Ordered Arrangement and Optical Properties of Silica-Stabilized Gold Nanoparticle–PNIPAM Core–Satellite Clusters for Sensitive Raman Detection

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Gold–polymer hybrid nanoparticles attract wide interest as building blocks for the engineering of photonic materials and plasmonic (active) metamaterials with unique optical properties. In particular, the coupling of the localized surface plasmon resonances of individual metal nanostructures in the presence of nanometric gaps can generate highly enhanced and confined electromagnetic fields, which are frequently exploited for metal-enhanced light–matter interactions. The optical properties of plasmonic structures can be tuned over a wide range of properties by means of their geometry and the size of the inserted nanoparticles as well as by the degree of order upon assembly into 1D, 2D, or 3D structures. Here, the synthesis of silica-stabilized gold–poly(N-isopropylacrylamide) (SiO₂-Au-PNIPAM) core–satellite superclusters with a narrow size distribution and their incorporation into ordered self-organized 3D assemblies are reported. Significant alterations of the plasmon resonance are found for different assembled structures as well as strongly enhanced Raman signatures are observed. In a series of experiments, the origin of the highly enhanced signals can be assigned to the interlock areas of adjacent SiO₂-Au-PNIPAM core–satellite clusters and their application for highly sensitive nanoparticle-enhanced Raman spectroscopy is demonstrated.

1. Introduction

The unique properties of metal nanoparticles (NPs), that is, gold or silver nanoparticles, and assemblies thereof, motivated the synthesis of many different kinds of nanoparticle architectures, starting off with 1D NP dimers and NP chains, 2D-ordered sheets, and 3D clusters, pyramids, etc.[1] Depending on their geometry, material composition, degree of order, and periodicity, these nanoparticle assemblies show a large variety of interesting optical phenomena. Besides their ability to generate highly localized and enhanced electric fields, coupling of supported localized surface plasmon modes can induce Fano-resonances[2] and magnetic modes.[3] As a consequence, plasmonic building blocks and assembled structures thereof have gained increasing interest for applications in, for example, sensor devices, drug detection, and chemical analysis-based on vibrational spectroscopy,[4] that is, surface-enhanced Raman spectroscopy (SERS)[5] and surface-enhanced IR absorption (SEIRA) spectroscopy.[6] The high sensitivity of the near-field and far-field response to the gap size further attracted large interest to employ hybrid nanostructures for plasmon-stimulated processes, such as catalytic reactions,[7] or to study plasmon-mediated quantum transport phenomena, etc.[8]
The occurrence of localized surface plasmon resonances (LSPRs) and the capacitive coupling of the LSPRs in confined nanoparticle configurations results in the formation of hot spots.\cite{9} The strongly enhanced and confined electromagnetic fields in the gap regions are associated with a gap plasmon mode and can be used to boost optical signals.\cite{10} These strong electromagnetic fields can, for example, be used to increase the sensitivity of Raman spectroscopy up to a factor of $10^{10}$ compared to classical Raman experiments.\cite{11} Therefore, the development of surfaces featuring gap plasmons is a topic of increasing interest and different substrate designs have been proposed,\cite{12} in certain cases demonstrating a Raman sensitivity down to the single molecule level.\cite{13} In particular for the analysis of low abundant analytes, a high detection sensitivity is indispensable. As a consequence, major goals for the development of suitable substrates are to improve the reliability of measurements as well as to decrease the required amount and concentration of the analyte solutions. One approach is the synthesis of nanoparticles that can be used to induce enhanced Raman signals, and which can be coated on virtually any surface to achieve high enhancement factors of the Raman signatures. As a consequence, a large number of nanoparticles have been tested for this nanoparticle-enhanced Raman spectroscopy approach. 

On the one hand, design rules of these NP substrates comprise the choice of the nanoparticle material, its geometry, size, and, on the other hand, their distribution, fill factor and their degree of order within the plasmonic material. Tested systems include, among others, fractal nanoparticle aggregates,\cite{14} dendritic nanoparticle structures,\cite{15} core–shell nanoparticles,\cite{16} as well as complex polymer–nanoparticle structures,\cite{17} that is, superclusters,\cite{18} and core–satellite nanoparticles.\cite{19} Moreover, utilizing such plasmonic building blocks for the fabrication of 2D arrays or 3D crystals adds further possibilities to tune their optical response.\cite{20} As such, their utilization in the formation of 3D metamaterials is of great interest, in particular for constructing active gain-based\cite{21} and hypobolic metamaterials.\cite{22} 

Recently, shell-insulated nanoparticles for enhanced Raman spectroscopy (SHINERS) were introduced as highly active materials for nanoparticle-enhanced Raman spectroscopy, which are applicable to arbitrary structures/surfaces.\cite{23} SHINERS consist of a metal nanoparticle acting as an enhancer for the Raman signals and feature additionally a pinhole-free shell of a dielectric layer consisting of silica or aluminum oxide. These dielectric layers are thought to seal the nanoparticles and prevent the contamination of the metal surface that might impair the spectroscopic assessment of Raman signals generated by an analyte molecule. Here, we investigate the fabrication of silica (SiO$_2$)-stabilized metal–polymer hybrid core–satellite nanoclusters (Figure 1), consisting of a poly(N-isopropylacrylamide) (PNIPAM) core surrounded by a dense shell of small gold nanoparticles (AuNP) (in the following referred to as SiO$_2$-Au-PNIPAM) and discuss important issues regarding their integration into self-assembled, ordered, 3D structures acting as a platform for sensitive Raman investigations. Their properties are studied and their ability to strongly enhance Raman signals is demonstrated. Arrays and small aggregates of the SiO$_2$-Au-PNIPAM core–satellite clusters show a favorable activity for nanoparticle-enhanced Raman spectroscopy, despite the small size of the individual plasmonic metal particles being incorporated into the core–satellite Au-PNIPAM nanoclusters.

2. Results

The synthesis of the Au-PNIPAM core–satellite particles was carried out based on a procedure reported by Gawlitza et al.\cite{24} Cross-linked PNIPAM polymer nanoparticles with a cross-linker content of 10 wt% were synthesized and subsequently decorated with citrate-stabilized gold nanoparticles with a diameter of 13 nm. The micropel-like structure of the PNIPAM core allows the physical trapping of the Au nanoparticles preferentially at the outer surface of the PNIPAM core particle. Fairly high concentrations of the added gold nanoparticles resulted in the formation of a dense shell of gold nanoparticles surrounding the PNIPAM core as shown in Figure 2a. This type of metal–polymer hybrid nanoparticles, in the following termed superclusters, was used by Gawlitza et al. to study the thermoresponsive behavior of the Au-PNIPAM nanoparticles in relation to the applied loading density with Au nanoparticles as well as for different cross-linker ratios. The particles fabricated following this procedure revealed the reported thermoresponsive behavior in solution and the particle diameter varied with respect to the

Figure 1. a) Schematic representation of the satellite SiO$_2$-Au-PNIPAM-gold core–shell nanoparticles and their incorporation into small aggregates and 3D self-assembled arrays. b) Backscattered electron microscopy image of the synthesized clusters.
temperature of the particle solution (Figure S1, Supporting Information). This particle system, however, turned out to be not suitable for the self-assembly into 3D structures of higher order. As can be observed by transmission electron microscopy (TEM) investigations, the superclusters tend to collapse when they are prepared on a substrate after the evaporation of the solvent. Figure 2a,b depicts representative TEM images of an individual Au-PNIPAM nanoparticle. Figure 2a shows the top-view analysis, while Figure 2b depicts the same particle being investigated under a tilt angle of $52^\circ$. It can be clearly seen that the Au-PNIPAM nanoparticles are not round-shaped, but feature a rather flat, disc-like structure. The lack of stability upon drying prevents their use as building blocks for the self-assembly of well-ordered 3D arrays. Figure 2c depicts an experiment that aimed at the formation of a 3D array consisting of Au-PNIPAM superclusters. It can clearly be observed that the Au-PNIPAM nanoparticles completely disintegrate and no organized multilayer of the hybrid nanoparticles could be obtained. For the purpose of fabricating 3D organized arrays of Au-PNIPAM superclusters two requirements are mandatory: First, the particle size has to feature a narrow size distribution and, second, the particles need to maintain their spherical shape. While the first requirement is fulfilled by the introduced synthesis approach and a narrow size distribution of the particles is observed, the synthetic strategy had to be optimized in terms of particle stability.

Figure 2. TEM images of Au-PNIPAM core–satellite nanoparticles on a TEM grid: a) Top-view and b) structure at a tilt angle of $52^\circ$. The structures are not stable and the spherical shape of the nanoparticles is destroyed during the solvent evaporation process. c) SEM image of the nanoparticles deposited onto a silicon wafer. Also in this case the structures are damaged within the preparation process. TEM images of silica-stabilized SiO$_2$-Au-PNIPAM nanoparticles: d) Top-view and e) structure at a tilt angle of $45^\circ$. f) SEM image of several SiO$_2$-Au-PNIPAM nanoparticles arranged on a substrate (cross-sectional view). The SiO$_2$-Au-PNIPAM core–satellite clusters maintain their spherical shape and show an improved stability.

One possible approach is to stabilize the Au-PNIPAM clusters with a thin silica shell (SiO$_2$-Au-PNIPAM). First of all, this thin silica shell enables to improve the shape stability and allows preparing the nanoparticles onto surfaces by evaporation of the solution without loss of their spherical shape. Moreover, the silica shell could potentially improve the Raman enhancement of the individual plasmonic Au nanoparticle building blocks located in the shell of each supercluster due to the higher refractive index and the formation of ordered resonant gap structures. For this purpose, the Au-PNIPAM solution was treated with diglycerylsilane, which resulted in the formation of a thin silica layer on the surface of the Au-PNIPAM nanoparticles. The typical thickness of the silica layer is in the order of less than 2–3 nm (Figure S3a, Supporting Information). As expected, the addition of the silica shell of the Au-PNIPAM clusters impairs the thermoresponsive properties of the SiO$_2$-Au-PNIPAM superclusters (Figure S2, Supporting Information). However, their shape is successfully stabilized as can be seen from the respective TEM and scanning electron microscopy (SEM) images of the obtained SiO$_2$-Au-PNIPAM superclusters (Figure 2d,e). The spherical shape of the Au-PNIPAM nanoparticles is clearly visible even at a tilt angle of $45^\circ$ (Figure 2e), suggesting that the spherical shape of the nanoparticles is preserved in the dry state. To confirm this assumption, additional SEM investigations of arranged SiO$_2$-Au-PNIPAM particles (Figure 2f) were conducted. The structure of individual SiO$_2$-Au-PNIPAM was moreover accessed by SEM investigations of a cross-sectional break junction (Figure S3b, Supporting Information) as well as by a TEM tomography series (Figure S3c, Supporting Information). Both methods
confirmed the spherical shape of the SiO₂-Au-PNIPAM superclusters and can prove the assembly of the gold nanoparticles exclusively in the shell on the outside interface of the PNIPAM core–particles. As a main feature of the synthesized structures, their homogeneous size distribution, their fairly dense shell consisting of 13 nm Au nanoparticles, and their shape persistence have to be emphasized. These properties are a prerequisite to assemble these superclusters into regular, ordered 3D structures.⁹

In order to obtain highly ordered 3D structures consisting of SiO₂-Au-PNIPAM core–shell clusters, a structured layer of photoresist was fabricated to provide microstructured “molds” with a typical size between 37 µm × 37 µm and 90 × 90 µm and a depth of ≈1.0 µm (Figure S4, Supporting Information). After exposure of the substrates through a photomask (here conventional TEM grids were used (mesh 400 and mesh 200, respectively)) with light, the exposed parts of the photoresist were washed off. The obtained molds were used to deposit the SiO₂-Au-PNIPAM cluster solution. The arrangement of the nanoparticles within these mold structures critically depends on the evaporation conditions of the solution. Simple deposition of the solution and evaporation of the solvent at room temperature did not result in the formation of well-organized 3D patterns of silica-stabilized SiO₂-Au-PNIPAM nanoparticle clusters. In order to achieve a good packing of the SiO₂-Au-PNIPAM nanoparticles, sodium dodecyl sulfate (SDS) was added to the SiO₂-Au-PNIPAM solution. The substrates were preheated to 90 °C, the solution was deposited onto the hot substrates and the solution was subsequently allowed to dry at 90 °C. After a few minutes the substrate was cooled to room temperature and the remaining photoresist was removed by acetone. Alternatively, ethylene glycol can be added to the cluster solution to achieve a good packing of the superclusters. In this case, the samples were dried at room temperature, which required considerably more time. A typical microstructure of organized SiO₂-Au-PNIPAM nanoparticles is depicted in Figure 3a, resembling a “crystal-like” arrangement of the plasmonic superclusters with domain sizes of 2–5 µm. These domains are characterized by a reasonably well-ordered 3D arrangement of the plasmonic superclusters as shown in Figure 3b and the cross-sectional SEM view (Figure 3c). Based on the depth of the utilized molds (Figure S4, Supporting Information) up to three to four layers of superclusters can be formed. However, one could possibly also use thicker photoresist layers. SEM investigations suggest a body-centered cubic (bcc)-like organization at least in the top layers. The boundaries of the domains indicate stacking defects.

Based on these well-ordered layers there is a high probability for the interaction of individual plasmonic superclusters as well as of individual AuNPs in the contact regions of adjacent plasmonic superclusters. These feature two types of plasmonic gaps: (I) the gaps provided by the 13 nm Au nanoparticles in the shell of individual supercluster as well as (II) gaps formed when the Au nanoparticles interlock in the contact region of two adjacent superclusters. The diameter of the gold nanoparticles decorating the PNIPAM core is very small (i.e., 13 nm), and thus, their optical response is dominated by light absorption. Both gap types can potentially contribute to cooperative plasmon coupling effects, which are further investigated.

In order to evaluate the alterations induced by the coupling of individual plasmonic superclusters and of gold nanoparticles within the shell structures, the plasmon resonances of the individual building blocks as well as of small aggregates and larger 3D areas were investigated by means of spectrally resolved dark-field (DF) scattering as depicted in Figure 4.

For individual SiO₂-Au-PNIPAM core–satellite particles, a plasmon resonance peak at ≈600 nm is observed (Figure 4, spot 2–4). Compared to the plasmon resonance of the individual AuNPs with a diameter of ≈13 nm at 517 nm (Figure S5, Supporting Information), the peak position of the cluster is clearly red-shifted and also broadened. This shift is indicative for a capacitive mode coupling of the LSPRs of individual AuNPs within the shell on the PNIPAM core. This can be expected due to the rather high density of AuNPs within the shell, which results in small nanometric interparticle gaps. An estimation of the gap distances on the very top of individual silica-stabilized superclusters (to minimize distortions caused by the projection of the SEM imaging) suggests a nanoparticle distance of 4.7 ± 3.6 nm as a mean gap distance. No carbon or gold coating was applied in order to access the gap distances. It has to be mentioned that the limited obtainable resolution of the SEM might result in even significantly smaller inter-Au-nanoparticle gaps that cannot be.

![Figure 3. a) SEM image of a well-organized 3D arrangement of SiO₂-Au-PNIPAM nanoparticles after removal of the photoresist mold. Domain boundaries between highly organized areas of SiO₂-Au-PNIPAM particles are observed. The squares (I) and (II) denote regions of large ordered and densely packed SiO₂-Au-PNIPAM particles. b) Higher magnification SEM image of an ordered area. c) Cross-sectional SEM image of a two-layer system demonstrating the spherical shape of the SiO₂-Au-PNIPAM core–satellite superclusters.](image-url)
resolved properly. The recorded DF spectra (Figure 4b,c) on different nanostructures consisting most likely of individual and of only a few SiO$_2$-Au-PNIPAM superclusters arranged in a small aggregate first of all showed a sequential red-shift of the plasmon peak position with an increasing number of plasmonic supercluster constituents (similar to the marked area (I) in Figure 3a) and increasing packing density in the 3D aggregates. For packed domains (similar to the marked area (II) in Figure 3a), the plasmon peak further red-shifts and a new mode starts to emerge in the NIR regime. With a high degree of order of the SiO$_2$-Au-PNIPAM supercluster arrays the NIR mode was found to become strongly enhanced (Figure 4c). These decisive alterations of the shape of the plasmon peak can be assigned to a strong coupling of the LSPRs of individual plasmonic superclusters, potentially leading to the formation of hot spots which allows using these ordered structure as substrates for the sensitive detection of molecular tracers by measuring Raman spectroscopy.

In order to determine their suitability as a substrate for molecular sensing based on Raman spectroscopy, confocal Raman spectra were recorded at different locations. Figure 5 displays typical spectra obtained for a confocal laser illumination with excitation wavelengths of $\lambda_{exc} = 532$ nm and $\lambda_{exc} = 632.8$ nm and at an excitation power of $P_L = 100$ µW. The chosen laser intensity is low and minimizes damage induced by the laser illumination. Both spectra show characteristic Raman bands and most of these peaks can be assigned to modes typical for $\mathrm{n}$-isopropyl acrylamide (NIPAM) (reference spectra in Figure 5d). In particular, the bands at 1620, 1589, and 1300 cm$^{-1}$ correspond to the amide I, amide II, and amide III bands, respectively. These vibrational modes can be clearly assigned to PNIPAM. Furthermore, a characteristic of the isopropyl CH$_3$ deformation band appears at $\approx$1375 cm$^{-1}$. While the peaks associated to the amide bands follow a single Lorentzian line profile, this is not the case for the CH$_3$ deformation band, which is known to appear as a double peak. A comparison of both spectra recorded at different excitation wavelengths shows that for an excitation at 632.8 nm, that is, close to the plasmon resonance peak position of the plasmonic substrate, the signal-to-noise ratio is clearly improved and distinct bands can be only clearly identified under these excitation conditions. This is in accordance with the observation that excitation conditions at wavelengths matching the LSPRs of the applied nanostructures lead to the highest electric fields and, thus, strong Raman enhancement factors.[27]

3. Discussion

In order to discriminate the origin of the observed PNIPAM signature several aspects have to be taken into consideration. First, it has to be tested if the PNIPAM Raman signals might stem from the core material of the SiO$_2$-Au-PNIPAM superclusters. Furthermore, it has to be elucidated which gap plasmons are primarily responsible for the enhancement of the Raman signals. To investigate these issues, a number of additional experiments have been conducted.

As already mentioned, the signals could originate from the PNIPAM within the SiO$_2$-Au-PNIPAM superclusters itself, however, it has to be taken into account that PNIPAM is only a poorly Raman active molecule and usually does not contribute to the Raman signal of PNIPAM clusters, as shown by Liz-Marzán and co-workers.[28] Figure 5c presents a respective control measurement on a PNIPAM film. Even for comparable integration times but five times larger excitation power no Raman signals could be detected and only a poor signal-to-noise ratio could be achieved. Only by extending the integration time to 20 min very faint vibrational signatures were found.

A closer inspection of the Raman spectrum acquired on the Si-Au-PNIPAM samples revealed additional Raman bands, which most likely arise from the formed silica shell. The peak at 456 cm$^{-1}$ can be assigned to Si vibrational modes. This supports the assumption that the Raman signal stems mainly from the electric field confined in the region of the silica shells. Remarkably, the Raman signals reveal no fluctuation in terms of its signal strength and the observed peak
positions over time and no degradation of the supercluster structures was observed. We ascribe this to the protective influence of the silica shell to prevent contamination of the AuNPs, similar to the effect observed for SHINERS.\[23\] To further clarify the origin of the strong enhancement of these Raman signatures, the contributions of the interlock regions of contacting superclusters and gaps formed within the shell surface of the individual AuNPs were further investigated. In a first step, the Raman activity of individual SiO$_2$-Au-PNIPAM core–satellite nanoclusters was addressed. In the case that the interparticle gaps of the 13 nm AuNPs attached on the superclusters’ surface primarily contribute to the total electric field enhancement and, thus, already mediate the enhancement of the Raman signals. It is expected that even individual superclusters show a high Raman activity for PNIPAM, as they are in direct contact. It is hence also reasonable to assume that the obtained signals stem from residual PNIPAM molecules still present in the solution. Even though the cluster solution was carefully purified before use by repeated centrifugation and redisperision, it is likely that a low number of residual molecules are still present in the solution. During the assembly of the plasmonic superstructures into the 3D structure these residual molecules are likely to be trapped in the gap regions of AuNPs formed by two adjacent SiO$_2$-Au-PNIPAM core–satellite clusters of the arranged array. Similarly, a Raman signature of the SDS (reference Raman spectrum in Figure 5e) largely overlaps with bands also observed for the PNIPAM Raman peaks. Thus, a clear discrimination of these molecules is not possible. Interestingly, the number of interlock areas in the analysis volume of the confocal microscope is rather low. Taking into account the size and excitation/detection volume, the recorded Raman signal stems only from a few interlock regions, thus, suggesting an excellent sensitivity of the SiO$_2$-Au-PNIPAM cluster.

Remarkably, neither for an individual supercluster nor for small aggregates thereof Raman signatures of PNIPAM were detectable. Therefore, it is not likely that the gaps formed by the Au nanoparticles directly on the shell structure of the SiO$_2$-Au-PNIPAM superclusters are the main origin for the extraordinary high Raman intensities of the observed PNIPAM peaks in 3D arrangements. Thus, rather the gaps formed by the interlock of the superclusters could be the cause of the enhancement effect, although aggregates of only a few SiO$_2$-Au-PNIPAM core–satellite clusters formed by drop-casting do not reveal any related effects. Here, the formed interlocks might be less tight than for 3D structures formed in the confinement of the template structure.

The predominant role of the interparticle gaps becomes even more evident if an analyte is used. Therefore, ascorbic acid was mixed with SiO$_2$-Au-PNIPAM particle solution and samples were allowed to dry on a double-side polished silicon wafer. This procedure results in the formation of small cluster arrangements with typically 5–25 Au-PNIPAM nanoparticles.

Figure 5. Raman spectroscopy of 3D arranged SiO$_2$-Au-PNIPAM stacks for an excitation wavelength a) $\lambda_{\text{exc}} = 532$ nm and b) $\lambda_{\text{exc}} = 632.8$ nm. c) Control measurements on pure PNIPAM films utilizing the same setup. Reference Raman measurements on d) NIPAM and e) SDS powder samples.
Figure 6 (middle) displays the obtained Raman spectra. For reference, corresponding Raman spectra were recorded on NIPAM (top) and ascorbic acid (bottom) alone. It is clearly visible that the peaks are entirely generated by the ascorbic acid and no signals can be found that originate from the PNIPAM. This is in particular visible by analyzing the spectral range from 2500 to 3500 cm\(^{-1}\).

The experiments performed on the Si\(_2\)-Au-PNIPAM clusters feature additional peaks at ≈900 and 1415 cm\(^{-1}\), which are not observable in the reference spectra obtained with pure ascorbic acid solution. These peaks are also not observed in this position in the reference spectrum of NIPAM, indicating an excellent sensitivity of the Raman spectra obtained on the Si\(_2\)-Au-PNIPAM supercluster aggregates.

The assumption that the interlock regions provide the areas of high Raman enhancement is further supported by the investigation of small supercluster aggregates, which were assembled onto a nonstructured substrate by drop-casting. No distinctive Raman signatures of the PNIPAM were found, most likely because of a reduced probability of PNIPAM to integrate into the interlock area of the superclusters and for the formed gap sizes. However, on these small aggregates of Si\(_2\)-Au-PNIPAM superclusters a variety of other Raman peaks is observed. These are characterized by rapid fluctuations of changing Raman bands which appear and disappear in a random pattern (Figure 7a,b), suggesting that the peaks originate from randomly adsorbing molecules from the environment, which are either degraded or, more likely, desorb from the silica shell in the interlock area. The presence of intense CH\(_3\) vibrations in most of the spectra suggests that carbohydrates from the environment were transiently adsorbed onto the structures, preferentially in the gaps formed in the interlock regions.

Each spectrum was recorded within 10 s at an excitation power of only 500 \(\mu\)W. Individual traces clearly show the high sensitivity of the Si\(_2\)-Au-PNIPAM clusters for nanoparticle-enhanced Raman spectroscopy. These fluctuating Raman signatures were not observed on isolated superclusters, hence, further confirming that interlock areas are the main source for the highly enhanced Raman signals, rather than the gaps formed by individual Au nanoparticles of the shell.

These results verify that the interlock areas are the primarily areas of high electromagnetic field strength and also rule out that the adhesion sites of the Au nanoparticles on the PNIPAM core interface act as potential hot spots mediating the strong Raman signatures of PNIPAM.
4. Conclusions

The presented studies can shows the high sensitivity of the synthesized SiO$_2$-Au-PNIPAM core–satellite nanoparticles in terms of Raman sensitivity. Experiments demonstrated that the gap modes in the interlock area, where the superclusters touch each other, strongly contribute to the Raman enhancement and result in strong Raman signatures even at low excitation powers as well as rather short spectra acquisition times. A number of experimental parameters have so far not been studied in detail, for example, the influence of the silica shell thickness, the diameter of the PNIPAM core particle diameter, as well as the influence of the packing density and size of the individual Au particles within the SiO$_2$-Au-PNIPAM supercluster shell. These parameters can certainly further optimize the achievable Raman enhancement. Besides their application to Raman chemical analysis, their construction from small AuNPs and scaffolding PNIPAM spheres opens up further modification possibilities toward plasmonic superclusters with higher complexity, that is, core–shell–shell atoms, which would enable to explore the rich plasmonic properties of these structures in terms of plasmon mode coupling, stimulation of Fano-resonances, etc. The presented approach to form stable and well-ordered 3D structures with controllable plasmonic properties provides the perspective to exploit them as multifunctional platforms with advanced optical and catalytic properties. For this application, large-area, well-ordered, 3D stacks are ideally suited to engineer composite materials, which could be explored to probe reactions under low light conditions, or even could constitute the framework for active plasmonic metamaterials by the integration of an optical gain medium. A major advantage of the presented superclusters is their applicability to arbitrary-shaped interfaces as well as their high temperature and environmental stability, which enables their use in gas detection systems, microfluidic devices, and at solid interfaces.

5. Experimental Section

Materials and Instrumentation: Glycerin (p.a. 99.5%, anhydrous), ethylene glycol (99.8%, anhydrous), tetraethylorthosilicate, SDS (99%), and N,N'-methylenebisacrylamide (99%) were received from Sigma-Aldrich. NIPAM (>98%) was purchased from Fluka. Sodium hydroxide (99%) and polyvinylpyrrolidone K25 were obtained from Carl Roth. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar. Hydrogen tetrachloroaurate(III) trihydrate (99.99%) was purchased from Alfa Aesar.

UV–vis spectra were recorded on a Perkin Elmer Lambda 750 spectrometer in 1 cm quartz cuvettes at room temperature (temperature responses were investigated at variable temperatures). Spin-coating experiments were executed using a WS-400B-6NPP/LITE (Laurell Technologies Corporation). TEM measurements were performed on a FEI Technai G2 20 cryo-Transmission Electron Microscope at 200 kV and SEM images were acquired on a ZEISS Sigma VP. The carbon-supported TEM grids (Mesh 400, Quantifoil) were cleaned by argon plasma treatment for 30 s prior to the preparation of the samples. Determination of the particle size was done using the software ImageJ by measuring at least 100 particles per sample. Centrifugation was performed with a Heraeus Biofuge Primo with a fixed angle rotor in 1.5 mL Eppendorf tubes.

Experiments employing ascorbic acid as analyte were performed with a Bruker Senterra system and an excitation wavelength of 532 nm and a laser power of 20 mW (prior to pass through the optics). $1 \times 10^{-3}$ m stock solutions of ascorbic acid dissolved in water were mixed with the SiO$_2$-Au–PNIPAM nanoparticle solution and were drop-cast on a clean silicon wafer. Integration times of 50 s were used. All other spectroscopic measurements were conducted with a home-built Raman system composed of an Acton 300i spectograph with liquid N$_2$ cooled Pylon CCD sensor connected to an inverse microscope (Ti-U Nikon, Japan) equipped with an oil immersion objective (NA 1.49) and suitable Razor edge filters LP03-532RE and LP03-633RE (Semrock, USA).

Synthesis of Citrate-Stabilized Gold Nanoparticles: In a 250 mL round bottom flask, 200 mL of a HAuCl$_4$ $\times$ 3H$_2$O (1 $\times$ 10$^{-3}$ m) solution was heated to 100 °C while stirring at 700 rpm. To the refluxing solution 1 mL of a sodium citrate solution (0.78 m) was added at once. The color of the solution turned red after $\approx$30 s. Heating was continued for 30 min, afterward the solution was cooled and stored in the dark at 4 °C.

Preparation of the Au-PNIPAM Clusters: PNIPAM nanoparticles with 10% cross-linker were prepared according to a literature procedure.[24] Briefly, a surfactant-free precipitation polymerization protocol was employed to fabricate uniformly sized PNIPAM
microgel-like particles. Afterward, loading with the citrate-stabilized gold nanoparticles was performed by adding these to the PNIPAM nanoparticle solution. After homogenization for 10 min the obtained solution was purified by centrifugation (8000 rpm, 5 min), the supernatant was removed and the Au-PNIPAM clusters were redispersed in water. The purification cycle was repeated three times.

Preparation of the SiO$_2$-Au-PNIPAM Clusters: Diglycercylsilane was prepared according to the procedure described in Ref. [29]. 1 mL of the initial polymer particle solution was centrifuged at 1000 rpm for 5 min and 900 µL of the supernatant solution was taken off. 100 µL of this solution were diluted with 900 µL water and centrifuged four times at 10000 rpm for 5 min. Each time 950 µL of the supernatant solution were taken off and replaced with 950 µL fresh water. The particles were redispersed by shaking and ultrasonication. 500 µL of the purified PNIPAM particle solution were added to 10 mL of citrate-stabilized gold nanoparticles. The mixture was shaken for 3 h, then a freshly prepared solution of diglycercylsilane (100 µL, 100 mg mL$^{-1}$) was added and the solution was stirred for 24 h at 100 rpm. 1 mL of this solution was centrifuged four times at 1000 rpm for 10 min in a glass (I) vial. Each time 900 µL of the supernatant solution was taken off and replaced with 900 µL fresh water. For the last centrifugation cycle no water was added and the particles were redispersed in 100 µL of the residual solution.

Photolithography: Thin glass substrates were sprayed with the photoresist and immediately afterward placed in a spin-coater and rotated at 500 rpm for 1 min. Subsequently, the samples were dried in the dark for 10 min at 70 °C. Afterward, the glass slides were transferred on a black background and TEM grids were placed on the substrates. From a distance of ~20 cm the slides were irradiated with a commercial 35 W halogen lamp for 10 min. Finally, the developed slides were immersed in a NaOH solution (70 g L$^{-1}$) for 30 s under slight swiveling, washed with water, and then dried.

Deposition of the Cluster Arrays: 1 µL SDS solution (10 vol%, 1 mg mL$^{-1}$) was mixed with 10 µL of the cluster solution in an Eppendorf vial to improve the surface tension. The glass substrates were preheated in an oven to 90 °C. 0.5 µL of the particle solution were placed on the grid structures and after 5 min the substrates were taken out of the oven and cooled to room temperature. Finally, the substrates were swiveled in acetone in order to remove the photoresist and then dried.

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.


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