Gas-phase synthesized nanoparticles (NPs) possess ultraclean surfaces which mostly preserve the pristine energetic properties as they are. This feature largely benefits the potential uses of such NPs in sensors and catalysts. However, precise control of their configuration and properties is still a big challenge because the growth mechanism and phase evolution dynamics in these NPs are very hard to unveil. Here, we report a strategy to investigate the phase evolution dynamics in binary NPs by using e-beam assisted ultrafast local heating and cooling inside a transmission electron microscope. With this strategy, the phase segregation and corresponding shape evolution of PbBi NPs are in situ revealed. It is found that the as-prepared PbBi alloy NPs will transform into heterostructures under e-beam stimulated structural relaxation, leading to the formation of featured Janus configurations with faceted Bi polyhedron parts and intermetallic hemisphere parts. During phase segregation, Pb$_1$Bi$_1$ and Pb$_7$Bi$_3$ phases are captured and identified, and a model of phase and shape evolution of PbBi nanoalloys is developed and contrasted with that of their bulk counterparts. These findings benefit the understanding of the phase dynamics of binary NPs and can provide in-depth information for engineering their structures for practical applications.

**KEYWORDS:** phase segregation, binary nanoparticles, ultrafast heating/cooling, in situ, Janus structure

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properties differing from their bulk counterparts.\textsuperscript{20−23,25,26} Such inconsistencies between NPs and bulk materials naturally raise questions such as whether binary nanoalloys still follow the rules established based on the bulk counterparts, for example, the phase diagram and the thermodynamic equilibrium states. Unfortunately, rare investigations have been performed and current knowledge remains insufficient.\textsuperscript{27−29}

On solving the above questions, two issues should be dealt with carefully during the experimental investigation. One is that researchers should keep the binary NPs from surface contamination to unveil their pristine property and behavior. The other is that advanced techniques are required to be able to control the phase evolution stepwise together with synchronous observation. Such requirements bring enormous challenges to conventional techniques both in NPs fabrication and in structure characterization, and hence leave the questions remaining. In this paper, we report a delicate in situ method based on transmission electron microscopy (TEM) to probe into the phase dynamics in binary NPs. Using PbBi alloy as a sample, we show that ultraclean binary NPs can be in situ obtained designedly, and that the phase evolution of these obtained binary NPs can be maintained precisely by ultrafast heating and cooling. Therefore, the phase segregation process in the NPs, as well as the discrepancy between them and their bulk counterpart, can be creatively unveiled and verified.

**RESULTS AND DISCUSSION**

Figure 1 shows the illustration of fabricating PbBi NPs using our previously developed method, that is, the in situ evaporation-and-deposition (EAD) method.\textsuperscript{30} Generally, microsized alloy balls are used as the initial substance source. With intense electron beam (e-beam) irradiation, thermal accumulation can be achieved and localized at these microballs, and atoms are then sublimated/evaporated and later deposited on the supporting substrates nearby the microballs (see experimental section and Supporting Information for details). Benefiting from this in situ growth strategy, the newly formed NPs possess ultraclean surfaces and their sizes can be monitored and precisely controlled by rapidly halting the growth process. Figure 2a shows the initial morphology of typical as-fabricated PbBi alloy NPs with a mean size of around 23 nm. Apparently, the as-fabricated NPs present spherical shapes and uniform structures, representing a well-mixed solid solution phase. High-angle annular dark-field (HAADF) mappings of these NPs by scanning-TEM characterization further confirm this conclusion (see more details in the Supporting Information). The PbBi alloy NPs can retain their even phase if no further irradiation is exerted on them. Otherwise, phase segregation will take place together with obvious shape transformation. Figure 2b shows the morphology of the phase-segregated PbBi NPs which have been irradiated under an e-beam intensity of about 110 A·m\textsuperscript{−2} for 40 s. It can be seen that most of the NPs have changed their shapes from spherical to irregular. Meanwhile, some of the NPs increase in size apparently, which is possibly due to the Ostwald ripening or the coalescences that occurred between them.\textsuperscript{30}

As indicated by the yellow dashed circles, the large NPs present different contrasts, revealing heterojunction structures with a hemisphere part and a faceted polyhedron part. Generally, the faceted polyhedron parts can be classified into two types from their shapes, that is, one type has a half-hexagon profile while the other type has a truncated rectangular profile. Figure 2 panels c−f give both the bright-field images and HAADF mappings of these two types of heterostructured NPs, respectively. Correspondingly, the sharp image contrasts in each NP suggest that phase separation has happened and accounts for the NP shape transformation. Since the HAADF mappings (Figure 2d and Figure 2f) reflect strong Z-contrast,\textsuperscript{31} the gray parts with facets in comparison to the bright hemispheres thereby imply that Bi element has segregated from the initial alloy. Figure 2h shows an atomic-resolution TEM image of the area marked by the blue dashed box in Figure 2e. The measured 0.33 nm lattice spacing in the upper part (the segregation part) together with an included angle of 87.6° (measured from the inset fast Fourier transformation pattern) well corresponds to the (012) and (10−2) planes of Bi crystal, confirming that the segregation part should be pure Bi. In comparison, the lattice spacings of 0.26 and 0.30 nm measured in the lower spherical parts cannot coincide with pure Bi or Pb crystal, indicating that they possibly retain the alloy phase. The formation of featured facets on the Bi segregations implies that surface energy overwhelmingly governs the geometric shape of these ultraclean NPs. Such a featured configuration should be a kind of the Wulff shapes frequently revealed in monocrystalline NPs.\textsuperscript{32} By statistically calculating the indices of the formed facets, as shown in Figure 3g, the preferred low-energy surfaces are identified as \{012\}, \{003\}, \{110\}, \{104\}, and \{101\} groups, well in agreement with the results found in Bi polycrystals (see more details in the Supporting Information).

The occurrence of phase separation on the PbBi alloy NPs under intense irradiation indicates that the e-beam can be used as a controllable stimulus to probe into the phase dynamics of such nanoalloys. The confined heating effect and fast response of the e-beam can provide quite a delicate condition to reveal the transient states together with their evolution processes that
are hardly observed in a conventional thermal heating approach. Since the energy comes only from the e-beam, the heating region can thus be easily adjusted by spreading or focusing the beam size. The heat-up speed is balanced by the heat accumulation from beam irradiation and the heat dissipation from the supporting holey carbon film over the copper grid. Typically, the heating and cooling speed in the NPs can reach the order of $10^{11} \sim 10^{12}$ °C/s by a rough estimation from the experimental conditions (see more details in the Supporting Information). Such a fast response makes the e-beam serve as the nanoswitch, which can activate or freeze the phase and shape evolution of each NP.

Figure 2i shows the HAADF mapping of the PbBi alloy NPs after an irradiation flush with beam intensity of around 85 $\text{A} \cdot \text{m}^{-2}$ for 10 s. It is very interesting to find that some NPs present pac-man shapes, implying the emergence of early stage phase segregation. According to the contrast discrepancy in the HAADF mapping, the narrow gray lamella should be the initially segregated Bi nanocrystals. With more irradiation flushes, as shown in Figure 2j, phase segregation emerges in almost all the PbBi NPs. Despite the lamella sizes varying from single nanometers to over ten nanometers (marked by the yellow arrows), three types of segregation morphologies are identified distinctly. As indicated by the red dashed circles, embedded structures (type (ii)) and Janus configurations (type (iii)) are also observed beside the pac-man ones (type (i)). The Janus configurations seem to derive from the pac-man ones, due to the further growth of Bi lamellae in subsequent structural relaxation. Noticeably, the Janus PbBi NPs mostly remain spherical in this stage. They still need further structural relaxation to reconstruct their low-energy facets.

To reveal the dynamics of phase segregation, several as-fabricated PbBi alloy NPs are in situ monitored to track their structure and shape evolution during e-beam irradiation. It is found that phase segregation and formation of facets occur very quickly in this continuous irradiation condition (under a beam intensity of around 110 $\text{A} \cdot \text{m}^{-2}$), as shown by the Supplementary video 1 and video 2. It seems that the PbBi alloy NPs behave as quasi-liquids. This feature enables the fluctuation of particle surfaces, which facilitates the nucleation of facets so as to reduce the systemic Gibbs free energy. Meanwhile, the continued segregation of Bi atoms from the alloy body leads to an epitaxial-like growth of the Bi crystal, as evidenced by the continuously receding interface toward the alloy side (video 1). Figure 3 panels a and b give the illustration of this shape and phase evolution process together.
with the snapshots of a typical PbBi alloy NP undergoing such evolution. With an interval of 0.5 s per frame, it can be seen that initially, the segregation process is quite fast, and later slows drastically. Besides this single-end nucleation mode (marked as type I), Bi segregation from multi-ends during irradiation can also be observed in some NPs. As shown in Figure 3 panels c and d, the surface instability gives rise to two segregation sites (marked as type II and indicated by the red
arrows) at the particle surface, leading to the evolution of the NP changing from a Janus shape to a sandwich-like one. With more irradiation time, the sandwich-like shape eventually recovers its Janus shape, probably due to atom diffusion and phase fusion inside the NP. Supplementary video-3 shows the dynamic phase evolution of a NP undergoing such a transition. The flickering of the interface implies that energy relaxation inside the NP may last during the whole segregation process. Aside from these two main types of shape and phase evolution that occurred inside single NPs, similar phenomena are also observed in NP dimmers accompanying by coalescence and particle growth (Supplementary video-4). As a result, several Janus NPs after phase transition are significantly bigger than the as-fabricated ones.

The growth of Bi segregation seems to be suspended when the alloy body part reaches certain equilibrium states. Figure 4 panels a–c show the atomic structures of the Janus PbBi NPs which have been irradiated for 5 min and reached an equilibrium state. The lattice spacings and correlated included angles are measured and partially marked in the NPs (see more details in the Supporting Information). Interestingly, the Pb$_7$Bi$_3$ phase is identified in the remaining hemisphere body.
parts, indicating that this phase is an energy-preferred phase during the segregation evolution. Meanwhile, flat interfaces along with the Bi-(012) plane are also frequently observed in the Janus NPs. This suggests that this featured interface should also be the energy-preferred one. As a result, the codetermination of surface energy and interface energy finalizes this special geometry of the heterostructured NPs. The formed Pb$_7$Bi$_3$ phase from the Birich alloy is close to the lead–bismuth eutectic point (44.5 at. %Pb – 55.5 at. %Bi) in the phase diagram. It is found that more irradiation time (typically longer than 20 min) can effectively enable further structural relaxation. As evidenced in Figure 4 panels d–f, the Pb$_7$Bi$_3$ phase (i.e., the ε-phase in the phase diagram) is later formed in the remaining hemisphere part. This transition from Pb$_7$Bi$_3$ phase to Pb$_1$Bi$_1$ phase (ε-phase) releases more Bi atoms and further enlarges the Bi crystal part by receding the interface inside the Janus structure.

Although the crystalline structures of the Janus NPs provide substantial evidence for identifying the intermetallic phases, the elemental distributions of Pb and Bi as well as their evolution trends are hardly clear judging only from the lattice parameters, especially taking into account the homogeneity in different NPs. Thereby, energy-dispersive spectrum (EDS) mappings are performed to semiquantitatively verify the phase and elemental evolution. Figure 5 shows the EDS results of the PbBi NPs at different evolution stages. As can be seen in Figure 5a where the NPs are in their as-fabricated state, the even distribution of Pb and Bi elements corroborates the uniformly alloyed structure. Even for those ultrasmall ones, no significant phase separation is observed. Semiquantitative calculations from the EDS mappings (Figure 5c) indicate that the atomic fraction of Bi element is larger than that of Pb, showing a composition around 38 at. %Pb–62 at. %Bi. In contrast, the Janus NP where phase segregation has happened shows a quite different elemental distribution (Figure 5b). The Bi segregation mostly occupies half of the volume in each NP. Figure 5c gives a refined EDS mapping of a typical Janus NP marked by the blue dashed box in Figure 5b. It can be seen that the upper part only shows strong Bi signals while the lower part has mixed Pb and Bi signals. By semiquantitative calculations, as shown in Figure 5f, the upper part (i.e., the Bi segregation part) has a composition of 6.5 at. %Pb–93.5 at. %Bi in atom fraction, while the lower part has that of 67 at. %Pb–33 at. %Bi. In consideration of the noise level and the accuracy of EDS signals on single NPs, it is reasonable to ascribe the upper part as pure Bi crystal. Meanwhile, the lower part with a Pb/Bi ratio of around 2 (i.e., 67/33 ~ 2.03) is also close to the intermetallic phase Pb$_7$Bi$_3$ (7/3 = 2.33) measured from the crystal lattices (Figure 5d). Since the ε phase in the phase diagram has a Pb/Bi ratio ranging from 1.32 to 2.7 in atom fraction, it is thus credible to attribute the lower part as the ε phase.

It should be noticed that long-time irradiation during EDS mapping (e.g., in Figure 5c) can induce surface modifications on the surface of the ultraclean NPs. Thin lead oxide shells are frequently found on both the residual ε-phase parts and the Bi-segregation parts (see more discussion in the Supporting Information). The oxidant source is probably generated by the diffusion and decomposition of the organic molecules adsorbed on the supporting Formvar films over the copper grid. The oxidation process is thus very slow and also restricted by the amount of the residual oxidant source. It can be
found that even though the oxidation shells are atomically thin, much fewer facets are formed on the Bi crystals, differing from those well-shaped ones. This surface-condition-induced geometric discrepancy further implies that surface energy and surface condition play critical roles in the energy relaxation of the as-prepared PbBi NPs. In other words, even though the surface contamination is very tiny, it will severely change the surface reconstruction of such delicate NPs, losing the chance for realizing the essential behaviors and properties of pristine gas-phase synthesized NPs.

The shape evolution of the PbBi NPs demonstrates that the free surfaces play a critical role in finalizing the eventual NP configuration, showing a strong surface effect. In terms of the phase evolution, whether the size effect or surface effect would generate an un-neglectable influence is still unclear. To make a comparison with the bulk counterpart, the phase diagram of bulk PbBi alloy and its normal precipitations during cooling are illustrated in Figure 6a—c. Taking the composition ratio similar to that of the initial PbBi NPs obtained in our experiments (i.e., around 38 at. %Pb—62 at. %Bi), as indicated by the arrow in Figure 6b, the molten bulk alloy will first precipitate solid Bi (marked as $B_i$) during slowly cooling down, and then form eutectic structures ($B_{II}$+$ε$ phase) and complete the liquid-to-solid transition according to the phase diagram. Under further structural relaxation, some extra Bi (marked as $B_{III}$) may precipitate from the $ε$ phase when the temperature further declines. Finally, composite microstructures including $B_i$, $B_{II}$+$ε$, and $B_{III}$ account for the final stable phases, as illustrated in Figure 6a. As for the PbBi NPs, the formation of Bi crystals and the $ε$ phase generally coincide with the bulk alloy. This suggests that the phase diagram is still valid at this scale for the prediction of phase evolution in NPs, though the exact temperatures at which phase transitions occur may slightly vary due to the size effect. Nevertheless, significant differences between the NPs and the bulk alloy in phase distribution can be clearly identified. That is, instead of forming eutectic structures, as illustrated in Figure 6d, the Bi precipitate tends to grow up, and the whole NP will finally transform into a Janus heterostructure. In this process, the free surfaces probably have provided an extra route for atom diffusion, which thereby inhibits the growth of more Bi lamella in the NP.

CONCLUSIONS

In summary, we have reported a strategy to unveil the phase evolution and dynamics in gas-phase fabricated binary NPs. We show that the e-beam can be used as a stimulus to create local heating with ultrafast response beyond conventional heating techniques. This enables the in situ synthesis of ultraclean binary NPs, as well as the manipulation of their phase and shape relaxation process. Using PbBi alloy as a demonstrative sample, it is revealed that PbBi alloy NPs show a featured phase transition scenario, that is, from an even alloy phase to a pac-man or a sandwich-like phase first, and then to a Janus phase with Bi segregations mostly faceted with (012) surfaces. Aside from the segregated Bi parts, the alloy parts undergo an intermetallic $\text{PbBi}_2$ phase first, and then further transform into the $\text{PbBi}_3$ phase ($ε$ phase). The observed phase and shape evolutions in PbBi NPs are also compared with their bulk counterparts. The validity of the phase diagram as well as the discrepancy between the precipitations are also discussed and attributed to the pronounced size and surface effects.

METHODS

The Bi$_4$Pb$_3$Sn$_{12}$In$_{21}$ bulk alloy (MAT-CN company) was used to fabricate the microballs. For a typical synthesis procedure, a fragment of the bulk alloy was peeled off and put into a beaker filled with hot deionized water (around 80 °C). When the alloy fragment melted, the beaker was transferred to an ultrasonic oscillator and sonicated for 60 s. During this process, the molten alloy was drastically dispersed into many small drops, and the clean deionized water turned into a turbid solution accordingly. Then, a drop of the turbid solution was absorbed using a glass pipet and dispersed onto the holey carbon film-supported copper grid for further experiments.

An aberration-corrected high-resolution TEM (FEI Titan 80–300) was used to perform the EAD experiments with an accelerating voltage of 300 kV. A weak e-beam was used for normal imaging while an intense e-beam was used to activate the EAD process. To verify the exact starting condition of the EAD process, the e-beam was first spread out to have quite a low beam intensity during sample searching. When the target sample was selected, the e-beam was focused on the microball step by step until the EAD process started. The corresponding beam intensities were recorded and set as the threshold values for alloy microballs having similar sizes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c08500.

More details for the EAD method, size distribution and composition of the obtained NPs, discussion on the beam effects, estimation of the cooling speed on the NP, discussion on the facets of the segregated crystals, discussion on the influence of surface oxidation, data on measured interfacial angles in the segregated crystals (PDF)

Dynamic phase segregation and facet formation in a typical PbBi NP (AVI)

Formation of facets on PbBi NPs at the initial stage (AVI)

Dynamic fusion of two Bi segregations in a PbBi NP to form a Janus structure (AVI)

Shape and phase evolution of a large PbBi NP formed by coalescence (AVI)

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Author Contributions
L.H. and L.S. proposed the project. L.S and Y.Z conducted the in situ TEM experiments. L.S., L.H., J.W., and L.S. performed data analyses. L.H. and L.S. organized and wrote the manuscript. All authors contributed to the discussion of the results and have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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