RESEARCH ARTICLE

Impressively printing patterns of gold and silver nanoparticles

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Abstract
The optical and chemical properties of gold and silver nanoparticles make them useful for many applications, including surface enhanced spectroscopy-based biosensors, photostable colorants, enhanced photovoltaic, and nanoscale optical elements. We report a simple technique to generate patterns of gold and silver nanoparticles with controlled shape and shape-dependent optical properties using metal stamps to impress them onto a glass substrate or flexible polymers. The pressure flattens the nanoparticles, converting initially spherical nanoparticles into discs with reduced height and increased diameter. This deformation causes their localized surface plasmon resonance wavelength to red-shift. Nanoparticles were characterized by electron microscopy, atomic force microscopy, and dark field optical scattering spectroscopy. The deformed nanoparticle patterns had a lateral resolution limited by the nanoparticle diameter (single particles are partly flattened only where they contact the stamp). The method also (i) transfers the stamp’s topography, with smooth stamps generating flattened nanoparticles with uniform height, and small changes in stamp height are evident in the nanoparticle height and scattering wavelength, and (ii) allows facile removal of undeformed nanoparticles using scotch tape, and patterns of deformed nanoparticles can be transferred to a flexible polymer film. The patterning process is simple and inexpensive. It can be performed by hand.
for demonstrations or artistic applications, with controlled force for plasmonics research, and potentially automated on reel-to-reel presses for large scale production.

**KEYWORDS**
lithography, LSPR, mechanical deformation, patterning

# 1 INTRODUCTION

Light irradiating plasmonic gold and silver nanoparticles (AuNPs and AgNPs) is strongly absorbed and scattered at wavelengths that depend upon the nanoparticle’s size, shape, and the refractive index of its surroundings. These optical properties arise from optically-driven resonant oscillations of conduction electrons in the nanoparticle, termed as the localized surface plasmon resonance (LSPR). Plasmonic nanoparticles are used in a variety of applications, including as labels in immunoassays, agents for photothermal therapy, lithographic fabrication, photostable colorants for printing, staining glass windows, components in nano-optical switches and waveguides, meta-materials with negative refractive indices, catalysis, and biosensors and labels based on surface enhanced spectroscopies. While considerable effort has been directed towards the synthesis of noble metal nanoparticles with a controlled size and shape, printing patterns of metal nanoparticles with different shapes on a solid substrate remains challenging.

To form patterns of plasmonic nanoparticles, top-down lithographic approaches are commonly used. For example, ion beam etching can be used to etch away a film into arrays of nanoparticles with a precisely controlled shape and pattern. Once a master pattern is formed using slow lithographic approaches, it can then be used to make submasters which in turn can be used as stamps in nanoimprint lithography via contact printing or chemical etching. Such nanoimprint lithography can be made compatible with reel to reel processes for rapid reproduction over large areas. However, generating the master stamp is slow and expensive, and the remaining processes require multiple steps such as heating the substrate to appropriate temperature, performing photolithography exposure/baking/development steps, and/or vapor depositing gold or silver. Several other techniques have been developed to pattern nanoparticles using pulsed laser writing, nanosphere lithography (also called colloidal lithograph), and others, but these are still relatively slow and require processes such as vapor deposition which are rarely available outside of academic or industrial laboratories. Although these techniques allow a careful control over nanoparticle height and aspect ratio through the vapor deposition thickness, they are ill-suited for studying the effects of nanoparticle shape while conserving volume, or for applications in low resource lab settings.

In a previous study, we described a simple technique to alter the shape of AgNPs by rolling a glass tube over them with a controlled force to compress them mechanically. The resulting shape change induces a red-shift in the LSPR scattering spectrum and exposes new surface areas. Herein we report an expansion of our previous work that shows the versatility of the deformation technique by using a stamp to create complex and high-fidelity patterns. We also show that gold nanoparticles as well as silver nanoparticles can be deformed using a rolling pin and/or stamp. This is important for long-term applications because gold, unlike silver, does not oxidize. Additionally, we show that the approach is simple enough that it can be performed by hand for minting, printing, and crafting applications, as well as educational activities such as the scientific outreach programs. To provide more uniformity mechanical systems with fixed force are used. Finally, we show how to isolate the pattern on a glass slide and to transfer the nanoparticles to flexible substrates.

# 2 RESULTS AND DISCUSSION

## 2.1 Manual and force-controlled nanoparticle deformation

Gold and silver nanoparticles can be deformed by applying pressure to them. We had previously demonstrated this with silver nanoparticles using a constant pressure device, here we extended to more chemically inert gold nanoparticles and showed that this could be done by hand. Spherical AuNPs of diameters 72 and 94 nm, and AgNPs of diameter 97 nm were used for preparing patterned nanoparticle surfaces (Figure S1). Initially, a colloidal AuNP suspension was deposited onto a PVP functionalized glass substrate and the nanoparticles were deformed by manually rolling a glass rod over them (Figure 1A). When these AuNPs (before deformation) were illuminated with white light...
they appear as bright green diffraction-limited points under a dark field microscope. After deformation, however, these nanoparticles appeared red-colored in the dark field image because their shape had changed from approximately spherical to flattened discs which altered the conditions for localized surface plasmon resonance.

Although nanoparticles can be easily deformed manually, this method suffers from two major drawbacks: (i) the compressive force exerted on the nanoparticles may not be uniform when the glass rod is manually rolled over the nanoparticles, and (ii) if the glass rod is not held properly, it could slide across the surface instead of rolling over it. To apply a consistent and controllable compressive force to deform the nanoparticles, we used a materials testing stand (Model ESM 303, Mark-10 Corporation, Copiague NY, USA) which pressed a glass “rolling pin” (a ¼ inch glass tube with a metal pin through it, Figure 1B) against a nanoparticle-coated sample attached to a computer-controlled stage. We deposited AuNPs onto a PVP functionalized glass substrate and mechanically deformed them using the rolling pin (Figure S2). The colloidal AuNPs (~72 nm diameter as determined by SEM) dispersion used in this experiment exhibited a strong extinction peak at around 520 nm (Figure S1). A glass slide with undeformed and deformed AuNPs regions was imaged using dark field microscopy; the undeformed particles at the bottom of the slide appeared as bright green diffraction-limited spots, while the deformed particles at the top of the slide appeared red as shown in Figure 1C. Dark field hyperspectral images showed single nanoparticles as diffraction limited spots for both the deformed (Figure 1D) and undeformed (Figure 1E) AuNPs. In Figures 1D and 1E, four representative particles are labelled 1–4, and their corresponding single particle scattering spectra are shown in Figures 1F and 1G, respectively. These results show that individual nanoparticles in the ensemble have similar spectra to each other, and that deformation causes a significant red-shift from ~565 nm to ~760 nm. Our previous work showed similar results with AgNPs; Figure S3 shows a comparison.\[16\]

The undeformed (Figure 2A1) and deformed AuNPs (Figures 2B1 and C1) were imaged using SEM. Figures 2A2, B2 and C2 show the corresponding histograms which revealed the effective nanoparticle diameter for the undeformed and deformed AuNPs (calculated from the area of each particle assuming a disc shape). The SEM images revealed that the AuNPs diameter and shapes varied as the applied load increased. The unmodified AuNPs had a roughly spherical shape with a mean diameter of 72 nm and a 6.9% of coefficient of variation (CV), Figure 2A. Rolling over the particles caused them to deform from spheres into discs and their mean diameters to increase in a load-dependent manner, increasing to 173 nm (CV-5.8%) with a 30 N load and 183 nm (CV-13%) with a 50 N load.
In our previous study, the deformation of AgNPs produced mostly ellipse-shaped nanodiscs with some sharp features, while the deformed AuNPs produce in this study were more circular nanodiscs according to the SEM images. This difference in shapes is attributed to the high crystallinity nature of AgNPs, which may have resulted in different deformation along different crystalline axes. In contrast, the AuNPs exhibited smaller crystal domain sizes with no preferred deformation axes. Further, at lower particle concentrations where individual particles could be resolved, the ellipse-shaped silver nanodiscs produced show polarization-dependent scattering properties (Figure S4). The random orientation and polarization dependence along with random nanoparticle positioning and color is an important feature for making unique irreproducible patterns for anti-counterfeiting/tamper-proof applications for uncirculated mint coins, electronic components, legal documents, etc. For these applications, stamp patterning is helpful for rapidly identifying a region of interest with the nanoparticles on it. After deformation, both Ag and AuNPs remain well-separated (except at higher concentrations where particles begin to touch).

We next studied the LSPR properties of the undeformed and deformed AuNPs by recording the dark field single nanoparticle scattering spectra for undeformed and deformed AuNPs on the glass substrate, as shown in Figure 2D1. The LSPR peak red-shifts and broadens with increasing applied load due to the increasing AuNP diameter and associated change in the aspect ratio (diameter/height). An overall LSPR shift of ~195 nm was observed when the applied load increased from 0 to 50 N, implying that the LSPR could be systematically red-shifted with increasing force and shape change. The data in Figure 2D2 illustrate the correlation between the maximum LSPR wavelength of undeformed and deformed AuNPs and applied load. The maximum LSPR wavelength increases rapidly with load for applied loads below between 0 and 10 N, after which the rate of red-shift decreases when the
applied load is varied from 10 to 50 N. This is in part due to a slower increase in the nanoparticle diameter relative to the initial NP diameter. Similarly, the glass rolling pin deforms slightly (on a \(<\ 100\) nm scale) with pressure, increasing the contact area with adjacent particles and glass substrate, thus exerting less force on each particle.\cite{16} In addition to the deformation not scaling with force the spectral shift is not expected to scale with force either because the phase of the incident light varies across the AuNPs, requiring consideration of dynamic depolarization and retardation effects.\cite{20}

### 2.2 Stamping deformation patterns

To rapidly generate patterns of deformed plasmonic nanoparticles, a stamp can be placed between the rolling pin and nanoparticles. To show this principle, we used TEM grids (SPI supplies, Crosby, TX) and VACCO grids (precision etched parts, South El Monte, CA) as stamps. TEM grids have a grid pattern on which samples are typically deposited prior to imaging, with the grid designed to rapidly select sample areas; these grids have uniform heights and precise boundaries, are relatively inexpensive and can be bought in large quantities. VACCO grids are designed as demo pieces to show capability to etch patterned metal substrates for a wide range of applications from physical filters to fluid control products (regulators and valves). The VACCO grids were larger than the TEM grids, had a rougher surface, and were reused several times in our experiments. We first performed the experiment by manually rolling a glass stir bar over either TEM or VACCO grids to press it into the silver nanoparticle covered glass slide. For the relatively large VACCO grid, the deformation pattern can be observed clearly by eye (Figure S6). The sample in Figure S6 was made and photographed during a public outreach event, Upstate!MAGINE Greenville South Carolina, which exemplifies the simplicity of the technique and hence its potential applicability to science demos as well as potentially for printing and artistic applications.

For more precise work, the mechanical test system was used to apply a uniform force. Figure 3 shows how deformed and undeformed areas can be easily distinguished by darkfield microscopy, SEM (Figure S7) and AFM (Figure S8). Nanoparticles in the deformed regions were disc shaped and had a larger diameter and smaller height than the undeformed approximately spherical (or polygonal) nanoparticles. The boundary between deformed and undeformed nanoparticles was very close to a straight line; occasionally a nanoparticle was found on the boundary itself and was deformed only where the grid was in contact with a region of the particle that remained unflattened (e.g., Figures 3A3 and B3). These observations were confirmed by AFM topographic scanning (Figure S9) using AgNPs. The zoom-out AFM image (20 × 20 microns) shows that under the mechanical force, the original polygonal AgNPs (∼97 nm) were uniformly deformed into flattened particles (∼24 nm height, Figure S10). Interestingly, AgNPs located at the border between original AgNPs and deformed AgNPs were partially deformed with one part of the particle essentially unchanged, while the part under pressure was flattened (larger diameter and reduced height).

The pattern was controlled by the stamp shape. If the stamp surface was uneven, the pattern reproduced some of the stamp features on the nanoparticle deformation pattern. For example, in place of a smooth copper TEM grid, a hexagonal patterned metal grid from VACCO was used as a stamp to deform ∼100 nm silver nanoparticles. The stamp finishing produced an uneven finish with clear streaks along one axis (Figure 4A1) causing ∼200 nm height variation along 20 µm laterally as shown in Figure 4A2. This caused similar features in the deformation (Figures 4B1 and B2) of Au and (Figures 4C1 and C2) AgNPs. This experiment demonstrates that stamps with smooth surfaces are needed to generate uniformly deformed nanoparticles, and that the surface height changes present in the stamp can be transferred to the deformed nanoparticle pattern which can be visualized both optically and using AFM (Figure 4). Individual nanoparticles with rougher features imprinted on them may be useful in applications such as sensors and catalysis, and other applications that could benefit from the relatively larger surface area when compared to that of the nanoparticle with smoother features (Figure S11).

For some applications, such as for printing non-bleaching colorants, it would be useful to generate patterns of only deformed particles with dark nanoparticle-free regions. We found that simple adhesive tape could remove undeformed particles from the substrate. Figures 5(i, ii, iii) illustrate the principle of this method schematically. Figures 5A1 and B1 show hyperspectral dark field images of AuNPs and AgNPs deformed under a copper TEM-grid pattern, respectively. The deformed and undeformed areas can be clearly distinguished in these images. Figures 5A2, A3 and B2, B3 show the hyperspectral dark field images of patterned AuNPs and AgNPs after removal of undeformed NPs using adhesive tape, respectively. This figure further confirms that this method is an effective way to remove undeformed nanoparticles from the surfaces and make patterned nanoparticle substrates. Furthermore, the approach also generated clear patterns without residues between lines (Figure 5B3). The preferential removal of undeformed spherical particles was likely due to the small contact area between the spheres and surface compared to the much larger contact area after deformation.
Scotch tape has previously been used to capture NPs such as Ag, Au, Cu and Pd onto a flexible surface\cite{21} for numerous applications including point of care detection of bacterial infections and detecting pesticides on fruits and vegetables using Surface Enhanced Raman Spectroscopy (SERS)\cite{22}. Although the scotch can provide a background signal in these sensing applications, analyte can be distinguished and detected. There was no obvious residue from the tape in the dark field images or electron microscopy and AFM images, however, it is possible that a thin residue could be left behind, which could provide a background signal in sensing applications which would require either chemical removal (e.g. alcohol washing) or plasma treatment.

Patterned nanoparticle arrays could also be transferred to a flexible polymer surface. We used First Contact Polymer (Platteville, WI) which is generally used to remove dust, fingerprints, residues and contaminants from precision surfaces such as lenses. Clear First Contact Polymer is a colorless solution that dries into a flexible thin-film at room temperature, and can be peeled off easily. Moreover, it can be either stretched or bent, and after the force is removed its original shape and size are restored (Figure S12 A1-3). By applying liquid polymer onto the patterned region and allowing it to dry, the NPs can be transferred onto the polymer surface. When the polymer solution is dried fast (dried within 5 minutes) on a NPs coated glass slide, the undeformed NPs are transferred onto the thin film leaving deformed NPs on the glass slide (Figure 6B i-iii). When the polymer solution is dried slowly (dried within 30 minutes), both undeformed and deformed NPs are transferred onto the thin film (Figure 6 C i-iii). The
slower evaporation results in uniform, resilient and good quality thin film that is in contact with the top and sides of the NPs, including any overhang. Before transferring NPs onto thin-film about 10 particles per μm² were present (forming continuous colored regions in the diffraction limited dark field images but countable in SEM images); after transferring the NPs the remaining particles on the glass slide could be clearly distinguished and counted in dark field imaging and had a concentration of ~0.6 particle per μm² (Figure S12 B1-2). After removing undeformed NPs using a scotch tape, the deformed nanoparticles in the patterned region can also be transferred onto a polymer surface (Figure 6D i-iii). Both clear and red First Contact Polymer can be used to remove nanoparticles.

3 | CONCLUSIONS

We demonstrated a simple method to pattern gold and silver nanoparticles and control their shapes by pressing a stamp onto the particles coating on a glass substrate. The resulting nanoparticle shape change induces a red-shift in the localized surface plasmon resonance, while regions untouched by the stamp remain unchanged. Using this
method, we demonstrated that a single nanoparticle can be partially patterned or deformed. Furthermore, (i) regions with only deformed nanoparticles present on the glass substrate can be prepared by removing undeformed nanoparticles with a tape, and (ii) patterns of both deformed and undeformed nanoparticles can be transferred onto a thin polymer film. This is a simple, inexpensive and yet effective technique to control the size and shape via patterning to tune the optical properties of nanoparticles. Future work will involve studying how changes in the nanoparticle surface roughness influence the catalytic and sensing properties of AuNPs and AgNPs.

4 | EXPERIMENTAL SECTION

4.1 | Methods and instrumentation

All chemical reagents were obtained from Sigma Aldrich and used as received. All aqueous solutions were
**FIGURE 6** A i–A iii, Schematic illustration of the transfer of NPs onto a clear polymer-film. (A i) Patterned and undeformed NPs on glass slide; (A ii) applying Clear First Contact polymer, letting it dry and peeling off (NPs transferred onto the polymer-film); (A iii) NPs remained on the glass slide. Dark field microscope images of patterned and undeformed NPs on (B i) glass slide and (B ii) undeformed NPs on polymer-film, (B iii) remaining NPs on the glass slide. Dark field microscope images of patterned and undeformed NPs on (C i) glass slide and (C ii) on polymer-film, (C iii) remaining NPs on the glass slide. Dark field microscope images of patterned NPs on (D i) glass slide after removing undeformed NPs and (D ii) patterned NPs on polymer-film, (D iii) remaining NPs on the glass slide.
prepared using deionized (DI) water (18.2 MΩ cm). Poly(4-vinylpyridine) (PVP) (M_w = 60,000 Da) was prepared by dissolving a weighed quantity of PVP into ethanol. Indium–tin oxide (ITO) coated glass (100 Ω cm⁻¹) was purchased from Delta Technologies, Limited. Samples were characterized using enhanced dark field transmission optical microscopy (Olympus BX4i) equipped with hyperspectral imaging spectrophotometer (CytoViva Hyperspectral Imaging System (HSI), Auburn, AL). Scanning electron microscopy (SEM) images were collected using a Hitachi SEM-4800 field emission (Hitachi, Japan) electron microscope operating at an accelerating voltage of 15 kV and an average working distance of 8.4 mm. The average nanoparticle size and particle size distribution were obtained using the ImageJ software. Alteration of the height of particles was measured using a AIST-NT SmartSPM in non-contact mode with HQ:NSC14/AL BS cantilevers from Mikro-Masch with spring constant of ca. 5.0 N m⁻¹. Absorbance spectra were collected using a Shimadzu UV-2501 PC spectrometer.

4.2 | Poly(4-vinylpyridine) functionalization of glass substrates

Both ITO-coated and normal glass substrates were cleaned by sonication in nanopure water for 15 minutes followed by drying inside a desiccators and plasma treating for 10 minutes (Harrick Plasma Cleaner PDC – 32G). The cleaned glass substrates were poly(4-vinylpyridine) (PVP) functionalized according to a previously reported method.[23] After modification with PVP, substrates were thoroughly rinsed in reagent ethanol to remove all weakly bound polymer molecules leaving only a monolayer directly adhered to the surface. Next, the PVP modified substrates were annealed at 120°C under ambient atmosphere for a few hours. For the experiments, both ITO-coated and normal glass substrates were used. No significant impact on experimental results was found with either because the NPs are deformed by the pressure exerted by the rolling pin, which is independent of the nature of the substrate. However, ITO-coated glass substrates were mostly used for scanning electron microscopy due to their electrical conductivity.

4.3 | AuNP and AgNP synthesis

AuNPs were prepared using the seeded growth method.[24] Briefly, a solution of 2.2 mM sodium citrate in 150 mL of nanopure water was heated in a three-necked round-bottom flask attached to a condenser for 15 minutes under vigorous stirring. After boiling had commenced, 1.0 mL of 25.0 mM HAuCl₄ was injected. After appearance of a deep red color, which indicates the formation of gold seeds, the mixture was boiled and stirred for another 10 minutes. Next, the mixture was cooled to 90°C and 1.0 mL of 25.0 mM HAuCl₄ was injected. After another 30 minutes the reaction was completed. This process was repeated twice. Then, the sample was diluted by extracting 55 mL of sample and adding 53 mL of nanopure water and 2.0 mL of 60.0 mM sodium citrate. This solution was then used as a seed solution and the process was repeated until the AuNPs had grown to the desired size. The AuNPs with average diameter of ~94 nm exhibited a maximum extinction wavelength of 561 nm (Figure S1). We also used commercially purchased AuNPs (EM.GC100, BBI Solutions, Anaheim, CA, USA) with average diameter of ~72 nm that exhibited a maximum extinction wavelength of 520 nm (Figure S1).

AgNPs were synthesized using the hydrogen reduction method developed by Evanoff and Chumanov.[25] Briefly, Ag₂O was added to deionized water in a ratio of 1.0 g L⁻¹ in a quartz reaction vessel. Next, 1.0 mM sodium silicate was added to promote stabilization of the resulting AgNPs. The mixture was then shaken well before connecting to the condenser and a hydrogen line. A heating mantle was placed under the vessel and its contents heated and maintained at 70°C with constant stirring. Once the temperature equilibrated, the vessel was flushed with H₂ (99.9% purity) and pressurized to 10 psi. Hazard: over pressurizing or using a defective vessel may result in explosion and cause severe injuries. Within 10–15 seconds of the initial pressurization, the contents of the vessel turned faint yellow in color indicating the formation of metallic silver particles 10–15 nm in diameter. As the reaction progresses, aliquots can be taken through the spout. Removing the aliquots from the reducing environment stops further growth of the particles. Likewise, the reaction can be stopped at any time simply by releasing the gas from the vessel. In this way, control of the particle diameter is purely a function of total reaction time. AgNPs with 97 nm average diameter had a maximum extinction wavelength of 502 nm (Figure S1).

4.4 | Deposition of nanoparticles on PVP functionalized ITO glass slides

To prepare the samples for deformation, both colloidal AuNPs (72 nm and 94 nm) and AgNPs (97 nm) were diluted with deionized water to an optical density (O.D.) of 1 (using wavelength at dipole maximum and 1 cm path length). This absorbance corresponds to ~2.3 × 10¹² particles per mL for 97 nm AgNPs and ~2.6 × 10¹⁰ particles per mL for 72 nm AuNPs and ~8.3 × 10⁹ particles per mL for 94 nm AuNPs based upon a previous study counting the
number of particles absorbed onto a surface with well-known dimensions and measuring decrease in optical density of nanoparticle solution.\[23\] PVP coated glass substrates were immersed in the diluted aqueous suspension of colloidal either AuNPs or AgNPs overnight at room temperature to form a monolayer of nanoparticles, then rinsed with reagent ethanol and dried overnight at room temperature in a desiccator connected to a vacuum pump. This leads to a well-dispersed configuration of colloidal either AuNPs or AgNPs on the substrate surface.

### 4.5 Mechanical deformation of nanoparticles

Nanoparticles deposited on a glass slide can be manually deformed by rolling a simple glass stirring rod over them while applying downward pressure (Figure 1). The pressure was be more easily applied by replacing the stirring rod with a simple rolling pin (a ¼ inch diameter glass tube with a metal rod through it). For controllable and uniform deformation, the rolling pin was attached to an ESM 303 mechanical test stand equipped with a 1000 N Mark-10 Force gauge with computer-applied force. Nanoparticles immobilized on a PVP functionalized ITO glass substrate were then clamped to a linear motorized stage LTS 300 (Thorlabs, City State). The rolling pin was placed on one end of the slide to begin with. Mechanical force was applied by the ESM 303 and the stage was moved forward and back to roll the glass tube over the length of the glass substrate 10 times (Figure S2). Our previous study showed a similar effect with a single roll.\[24\] However, single rolled deformed particles appear to have sharper edges compared to the particles deformed by rolling the glass rolling pin 10 times.\[24\] The applied force was varied from 0 to 50 N with the number of times the slide was rolled and rolling speed (500 µm s\(^{-1}\)) were kept consistent for each experiment. The glass tubes were cleaned several times using acetone and distilled water prior to use.

### 4.6 Dark field optical imaging

Optical scattering from patterned AuNPs and AgNPs was observed with a Nikon TE2000 microscope in a transmission dark field imaging configuration using a 0.95-0.8 numerical aperture (NA) condenser and 100X oil immersion objective with a variable aperture stopped down to just below 0.8 NA. Images were acquired on a Nikon D90 camera; all parameters of the camera were controlled by Camera Control Pro2 software (Nikon Instruments Inc., Melville, NY, USA).

### 4.7 Hyperspectral dark field imaging

Both undeformed and deformed AuNPs and AgNPs on PVP-functionalized glass substrates were examined using enhanced dark field transmission optical microscope (Olympus BX41) equipped with hyperspectral imaging spectrophotometer (CytoViva Hyperspectral Imaging System (HSI), Auburn, AL). The concentric imaging spectrophotometer was used to record optical scattering spectra from visible and near infrared wavelengths (400-1000 nm) at a spectral resolution of 1.5 nm with 10 nm scan size and pixel size 25 nm. The customized hyperspectral imager (mounted on a microscope and controlled by Environment for Visualization software) was extracted with complete spectral information from single or multiple pixels. All images were acquired using a 40X oil with iris objective at identical gain (gain = 5) and exposure time (0.1 ms).

### 4.8 Atomic force microscopy (AFM)

AFM images were collected for patterned AuNPs and AgNPs adsorbed on PVP functionalized ITO glass substrates using an AIST-NT SmartSPM in non-contact mode with HQ:NSC14/AL BS cantilevers from Mikro-Masch with spring constant of ca. 5.0 N m\(^{-1}\). These cantilevers had an uncoated tip radius of about 8 nm with a 40° full tip cone angle. AFM image processing was carried out with AIST-NT SPM Control Software. Polynomial background subtraction and line fit corrections were employed in some AFM images. Histograms of undeformed and deformed NPs sizes were based on statistical analysis of ~100 nanoparticles to calculate average size with standard deviation.

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### CONFLICT OF INTEREST

The authors declare no competing financial interest.
AUTHOR CONTRIBUTIONS
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Fathima S. Ameer, Meenakshi Ranasinghe, Shilpa Varahagiri Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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