Yolk-Shell AuAgPt Alloy Nanostructures with Tunable Morphologies: Plasmon-Enhanced Photothermal and Catalytic Properties

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1. Introduction

Localized surface plasmon resonance (LSPR) is one of the unique physiochemical properties for noble metal nanostructures.\(^1\) It occurs when the frequency of incident light is equal to the intrinsic oscillation frequency of metal surface electrons.\(^2\) The energy of incident light would be greatly absorbed and converted into other forms, such as internal energy. Based on this, a myriad of techniques has been developed. A typical example is the sensitive detection of functional molecules.\(^3\) For instance, the colloidal gold (Au) nanoparticles exhibit the red color while the addition of sulfuric species (i.e., L-Cysteine) would cause the aggregation of Au nanoparticles via the Au–S covalent bond and thus the redshift of the absorption peak in UV–vis extinction spectrum.\(^4\) Recent research progress have also demonstrated that the LSPR can be extended to other areas and utilized in a more comprehensive way, such as photothermal heat conversion and plasmon-enhanced catalysis.\(^5\) In particular, the photothermal heat conversion can sustainably transform the light energy of...
into thermodynamic one, while for plasmon-enhanced catalysis, the enhanced electromagnetic field would be beneficial to transfer the non-adiabatic energy from hot electrons that transiently populate the unoccupied electronic orbitals of the adsorbate to the vibrational modes of the adsorbed reactants and thus change the reaction pathways.\[^9\] It is worth pointing out that the morphology control could be an effective knob to maneuver the LSPR properties of noble metal nanostructures, which can further affect their performance for LSPR-based applications.\[^7\] Taking hollow nanostructures for example. Creating hollow interiors in the nanoparticle body not only leads to the enriched oscillation modes, but also induces multiple reflections of light within the hollow cavity, enhancing the utilization efficiency of incident light energy.\[^8\] Among those hollow structures, the yolk-shell or “rattle-typed” one containing a particle core inside the hollow shell is interesting, owing to their dual functionality arising from both core and shell parts.\[^9\] In addition, overlapping the plasmon of the two parts can bring in a more intense electromagnetic field and thus increase the density of hot electrons.\[^10\]

Thanks to research efforts from many groups, it is now possible to create yolk-shell nanostructures with the elemental compositions covering many noble metal combinations.\[^11\] Typical route involves the galvanic replacement reaction (GRR) between a core-shell particle and an etchant, where the metallic shell can be etched to form pores or cavities.\[^12\] If the etchant is a metal precursor, due to the difference in reduction potential, the reduction and deposition of the etchant atoms can change the types of constitutional elements.\[^13\] We noted that for most of these products, there is still lack of control over two important structural characters: i) the core and shell part are typically composed of different noble metals. Despite the presence of separated phase allows each component to play their individual role, the homogeneous distribution of all metals could facilitate the interaction between them and thus the potential synergetic effect can be expected;\[^14\] ii) achieving the frame-like morphology for outer shell is still facing technique challenging, especially for two metals with noticeable lattice mismatch. Compared to other hollow structures, the frame-like shell effectively removes the most part of side wall and reserves the corner and edge part, allowing the maximized exposure of surface atoms and hollow interiors.\[^15\] Meanwhile, the diffusion resistance can be significantly reduced, which makes the intensive interaction between the core material and reactants during catalysis feasible. However, during the GRR process, if the effective control over reaction kinetics and surface capping is absent, the etching and regrowth cannot typically conduct in a face-selective manner. In this case, the random destruction of edge regions would cause the collapse of the whole yolk-shell structure and thus the loss of well-defined frame-like shell. To this end, it is highly desirable to develop effective method to overcome these problems for a more versatile control over the morphology and elemental distribution.

Herein, we report the fabrication of yolk-shell AuAgPt nanostructures with tunable morphologies and examine their performance for LSPR-based performance for photothermal conversion and plasmon-enhanced catalysis. In particular, by mildly reacting Au@Ag core-shell nanocubes (NCs) with H$_2$PtCl$_6$, the resultant product took a well-defined yolk-shell structure containing cubic nanoframes. The morphology of the nanoframe can be controlled to be smooth and dendritic, respectively, when the amount of Pt precursor was tuned. Accompanied by the GRR between Ag and H$_2$PtCl$_6$, the Pt precursor can also diffuse inward and etch the Au core upon the formation of hollow interior. Meanwhile, the presence of reductant allows the regrowth of Au and Ag atoms, which makes the homogeneous distribution of the three metals over the whole particle. In addition to structural analysis, we also evaluated their performance toward two LSPR-based applications, including photothermal heat conversion and simulated sunlight-assisted reduction of 4-nitrophenol (4-NP). Due to the unique structure and elemental distribution, they exhibited a satisfactory activity in both measurements, and the mechanism for enhancement was also validated by finite-difference time-domain (FDTD) simulations.

2. Results and Discussions

2.1. Synthesis of AuAgPt Alloy Yolk-Shell Nanostructures with Tunable Morphologies

The current synthesis of AuAgPt yolk-shell nanostructures involves a stepwise design (Figure 1a). Typically, Au@Ag core-shell NCs were prepared using the protocol as developed by Xia and coworkers.\[^16\] We found that the use of docosyltrimethylammonium chloride (DTAC), instead of CTAC, as the capping agent, could improve the yield of cubic particle in final products (Figure S1, Supporting Information). Then, these Au@Ag NCs were directly mixed with Pt precursor solution to allow the GRR between them to occur. The residual AA involved in the solution could allow controlled reduction integrated in the GRR process. To track the shape evolution pattern, we made one batch of Au@Ag NCs react with different volumes of H$_2$PtCl$_6$ (20 mM) solution and recorded their shapes using scanning electron microscopy (SEM) and transmission electron microscope (TEM). As shown in Figure 1b,c, the Au@Ag NCs became etched after the reaction with Pt precursor. Some pores and voids could be observed in the particle. When the volume of H$_2$PtCl$_6$ (20 mM) solution reached 12 μL, the resulting products displayed the morphology of well-defined cubic frame in the shell part (Figure 1d,e). The average frame width was measured to be 8.7 ± 1.6 nm (Figure S2, Supporting Information). Further addition of H$_2$PtCl$_6$ solution made the product exhibit dendritic shape (Figure 1f,g). In particular, the cubic frame-like structure was maintained but high density of nanodendrites covered both the edge and interior of the particle. For convenience, the
as-mentioned three AuAgPt products were labeled as AuAgPt-6, AuAgPt-12, and AuAgPt-25, for further discussion.

The size variation of these AuAg-based products was statistically analyzed by counting 100 typical particles in corresponding electromicroscope images. As shown in Figure 2a, the edge length gradually increased as more H$_2$PtCl$_6$ was introduced (e.g., d(Au@Ag NCs): 38.3 ± 3.0 nm; d(AuAgPt-6): 42.5 ± 2.4 nm; d(AuAgPt-12): 47.1 ± 2.2 nm; d(AuAgPt-25): 55.6 ± 4.5 nm). Their elemental compositions were determined using inductively coupled plasma optical emission spectroscopy. The atomic molar ratio of Au:Ag:Pt for Au@Ag NCs, AuAgPt-6, AuAgPt-12, and AuAgPt-25 was measured to be 1.7:98.3:0, 1.2:87.1:11.7, 0.7:79.6:19.7, 0.1:63.8:36.1, respectively (Figure 2b). The increased percentage of Pt along with decreased percentage of Ag in resulting products confirmed the successful occurrence of GRR. The percentage of Au also became lower when more H$_2$PtCl$_6$ was introduced, which should be possibly attributed to the GRR between Au and PtCl$_6^{2-}$ and the partial loss of Au seeds during the formation of yolk shell structure.[17]

In addition to track the variation in morphology and elemental compositions, we also analyzed their crystal structure using XRD. As shown in Figure 2c, these peaks could be mainly indexed to the (111), (200), and (220) crystal planes of face-centered cubic (fcc)-Ag or Au, respectively, as their lattice constants are too close. The patterns also showed a small shift to the low-angle direction compared with the JCPDS data of fcc-Au and/or Ag, which could be related to partial oxidation of surface atoms or the presence of residual Cl$^-$/I$^-$. This is because the two theta value of Ag$_{2}$O (111) and AgCl (111) crystal plane is 32.790° (JCPDS No. 43-0997) and 27.831° (JCPDS No. 31-1238), respectively, which are both smaller than that of Ag (111). As indicated in previous studies, Ag nanocrystals tend to form a thin Ag$_{2}$O layer on the particle surface upon exposure in air, which affects their LSPR properties significantly (e.g., the LSPR peak of Ag@Ag$_{2}$O core-shell particles redshifts as compared to pure Ag nanoparticles of the same size with no oxide layer on the surface).[18] After the GRR with H$_2$PtCl$_6$, each diffraction peak of the resultant product became shifted to a larger two-theta value, respectively. The shift was more prominent when more H$_2$PtCl$_6$ was participating in the reaction. The detailed peak positions were listed in Table S1, Supporting Information, for comparison. Given the fact that only the diffraction peak lies between the corresponding peaks of fcc-Au/Ag and fcc-Pt and no additional diffraction peak for fcc-Pt appeared, we can confirm an alloy phase formed in the final.

Figure 1. a) Schematic illustration showing the shape evolution process of AuAgPt yolk-shell nanostructures. b,d,f) scanning electron microscope (SEM) and c,e,g) transmission electron microscope (TEM) images of yolk-shell AuAgPt nanostructures (AuAgPt yolk-shell nanostructures [YSNSs]) obtained by reacting one batch of Au@Ag core-shell NCs with aqueous H$_2$PtCl$_6$ (0.5 mM) solution at the volume of b,c) 6 μL, d,e) 12 μL, and f,g) 25 μL, respectively. For convenience, the three samples are labeled as b,c) AuAgPt-6 YSNSs, d,e) AuAgPt-12 YSNSs, and f,g) AuAgPt-25 YSNSs, respectively.
products when Au@Ag core-shell NCs reacted with H₂PtCl₆ under current conditions.

2.2. Morphology and Structural Characterizations of AuAgPt Alloy YSNSs

To further elucidate their structure, we took the as-prepared AuAgPt-12 alloy yolk-shell nanostructures (YSNSs) for systematic characterizations using other techniques, such as high-angle annular dark-field scanning TEM (HAADF-STEM), energy-dispersive X-Ray STEM (EDX-STEM), selected-area electron diffraction (SAED), high-resolution TEM (HRTEM), and X-Ray photoelectron spectroscopy (XPS). As shown in Figure 3a, the HAADF-STEM image further confirmed their yolk-shell structure with well-defined cubic frames. EDX-STEM elemental mapping images (Figure 3b–e) suggested that all the three metal atoms can be found over the whole particle. Compared to yolk-shell products documented in literature having a distinct core-shell elemental composition, the current AuAgPt nanostructures featured with homogeneous distribution of all elements, which should be related to the etching–regrowth mechanism as described in our previous work.[19] The SAED pattern of an individual particle clearly shows the diffraction pattern of fcc metal viewed along the [004] direction, suggesting the particle was sitting on the copper grid on the exposed {100} facets (Figure 3f). The lattice fringe of 0.20 nm measured in the HRTEM image of the shell part should be indexed to the alloy phase of AuAgPt (Figure 3g). Line-scan profile shows that the distribution of Pt and Au over the whole particle was relatively close, while Ag has a higher atomic percentage than both Au and Pt in the shell part (Figure 3h). In addition, their electronic states were evaluated using XPS. As shown in Figure 3i–k, typical doublets could be observed in Au 4f, Pd 3d, and Ag 3d XPS spectra, confirming their zero-valent states. The signal intensity of Au was relatively weak, which should be its limited atomic percentage in the product (<1%). In addition, the presence of residual Cl⁻ ions was validated from the wide XPS spectrum (e.g., 206.8 eV, Cl 2p band) (Figure S3, Supporting Information). The structural characterizations of Au@Ag NCs, AuAgPt-6 YSNSs, and AuAgPt-25 YSNSs, such as HAADF-STEM and EDX-STEM mapping images were illustrated in Figure S4–6, Supporting Information. Based on these data, it can be seen that the Au@Ag NCs exhibited a clear core-shell elemental configuration. For AuAgPt-6 and AuAgPt-25 YSNSs, despite all the elements can be found over the whole particle based on the EDX-STEM mapping images, the line-scan results suggested a more accurate elemental distribution feature. For example, for AuAgPt-6, the Ag mainly was distributed in the shell regions while the core was mainly composed of Au and Pt. In contrast, for AuAgPt-12, both Ag and Pt could be found in the shell part, while the core was mainly containing Au. Taken together, the use of different Pt contents in GRR could influence the elemental distribution of Au, Ag, and Pt in resultant products.
2.3. LSPR Properties

The as-prepared AuAg-based nanocrystals were suspended in water for measurement via UV–vis–NIR extinction spectroscopy. As shown in Figure 4a, the extinction spectrum of Au@Ag core-shell NCs showed the major peak located at 444 nm, corresponding to the dipole resonance mode of Ag. Moreover, two shoulder peaks located at 350 and 388 nm were also observed, which was ascribed to the quadrupole resonance mode of Ag and indicated the formation of cubic morphology of Ag-based nanocrystals featured with sharp corners.[20] After the GRR with H₂PtCl₆, their major peaks became gradually broadened from the visible to near-infrared region. Accordingly, the color of the aqueous suspensions was gradually changed from yellow to black as the Pt content increased in the products of AuAgPt alloy YSNSs. Compared to the metal nanoparticles with narrowband
plasmonic resonance which only allows the utilization of a small portion of light in the solar spectrum, the AuAgPt alloy YSNSs with broadband light absorption will be beneficial to enhance the utilization efficiency of sunlight energy and also avoid the wavelength limitation of light sources. This superior “black gold/silver”-like character enables the AuAgPt alloy YSNSs to have promising applications such as LSPR-based photothermal water purification/desalination, photothermal sensing/imaging, and plasmon-enhanced catalysis.\textsuperscript{[21]}

2.4. Plasmon-Enhanced Photothermal Conversion

The plasmon-enhanced photothermal properties of as-prepared AuAgPt alloys YSNSs were examined by measuring the temperature elevation of pure water and aqueous suspensions of Au@Ag NCs and AuAgPt alloys YSNSs with different Pt contents, respectively, under the irradiation of an 808 nm laser with a power density of 0.92 W cm\textsuperscript{-2}. As shown in Figure 4b, the temperature of the three aqueous suspensions of AuAgPt alloys YSNSs all increased from room temperature rapidly to over 35 °C in 15 min (e.g., T = 43, 40, and 38 °C, for AuAgPt-6, AuAgPt-12, and AuAgPt-25 alloy YSNSs, respectively, at t = 15 min with 300 μL aqueous suspensions). In contrast, there was no obvious change in the temperature of pure water and the aqueous solution of Au@Ag NCs, indicating that the light energy can be efficiently absorbed and converted into heat using AuAgPt alloys YSNSs. In particular, the average heating rate for aqueous suspensions of AuAgPt-6 alloys YSNSs reached 1.33 °C min\textsuperscript{−1} during 15 min laser irradiation, which showed the best photothermal heat conversion among the four AuAg-based samples. Figure 4c shows photothermal images of all the measured samples, which were recorded using an IR camera with the NIR laser at 10 min. The signal of temperature (in color) changed most prominently for AuAgPt-6 alloys YSNSs, validating the temperature variation results as displayed in Figure 4b. It also showed an excellent photothermal stability during five cycles of on/off laser irradiation, where no decay in the temperature was observed after 12 min irradiation for each cycle (Figure 4d). The photothermal heat conversion efficiency of AuAgPt-6 alloys YSNSs was measured to be 12.9% (Figure S7, Supporting Information), which is comparable among typical AuAg-based nanostructure reported in previous studies. In addition, unlike the shape evolution observed in Au–Ag hollow nanostructures after laser irradiation,\textsuperscript{[22]} the current AuAgPt-6 alloys YSNSs still maintained its unique yolk-shell frame-like morphology after photothermal treatment, which could be attributed to the synergetic effect of all three metals present homogeneously in one particle body (Figure S8, Supporting Information).
It is worth pointing out that the use of a simulated sunlight as the light source would lead to a different photothermal performance for these samples. As shown in Figure S9, Supporting Information, we tried to replace the 808 nm laser with a 500 W Xe lamp as the light source and reconducted the photothermal measurements. In this case, AuAgPt-25 YSNSs exhibited best photothermal conversion among the three AuAgPt samples. It is possible that the increase of Pt content in AuAgPt alloy YSNSs makes the plasma resonance of the material change from narrow band to wideband, which can improve the utilization efficiency of simulated sunlight. However, all these samples exhibited very limited temperature increases (e.g., less than 5 °C) upon such irradiation condition, suggesting the necessary use of 808 nm laser in evaluating their photothermal properties. It is possible that insufficient irradiation energy was provided at the appropriate wavelength that can be effectively absorbed.

2.5. Plasmon-Enhanced Catalysis

Since the as-prepared AuAgPt YSNSs had a strong absorbance in the visible region, their LSPR properties could also be utilized to enhance the catalytic performance under simulated sunlight irradiation as caused by the effect of plasmon enhancement. Herein, we chose the reduction of 4-NP under the irradiation of simulated sunlight as the model reaction since all the three metals have been demonstrated catalytic effective toward the reaction. The catalytic measurement were conducted according to the protocol as described in our previous study. For each catalyst, two sets of measurements with the same operational steps were conducted except for the irradiation condition. Each measurement continued for 25 min and time-dependent UV–vis extinction spectra were recorded at set intervals (Figure S10, Supporting Information). As shown in Figure 5a, the characteristic absorbance of 4-NP located at 400 nm in UV-vis extinction spectra became gradually smaller, showing the catalytic consumption of 4-NP. By the time point of 25 min, the conversion percentages of 4-NP for these catalysts under light on/off conditions were as follows (Figure 5c): i) Au@Ag NCs, 87.5% (light on) versus 85.3% (light off); ii) AuAgPt-6 YSNSs, 45.0% (light on) versus 35.0% (light off); iii) AuAgPt-12 YSNSs, 97.1% (light on) versus 95.8% (light off); iv) AuAgPt-25 YSNSs, 81.3% (light on) versus 67.5% (light off). The difference in conversion of 4-NP as catalyzed by these metallic nanoparticles should be attributed to the variation in both structure and elemental compositions. We noticed that for all these catalysts, the reduction of 4-NP became noticeably accelerated under light-on condition, indicating the contribution brought by plasmon-enhancement effect. For quantitative comparison, their apparent rate constants (k) were obtained by plotting \( \ln(I_0/I) \) versus reaction time and calculating the slope using the linear fitting method (Figure S11).

**Figure 5.** Simulated sunlight-assisted reduction of 4-NP using Au@Ag NCs and AuAgPt alloy YSNSs as the catalyst. a,b) Plots showing the absorbance at 400 nm versus time for different catalysts under a) light-off and b) light-on conditions. c,d) Histograms comparing the c) conversion of 4-NP and d) apparent rate constants for different catalysts under different irritation conditions.

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Supporting Information). These data were summarized and compared in the histogram (Figure 5d), where the AuAgPt-12 YSNSs catalyst showed the largest k value of 0.155 min⁻¹ for 4-NP reduction under the light-on condition.

In addition, we supplement the catalytic experiments without adding metal catalyst (namely, blank group). The k was measured to 0.003 and 0.004 min⁻¹ for 4-NP reduction with and without the irradiation of simulated sunlight, respectively (Figure S12, Supporting Information). Such slow reduction indicated the essential role of a metallic catalyst. The possible photothermal contribution was also largely excluded since the increase in the reaction temperature upon visible light irradiation was less than 2 °C, which should not be the leading cause for the improvement in apparent reduction rate. This is because the light source used in photocatalytic reduction of 4-NP is not a laser and the power was limited.

Moreover, we also conducted the catalytic reduction without the use of NaBH₄ as the reductant. As shown in Figures S13, S15, Supporting Information, the reduction still occurred and the light irradiation also promoted a faster and more complete reduction. However, the conversion was relatively lower as compared to the values obtained with the presence of NaBH₄, and the apparent rate constants was limited to be less than 0.025. These results suggested the following facts: i) 4-NP is not stable in water when metallic catalyst presents, and possibly decomposes into other forms; ii) the irradiation of plasmonic nanoparticles may cause the generation of hot electrons above Fermi Level, which may work as the reductant to facilitate the utmost reduction of 4-NP; iii) the amount of hot electrons may not be sufficient enough to be comparable to that provided by NaBH₄, thus dampening the conversion and the reduction rate.

2.6. Mechanistic Studies

The active role but different physiochemical behavior of AuAgPt alloy YSNSs in both photothermal conversion and plasmonic-assisted catalysis should be mainly ascribed to both elemental and geometric effects. For the elemental effect, it is well accepted that Au, Ag, and Pt has the respective coefficients, unlike the Au@Pt core-shell NCs with a solid interior, the three AuAgPt yolk-shell nanoparticles exhibit different structural parameters for internal part, such as the size/volume/position of pores or cavities, which would affect the mass transfer/diffusion rate and/or resistance of reactants during catalysis and the possible reflection modes of light within the hollow cavity. For example, as indicated in previous studies, a rough surface could be beneficial for the catalytic reaction.

However, the k_app of AuAgPt-6 and AuAgPt-25 YSNSs were obviously lower than that of the AuAgPt-12 YSNSs. Considering the fact that AuAgPt-6 had less hollow interior space and the hollow void of AuAgPt-25 YSNSs was partially filled, the effect of hollow structural feature on catalytic efficiency enhancement should be more important and dominant in current case.

To verify this assumption, we also synthesized two other types of nanocrystals with a similar structure but smaller or even no hollow interior, Au@Pt NCs (Figure S16, Supporting Information) and AuAgPt YSNSs with a 32 nm Au core (Figure S17, Supporting Information), followed by employing them as the catalyst in simulated sunlight-assisted reduction of 4-NP. As shown in Figures S18, S19, Supporting Information, despite the reduction was relatively faster under light assistance, the apparent rate constants were determined to be 0.0018 and 0.0008 min⁻¹, under light-on and light-off conditions, respectively, for Au@Pt core-shell NCs; 0.0069 and 0.0036 min⁻¹, under light-on and light-off conditions, respectively, for AuAgPt YSNSs with a 32 nm Au core. All these values were worse than that of those AuAgPt YSNSs with the 10 nm Au core. Such poor catalytic performance also are attributed to the insufficient interior space as arising from the increase in the size of Au core for AuAgPt YSNSs with a 32 nm Au core and the absence of hollow part in Au@Pt core-shell NCs.

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for AuAgPt-12. In a sense, these structural feature deviations lead to a different spectral feature as compared to the theoretical simulation.

Moreover, the electric field distributions of the Au@Ag NCs and the above three kinds of AuAgPt alloy yolk-shell nanostructures were also simulated, respectively. The profiles of electric

Figure 6. Finite-difference time-domain (FDTD) simulations of Au@Ag NCs and AuAgPt alloy YSNSs, including their extinction and scattering spectra as well as electric field distributions with an incident light of 808 nm: a,e) Au@Ag NCs; b,f) AuAgPt-6 YSNSs; c,g) AuAgPt-12 YSNSs; d,h) AuAgPt-25 YSNSs.
fields (described by $|E|^2/|E_0|^2$) were obtained when the 808 nm incident light is perpendicular to one of the facets. As shown in Figure 6e–h, whether solid Au@Ag NCs or hollow AuAgPt alloy yolk-shell nanostructures, strong LSPR-induced electric field enhancement at the corners of the cubic structures was all observed, which is identical with previous reports.[28] However, compared to that of solid Au@Ag NCs, the electric field enhancement at the corners of the hollow AuAgPt alloy YSNSs is more remarkable. This phenomenon is in line with the simulated spectra since extinction peak at longer wavelength better fits with the wavelength of incident light and thus gets more power from the light source. In addition, the electric field around the surface of Au core in the three hollow structures becomes intense, which might be attributed to plasmon coupling between the inner core and outer box.[29] Based on the FDTD simulation results, we can confirm the plasmon-enhanced photothermal properties of hollow AuAgPt alloy yolk-shell nanostructures. Specifically, all these AuAgPt yolk-shell nanoparticles exhibit similar optical response in terms of both absorption and scattering. In this case, the difference in photothermal conversion efficiency should mainly attributed to the geometric effect. Among the three types of YSNSs, the smooth-edged nanoframes showed the best photothermal conversion efficiency, which should be attributed to its relative large ratio of outer edge length to wall thickness and highly open structure.

When these AuAgPt alloy YSNSs worked as the photocatalyst assisting the reduction of 4-NP, the mechanism underlying the outcome catalytic activity should be unraveled by taking account of both the elemental and geometric effects. As indicated in previous studies, the apparent rate constant of both Ag and Au nanoparticles for catalytic reduction of 4-NP under the same conditions could be much higher than that of Pt nanoparticles (e.g., $k_{app} = 2.1482, 1.1167, 1.088 \times 10^{-1} \text{min}^{-1}$, for Ag, Au, and Pt nanoparticles, respectively, as indicated by in the previous study by Noveron and coworkers).[24] Therefore, regardless of irradiation conditions, the alloying of Au@Ag NCs with Pt could dampen the catalytic activity based on the elemental effect. However, when the yolk-shell nanostructures formed, the hollow interiors enable a rapid mass transfer/diffusion, which could result in the enhancement in catalytic activity arising from the structural advantage. Meanwhile, as the etching and regrowth proceeded, the exposure of Au core as well as the increment of Au as one of the alloyed components can also beneficial for improving the catalytic performance since Au has a higher catalytic activity than Pt. Therefore, the increase in Pt content and the creation of hollow part in the particle body could affect the catalytic process by applying opposite effects, making the change in catalytic activity exhibit a volcano-like trend when more Pt was introduced. For example, under light-off condition, the $k_{app}$ of AuAgPt-6 YSNSs reached 0.017 min$^{-1}$, much lower than that of Au@Ag NCs (0.102 min$^{-1}$). The weakened catalytic activity should be mainly caused by the deposition of Pt atoms on the outer shell. In contrast, when a fully open frame-like nanostructure formed, the $k_{app}$ of AuAgPt-12 YSNSs reached 0.142 min$^{-1}$, which was the best among the four samples. Further increment in Pt content led to the formation of rough edges and thus the occupation of more hollow interior space. In this case, the $k_{app}$ of AuAgPt-25 YSNSs declined to be 0.05 min$^{-1}$. For all the four samples, the reaction kinetics became improved when the incident UV–vis light was present, demonstrating the positive role of plasmon enhancement in catalysis.

In addition, we noted that the photothermal heat conversion efficiency of AuAgPt-6 alloys YSNSs was the highest, but the conversion percentages of 4-NP and apparent rate constants ($k$) under light-on/off conditions were the smallest. Such contrast should be attributed to the different mechanisms underlying the two applications. For metal nanocrystals, upon irradiation of UV–vis light, both the incident electromagnetic wave and the resonant frequency of conduction electrons are in phase, thus maximizing the electric field on the particle surface. The energy stored in surface plasmons can decay through either radiative (as reemitted photons) or non-radiative (electron-hole pair excitations and electron–electron collisions) ways. For photothermal heat conversion, non-radiative decay may produce local heating as the electronic kinetic energy can be transmitted to metal lattice phonons. In addition, plasmon energy can be non-radiatively dissipated by absorption within the metal nanocrystals, generating energetic hot charge carriers via electronic collisions with the surface of the plasmonic structure (surface scattering, also known as “Landau damping”).[30] Hot carriers are able to escape from the plasmonic NPs to be above the Fermi level, and thus be collected to induce the redox reactions.

3. Conclusions

In summary, AuAgPt alloy yolk-shell nanostructures have been successfully prepared with tunable elemental compositions and morphologies and explored in applications of photothermal conversion and plasmon-driven catalytic of 4-NP. Starting with uniform Au@Ag core-shell NPs, the introduction of H$_2$PtCl$_6$ not only generated hollow interiors inside the particle via GRR, but also distributed all the three metals over the whole particle via the unique “etching and regrowth” mechanism. When serving as the LSPR agents for applications, they exhibited satisfactory performances in terms of energy conversion and catalytic efficiency, where the synergetic effects arising from both elements and geometry have been analyzed. The mechanism for plasmon enhancement has been investigated using FDTD simulation, where remarkable electric field enhancement at the corners of cubic frame and around the Au core could be observed. The current work illustrates a feasible route to producing trimetallic cubic yolk-shell nanostructures with controlled compositions and validated their promising use in plasmon-driven applications, which could be extended to other noble metals and alloys and inspiring for rational design over plasmonic nanomaterials.

4. Experimental Section

**Materials:** Gold(III) chloride trihydrate (HAuCl$_3$·3H$_2$O, 99.9%), ascorbic acid (AA, 99.0%), hexadecyltrimethylammonium bromide (CTAB, 99%), and hexadecyltrimethylammonium chloride (CTAC, 97%) were all obtained from Aladdin Chemical (Shanghai, China) and used as received. Silver nitrate (AgNO$_3$, ≥99.8%), chloroplatinic acid hexahydrate (H$_3$PtCl$_6$·6H$_2$O, AR), sodium borohydride (NaBH$_4$, 98%), and 4-NP (≥98.5%) were obtained from Sinopharm (Shanghai, China) and used as received. DTAC (85%) was obtained from Degussa and used as received.

In all experiments, we used deionized water with a resistivity of 18.2 MΩ cm, which was prepared using an ultrapure water system (Ulupure, China).
Preparation of AuAgPt Alloy YSNSs: The 10 nm Au nanospheres were prepared using the method as described in our previous study. They were washed and re-dispersed in water at the mass concentration of 0.2 mg/mL as stock solution. The Au@Ag core-shell NCs were prepared by mixing the aqueous solutions of DTAC (20 mM, 3 mL), Au nanosphere stock solution (20 μL), AgNO3 (2 mM, 0.5 mL), and AA (10 mM, 0.5 mL) sequentially in a 20 mL glass vial and aged for 3 h at 60 °C. Then, one batch of aqueous suspensions of Au@Ag core-shell NCs were mixed with aqueous H2PtCl6 (20 mM) solution and aged at 60 °C for another hour to obtain AuAgPt alloy YSNSs. See main text for the volume of aqueous H2PtCl6 solution. The products were collected via centrifugation (16 000 rpm, 10 min) and washed with water once prior to further use.

Photoradiation Measurement: The photothermal effect of the AuAgPt alloy YSNSs was measured using an 808 nm laser and a digital thermometer. Typically, the aqueous suspensions of AuAgPt alloy YSNSs (particle concentration = 3.8 × 10^10 cm⁻³, total volume = 300 μL) were added to the 96-well plates, followed by the irradiation under the laser (0.92 W cm⁻²) for 12 min at the vertical distance of 20 cm. Throughout the measurement, the solution temperature was monitored using a digital thermometer, data was recorded at the set interval of 20 s, and the T-t curve was simultaneously mapped.

Recordings Method for Thermal Image: First, the thermal imager (FOTRIC 220s) with PC AnalyzIR software was connected, and the working area of the FOTRIC 220s was opened to ensure that the interface of software could record data. Then, the lens of the thermal imager was adjusted to align vertically with the sample (a vertical distance of 15 cm) to ensure that the sample image could be collected. The 808 nm near-infrared laser (0.92 W cm⁻²) was turned on with the vertical distance between the light source and the sample at 15 cm, and recording data with AnalyzIR software was started at the same time. After that, AnalyzIR software thermal imaging working area was used for data processing, the specific method was as follows: the sample solution imaging area was selected, and the curve between average temperature data and time change was automatically generated through the software.

Simulated Sunlight-Assisted Reduction of 4-NP: The mild test conditions (i.e., room temperature, neutral solution, and simulated sunlight [500 W halide lamp; Philips]) were adopted. Typically, 0.2 mL of aqueous 4-NP (5 mM) solution was added to 12.7 mL of deionized water and stirred thoroughly. After that, 0.1 mL of the as-prepared AuAgPt alloy YSNSs stock solution containing 40 μg of catalysts was added to the reaction mixture. Finally, 2 mL of a fresh, aqueous NaBH4 (500 mM) solution was added, and the solution was stirred throughout the reaction in a photocatalysis evaluation system (CEAulight Co., Beijing, China). Aliquots were taken out at set intervals, and the absorbance of the solution was measured using the UV–VIS–NIR spectrophotometer.

Instrumentations: Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), SAED (HAADF-STEM), and EDX-STEM mapping images were obtained using a Talos F200X (FEI, USA) microscope operated at 200 kV accelerating voltage. SEM images were obtained using a Zeiss Ultra60 microscope operated at 12 kV. The crystalline structures were analyzed with a MiniFlex600 X-Ray diffractometer (XRD, Rigaku). XPS measurements were performed using a Thermo Fisher Scientific KALPHA XPS with monochromatic Al Kα radiation (hν = 1486.6 eV). All extinction spectra were recorded using a T9 dual-beam UV–vis–NIR spectrometer (PERSEE, China). Inductively coupled plasma analysis was conducted on an ICAP-5000 inductively coupled plasma optical emission spectrometer (Focused Photonics Instrument, China).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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