Two Birds with One Stone: Spontaneous Size Separation and Growth Inhibition of Femtosecond Laser-Generated Surfactant-Free Metallic Nanoparticles via ex Situ SU-8 Functionalization

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ABSTRACT: Laser ablation in liquids (LAL) offers a facile technique to develop a large variety of surfactant-free nanomaterials with high purity. However, due to the difficulty in the control of the particle synthesis process, the as-prepared nanomaterials always have a broad size distribution with a large polydispersity (σ). Surfactant-free properties can also cause problems with particle growth, which further increases the difficulty in size control of the colloids. Therefore, searching for strategies to simultaneously unify the sizes of colloids and inhibit particle growth has become significantly important for LAL-synthesized nanomaterials to be extensively used for biological, catalytic, and optical applications, in which field particle size plays an important role. In this work, we present a facile way to simultaneously realize these two goals by ex situ SU-8 photoresist functionalization. Ag nanoparticles (NPs) synthesized by femtosecond laser ablation of silver in acetone at laser powers of 300 and 600 mW were used as starting materials. The synthesized Ag NPs have a broad size distribution between 1 and 200 nm with an average size of ca. 5.9 nm and σ of 127−207%. After ex situ SU-8 functionalization and 6 months storage, most particles larger than 10 nm become aggregates and precipitate, which makes the size distribution narrow with an average diameter of 4−5 nm and σ of 48−78%. The precipitation process is accompanied by the decrease in colloid mass from the initial ∼0.2 to 0.10−0.11 mg after ex situ SU-8 functionalization and 6 months colloid storage. Morphology analysis indicates that ex situ SU-8 functionalization inhibits the particle growth into polygonal nanocrystals. Radical polymerization of SU-8 on Ag NPs is considered to be the reason for both spontaneous size separation and growth inhibition phenomena. Benefiting from Ag NPs' embedment and acetone dissolution, the glass-transition temperature of SU-8 photoresist increased from 314 to 331 °C according to thermogravimetric analysis. The universality of ex situ SU-8 functionalization-induced growth inhibition and size separation behaviors is further proved using the Au colloids generated by LAL in acetone. This work is expected to provide a new route for better size control of LAL-synthesized colloids via ex situ photoresist functionalization, although a half of colloidal mass is wasted due to radical polymerization-induced colloidal precipitation.

INTRODUCTION

In over last 2 decades, a newly emerged nanoscience technique known as laser ablation in liquids (LAL) has demonstrated its ability for the convenient synthesis of a large variety of nanomaterials composed of metallic, alloy, doped oxides, and particle–polymer composites.1−7 LAL is also possible to be implemented in the presence of an external electric or magnetic field10,11 to produce nonspherical nanostructures.5 Downstream treatment, such as ex situ conjugation,3,12−14 enables researchers to construct particle–polymer or particle–
biomolecule composites, respectively. Currently, the productivity of LAL has already reached 4 g/h,15,16 almost comparable to that of wet-chemistry methods. For a long-term nanomaterial production, LAL becomes much cheaper than the wet-chemistry technique17 so that industrial applications of LAL-generated nanomaterials in the future are envisioned, which is one of the main driving forces for the rapid expansion of LAL all over the world in recent years.1

In the absence of surfactants during the fabrication procedure, the as-prepared nanomaterials always possess high purity,1 which makes them very appealing for catalytic and biological applications.2 On the other hand, high purity also means that the surfactant-free particles suffer from spontaneous growth21 due to colloidal Brownian collision, which leads to their evolution into different structures, such as nanocubes,22 nanowires,24 onion-structured spheres,26 nanofibers, and nanosheets.23 This issue further gives rise to the broad/bimodal size distribution problem of LAL-synthesized colloids being closely related to different mechanisms and the complex gas-phase/liquid-phase processes, involving particle nucleation and growth.27

Two options, laser modulation and surface chemistry manipulation, are available for size control of LAL-synthesized nanomaterials.1 The former strategy is mainly implemented by changing laser parameters such as laser power,39 pulse duration,40 repetition rate, and beam shape,41 fragmenting particles into smaller particles,42 or melting the particles into submicrospheres.43 The latter strategy relies on either the conjugation of the particles by polymers,39 or biomolecules40,41 or the inhibition of particle growth by salts,42 surfactants,43 or carbon clusters while implementing LAL in organic solvents.46 As easily deduced, even though the particle sizes are tailored, the particles obtained by laser modulation are still surfactant-free, which inevitably induces particle growth. For example, we have recently observed that ultrasmall Ag nanoparticles (NPs) grow into polygonal nanocrystals accompanied by an increase in the particle size during storage of the colloid for 6 months.47 Therefore, tailoring the colloidal surface chemistry by ex situ functionalization would be a better solution to accurately control the particle size. However, some problems still arise when adopting this strategy. For example, Dell’Aglio et al. observed the rapid colloidal aggregation after ex situ conjugation of ubiquitin on bare Ag NPs, which led to an obvious red shift of the colloidal surface plasmon resonance (SPR) band and a decrease in the SPR intensity.48 A similar trend was observed by Meneghetti’s group when they performed ex situ functionalization of Ag NPs with α-lipoic acid and dodecanethiol molecules.49 Therefore, finding a suitable carrier that can not only inhibit particle growth without strong colloidal aggregation but also can bring new functions to the particles is of great importance. In this regard, photoresists that can be used to construct three-dimensional (3D) functional structures and films50,51 are considered as good candidates for a thorough investigation. Barcikowski’s group introduced LAL-synthesized Ni–Fe nanoparticles in SU-8 to linearly align the magnetic particles with the aid of an external magnetic field.52 Jonušauskas et al. embedded LAL-synthesized Au particles inside a negative photoresist (zirconium/silicon hybrid sol–gel SZ2080) and implemented the Au NPs plasmon-assisted three-dimensional (3D) microstructuring.53 Although SZ2080 could increase the stability of Au NPs in isopropanol for months,53 the issues regarding how the fresh surfactant-free LAL-generated colloids behave in the presence of photoresist polymers, whether colloidal aggregation occurs, the extent to which the colloids become aggregated after ex situ polymer functionalization, and whether the aggregated colloids stay inside the liquids or precipitate over time, are still seldom studied. All of these
issues should be clarified to establish a steady foundation for the controllable 3D printing of particle–photoresist nano-composites.

In this work, Ag particles freshly synthesized by femtosecond LAL in acetone at laser powers of 300 and 600 mW for 60 min were used as the starting materials. We demonstrate that ex situ photoresist SU-8 functionalization does not only spontaneously narrow the colloidal size distribution due to the precipitation of large particle aggregates, but also inhibits particle growth into polygonal crystals. The variation in the absorbance of the ex situ functionalized Ag–SU-8 composite colloids was recorded using a UV−vis spectrometer. Particle size analysis based on transmission electron microscopy (TEM) observation of the fresh Ag colloids and 6 months-aged SU-8-functionalized Ag colloids provided evidences of both the size separation and growth inhibition phenomena. Analysis of the Ag NPs surface chemistry and the surface groups of SU-8-functionalized Ag NPs by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) measurements was performed to clarify the chemical bonding between SU-8 and Ag particles. Differential scanning calorimetry−thermogravimetric analysis (DSC−TGA) was implemented to evaluate how acetone dissolution and embedded Ag NPs alter the thermal properties of the SU-8 photoresist polymer.

## RESULTS AND DISCUSSION

Figure 1a−d shows the change in absorbance of the ex situ SU-8-functionalized Ag NPs within 32 h and after storage for 6 months. As the aging time increases, the SPR peak first red-shifts from 404 to 410 nm after 32 h colloidal storage and further red-shifts to 422 nm after storage of both colloids for 6 months. A difference was observed for different laser powers in that the SPR intensity of SU-8-functionalized Ag NPs changed with time. For the composite colloid produced by 300 mW LAL, the SPR peak intensity was almost unchanged within 32 h (Figure 1a), but was significantly decreased from 3.5 to 2.0 (au) after 6 months of storage (Figure 1c,d) due to the slow precipitation of Ag NPs. In contrast, the SPR intensity for 600 mW LAL quickly decreased from 3.5 to 3.2 after storage for 32 h and then further decreased to 1.3 after storage for 6 months, which indicates the rapid precipitation of Ag NPs. The initial masses of the Ag colloids in both cases were ca. 0.20 mg. After storage for 6 months, the residual masses of Ag colloids inside the liquids changed to 0.11 and 0.10 mg for 300 and 600 mW LAL colloids, suggesting almost a half of Ag colloids in weight precipitated over time. The inset of Figure 1c shows the photographs of the composite colloids stored for 6 months. Despite almost the same initial SPR peak intensity corresponding to the same initial Ag NP concentration (Figure 1a), the SU-8-functionalized Ag colloids prepared by 300 and 600 mW LAL were orange and yellow after storage for 6
months, respectively, indicating a lower concentration of Ag NPs in the liquid for the latter case, in accordance with the SPR intensity difference shown in Figure 1d. At the bottom of the colloidal container, the precipitated particles (Figure 1c, black arrows) were clearly evident, as expected.

Figures 2a−c and 3a−c show the TEM images and the size distributions of the fresh Ag NPs synthesized by LAL at laser powers of 300 and 600 mW, respectively. The overall average sizes of the fresh 300 and 600 mW LAL−Ag NPs were 5.93 ± 7.55 nm (polydispersity (σ) = 126.7%) and 5.88 ± 12.18 nm (σ = 207.1%). Similarly to most of other LAL results,1 the Ag colloids synthesized in this work have a broad size distribution with size variation from 1 nm to several hundred nanometers. LAL at higher laser power has higher NP productivity;47 therefore, a larger amount of both large and small particles with diameter lower and higher than 10 nm (Figures 2a vs 3a) are generated by 600 mW LAL, and the average size of the 600 mW LAL−Ag colloid is slightly smaller than that of the 300 mW LAL colloid. Such a broad size distribution will cause a severe problem for colloidal applications such as catalysis2 because of the difficulty in clarifying the size effect.

In our cases, small particles of 1−10 nm in diameter occupy 88 and 91% number frequency of the entire amount for 300 and 600 mW, respectively. A detailed analysis of the particle sizes in the range of 0−10 nm shows that the colloids are mainly composed of Ag clusters of ca. 2 nm in diameter (insets of Figures 2g and 3g) with average sizes of 3.89 ± 1.98 nm (σ = 50.9%) and 3.69 ± 1.88 nm (σ = 50.9%) for 300 and 60 mW, respectively, which are almost of the same size as that of metallic colloids obtained by laser fragmentation in liquids.24 Therefore, as deduced from our experimental results, long-period femtosecond LAL in organic solvents is an attractive method to synthesize small metallic particles, as also indicated in ref 21.

The UV−vis spectra and photographs of the ex situ SU-8-functionalized Ag colloids (Figure 1) after storage for 6 months indicated a large amount of particles precipitated at the bottom of the colloidal container, while others remain stably dispersed in the solution. Analysis and comparison of the stable colloids and the precipitated particles were thus performed. Figures 2d−f and 3d−f show the morphologies of the stable Ag−SU-8 colloids after storage for 6 months. Compared to the fresh Ag colloids, which have broad size distributions, the as-aged stable ex situ SU-8-functionalized colloids have narrower size distributions. Particles larger than 30 nm were not detected. Approximately 99% number frequency of the stable particles is in the range of 1−20 nm for both cases (Figures 2h and 3h). Therefore, the spontaneous size separation phenomenon caused by large particle precipitation is evident for the ex situ SU-8-functionalized Ag colloids. The average sizes of the ex situ SU-8-functionalized 300 and 600 mW LAL−Ag NPs are 5.81 ± 4.55 nm (σ =
78.3%) and 5.07 ± 2.42 nm (σ = 47.7%), respectively, which are significantly smaller than those of the fresh Ag NPs used for ex situ functionalization and those Ag colloids stored for 6 months (7.40 ± 7.56 nm (σ = 102.2%) for 300 mW LAL and 7.82 ± 8.17 nm (σ = 104.5%) for 600 mW LAL), as shown in ref 47. Size separation phenomenon for the LAL−Ag colloids was also observed, where carbon shells, carbon clusters in liquids, and self-assembled carbon sheets acted to capture large particles and resulted in precipitation. However, compared to ex situ SU-8-functionalized Ag colloids, many particles larger than 30 nm were still stable in liquids. Precipitation of lesser amounts of large Ag particles and no colloidal dilution meant that the concentrations of as-aged LAL−Ag colloids without SU-8 functionalization were much higher than those of stable SU-8-functionalized Ag after storage for 6 months, as evidenced by the SPR peak intensities after storage for 6 months (2.0 and 1.3 for ex situ SU-8-functionalized 300 and 600 mW LAL colloids, respectively (Figure 1c,d); 5.0 and 4.5 for 300 and 600 mW LAL colloids, respectively47). These results suggest: (1) ex situ SU-8 functionalized 600 mW LAL−Ag colloid possess higher efficiency and higher ability for size separation than the functionalized 300 mW LAL−Ag colloid; (2) ex situ SU-8 functionalization is much more efficient for size separation than the LAL colloids as evidenced by a significant decrease in the SPR peak intensity, which corresponds to stable colloidal concentrations.

The morphologies of the precipitated particle aggregates for ex situ SU-8-functionalized 300 and 600 mW LAL colloids are shown in Figure 4a–f, respectively. The maximal sizes of the aggregates are in the micrometer scale (Figure 4b,e), and these are mainly composed of particles larger than 10 nm (Figure 4g,h). The average sizes of the precipitated particles are 29.71 ± 34.25 nm (σ = 115.3%, Figure 4g) for 300 mW LAL and 36.66 ± 37.78 nm (σ = 103.1%, Figure 4h) for 600 mW LAL. As reported elsewhere,47 Ag NPs larger than 30 nm are encapsulated by carbon shells. During the precipitation of large particles, the carbon shells should also capture a large amount of smaller Ag NPs (Figure 4c,f) to be precipitated. That is why, the precipitated particles include 22.5% (Figure 4g) and 16.5% (Figure 4h) small particles with sizes of 0−10 nm.

Although aggregation induced by ex situ functionalization significantly reduces the Ag colloidal concentrations, it facilitates the development of stable composites with narrower size distribution. Within the range of 1−10 nm, the average sizes of ex situ SU-8-functionalized Ag NPs for 300 and 600 mW LAL are 4.04 ± 1.07 nm (σ = 26.5%) and 4.79 ± 1.57 nm (σ = 32.8%), respectively. Therefore, the polydispersities of tiny Ag NPs (1−10 nm) also reduced from 50.9 to ca. 30% after ex situ SU-8 functionalization. As reported elsewhere,47 without ex situ functionalization, the surfactant-free LAL-synthesized tiny Ag particles grow into 7−50 nm polygonal nanocrystals (Figure 5a). In contrast, the ex situ SU-8-
functionalized Ag colloids are spherical in shape (Figure 5b,c). Therefore, it is reasonable to deduce that besides size separation ability, ex situ SU-8 functionalization can also inhibit the particle growth. Different from the regular Ag colloids stored for 6 months where large particles with diameters of several hundreds of nanometers are stable, no such large particles are found in the six ex situ SU-8-functionalized Ag colloids stored for 6 months (Figures 2d and 3d). This means that the polymer does play an important role in the precipitation of large particles.

The surface chemistry of LAL–Ag particles was examined by XPS (Figure 6a). The percentages of Ag, C, and O quantified by XPS analysis are 16.82, 63.08, and 2.93%, indicating that the LAL-synthesized Ag particles were covered by a thick layer of carbon. The peak fit of the high-resolution C 1s spectrum by deconvolution (Figure 6c) confirmed the formation of both sp² C–C and sp³ C–C, which correspond to the characteristic peaks at 284.5 and 285.2 eV.⁵⁴ The presence of sp² and sp³ carbon corresponds to hybridized C–C disordered graphite and crystalline diamond or soot, respectively. The sp²/sp³ area ratio was calculated to be 59.29:20.00 ≈ 3:1, which indicates that the outermost surface layers of the particles are mainly covered by disordered amorphous carbon. Given that (1) the detection depth is only 5 nm for XPS characterization and (2) Ag cores can be detected by XPS, the average thickness of carbon shells is less than 5 nm. The high resolution of the XPS Ag 3d image (Figure 6b) has two peaks of Ag 3d₅/₂ and Ag 3d₃/₂ at binding energies of 368.0 and 374.1 eV, which is in good agreement with the peaks of pure Ag.⁵⁵ No other peaks corresponding to AgO (367.3 eV) or Ag₂O (367.8 eV)⁵⁶ were observed; therefore, it can be concluded that pure Ag particles are generated by femtosecond LAL of Ag in acetone. High-resolution XPS O 1s (Figure 6d) and C 1s (Figure 6c) images show that C=O carboxyl group (531. 0 eV in the O1

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Figure 5. (a) TEM image of the Ag colloid stored for 6 months, whereby particle growth into polygonal nanocrystals occurs. (b, c) TEM images of ex situ Ag–SU-8 Ag colloids stored for 6 months, where most of Ag particles are spherical, which indicates that particle growth is inhibited by ex situ SU-8 functionalization.

Figure 6. (a) Wide XPS scan of the Ag@C particles synthesized by laser ablation of Ag in acetone. High-resolution spectra of (b) Ag 3d, (c) C 1s, and (d) O 1s and the deconvoluted peaks.
The bonding between SU-8 and Ag NPs alters the glass-transition temperature (T_g) of SU-8 polymer, which increases T_g from 314 °C (pure SU-8) to 331 °C after ex situ embedding of LAL−Ag NPs in SU-8, as shown in the TGA profile (Figure 7b). Both T_g values of acetone-dissolved SU-8 and SU-8−Ag composites are larger than 136 °C for pure SU-8 gel (Figure 7b), which is close to 25 wt % pyrolysatereported elsewhere. Deduced from the TGA curve, the Ag NP content is estimated to be 4 wt %, Epoxide rings are good synthetic intermediates; therefore, it is speculated that the epoxy groups of SU-8 should be first converted into hydroxyl groups and then act as initiator sites for the free-radical polymerization of SU-8 photoresist.

To confirm this speculation, FTIR analysis of chemical groups that are conjugated on the precipitated Ag NPs was performed, and the results are shown in Figure 8. For a better understanding of how chemical groups of SU-8 change after LAL−Ag NP binding, FTIR spectra of the pristine SU-8 and ex situ synthesized Ag−SU-8 composites (from the stable colloids) are also shown (blue and red curves in Figure 8, respectively). The chemical groups, wavenumbers for different peaks, and the vibrational bindings are summarized in Table 1. The vibration bands at 1242, 833, and 912 cm⁻¹ are related to the symmetrical and asymmetrical stretching peaks of the −CH₂, −CH₃, and −CH₃ groups and then act as initiator sites for the free-radical polymerization of SU-8 photoresist.

Figure 7. (a) DSC and (b) TGA analyses of SU-8 gel, acetone-dissolved SU-8 polymer, and Ag−SU-8 composites synthesized by ex situ mixing of LAL-synthesized colloids and SU-8 solution.
CH stretching. The broad band at 3480 cm⁻¹ of the SPR band has been attributed to variation of the surface construction of 3D structures or functional SU-8 composite could also occur similarly to that of pristine SU-8 for the concentration, means that polymerization of the composites alized 600 mW LAL at a higher power, which explains why the ex situ function-
ized 600 mW LAL for the stable ex situ Ag precipitated Ag NPs, while the C=O stretch of epoxy rings was detected from the FTIR spectra (Figure 8 and Table 1), no CH₂=O=CH band of epoxy rings was detected from the precipitated Ag NPs, while the C–O–H group appears, both of which indicate the free-radical polymerization of SU-8 photoresist with Ag NPs according to the scheme shown in Figure 9. The radicals are due to acetone decomposition during LAL. Higher amounts of radicals are generated by LAL at a higher power, which explains why the ex situ functionalized 600 mW LAL–Ag NPs undergo a quicker precipitation while ex situ functionalized 300 mW LAL–Ag NPs undergo a slow precipitation (Figure 1). The preservation of epoxy rings for the stable ex situ Ag–SU-8 composites, despite the low concentration, means that polymerization of the composites could also occur similarly to that of pristine SU-8 for the construction of 3D structures or functional SU-8 composite films, which will be examined in our future work. The red shift of the SPR band has been attributed to variation of the surface chemistry or an increase of the particle size. In the present case, due to the decrease in the Ag particle size after colloidal storage for 6 months (Figures 2d–f and 3d–f), it can be concluded that alteration of the surface chemistry of Ag NPs caused by ex situ SU-8 functionalization leads to the red shift of the SPR band of the Ag colloids from 404 to 422 nm (Figure 1). Due to surface chemistry alternation, the hydrodynamic diameters of the SU-8-functionalized Ag NPs significantly increased to 187.6 ± 41.2 (Figure 10a) and 254.6 ± 61.1 nm (Figure 10b) after 6 months storage. The larger hydrodynamic sizes and broader hydrodynamic size distributions of Ag–SU-8 composites using 600 mW LAL–Ag colloids should be attributed to higher amounts or stronger bindings of SU-8 molecules on Ag NPs originating from more radicals generated during 600 mW LAL.

To demonstrate the universality of simultaneous particle growth inhibition and size separation phenomena induced by spontaneous radical polymerization after ex situ SU-8 functionalization, the absorbance difference between 3 weeks-aged Au colloid synthesized by LAL in acetone and the Au colloid ex situ functionalized by SU-8 is shown in Figure 11 for comparison. Similarly to the case of Ag colloids shown in Figure 1, the SPR intensity of SU-8-functionalized Au colloid significantly decreases from 2.3 to 0.4 after 3 weeks storage. In comparison, the SPR intensity of 3 weeks-aged Au colloid without SU-8 functionalization slightly increases from 2.3 to 2.7 due to acetone volatilization-induced AuNP concentration increase. That is why, the optical transparency of the aged Au and SU-8–Au colloids is very different, as indicated by the inset optical images in Figure 11a. After 3 weeks storage, the SPR peak positions of Au colloid and the SU-8–Au composite colloid shift from 531 to 533 and 537 nm, respectively, indicating the particle growth of Au particles during storage and the surface alteration of Au particles after SU-8 functionalization, respectively. Figure 12 shows the TEM images of the Au colloid (Figure 12a–c) and SU-8-functionalized Au colloid (Figure 12d–f) and the calculated size distributions (Figure 12g.h). As clearly shown, the aged Au colloid has large particles with maximal size up to 87 nm, while in comparison, the maximal size of SU-8-functionalized supernatant Au colloid after 3 weeks storage is only 25 nm. Many polygonal Au particles are found from the aged Au

Table 1. IR Absorption Modes of Pristine SU-8 and SU-8–Ag Composites

| chemical group | wavenumber (cm⁻¹) | assignment |
|---------------|------------------|------------|
| epoxy rings   | 1242             | C–O–C asymmetric stretch⁶⁶ |
|               | 833              | C–O–C symmetric stretch⁶⁶ |
|               | 912              | CH₂–O–CH bend⁶⁸ |
| benzene rings | 1607             | 1st pair of para/ortho-substituted benzene⁶⁸ |
|               | 1500             | 2nd pair of para-substituted benzene⁶⁶ |
|               | 1472             | 2nd pair of ortho-substituted benzene⁶⁸ |
| ether groups  | 1183             | –C=C–O–C– stretch⁶⁸ |
|               | 1126             | –O–C–C– stretch⁶⁸ |
|               | 1032             | –C–O–C– stretch⁶⁸ |
| others        | 1295             | C–O–H stretch⁶⁶ |
|               | 1728, 1792       | C=O stretching⁷⁰ |
|               | 2872             | asymmetrical –CH₂ stretch⁷¹ |
|               | 2923             | symmetrical –CH₂ stretch³¹ |
|               | 2964             | CH stretch⁷¹ |
|               | 3480             | OH–⁷² |

Figure 9. Scheme for the free-radical polymerization of SU-8 on surfactant-free Ag NPs.
colloid (Figure 13a) but seldom found from the SU-8-functionalized Au colloid (Figure 13b). This phenomenon indicates that SU-8 functionalization indeed inhibits the particle growth, which can also be deduced from the smaller average sizes of SU-8-functionalized Au particles in the range of $0^{-10}$ nm (Figure 12g,h; $3.98 \pm 1.62$ and $3.66 \pm 1.54$ nm for aged Au particles and SU-8-functionalized Au particles, respectively). Taking together, the above-mentioned findings give an evidence that radical polymerization between SU-8 molecules and LAL-generated Au particles causes the precipitation of large particles and inhibits the particle growth, similarly to the case of ex situ SU-8-functionalized Ag colloids.

Recently, we have shown that the carbon clusters and the carbon shells of metal particles can behave as captors to capture large particles to become nanoaggregates and make them precipitate over time.47 The precipitation of Au colloids also occurred during the storage. Due to similarity to Ag colloids, analysis of the precipitated Au particles was not performed in this work. In both cases, many large particles are still stable in the liquids even after storage for 6 months. In contrast, the size separation ability of ex situ SU-8 photoresist functionalization is more efficient in spite of severe colloid precipitation.

### CONCLUSIONS

This work has demonstrated that ex situ SU-8 functionalization of surfactant-free Ag NPs not only allows the size selection of small particles, but also enables the inhibition of particle growth into polygonal nanocrystals. Spontaneous aggregation and precipitation of the large particles with diameters of $10^{-300}$ nm occurred during long-term storage for 6 months, irrespective of the initial amount of the large particles synthesized by LAL at laser powers of 300 and 600 mW. The colloidal concentrations thus significantly decreased, and the size distributions of the colloids narrowed with the polydispersity of the overall sizes changing from initial $126^{-207}$ to final $50^{-80}$. As for the predominantly small ($1^{-10}$ nm) particles with average sizes of $4^{-5}$ nm that occupied $82^{-96}$% number frequency of the stable SU-8-functionalized Ag NPs, the polydispersity decreased from 50.9 to 26.5–32.8%. XPS and FTIR joint analysis confirmed free-radical polymerization of SU-8 on surfactant-free Ag NPs, which is considered to be the underlying mechanism for both spontaneous size separation and growth inhibition phenomena. The acetone dissolution and the interaction between the SU-8 molecules and surfactant-free LAL-generated Ag NPs also altered the thermal properties of SU-8 photoresist. Three new endothermic peaks (199, 253, and 419 °C) were observed in the DSC curve, while the glass-transition temperature of SU-8 increased.
from 314 to 331 °C when the ex situ SU-8-functionalized Ag NP was ca. 4 wt % of the overall weight of the composites. Successful narrowing of the size distribution of metallic colloids by ex situ photoresist functionalization and long-term storage may offer a solution to solve the broad size distribution problem of LAL colloids. It is noteworthy that if adopting this method for size control, precipitation-induced decrease in the colloid concentration will significantly lower the mass for practical applications.

**METHODS**

Silver colloids were synthesized by laser ablation of Ag in acetone for approximately 60 min using a femtosecond laser (FGPA μJewel D-1000-UG3, IMRA America Inc., Ann Arbor, MI) with pulse duration, wavelength, and repetition rate of 457 fs, 1045 nm, and 100 kHz, respectively. Two laser powers of 300 and 600 mW were adopted for LAL. A 20 mm diameter and 1 mm thick silver plate was placed inside a glass dish (45 mm diameter and 18 mm height) filled with 8 mL of acetone for LAL. A 10 mm diameter and 5 mm thick gold target was placed inside a smaller glass dish (35 mm diameter and 15 mm height) filled with 8 mL of acetone for LAL. The thickness of the liquid was approximately 5 mm above the target surface. The femtosecond laser beam was focused on the Ag plate surface using a 20× objective lens (numerical aperture = 0.4, Mitutoyo, Japan). An area of 3.5 × 3.5 mm² was scanned at a scan speed of 1 mm/s. The parallel-line scanning method described in refs 76−78 was adopted with an adjacent line interval of 5 μm. After synthesis, the colloids were directly mixed with the acetone-dissolved SU-8 (SU-8 2050, MicroChem) polymer solutions to make the weight ratio of Ag or Au colloids (including the acetone solvent used for LAL) occupy 12 wt % of the mixed solution. The colloids were stored and sealed in a glass container at room temperature. After storage...
for 6 months, both the colloids in the liquids and the precipitated particles at the bottom of the glass container were characterized by TEM and UV–vis spectroscopy. The masses of the synthesized Ag colloids obtained by LAL at 300 and 600 mW were measured by comparing the weight of the Ag target before and after LAL. The residual masses of stable supernatant Ag colloids after 6 months storage were estimated by comparing the peak intensity of the fresh Ag colloids diluted by acetone with dried SU–8 Ag composite films. The weight ratios of acetone in both supernatant SU–8 composites were measured by comparing the weight of glass slides used for composite film deposition, the weight of the colloid used for film deposition, and the glass slides with dried SU–8–Ag composite films. The weight ratios of acetone in both supernatant SU–8–Ag composite colloids, which were stored for 6 months, were ca. 89 wt %.

Transmission electron microscope (Jeol JEM-1230) and UV–vis spectrometer (Shimadzu UV-3600 Plus) were used to characterize the morphologies of Ag NPs and Ag–SU–8 composites and record the variation in the absorption spectra of composite over time. For XPS (Rigaku SmartLab-R 3 kW) characterization, the colloids were centrifuged by a centrifuge (Eppendorf Centrifuge 5430, Germany) at a rotation speed of 14000 rpm for 10 min and then deposited on the glass substrates. The surface chemistry of the Ag particles was analyzed by FTIR spectrometer (Shimadzu, Prestige-21). The Ag NPs precipitated at the bottom of the container were separated from the stable composite colloids and then washed twice with acetone. After each washing, the precipitated colloids were centrifuged and separated from the upper solutions to ensure that the remaining SU–8 in the liquid was removed from the precipitated Ag NPs. Then, the precipitated Ag–SU–8 composites were then directly used for FTIR characterization. For DSC–TGA (Mettler Toledo, TGA/DSC2, Greifensee, Switzerland) and FTIR characterization of the acetone-dissolved pure SU–8 and the ex situ functionalized Ag–SU–8 composites, the solutions were deposited on glass substrates and then dried in an oven at 60 °C for 10 h. The DSC–TGA measurement of pure SU–8 gel without acetone dissolution was also performed for comparison. DSC–TGA measurements were implemented in nitrogen gas at a heating rate of 20 °C every 5 min. After solidification, small pieces of the dried SU–8 and Ag–SU–8 composite films were peeled off from the glass and used for FTIR characterization. A particle size analyzer (ELSZ-2PL, Phototal, Osaka, Japan) was used to measure the hydrodynamic diameters of 6 months-aged SU–8-functionalized Ag particles.

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**Author Contributions**
D.Z. and K.S. conceived and designed the experiments. W.C. performed the experiments. D.Z. characterized the particles and analyzed the data. K.Y., A.T., and K.N. performed the TGA–DSC measurement. H.-P.L., Y.K.L., and Y.I. performed the DLS measurement. D.Z. wrote the paper, and all authors read and revised it. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

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