Synthesis of size-controlled silver nanodecahedrons and their application for core–shell surface enhanced Raman scattering (SERS) tags†

Haifei Lu,ab Zhiwen Kang,a Haixi Zhang,ab Zhili Xie,c Guanghui Wang,ac Xia Yu,b Huiyu Zhang,c Ken-Tye Yong,c Ping Shumc and Ho-Pui Hob

We report the synthesis of silver nanodecahedrons (Ag NDs) and their use as surface enhanced Raman scattering (SERS) nano-composites. The as-prepared Ag NDs possess strong localized surface plasmon resonance (LSPR) with widely tunable peaks between 420–660 nm, which was formerly not possible, thus greatly improving the prospect of using silver nanoparticles for SERS applications. The growth of large size Ag NDs (LSPR peak longer than 490 nm) results from a seed-mediated step involving the reduction of silver cations by photo-excitation (illumination wavelength at 500 nm). Ag ND-SERS composites formed from a layer-by-layer coating technique show strong Raman signal enhancement and good material stability because of passivation effects from the coating. The reported silica-coated Ag NDs may be used with other molecular species to take advantage of field enhancement for a variety of applications, including non-linear harmonics generation and fluorescence enhancement.

Introduction

Surface enhanced Raman scattering (SERS) has been studied extensively in the areas of physics, chemistry, colloid science, plasmonics, technology, engineering, and biology since its discovery in 1974.1 Applications based on SERS have been under intense investigation in recent years.2–7 Also, colloidal metal nanoparticles of controllable shapes and sizes,8–14 and metal nanostructures on solid substrates15–17 are the most popular options for the application of SERS. While fluorescence is still a dominant signal reporting agent for a number of bio-detection applications, including clinical diagnostics, drug delivery, food safety and environmental monitoring, SERS has been reported to be a promising alternative because of the abundance of Raman reporting tags with good biocompatibility and amplified sensitivity associated with localized field enhancement.18–22 Typical SERS tags are made from coating organic Raman reporters on inorganic noble metal nanoparticles (NPs). If properly engineered, these NP composites are chemically stable and may be readily functionalized with biomolecular species. In order to achieve high Raman intensity from the SERS tag through the use of hot-spots between nanoparticles, silver or gold nanoaggregations,23,24 and polymer or silica microspheres assembled with noble metal nanoparticles25–27 have been investigated. On the other hand, the prospect of using single NP based SERS tags for high sensitivity bio-detection is limited because the nanoparticle alone provides relatively low electric field enhancement. It is well known that silver is a better choice than gold in terms of field enhancement because of its lower loss. However, conventional silver nanoparticles only offer LSPR peaks in the UV-blue region. Their potential for typical Raman detections cannot be ideally performed if using laser lines at 488 nm, 514 nm and 633 nm. Moreover, silver nanoparticles without surface protection are prone to oxidation and aggregation.28 With the objective to address the aforementioned issues, we report herein our study on silver nanodecahedrons (Ag NDs), which have been shown previously to provide ~109 SERS average enhancement factor (EF) for each reporter molecule on the surface because of their sharp tips and edges.29

In this work, Ag NDs with LSPR peaks ranging from 420 to 660 nm have been firstly synthesized through a photochemical method. Raman reporters (4-aminothiophenol and 4-mercaptobenzoic acid) have been added to the Ag ND surface in a monolayer form. We use a layer-by-layer (LBL) technique to produce several polyelectrolyte layers on the Ag NDs in order to facilitate the formation of a silica coating on top of the Raman
reporter monolayer. Strong Raman signals have been observed from the Ag ND-based SERS tags, thus confirming the possibility of using such nano-materials to replace fluorescence reporters in a wide range of bio-detection applications.

**Experimental**

**Materials**

Silver nitrate (ACS reagent, \( \geq 99.0\% \)), poly(vinyl pyrrolidone) (PVP, \( M_w = 40,000 \text{ g mol}^{-1} \)), 4-mercaptobenzoic acid (4-MBA) (98%), 4-aminophenol (4-ATP) (97%), poly(allylamine hydrochloride) (PAH, \( M_w = 15,000 \text{ g mol}^{-1} \)), poly(sodium styrenesulfonate) (PSS, \( M_w = 70,000 \text{ g mol}^{-1} \)), tetraethyl orthosilicate (TEOS), hydrogen peroxyde (\( \text{H}_2\text{O}_2 \)) solution (30 wt.% in \( \text{H}_2\text{O} \)), and ammonium hydroxide solution (30–33% \( \text{NH}_3 \) in \( \text{H}_2\text{O} \)) were purchased from Sigma-Aldrich. Sodium citrate dehydrate and sodium borohydride (99%) were purchased from FisherScientific. All chemicals were used with no further purification. Water used in the synthesis experiment was purified by Spectra-Teknik ultra-pure water purification system. High-brightness light-emitting diodes (LEDs) with emission peaks at 465 nm and 500 nm were purchased from Fisher Scientific.

**Synthesis of Ag nanodecahedrons**

Silver nanodecahedrons (Ag NDs) were prepared using the method reported in ref. 29 with a slight modification. Typically, 80 μL ice cold sodium borohydride (0.1 M) was rapidly injected into five ice bathed beakers containing 8 mL aqueous mixtures of silver nitrate (0.1 mM), poly(vinyl pyrrolidone) (0.2 mM) and different amount of sodium citrate to make sodium citrate/silver nitrate at different molar ratios, under continuous stirring for 30 min. The five solutions were then incubated for 12 h in a dark environment at 4 °C. The final bright yellow solutions were exposed to 465 nm radiation from a blue LED for 7 h at room temperature.

In this work, we adopted an improved method for the preparation of larger size (i.e. LSPR peak longer than 490 nm) Ag NDs, where only one kind of LED (emission peak at 500 nm) was used for the regrowth step. 4 mL of as-prepared Ag NDs seed colloid (prepared from molar ratio of sodium citrate/silver nitrate at 30) was centrifuged for 30 min at 5000 rpm. The sediment was dispersed into 8 mL mixture of trisodium citrate (3 mM) and poly(vinyl pyrrolidone) (0.2 mM). Ag NDs were synthesized by adding the silver nitrate solution to the mixture, followed by exposure to 500 nm LED illumination. The final size of the Ag NDs was controlled by varying the amount of silver nitrate and illumination duration. All experiments were conducted at room temperature.

For the synthesis of Ag NDs with smaller sizes (i.e. LSPR peak in the range 420–480 nm), 20 μL, 80 μL, 140 μL and 260 μL of \( \text{H}_2\text{O}_2 \) aqueous solution (0.5 mM) were added to four samples of 3 mL as-prepared Ag ND seed colloids (prepared from molar ratio of sodium citrate/silver nitrate at 30). Consequently, oxidation of Ag NDs resulted in the production of small size silver nanoparticles. The four samples were left to stabilize for 2 h. Finally Ag NDs were collected from the four samples by centrifugation followed by dispersion in PVP solution.

**Synthesis of silver nanodecahedrons based SERS tags**

Two kinds of Raman reporters (4-ATP and 4-MBA) were used in our experiments for the formation of silica coated Ag ND-SERS tags. Firstly, 4 mL of Ag ND solution with LSPR at about 510 nm was centrifuged, and the sediment was dispersed in 2 mL de-ionized (DI) water. Then the 2 mL Ag ND solution was slowly added drop-wise into 4 mL of 4-ATP aqueous solution (0.15 mM) under vigorous stirring and left for 30 min. This procedure resulted in the formation of a self-assembled monolayer (SAM) of 4-ATP molecules on the Ag ND surface. The modified Ag ND solution was centrifuged twice at 5000 rpm for 30 min to remove unbounded 4-ATP molecules and the precipitate was re-dispersed in 2 mL of DI water. The 2 mL Ag ND solution was added drop-wise to 4 mL of PSS (2 g L\(^{-1}\), 6 mM NaCl) aqueous solution under vigorous stirring. After 3 h continuous stirring, the solution was centrifuged twice at 5000 rpm, to remove excess polyelectrolyte, and re-dispersed in 2 mL of DI water. Thereafter, the solution was added drop-wise to 4 mL of PAH (2 g L\(^{-1}\), 6 mM NaCl) aqueous solution under vigorous stirring. Stirring was continued for another 3 h, centrifuged twice at 5000 rpm, to eliminate excess PAH, and re-dispersed in 2 mL DI water. The 2 mL 4-ATP/PSS/PAH coated Ag ND solution was mixed with 4 mL of PVP (4 g L\(^{-1}\)) aqueous solution and stirred for 12 h. The mixture was centrifuged at 5000 rpm, the clear supernatant discarded and the precipitate re-dispersed in 1 mL of water. The aqueous dispersion of PVP coated Ag ND solution was added to 4 mL of ethanol drop-wise and under vigorous stirring. Then 0.06 mL of ammonia solution (30–33% in water) was added under vigorous stirring and immediately 0.02 mL of a solution of TEOS in ethanol (1 vol.% of TEOS) was added under gentle stirring. The reaction mixture was allowed to react for 2 h. Then, 4-ATP modified silica coated SERS tags were collected by centrifugation.

For the synthesis of 4-MBA modified silica SERS tags, a similar method was adopted, except PAH was used to coat 4-MBA SAM modified Ag NDs as the first polyelectrolyte layer. Then, another three layer of PSS, PAH and PVP were coated sequentially on the Ag NDs. Finally, silica coating was realized after transferring the nanoparticles into an ethanol–water mixture followed by adding suitable amounts of ammonia solution and TEOS.

**Characterization**

Transmission electron microscopy (TEM) images were acquired using a FEI CM120 microscope at 120 kV. Scanning electron microscope (SEM) imaging was performed in a FEI Quanta 400 FEG microscope. Extinction spectra were measured using a Hitachi U-3501UV-visible/NIR spectrophotometer. SERS spectra were recorded using a Renishaw RM-1000 Micro Raman spectrometer coupled to a Leica microscope. Backscattered photons were collected using a 50× objective (NA = 0.75). The 514 nm excitation source (20 mW) was obtained from an argon laser. The scattering spectra were recorded in the range of 600–2000 cm\(^{-1}\) with 10% laser power and 10 s integration time.
Results and discussion

Regrowth of silver nanodecahedrons

While regrowth of Ag NDs is activated through photo-excitation from the LED, control of particle sizes and shapes are readily achieved by varying reaction parameters, including illumination wavelength, pH value, surfactants, constituent concentrations and their ratios.\textsuperscript{30–34} Generally, for the case of precursor-containing silver nanoparticles below 10 nm, varying illumination wavelength will change the shape of the product. For example, the use of 405 nm, 455–465 nm, 500–650 nm and 600–750 nm will, respectively, lead to the formation of silver spheres, nanodecahedrons, nanoprisms/nanoplates and nanorods.\textsuperscript{30,31,34} Former theoretical calculations indicate that small silver nanoparticles with different crystal structures, such as fcc, hpc, parallel twins, decahedra and icosahedra, can appear in the precursor because of errors in the stacking sequence of a fcc lattice.\textsuperscript{35} While each crystal structure is believed to require specific activation energy for material formation through photon absorption, one should be able to control the core structure of the silver nanoparticles for growth by varying the illumination wavelength. On the other hand, other small silver nanoparticles will be scavenged by oxidation into silver cations and serve as the silver source for the growth of the selected cores. 405 nm light favours the growth of small silver nanoparticles with icosahedral structures into nanospheres. 455–465 nm light favours the growth of small nanoparticles with decahedral (five-fold twins) structures into Ag NDs. On the other hand, silver nanoplates and nanoparticles will emerge from small Ag nanoparticles with parallel twins when the irradiation wavelength is 500–650 nm. With longer wavelengths of 600–750 nm, the final products become silver nanorods, which also evolve from small decahedral nanoparticles, but with higher growth speed on (111) than on (100) faces. However, the exact mechanism behind this selectivity of excitation wavelength in relation to the shape of the Ag nanoparticles is an issue yet to be clarified.

In our experiments, we first used 465 nm LED to irradiate a precursor prepared by adding NaBH\textsubscript{4} to silver nitrate solution in the presence of PVP and citrate. This process resulted in the generation of a large amount of Ag NDs in the final solution after 7 h of irradiation. Moreover, the production yield of Ag NDs was found to be very sensitive to the population ratio of nanocrystals with five-fold twinned defects over other products. The ratio between silver nitrate and sodium citrate actually provided us a pathway to control the five-fold twinned defects in the nanostructures during NaBH\textsubscript{4} reduction prior to subsequent photo-assisted Ag ND growth. Fig. 1 shows the extinction spectra of solutions prepared from different molar ratios of sodium citrate and silver nitrate after NaBH\textsubscript{4} reduction and incubation. As seen in the extinction spectra, a peak appears at the longer wavelength and its intensity increases with increasing ratio between sodium citrate and silver nitrate. A TEM image of the seeds prepared from solution with sodium citrate/silver nitrate at 30, as shown in the inset of Fig. 1, suggests that the longer wavelength extinction peak is associated with relatively large silver nanostructures containing multiple twins that also include decahedral defects. Fig. S1 in ESI\textsuperscript{†} shows the extinction spectra of nanoparticles grown from these solutions after irradiation by 465 nm LED. The TEM image in Fig. S2(a), ESI\textsuperscript{†} reveals that a large amount of silver nanoplates and nanoprisms were formed when the sodium citrate/silver nitrate ratio was relative low. On the other hand, a relatively high sodium citrate/silver nitrate ratio resulted in a much reduced amount of silver nanoplates and nanoprisms as shown in Fig. S2(b) and S2(c), ESI\textsuperscript{†}. However, a small amount of rounded nanoparticles with an irregular shape were found if the sodium citrate/silver nitrate ratio was 50. The density of these irregular nanoparticles increased dramatically when the sodium citrate/silver nitrate ratio was 70. It is believed that citrate acts as an agent for controlling the crystal imperfections in the silver nanocrystals.\textsuperscript{36} Low levels of sodium citrate/silver nitrate ratio favours the formation of single or parallel twinned silver nanocrystals, which can also grow under 465 nm light, as observed from Fig. S2(a), ESI\textsuperscript{†}. For the case of medium level citrate concentration, the higher population of large multiple twinned nanocrystals in the product also leads to a higher production yield of Ag NDs. However, it is not always the case that a high sodium citrate/silver nitrate ratio results in a high yield of Ag NDs. High citrate concentration also leads to high occurrence of crystal imperfections, such as stacking faults and partial dislocations, which tend to produce more irregular shaped silver nanoparticles, as shown in Fig. S2(d), ESI\textsuperscript{†}. The effectiveness of using the sodium citrate/silver nitrate ratio to control the seed nanostructures can be further demonstrated by comparing the effects of irradiating the seed solutions with a 520 nm light source. As mentioned earlier, 520 nm irradiation favours the pathway of growing nanoprisms and nanoplates from small silver nanoparticles with parallel twins. This point is further supported by the extinction spectra shown in Fig. S3, ESI\textsuperscript{†} and the SEM image in Fig. S4(a), ESI\textsuperscript{†} where we see that nanoprisms and nanoplates are the major products. We also notice that parallel twinned nanocrystals prevail over five-twinned nanostructures in solutions prepared...
from sodium citrate/silver nitrate molar ratios within the range between 1–10. In Fig. S3 and S4(b), ESI, we show the extinction spectrum and SEM image of products prepared with the molar ratio at 30. In this case, the population of silver nanoprism or nanoplasts is much lower. This result further supports our assumption that increasing the sodium citrate/silver nitrate ratio will improve the production yield of five-fold twinned nanocrystals. Finally, prolonged growth under 520 nm irradiation will produce silver nanodecahedrons with a distinctive LSPR peak at 540 nm.

Despite the aforementioned measures for optimizing the sodium citrate/silver nitrate ratio and employing photoexcitation at 465 nm to improve the production yield of Ag NDs, a certain quantity of silver nanoplats and nanoprism are still inevitable. Hence the centrifugation method is adopted to remove these relatively small size nanoplats, nanoprism, and unconsumed small silver nanoparticles. Another crucial point related to the purity and size range of silver NDs is the precursor added to the silver ND seeds for regrowth. Using the precursor composed of small silver nanoparticles, the largest LSPR of the acquired Ag NDs is about 560 nm.\(^3\) The plasmon-driven method, where the emission peak of the LED illumination coincides with the LSPR peak of the Ag ND seeds, can further promote the growth of even larger Ag NDs to 590 nm.\(^2\) However, the purity and uniformity of Ag NDs will be undermined if we use wavelengths away from the LSPR peak of the seeds for regrowth. On the other hand, if a mixture of sodium citrate, PVP, and silver nitrate is used for the precursor, and without the addition of NaBH\(_4\) to reduce silver cations into silver nanoparticles, the seeds contain Ag NDs only and this results in the generation of larger Ag NDs with a high degree of purity. Since Ag ND is the only nanostructure available in the mixture of silver ND seeds and precursor, silver cations in the solution will be reduced and then deposited on the Ag ND seeds upon receiving excitation from the incident photons. From our experiments, we have successfully synthesized a range of Ag NDs having LSPR anywhere between 490 and 660 nm with the use of a single LED wavelength at 500 nm. Fig. 2(a) shows the normalized extinction spectra of different sizes of Ag NDs with LSPR taking place at 494 nm, 520 nm, 543 nm, 575 nm, 600 nm, 630 nm and 660 nm. TEM images of Ag NDs having LSPR at 630 nm and 660 nm are shown in Fig. 3(a) and (b), and their edge lengths are measured to be 94.8 nm and 108 nm, respectively. Ref. 29 provides a detailed size distribution of Ag NDs with extinction peaks in 489–590 nm. In Fig. 2(b), we also present DDA (Discrete Dipole Approximation) results for Ag NDs having edge lengths of 50 nm, 70 nm, 90 nm, and 110 nm, whose extinction peaks are at 548 nm, 556 nm, 596 nm, and 630 nm, respectively. Apart from a slight red-shift of the major extinction peaks, the general spectral shape and red-shift trend with increasing nanoparticle size of the DDA results are in good agreement with experimental data, thus signifying that our Ag NDs are of good quality. Also, the slight discrepancy in the peak locations can be explained by the fact that our simulation assumes pure water as the dielectric environment surrounding the Ag NDs, while in the experimental case there should be a fair amount of surfactants (e.g. PVP and citrate).

Although the incident photons do not match with the LSPR of the Ag NDs, especially for the growth of large Ag NDs, a small degree of LSPR excitation may still be present. This inevitably leads to the generation of hot electron–hole pairs on the surface of the Ag NDs. Consequently, reduction of silver cations in the vicinity can still produce neutral silver for material growth on the Ag ND surface. Indeed the purity and uniformity of the final Ag NDs depend greatly on the material growth on the Ag ND surface. Indeed the purity and uniformity of the final Ag NDs depend greatly on the effectiveness of the separation step through which Ag NDs are extracted from other silver nanostructures. Compared to our previous plasmon-driven approach,\(^2\) which involves multiple growth steps and requires careful optimization between the seed characteristics and the light source for achieving good regrowth of Ag NDs, the new technique presented here overcomes the size limitation of using a single light source as reported in the previous method and readily produces a wide range of Ag ND sizes with LSPR anywhere between 490 nm and 660 nm through the use of a 500 nm LED. This greatly simplifies the Ag ND synthesis procedures, and therefore favours practical implementation.
H₂O₂ oxidation for the synthesis of small silver nanodecahedrons

H₂O₂ has been used as an oxidizing agent for selectively shortening single crystalline gold nanorods while keeping their diameter constant. Here, a similar method is adopted for the synthesis of silver nanoparticles with LSPR in short wavelengths, i.e. 420–480 nm. H₂O₂ may be added to the Ag ND colloid to induce oxidation of Ag NDs. Consequently a blue-shift in their LSPR will take place. Fig. 4 shows four extinction spectra and the photographs of silver colloids prepared by adding 20 μL, 80 μL, 140 μL, and 260 μL H₂O₂ aqueous solutions into silver nanodecahedrons colloids with a 489 nm extinction peak. Inset photographs are taken in reflection and transmission modes of the four colloids.

Two-mode phenomenon found in polygonal crystals. As revealed by TEM, two vertices of the two back-to-back penta-prisms and the five sharp tips of the Ag NDs have been truncated by oxidation. The preferential oxidation of the atoms
at tip areas could be due to their relatively higher chemical energy than the flat surface according to the Gibbs–Thomson equation. Increasing the amount of \( \text{H}_2\text{O}_2 \) results in a larger extent of the rounded tips in the silver NDs. Nonetheless, the truncated silver nanoparticles or truncated nanobicones in the present case are clearly five-fold twinned crystals still. Further increase of \( \text{H}_2\text{O}_2 \) inevitably converts the Ag NDs into spheres and the two LSPR modes will merge to become one.

**Layer-by-layer (LBL) method for the synthesis of SERS tags**

Because of their sharp tips and edges, Ag NDs have application potential related to their unique LSPR characteristics. Previous work has demonstrated that the average enhancement factor (average EF) of SERS can easily reach \( 10^6 \) when the Ag ND surface is functionalized with Raman reporter molecules.\(^{29}\) In order to highlight the merits of using Ag NDs for SERS, another three control samples, consisting of two different sizes of silver nanoprisms and one of gold nanoparticles were used in a Raman spectroscopy experiment in which their SERS capabilities were compared. Silver nanoprisms a and nanoprisms b were prepared using a photochemical method described in ref. 33. Gold nanoparticles were prepared using a classic citrate reduction technique.\(^{39}\) All the four samples had their nanoparticle concentration adjusted so that their major extinction peaks were of the same magnitudes. The results are shown in the left inset of Fig. 6. The same volume of the four colloids were mixed with four identical 4-MBA solutions with a concentration of \( 3.75 \times 10^{-5} \) M. A 785 nm laser from a Deltanu ExamineR modular system mounted on a Nikon inverted microscope was used to irradiate the samples, which took the form of liquid drops on a glass substrate, and the Raman signals were collected using a \( \times 20 \) objective. Raman spectra of the four samples shown in Fig. 6 reveal that Ag NDs produced by far the strongest SERS signal compared to the other three samples. Both of the two nanoprisms samples show similar Raman signal intensity, while the Raman signal obtained from gold nanoparticles is almost buried by noise. Using the area of the 1076 cm\(^{-1} \) peak, the SERS signal coming from the Ag NDs is 22–28 times stronger than the two samples containing silver nanoprisms and 255 times for the case of gold nanoparticles. Such a significant increase in Raman intensity over the other three samples could be attributed to the strong electric field enhancement from silver NDs.

In fact, proper choice of Ag NDs with LSPR located somewhere between the laser line and Raman scattering wavelength can provide a stronger Raman signal because LSP in the Ag NDs can enhance both the incident and scattering fields.\(^{40,41}\) Here, we propose to use Ag NDs as the core of SERS tags. The aim is to achieve highly sensitive immunosassays with broadly tunable Raman excitation wavelengths. Success of the proposed Ag ND approach depends crucially on the control of physical properties, including the intensity and location of the LSPR peaks, and uniformity of the nanoparticles. Reported efforts on the synthesis of SERS tags have mainly been based on coating a layer of Raman reporter molecules on the nanoparticles surface, followed by the addition of a silica or organic coating for further bio-conjugation or other functional applications. In the former cases, silver or gold nanoparticles modified with Raman reporter molecules are subjected to further surface treatment by (3-aminopropyl)trimethoxysilane (APTMS), (3-mercaptopropyl)trimethoxysilane (MPTMS) or poly(ethylene glycol) methyl ether thiol (mPEG-SH) in order to promote the formation of a silica coating.\(^{42-44}\) The introduction of these non-Raman active molecules would reduce the concentration of Raman reporters attached on the nanoparticle surface, which consequently weakens their Raman intensity. Hence, a SAM layer would be more preferable to be adopted as a Raman reporter coating on silver NDs. While the LBL technique can precisely tune the thickness of the dielectric layer on nanoparticles depending on the polyelectrolyte coating cycles,\(^{45}\) on the other hand, the polyelectrolyte layer will also facilitate silica coating on the nanoparticles. Here, multiple layers of polyelectrolyte involving PAH and PSS have been applied to the Ag ND surface before the final silica coating step, which includes a PVP treatment followed by mixing with an ethanol–water (4 : 1 in volume) solution with the addition of a proper amount of \( \text{NH}_2\text{OH} \) and TEOS.

The proposed procedure is depicted in Scheme 1. Two Raman tag molecules (4-APT and 4-MBA) are used here to demonstrate the synthesis of Ag ND-SERS tags. Silver nanodecahedron colloids with LSPR at 510 nm are added to 4-APT or 4-MBA solution with an adequate quantity of molecules. This promotes the formation of SAM on Ag ND because of a strong bonding between thiol group and silver. Once the Ag ND colloid is added to the Raman reporter solution, the colors of both solutions undergo a red-shift. The surface of Ag NDs becomes modified by \( -\text{NH}_2 \) or \( -\text{COOH} \) groups, thus making the surface positively or negatively charged, respectively. PSS and PAH are separately used for the first coating layer on the \( -\text{NH}_2 \) and \( -\text{COOH} \) terminated Ag ND surface because of electrostatic interactions. The outer layer of the treated Ag NDs should be PAH in order to ensure proper enclosure of the PVP, which has a slightly negative charge\(^46\) and acts as an interlayer for silica coating deposition. The occurrence of the LBL process can be observed with a red-shift of the colloid extinction spectra upon each polyelectrolyte
layer coating. Finally, NH4OH and TEOS are added to the mixture for the formation of a silica layer. The thickness can be tuned by adjusting the amount of TEOS. TEM images of our silica coated Ag ND-SERS tags are shown in the inset of Fig. 7. The top three core–shell nanoparticles are 4-ATP modified SERS tags while the bottom three are 4-MBA modified SERS tags.

Finally, the Raman spectra shown in Fig. 7(a) and 7(b) are typical ones obtained from 4-ATP and 4-MBA modified SERS tags. As marked on the Raman spectrum of 4-ATP, the peaks at 1007 cm\(^{-1}\), 1079 cm\(^{-1}\), 1183 cm\(^{-1}\) and 1585 cm\(^{-1}\) (marked with red) are attributed to the a\(_1\) mode of 4-ATP molecules while 1142 cm\(^{-1}\), 1389 cm\(^{-1}\) and 1433 cm\(^{-1}\) (marked with blue) are from the b\(_2\) mode of 4-ATP. The other two peaks, 1491 cm\(^{-1}\) and 1648 cm\(^{-1}\) (marked with black), are not yet well studied and there exist very few published data related to these two modes. Nonetheless, similar peaks also appear in SERS of 4-ATP modified gold nanorods when placed in an acidic environment.\(^{47}\) Moreover, Sun et al.’s simulation result indicates that four peaks 1039 cm\(^{-1}\), 1132 cm\(^{-1}\), 1483 cm\(^{-1}\) and 1627 cm\(^{-1}\) will appear upon protonation of 4-ATP adsorbed silver nanoparticles.\(^{48}\) Based on these experimental and simulation results, we can conclude that 1491 cm\(^{-1}\) and 1648 cm\(^{-1}\) are caused by protonation of 4-ATP in our experiment, thus providing strong evidence to indicate that 4-ATP in the Ag ND-SERS tags is protonated. This also suggests that 4-ATP is positively charged and is expected to enhance a strong electrostatic interaction with PSS.

The Raman spectrum obtained from 4-MBA modified Ag ND-SERS tags (see Fig. 7(b)) looks similar to that reported in ref. 49, where 4-MBA has been attached to silver nanoparticles at pH \(\sim 12.3\). The two strong bands at 1078 cm\(^{-1}\) and 1386 cm\(^{-1}\) are assigned to \(v_{\text{sa}}\) and \(v_{12}\) aromatic ring vibrations respectively. While the bands at 849 cm\(^{-1}\), 1425 cm\(^{-1}\) and a broad band 1370–1395 cm\(^{-1}\) (marked with red) are due to \(\delta(\text{COO}^-)\), the surface-bound COO\(^-\) groups and non-bonded COO\(^-\) groups of the more vertically oriented 4-MBA molecules. The band at 1707 cm\(^{-1}\) (marked with blue) is assigned to C–O stretching vibrations of non-dissociated COOH groups.\(^{50}\) However, the Raman intensity brought by COO\(^-\) groups is much stronger than brought by COOH groups, which reveals that most carboxylic acid groups of 4-MBA in SERS tags are present in COO\(^-\) forms. Consequently, PAH may readily bond to the 4-MBA modified Ag NDs through electrostatic interaction.

Indeed, apart from 4-ATP and 4-MBA, any molecule containing thiol, disulfide, isothiocyanate or benzotriazole groups and
possess strong signatures may act as the Raman reporter constituent in our Ag ND-SERS tags. The synthesis route is similar to those reported herein. A wide variety of sensitive multiplexed bio-detection and immunoassay applications may be contemplated. Finally, the stability of the silica coated SERS tags are performed by dispersing them into the conventional buffer solutions. Fig. 8 is the extinction spectra of the solutions after 6 h incubation. Because of the passivation of silica coating, the SERS tags are quite stable in these buffer solutions, and no obvious oxidation and aggregation happen even in the high concentration salt solution.

Conclusions

In summary, with the assistance of centrifugation, silver nanodecahedrons (Ag NDS) in high purity may be synthesized by irradiating the small size silver nanoparticle solution prepared from a proper sodium citrate/silver nitrate ratio. These Ag NDS can be used as the seed solution for further regrowth to produce large Ag NDS. A broad range of Ag NDS with LSPR peaks in the region of 490–660 nm can be produced by the reported seed-mediated method, where we use silver cations directly as silver source and a 500 nm LED as the light source for regrowth, and Ag NDS with LSPR below 480 nm can be produced by the oxidation of H₂O₂. These uniform Ag NDS with a broad range of sizes offer choices for users according their Raman excitation source and reporter type. We also introduce a general scheme for the synthesis of silica coated Ag NDS based SERS tags for achieving high Raman intensities. The layer-by-layer method reported herein provides a practical route for producing silica coatings on the Ag ND-SERS tags for further functionalization and protecting the composite nanoparticles against chemical modifications. These new SERS tags may become an excellent candidate for “nanobarcode” applications based on Raman signatures. A wide variety of labeling probes for sensitive and multiplexed immunoassay applications are contemplated.

Acknowledgements

The authors thank Dr Ning Ke for conducting TEM characterizations of the samples. The project is supported by A*STAR research grant SERC 0921450031. HFL’s research studentship and Group Research Projects 3110048 and 3110070 from The Chinese University of Hong Kong are gratefully acknowledged.

References