structures that exist in the constituent unary and binary systems. The XRD data show that the diffusion and nucleation steps are complete within 30 min of heating, yielding the desired ternary phase. This is in contrast to the standard procedure for synthesizing this material, which requires heating at 1000 °C for 2 h, followed by annealing at 550 °C for 3 days. These results establish that (a) the solution-based nanocomposite approach is applicable to ternary phases, (b) nanocomposite composites form between metals and semiconductors, and (c) these metal–semiconductor nanocomposite precursors react similarly to the metal–metal binary composites to form ternary phases.

**Morphologically Diverse Nanomaterials.** An important consequence of this solution-based synthetic approach is that it can be scaled up to yield morphologically diverse intermetallic and alloy materials. Multimetallic materials with controlled shape, size, and dimensionality can be readily accessed using solution-deposition techniques and nanoscale templating strategies. Such flexibility in materials processing is unprecedented for intermetallics and alloys.

Thin films of intermetallics and alloys can be prepared by common solution-deposition techniques, including evaporation and spin coating. Figure 9a shows an optically transparent film of intermetallic AuCu that was prepared by evaporating an aqueous solution of the binary Au–Cu nanocomposite onto a clean glass slide, and then annealing the film at 300 °C for 30 min. XRD patterns confirm the ordered intermetallic structure of AuCu. SEM micrographs (Figure 9b,c) show a uniform film with an average thickness of 10 µm. The enlarged region in Figure 9c highlights the nanoscale grains that comprise the films, as well as the local surface roughness. Preliminary evidence suggests that this approach to thin film growth can also be extended to polymer supports and spin-coated surfaces. In addition to planar films, this solution-based strategy can be used to synthesize intermetallic and alloy films on nonplanar surfaces. Figure 9d shows a photograph of a glass rod that was coated with a film of intermetallic AuCu by dipping the rod in a Au–Cu nanocomposite solution, allowing the solution to evaporate, and then heating the rod to 300 °C for 30 min.

By scaling up the thin film deposition process, free-standing multilmetallic films and membranes can also be formed by drying a nanocomposite solution onto a molded surface. Figure 9e shows a free-standing Au–Cu–PVP nanocomposite. The nanocomposite precursor thermally transforms to an intermetallic AuCu monolith, which is shown in Figure 9f. The change in color from black to metallic golden is indicative of the change in structure and grain growth that occur during thermal processing. Optical micrographs of the intermetallic AuCu monoliths acquired in reflection mode are shown in Figure 9g,h. The high reflectivity is consistent with the formation of a metallic film, and the etch marks conform to the container in which the monolith was molded. Thus, the resulting monoliths retain the macroscale features of the template.

Because of the PVP remains intact during the thermal processing at 200–300 °C. Thus, the monoliths represent a direct route to intermetallic/polymer composite films, which could be interesting materials for structural and corrosion-resistant applications. Burning off most of the polymer at higher temperatures yields free-standing intermetallic monoliths with minimal carbon residue.

By scaling up the reaction even further, gram-scale bulk powders of intermetallic AuCu can be synthesized by heating.
at 300 °C for less than 1 h, since the nanocomposite precursors guarantee nanometer diffusion distances regardless of sample size. A photograph of a 0.5 g sample is shown in Figure 9i, along with its bulk powder XRD pattern, which clearly shows the formation of nanocrystalline intermetallic AuCu. Longer annealing times sinter the nanoparticles, forming dense powders with submicrometer crystallites. Figure 9j shows an SEM micrograph of the nanocrystalline intermetallic powder.

Solution-templating methods for making nanostructured materials are well-known, but related methods that form multimetallic alloy and intermetallic materials are rare. Since the nanocomposite precursors are stable in solution, they can be infiltrated into nanoscale templates, dried, and thermally converted into alloys and intermetallics while retaining the morphology of the template. For example, a porous nanomesh of intermetallic AuCu was prepared by templating against a disordered array of polymer spheres (Figure 9k). Likewise, a periodic inverse opal structure of intermetallic AuCu was formed by templating against a colloidal crystal of polystyrene spheres (Figure 9l). Such materials are of interest for applications that include photonics, separations, sensors, and catalysts.

Physical Properties. A synthetic strategy is viable if it produces new materials that have useful physical properties. Indeed, multimetallic solid-state materials made using the metallurgy in a beaker approach are functional, yielding a variety of important properties. Films of intermetallic AuCu showed a resistivity of approximately 3200 Ω·cm, which is 1–2 orders of magnitude higher than previously reported for bulk AuCu and may be due to grain boundary effects. Field-dependent magnetic measurements confirm that our FePt sample is a room temperature ferromagnet, with a coercivity of 8000 Oe at 10 K (Figure 10a). This compares favorably to other Fe-Pt nanomaterials, considering that the coercivity is highly variable and depends on the annealing time and temperature and the Fe:Pt ratio. Figure 10b shows a plot of resistance vs temperature for FePt.
a piece of the Ag₃Pd₁S sample described in Figures 7 and 8. The data were acquired as a four-wire measurement, which included the resistance of two contacts to the sample. A sharp transition is seen near 1.10 K, where the slope reaches 8.0 Ω/K. For T < 1.10 K, the application of a magnetic field of H = 1.5 kOe restores the resistance to R = 0.165 Ω (not shown). These results indicate that our Ag₃Pd₁S sample is superconducting with Tₘ = 1.10 K. For the bulk material synthesized by a traditional solid-state reaction, Tₘ = 1.13 K.³³ (The resistance of the Ag₃Pd₁S sample below Tₘ is most likely due to contact resistance, but may also result from the large number of grain boundaries that are inherent in the low-temperature sintering process.) More detailed studies of the superconducting properties of Ag₃Pd₁S synthesized using nanoparticle precursors are currently in progress.

Despite the unknown surface chemistry of these multimetallic materials (e.g., impurities, reactivity, and accessibility of surface sites), preliminary evidence suggests that they can serve as active and selective catalysts. Figure 11 shows the catalytic formation of H₂O₂ over a AuPd₄ alloy catalyst. Nanocrystalline Pd is known to catalyze the formation of H₂O₂ from H₂ and O₂, and evidence exists that colloidal Pd is involved in the catalytic cycle.⁴⁵ The results in Figure 11 show that H₂O₂ is produced from H₂ and O₂ using the PVP-stabilized AuPd₄ alloy as a catalyst. Importantly, the selectivity for H₂O₂ formation is 65% for our unsupported AuPd₄ catalyst. This is significantly larger than the 45% selectivity obtained from standard Pd/SiO₂-supported catalysts.⁴⁶ These results clearly establish that (a) these multimetallic materials have accessible surfaces and (b) they can serve as stable, highly selective catalysts for important chemical transformations. Details of the surface chemistry remain unknown, and will be explored in detail in future work.

Conclusions

We have demonstrated that metal nanoparticles can be used as a robust solution-based toolkit for synthesizing intermetallic compounds and alloys within minutes at low temperatures. The strategy exploits the enhanced reactivity and nanoscale diffusion distances afforded by binary nanoparticle composites to eliminate the need for high-temperature heating and atomic-scale homogenization, which are necessary using traditional methods for solid-state synthesis. The composition of the product is related to the composition of the metal nanoparticle precursors, and multiple compounds in the same binary system can be readily accessed; e.g., AuCu, AuCu₁₁, Au₄Cu, and AuCu-II are all accessible in the Au–Cu system. This approach is general with respect to composition, crystal structure, and morphology, and is successful for both binary and ternary phases. A significant benefit of the low-temperature solution process is that morphologically diverse nanomaterials of complex compositions and structures can be accessed—surface-confined thin films, free-standing films, nanomesh materials, inverse opals, and gram-scale bulk powders with dense submicrometer crystallites. As shown previously, this approach can also yield discrete solution-dispersible intermetallic nanocrystals in the Au–Cu system.¹⁹ Such flexibility in materials synthesis and processing is unprecedented for intermetals and alloys.

This approach has several important implications for synthesizing new solid-state materials and for controlling critical aspects of materials processing. The ability to synthesize multimetallic solids at low temperatures without arc-melting or high-temperature annealing shifts the rate-limiting step from solid–solid diffusion to nucleation, and thus has the potential to yield new metastable, nonequilibrium, and interfacially stabilized phases as bulk materials. Likewise, the solution-based precursors provide access to complex nanostructured materials and thin films that would otherwise be inaccessible or require high-temperature or vacuum deposition techniques. Thus, this approach could open the door to intermetallic and alloy coatings on a variety of planar and nonplanar supports, flexible films on polymer substrates, high-surface-area materials for catalytic applications, and nanotemplated materials, such as inverse opals and possibly nanorods, for fundamental studies and devices that exploit nanoscale magnetic, electronic, and optical properties.

The materials synthesized using this metallurgy in a beaker strategy are inherently impure, since the synthesis relies on sacrificial polymers and other solution additives that are necessary for reducing the metal salts and inducing nanoparticle aggregation to form nanocomposites. However, we demonstrated that these materials can have properties that are comparable to or superior to those of materials synthesized through more traditional routes that generally have higher purities. Other alternative synthetic approaches yield highly pure materials, but require much more elaborate setups and are not as amenable to scaleup (e.g., thin films prepared by Johnson and co-workers using elementally modulated reactants).¹⁶ Our materials, although not as pure as those made by other routes, are easy to synthesize and scale up and may be appropriate for applications where low-level impurities are tolerable. There is a tradeoff between ultrapure materials and materials that are easy to process and simple to produce in large quantities with controllable compositions and morphologies. We believe that the approach described here could be a viable strategy for synthesizing complex nanostructured materials with useful, unique, and unanticipated properties.

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Supporting Information Available: Powder XRD patterns for intermetallic AuCu synthesized from bulk precursors and using PSS and PEO, deconvoluted XPS spectrum for the Cu 2p region of the Au–Cu nanocomposite precursor, and EDS spectra for the Ag₃Pd₃S nanocomposite (PDF). This material is available free of charge via the Internet at http://pubs.acs.org. JA043335F