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# Extending Surface-Enhanced Raman Spectroscopy to Liquids Using Shell-Isolated Plasmonic Superstructures

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**Abstract:** Plasmonic superstructures (PS) based on Au/SiO<sub>2</sub> were prepared for Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS) in liquid phase applications. These superstructures are composed of functionalized SiO<sub>2</sub> spheres with plasmonic Au nanoparticles (NPs) on their surface. Functionalization was performed with (3-aminopropyl)-trimethoxysilane, (3-mercaptopropyl)trimethoxysilane and poly(ethylene-imine) (PEI). Of these three, PEI-functionalized spheres showed the highest adsorption density of Au NPs in TEM, UV/Vis and dynamic light scattering (DLS) experiments. Upon decreasing the Au NP/SiO<sub>2</sub> sphere size ratio, an in-

## Introduction

Surface-enhanced Raman spectroscopy (SERS) is a valuable characterization tool for catalysis research due to the extremely high signals that can be obtained.<sup>[1,2]</sup> The key to the strong enhancement lies with the SERS-active substrates, generally consisting of Au or Ag nanoparticles (NPs).<sup>[3]</sup> These materials exhibit surface plasmon resonance when irradiated with laser light of the correct frequency, creating an electromagnetic field of high energy density around the NPs. The strong signals that have been observed originate from molecules that reside within this field, within a few nanometres from the SERS-active substrate. The strongest signals arise from so-called 'hot spots': locations where the surface plasmons have coupled between multiple particles to form pockets of high-energy electromagnetic fields that allow detection of single molecules.<sup>[4,5]</sup> This high sensitivity makes the technique a valuable tool in catalysis research, where the elucidation of reaction mechanisms is one of the main interests.<sup>[6,7]</sup> Several catalytic reactions have al-

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crease in adsorption density was also observed. To optimize plasmonic activity, 61 nm Au NPs were adsorbed onto 900 nm SiO<sub>2</sub>-PEI spheres and these PS were coated with an ultrathin layer (1–2 nm) of SiO<sub>2</sub> to obtain Shell-Isolated Plasmonic Superstructures (SHIPS), preventing direct contact between Au NPs and the liquid medium. Zeta potential measurements, TEM and SHINERS showed that SiO<sub>2</sub> coating was successful. The detection limit for SHINERS using SHIPS and a 638 nm laser was around  $10^{-12}$  m of Rhodamine ( $10^{-15}$  m for uncoated PS), all with acquisition settings suitable for catalysis applications.

ready been studied with SERS over the years, mainly electrocatalytic and photocatalytic reactions, a limitation being the interaction of reactants with 'hot electrons', highly energetic electrons originating from direct contact between the molecule of interest and the metal NP surface in the hot spots.<sup>[8–10]</sup>

Recently, Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS) has emerged to overcome this limitation by coating the Au or Ag SERS-substrates with a thin layer of dielectric oxide, like SiO2.[11] This layer prevents interference of hot electrons in the reaction of interest and increases the thermal stability of the NPs, which has extended the applicability of SERS to heterogeneous catalysis. For example, the group of Tian recently studied CO oxidation over Pt-Fe and Pd catalysts deposited on core@shell Au@SiO2 Shell-Isolated Nanoparticles (SHINs).<sup>[12]</sup> Our own group has recently reported on support effects in CO adsorption and hydrogenation over Ru and Rh catalysts assembled on Au@SiO<sub>2</sub> and Au@TiO<sub>2</sub> SHINs.<sup>[13]</sup> However, these studies were all limited to gas-solid phase heterogeneous catalysis, with the application of SERS and SHINERS to liquid phase heterogeneous catalysis still lacking. This is mainly due to the aforementioned requirement of hot spots, which are not present in stable dispersions of Au or Ag NPs. Furthermore, recently Zhang et al. reported that the monomeric Au NPs that are present in dispersions show negligible SERS-activity.<sup>[14]</sup> Therefore, a method to create hot spots in stable dispersions needs to be developed in order to extend the applicability of SERS and SHINERS to liquid-phase heterogeneous catalysis.

Numerous methods have already been explored, including synthesis of plasmonic nanoparticles with intrinsic hotspots,<sup>[15]</sup> self-assembly of plasmonic nanoparticles into complex super-



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structures<sup>[16]</sup> and assembly of plasmonic nanoparticles onto larger SiO<sub>2</sub> spheres.<sup>[17]</sup> Of these methods, adsorption of Au NPs onto large SiO<sub>2</sub> spheres may well be the most promising of all. This method is not only facile in preparation (simply mixing dispersions of Au NP and SiO<sub>2</sub> spheres with appropriate surface chemistry), it also provides easy tunability by simply adjusting Au NP size and/or SiO<sub>2</sub> sphere size, which can alter plasmon resonance wavelength or colloidal stability. Le Beulze et al. already showed that using this method, significant SERS-enhancement can be obtained with 10-50 nm citrate-stabilized Ag and Au NPs on 80–100 nm SiO<sub>2</sub> spheres.<sup>[17]</sup> However, we believe that increasing the SiO<sub>2</sub> sphere size will have a beneficial effect: larger plasmonic nanoparticles can be used, increasing the signal enhancement by creating stronger hot spots. However, sedimentation rate of these plasmonic Au/SiO<sub>2</sub> superstructures needs to be taken into account, as this will limit the time scale of experiments on reactions under investigation.

Citrate-stabilized Au NPs are susceptible to ligand exchange,<sup>[18]</sup> allowing not only for easy adsorption of the Au NPs onto functionalized SiO<sub>2</sub> spheres, but also coating of the resulting superstructures with a pinhole-free layer of SiO<sub>2</sub> using the method developed by Li et al.<sup>[11,19]</sup> Unlike SiO<sub>2</sub>-encapsulation using the Stöber method, the method by Li et al. yields nonporous, thin, uniform layers of SiO<sub>2</sub>, isolating the metal NP surface and preventing the interaction of plasmons and hot electrons with the substrates of interest.<sup>[8,19]</sup> Furthermore, this SiO<sub>2</sub> coating provides the possibility to adsorb catalytically active nanoparticles onto the (Au/SiO<sub>2</sub>)@SiO<sub>2</sub> superstructures, ultimately enabling investigation of heterogeneous catalytic processes in liquids using SHINERS.<sup>[12]</sup> Finally, as an added benefit, the use of superstructures large enough to visualize by optical microscopy enables single particle studies.

In this work, we investigate the optimum properties of Au NP/SiO<sub>2</sub> sphere plasmonic superstructures (PS) that display both SERS-activity and colloidal stability. We prepare SiO<sub>2</sub> spheres and functionalize their surface with different molecules: (3-mercaptopropyl)trimethoxysilane (MPTMS), (3-aminopropyl)-trimethoxysilane (APTMS), and poly(ethyleneimine) (PEI). Subsequently, we study the effect of these functional groups on the adsorption of citrate-stabilized Au NPs onto the SiO<sub>2</sub> surface. Moreover, we study the effect of size ratio between Au NPs and SiO<sub>2</sub> spheres for maximum surface coverage, plasmon coupling and colloidal stability. The plasmonic superstructures are analyzed by transmission electron microscopy (TEM), UV/Vis spectroscopy, dynamic light scattering (DLS), and Raman spectroscopy. Based on the experimentally determined optimum parameters, PS and shell-isolated PS (SHIPS) are synthesized. SERS-activity of the (SHI)PS is then measured on spin-coated single (SHI)PS by Raman microscopy and on dispersions of (SHI)PS using a Raman probe, both with 638 nm excitation.

#### **Results and Discussion**

In a first part of our study, the effect of functionalization on  $SiO_2$  spheres of 450 nm was investigated and the results are summarized in Figure 1. The surface of the  $SiO_2$  spheres under

study was modified with different functional groups, in particular thiols (signified as SiO<sub>2</sub>-SH) and primary amines (SiO<sub>2</sub>-NH<sub>2</sub>) through grafting with siloxane ligands, and with a combination of primary, secondary, and tertiary amines (SiO<sub>2</sub>-PEI) through adsorption of the polymer polyethyleneimine (PEI). The TEM (Figure 1a, b) results show that the physical dimensions of the spheres have not been affected by functionalization, whereas DLS results (Figure 1c, and Figure S1 in Supporting Information) show that the hydrodynamic radii are practically the same before and after functionalization, indicating that no particle clustering has occurred after functionalization. Note that the peak for SiO<sub>2</sub>-NH<sub>2</sub> is slightly shifted and broader than the other three, possibly due to a small fraction of particle doublets.

To evaluate whether functionalization had been successful and to probe the influence on the surface properties, the SiO<sub>2</sub> spheres were investigated with Raman spectroscopy and zeta potential measurements, respectively. Figure 1d shows the Raman spectra obtained of bare and functionalized SiO<sub>2</sub> spheres. In the spectral region of 200–1100 cm<sup>-1</sup> several Raman bands arise from the silica spheres and the tetraethoxysiloxane (TEOS) precursor, which is known to partially remain in the SiO<sub>2</sub>.<sup>[20-22]</sup> For example, a Raman band at 480  $\text{cm}^{-1}$  originates from the Si- $(OC_{2}H_{5})_{x}$  stretching vibration, next to a Raman band at 807 cm<sup>-1</sup> due to a Si–C vibration.<sup>[22]</sup> The presence of TEOS residue is confirmed by the presence of a weak, broad band in the C-H stretching vibrations centered around 2940 cm<sup>-1</sup>, assigned to C–H stretching vibrations of the residual ethoxy groups originating from TEOS.<sup>[21]</sup> Furthermore, surface silanols are observed at 980 cm<sup>-1</sup> (Si–OH vibrations) and in the high wavenumber region (>2500 cm<sup>-1</sup>: O–H vibrations).<sup>[22]</sup> For the amine-functionalized samples, these Raman bands are broader and more intense than for both the bare and thiol-functionalized spheres, in line with the presence of -NH<sub>x</sub> groups that participate in hydrogen bonding. Since thiols are generally not associated with hydrogen bonding, the O-H vibrations in SiO<sub>2</sub>-SH can be ascribed solely to Si-O-H. Additionally, the thiol-functionalized spheres exhibit a small Raman band at 2585 cm<sup>-1</sup>, ascribed to S-H stretching vibrations.<sup>[23,24]</sup> The presence of silanol groups despite the observation of the S-H stretching vibration is an indication that the SiO<sub>2</sub> surface is not completely covered in thiols, but rather a mixture of thiols and hydroxyls. Finally, the C-H stretching region exhibits sharp features at 2940 cm<sup>-1</sup> for SiO<sub>2</sub>-NH<sub>2</sub> and SiO<sub>2</sub>-SH characteristic for CH<sub>2</sub> stretching vibrations, arising from the propyl chain or methyl from the methoxy groups. SiO<sub>2</sub>-SH, SiO<sub>2</sub>-NH<sub>2</sub>, and SiO<sub>2</sub>-PEI all exhibit additional stretching vibrations at around 2985 cm<sup>-1</sup> which we assign to -CH<sub>2</sub> groups positioned next to either N or S, taking into account the structure of PEI.<sup>[24]</sup> In short, the Raman spectra show that modification of the surface of the SiO<sub>2</sub> spheres with functional groups was successful for PEI and NH<sub>2</sub>, and partially successful for SH.

Figure 1 e summarizes zeta potential measurements of all the SiO<sub>2</sub> spheres over the pH range 1–12. Note that the bare, primary amine-, and thiol-functionalized SiO<sub>2</sub> spheres all show a strongly fluctuating zeta potential at pH > 10.5 due to dissolution of SiO<sub>2</sub>.<sup>[25]</sup> The SiO<sub>2</sub>-PEI spheres do not display these fluc-

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**Figure 1.** Characterization data of the SiO<sub>2</sub> spheres under study. (a) Transmission electron microscopy (TEM) image of unfunctionalized SiO<sub>2</sub> spheres of 450 nm; (b) TEM image of 450 nm SiO<sub>2</sub> spheres functionalized with primary amines (SiO<sub>2</sub>-NH<sub>2</sub>). Grafting of the amine groups onto the surface has not altered the morphology of the spheres; (c) Intensity-weighted size distributions from dynamic light scattering (DLS) of bare and functionalized SiO<sub>2</sub> spheres. The hydrodynamic size of the spheres is comparable to the TEM size and is barely affected by functionalization, indicating that the spheres were dispersed individually, without clustering. (d) Bulk Raman spectra of the bare and functionalized SiO<sub>2</sub> spheres. The spectra of the introduced surface groups compared to the bare spheres. The spheres were dried on a Si wafer prior to Raman measurements. (e) Zeta potential measurements of the SiO<sub>2</sub> spheres over a pH range of 1–12. Similar behavior is observed for SiO<sub>2</sub> and SiO<sub>2</sub>-SH, indicating limited effect of the functionalized SiO<sub>2</sub> reference.

tuations, indicating that the polymer completely covers the SiO<sub>2</sub> surface, preventing direct contact with the medium. At pH < 8.5, the surface charge of SiO<sub>2</sub>-NH<sub>2</sub> spheres starts to deviate from the behavior exhibited by bare and thiol-functionalized SiO<sub>2</sub> spheres, while the latter two show nearly identical behavior, indicating that silanol groups dominate the charge on the surface as hinted upon in the Raman spectrum of SiO<sub>2</sub>-SH in Figure 1 d. Judging on the behavior of the surface charge of SiO<sub>2</sub>-NH<sub>2</sub> spheres above pH 8.5, these particles also exhibit silanol groups alongside the primary amines. Remarkably, both bare and thiol-functionalized SiO<sub>2</sub> spheres only reach the isoelectric point at pH < 2, meaning that the surface is dominantly negatively charged. Solely based on electrostatic interactions, repulsion between SiO<sub>2</sub>(-SH) and Au NPs will take place upon mixing, as citrate-stabilized Au NPs are negatively charged as well (See Figure S2). Both amine samples do pass their isoelectric points due to protonation of the amine groups; primary amine-functionalized samples at pH 7, and polymer-coated spheres at pH 10. Note that for both NH<sub>x</sub>-functionalized samples, zeta potential measurements below pH 2.8 were not reliable as the dispersions were no longer stable, resulting in poor reproducibility. The behavior of the SiO<sub>2</sub>-PEI spheres exhibiting a local minimum around pH of ca. 4.2 is attributed to a change in conformation of the polymer, exposing or shielding amine groups which in turn influences the surface charge. To summarize: based on electrostatic interactions solely, Au NPs should show increasing adsorption density in the order SH < NH<sub>2</sub>  $\le$  PEI.

Adsorption of Au NPs of 17, 40, and 63 nm (characterization data can be found in Figure S3) onto the functionalized 450 nm SiO<sub>2</sub> spheres was subsequently investigated. By using a large excess of Au NPs, maximum adsorption could be achieved while rendering differences in SiO<sub>2</sub> sphere concentration negligible. By using Au NPs of various sizes, the effect of size ratio was studied in addition to the effect of functionalization. By changing this ratio, the contact area between the two particles can be enlarged, which is expected to increase the formation and stability of the PS. We introduce an adsorption angle  $\theta$  that depends on the size ratio and is defined as follows [Eq. (1)]:

$$\theta = 2\tan^{-1}\left(\frac{r_{Au}}{r_{Au} + r_{SiO_2}}\right) \tag{1}$$

Here  $r_{Au}$  and  $r_{SiO_2}$  are the radii of the Au NPs and the SiO<sub>2</sub> spheres, respectively. The results for adsorption of different

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size Au NPs on 450-SiO<sub>2</sub> are summarized in Figure 2; The inset of Figure 2a represents a schematic depiction of this angle, and Figure 2b-j summarize the results of Au NP adsorption of different sizes on the three types of functionalized SiO<sub>2</sub> spheres. Upon comparison of the TEM results in Figure 2, we can observe several trends. First of all, affinity of Au NPs for the different types of SiO<sub>2</sub> seems to follow the trend predicted by the zeta potential measurements, namely:  $SH < NH_2 \le PEI$ , even though Au NPs are often assumed to bind strongly to thiols.<sup>[26,27]</sup> Second, for all types of SiO<sub>2</sub>, we see increasing adsorption density with decreasing Au NP size, or in other words, with decreasing  $\theta$ . Furthermore, analysis of the superstructures with DLS and UV/Vis spectroscopy as illustrated in Figure S4 and S5 supports these trends by, respectively showing a decrease in amount of free Au NPs in dispersion with an increase in hydrodynamic radius of the supporting SiO<sub>2</sub> spheres, and the emergence of an additional absorption band around 700 nm that can be attributed to the surface plasmon resonance (SPR) of coupled Au NPs, whereas the band arising from LSPR of free Au NPs at 540 nm decreases.<sup>[28]</sup>

Based on these results, PS with optimized adsorption density should consist of Au/SiO<sub>2</sub>-PEI with a  $\theta < 9^{\circ}$ . To optimize SERS activity, Au NPs should be around 100 nm.<sup>[29]</sup> Filling in Equation 1 for this Au NP size gives a required SiO<sub>2</sub> sphere size of 1.5  $\mu$ m, which in turn gives an estimated time of  $\approx$  45 minutes in a reactor cell of 2.5 cm in height before sedimentation of the PS is complete (See Supporting Information for more de-



**Figure 2.** Adsorption density of Au NPs of different sizes on 450 nm SiO<sub>2</sub> spheres. (a) Definition of the angle  $\theta$ ; (b–d) Au63, Au40, and Au17/SiO<sub>2</sub>-SH, resp.; (e–g) Au63, Au40 and Au17/SiO2-NH<sub>2</sub>, resp.; (h–j) Au63, Au40, and Au17/SiO<sub>2</sub>-PEI, resp. Increasing adsorption is observed in the order PEI > NH<sub>2</sub> > SH and with decreasing  $\theta$ . Note that the adsorption density in c and d seems similar due to poor contrast between large SiO<sub>2</sub> spheres and small Au NPs. Scale bars represent 500 nm.

tails on the estimation). Instead, we have opted to select a slightly smaller Au NP size of 61 nm on 900 nm SiO<sub>2</sub>-PEI spheres as a trade-off between SERS-activity and colloidal stability. For this PS,  $\theta$  equals 7.3° and its sedimentation time is estimated to be  $\approx$ 110 minutes in theory, in practice even longer (see Supporting Information), which will provide enough time to carry out experiments with dispersions of Au61/SiO<sub>2</sub>-900-PEI in several applications. The obtained PS is shown in Figure 3a, along with its UV/Vis spectrum in Figure 3c. It is clear that Au NPs have adsorbed onto the surface as expected and this is confirmed by the band around 750 nm in the UV/Vis spectrum that we can assign to coupling of Au NPs on top of the SiO<sub>2</sub> spheres.

In order for these structures to be used in heterogeneous catalysis, direct contact between the Au surface and reagents needs to be prevented, so that no plasmonic side reactions can occur.<sup>[8,11]</sup> Modifying the method by Li et al. for the synthesis of SHINs, we prepared Shell-Isolated Plasmonic Superstructures (SHIPS) by coating the entire PS with a thin layer of SiO<sub>2</sub>, as demonstrated in Figure 3 b. The top UV/Vis spectrum in Figure 3 c shows that the plasmonic properties of these SHIPS are preserved. Additional characterization data can be found in Figure S6 and Table S2. Subsequently, the SERS-activity of both the PS and the SHIPS was determined in two ways: Raman micro-spectroscopy was used to investigate single (SHI)PS deposited on a Si wafer, while Raman spectroscopy was used to determine the enhancement of (SHI)PS in dispersion, both using the same probe molecule.

First, the enhancing properties of single PS were tested. We did this by spin coating a droplet of Au61/SiO<sub>2</sub>-900-PEI and (Au61/SiO<sub>2</sub>-900-PEI)@SiO<sub>2</sub> dispersion onto a B-doped Si wafer, compatible for scanning electron microscopy (SEM). The obtained SEM images in Figure 4c showed that spin coating indeed causes deposition of individual PS over the wafer. As the Au61/SiO<sub>2</sub>-900-PEI superstructures have dimensions above the optical diffraction limit, the individual PS could even be distinguished using a Raman microscope, which allowed us to assess the enhancing properties of a single superstructure at a time using Rhodamine 6G as probe molecule. Rhodamine 6G is a dye molecule often used in Raman spectroscopy to test the signal enhancement of SERS substrates.<sup>[13,30]</sup> Its conjugated structure made up largely of aromatic rings is the basis for its inherently high Raman cross-section, which combined with its high stability against photobleaching makes Rhodamine 6G a suitable probe molecule for Raman measurements based on laser excitation and subsequent high photon flux.<sup>[31]</sup>

The SER spectra measured of a  $10^{-4}$  M Rhodamine 6G solution on a Si wafer with single superstructures are displayed in Figure 4a, with the inset in Figure 4c showing a microscopy image of an individual superstructure. Several superstructures were located dispersed over the 7 mm×7 mm Si wafer and tested for their Raman signal enhancing properties using 638 nm laser excitation. Normalized for laser power per cps (cps: counts per second, the general measure for intensity in Raman spectra), the SERS-activity of the different superstructures could be compared. Figure 4b shows the intensity of the highest peak in the Rhodamine 6G spectrum at 1364 cm<sup>-1</sup> (as-

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**Figure 3.** (a) TEM image of Au61/SiO<sub>2</sub>-900-PEI PS where clustering of the Au NPs on top of the SiO<sub>2</sub> sphere can be observed. (b) TEM image of  $(Au61/SiO_2-900-PEI)@SiO_2 SHIPS$ . A thin layer of silica (grey parts) can be observed around the Au NP (black parts). For clarity the silica layer is also indicated in the inset. (c) Normalized UV/Vis spectra of (yellow) parent Au61 NPs; (purple) Au61/SiO<sub>2</sub>-900-PEI, and; (grey) (Au61/SiO<sub>2</sub>-900-PEI)@SiO<sub>2</sub>. At 550 nm a band arising from localized surface plasmon resonance is present in all samples. The (SHI)PS show additional bands at longer wavelengths that can be attributed to coupling of the surface plasmon resonances of several Au particles and are thus an indication that hot spots are present on top of the SiO<sub>2</sub> spheres. The low signal-to-noise ratio in the (Au61/SiO<sub>2</sub>-900-PEI)@SiO<sub>2</sub> spectrum is caused by the low concentration of SHIPS.



**Figure 4.** (a) Typical SER spectra of a  $10^{-4}$  M Rhodamine 6G solution over single Au61/SiO<sub>2</sub>-900-PEI PS (top, purple) and over single (Au61/SiO<sub>2</sub>-900-PEI)@SiO<sub>2</sub> SHIPS (bottom, grey) deposited on Si wafers. Spectra are corrected for intensity differences due to exposure time and laser power for fair comparison. Enhancement is stronger for the uncoated plasmonic superstructures due to the increased distance between Au NPs and the probe molecule when a silica coating is present in between, as also shown in (b); Scatter plot of the intensity of the 1364 cm<sup>-1</sup> peak (C–C stretching in the xanthene ring) of Rhodamine 6G after baseline subtraction measured on different uncoated (purple) and coated (grey) superstructures. The average intensity on uncoated superstructures is over twice as high compared to SHIPS. These measurement points were corrected for differences in laser power and exposure times. (c) Scanning electron micrograph of a single plasmonic superstructure spin-coated on a Si wafer. The inset shows a microscopy image of an individual superstructure, as observed in Raman microspectroscopy experiments of (a) and (b); (d) S(HIN)ER spectra of Rhodamine 6G solutions of different molarities mixed with Au61/SiO<sub>2</sub>-900-PEI PS (pink) and SHIPS (grey). The lowest concentration in which Rhodamine 6G could be detected was found to be  $10^{-15}$  M for PS and between  $10^{-11}$  and  $10^{-13}$  M for SHIPS. Without any (SHI)PS a concentration of  $10^{-3}$  M Rhodamine 6G could be detected (top spectrum, marked with an asterisk). The broad band around 1640 cm<sup>-1</sup> is attributed to the bending mode of water.

signed to C–C stretching of the xanthene ring<sup>(32)</sup>) after baseline subtraction and accounting for laser power. We observe an average of 658 counts per second per laser power unit for PS, measured on 26 structures. These spectra were recorded at max  $1 \times 10$  s exposure time with 2.5 mW laser power on the sample. Comparing this with the SiO<sub>2</sub>-coated derivative of the

PS, we see a similar spectrum, at less than half the intensity ( $\approx 2.4 \times \text{less}$ ). This is indicative of a SiO<sub>2</sub> coating with minimal thickness, as was also observed in the TEM image in Figure 3 b and in zeta potential measurements in Table S2. Note that fluctuations in signal between different individual structures are larger for PS in absolute terms (standard deviation of 219

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counts for PS versus 126 counts for SHIPS), but are actually smaller in relative terms (33% vs. 51%, respectively). Fluctuations like these are common in S(HIN)ERS experiments.<sup>[33,34]</sup>

The enhancing properties of the (SHI)PS in dispersion were tested using a Raman probe with 638 nm excitation wavelength. (SHI)PS were mixed with Rhodamine 6G solutions of 10<sup>-4</sup>–10<sup>-15</sup> m, transferred to a quartz cuvette and subsequently placed in front of the probe. Spectra obtained of the PS-Rhodamine 6G and SHIPS-Rhodamine 6G mixtures are shown in Figure 4d. As in catalysis we often want to study low concentrations of reactants, the aim of this experiment was to find the lower limits for Raman measurements while maintaining acquisition conditions still suitable for in situ and operando experiments. In other words, spectra were recorded at a maximum total time of 30 s. The resulting spectra show that PS are more SERS-active than SHIPS, as the lower detection limit differs by several orders of magnitude ( $\approx 10^{-12}$  vs.  $10^{-15}$  M, respectively). Note that the signal intensities obtained for  $10^{-9}$  M and 10<sup>-12</sup> M Rhodamine 6G solutions are very similar. We attribute this similarity to adsorption of the dye molecule directly onto the Au/SiO<sub>2</sub>-PEI PS either through coordination of its amine group to the Au NP surface (that is still partially stabilized by carboxylic acid groups with a lower affinity to Au surfaces than amine groups) or due to interaction/hydrogen bonding with the amines present in the PEI polymer. This also in part accounts for the larger difference in signal intensity between PS and SHIPS compared to the micro-spectroscopy experiments on single superstructures. Additionally, the observed difference can be caused by a lower concentration of SHIPS compared to PS.

Furthermore, at higher concentrations the acquisition time and laser power could be lowered significantly, decreasing the potential of beam damage to the sample and minimizing physical effects of laser emission (e.g., temperature increase) on ongoing reactions.<sup>[35]</sup>

## Conclusions

SERS-active, colloidally stable superstructures of (Au/SiO<sub>2</sub>)@SiO<sub>2</sub> have been successfully prepared for reaction monitoring in heterogeneous catalysis applications. Two important properties were investigated: the effect of functionalization of SiO<sub>2</sub> spheres and the Au NP/SiO<sub>2</sub> sphere size ratio. Upon functionalization of the SiO<sub>2</sub> spheres with MPTMS, APTMS, and PEI we found that electrostatic interactions dominate the adsorption of Au NPs over intrinsic chemical affinity. For the size ratio a balance was found between the radius of the Au NPs and the SiO<sub>2</sub> spheres. For adsorption angle  $\theta < 9^{\circ}$  dense adsorption of Au NPs and plasmon coupling were observed. To maintain colloidal stability, the superstructures need to be as small as possible; however, SERS-activity of Au NPs increases with size. Au NPs of 61 nm on SiO<sub>2</sub> spheres of 900 nm were found to provide SERS-activity, while maintaining colloidal stability for a few hours. Finally, we showed that the obtained SERS-active superstructures can be coated with a thin layer of protective SiO<sub>2</sub>. These structures open up the possibility of using SERS to investigate liquid-phase systems, and specifically reactions related to heterogeneous catalysis.

### **Experimental Section**

#### Materials synthesis

Au NPs were synthesized using a seeded-growth method. First, seeds of 17 nm in MilliPore water (MQ, resistivity 18.2 M $\Omega$  cm at 20 °C) were synthesized following the Turkevich method using HAuCl<sub>4</sub>·3 H<sub>2</sub>O (99.99%, Alfa Aesar).<sup>[36]</sup> Seeds were grown to particles of 61 and 63 nm using hydroxylamine hydrochloride (99.995%, Sigma–Aldrich) as mild reducing agent.<sup>[37]</sup> Trisodium citrate dihydrate (99%, Sigma–Aldrich) was used as surfactant in both syntheses. Au NPs of 40 nm were obtained from British Biocell International (BBI) Solutions.

SiO<sub>2</sub> spheres were synthesized following the Stöber method.<sup>[38]</sup> In short, appropriate amounts of ammonia (VWR International, 28–30% in water) were mixed with absolute ethanol and MQ and subsequently tetraethoxysilane (TEOS) (Brunschwig Chemie BV) was added. First, small spheres were formed, and these were subsequently grown to particles of the appropriate size. The obtained SiO<sub>2</sub> spheres were washed with EtOH several times, and finally redispersed in MQ. The SiO<sub>2</sub> spheres were functionalized with (3-mercaptopropyl)trimethoxysilane (MPTMS) (95%, Alfa Aesar), (3-aminopropyl)trimethoxysilane (APTMS) (99%, Sigma–Aldrich), or poly(ethyleneimine) (PEI) (50% in H<sub>2</sub>O, Sigma–Aldrich) by first adjusting the pH of the solution to  $\approx$ 11 using NaOH, and then adding appropriate amounts of functionalizing agent, following the procedures by Claesson et al.<sup>[39]</sup> and Padmanabhan et al.<sup>[40]</sup>

Au/SiO<sub>2</sub> superstructures were synthesized by adding a small amount of functionalized SiO<sub>2</sub> spheres to a diluted Au NP dispersion. Typically 2.5 mL of an as-prepared Au NP dispersion was added to 2.5 mL of MQ. 125  $\mu$ L of functionalized SiO<sub>2</sub> spheres was added to the diluted Au NPs and this mixture was left to stir for 2 h. In all syntheses Au NPs were used in large excess to ensure maximum adsorption which was confirmed by the remaining pink color of the dispersions after adsorption. These excess Au NPs could easily be removed after centrifugation at low speed or gravitational sedimentation of the Au/SiO<sub>2</sub> superstructures.

(Au/SiO<sub>2</sub>)@SiO<sub>2</sub> SHIPS were synthesized by adjusting the method of Li et al.<sup>[19]</sup> Typically, 2 mL of superstructures was added to 8 mL of MQ. 0.1 mL of 1 mM APTMS solution was added and the mixture was stirred at room temperature for 15 min. Then, 0.2 mL of 0.54 wt.% sodium silicate solution (27%, Sigma Aldrich) with pH < 11 was added. This mixture was left to stir for 2 days at room temperature. The obtained SHIPS were washed by centrifugation three times and then redispersed in 2 mL of MQ.

#### Materials characterization

Transmission electron microscopy was carried out on a FEI Tecnai 12 and FEI Tecnai 20, operating at 120 keV and 200 keV, respectively. 20  $\mu$ L of colloidal dispersion was drop-cast on a 300 mesh Cu carbon/Formvar TEM grid (Van Loenen Instruments). TEM images were analyzed using iTEM and Fiji/ImageJ software. DLS and zeta potential measurements were carried out on a Malvern Zetasizer in disposable zeta potential cuvettes. Measurements were repeated at least 3 times. DLS measurements were carried out in backscattering configuration. UV/Vis spectroscopy was carried out on a Cary 60 UV spectrophotometer in quartz cuvettes with a path length of 10.00 mm. A blank was always recorded first. Spectra were measured using Scan Application software by Agilent Tech-



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nologies, version 5.1.0.1016. Raman micro-spectroscopy of (functionalized) SiO<sub>2</sub> spheres was carried out on a Renishaw InVia Raman microscope equipped with a 532 nm laser. Spectra were recorded with a 1200  $Imm^{-1}$  grating, a 50× objective, 10 s acquisition time, 1 accumulation and a laser power output of 37.1 mW. Wire 3.4 software was used to record spectra. SEM and Raman micro-spectroscopy samples of (SHI)PS were prepared by spin coating 15 µL of superstructure dispersion on B-doped Si wafers cut to dimensions of 7×7 mm. Si wafers were cleaned and made hydrophilic by ultrasonication in a 1:1:1 vol mixture of ethanol : acetone : MQ and subsequent rinsing with MQ. Spin coating was performed on an Ossila Spin Coater at 2500 rpm for 60 s per sample. SEM was performed on a FEI XL30sFEG and measurements were performed in UHR mode at a voltage of 5 kV and using a TLD detector. Due to charging of the sample images were recorded in 128x Integrated TV images mode and exported to Scandium 5.0. Raman microspectroscopy was carried out on a Horiba XPlora system equipped with a 638 nm laser. For measurements of dispersions the Horiba XPlora microscope was connected to a probe head compatible with 638 nm laser excitation. Laser power varied from 0.14 to 13.9 mW. Spectra were recorded with a static grating of 1200 lmm<sup>-1</sup>, with max. 10 s exposure time and 3 accumulations, which when combined would always result in a total acquisition time of max. 30 s. Raman spectra were analyzed using LabSpec software version 6.

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### **Conflict of interest**

The authors declare no conflict of interest.

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