Developing Superstructures to Study Heterogeneous Catalysis with Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy

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Abstract

In this project, superstructures consisting of colloidal catalyst nanoparticles deposited on shell-isolated nanoparticles (SHINs) were developed. These superstructures were applied to study catalytically active platinum-group metal nanoparticles with shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), using CO oxidation as a model reaction. Raman spectroscopy is a valuable tool to study catalysts under working conditions.

Plasmonic gold nanoparticles were synthesised by a seeded growth method. These Au NPs were applied to enhance the Raman signal. In order to improve the stability and reduce plasmon-driven side reactions, the Au NPs were coated with an ultrathin silica shell, producing Au@SiO₂ shell-isolated nanoparticles (SHINs). The silica shell can function as a support for catalyst materials, enabling the study of surface reactions over the catalyst nanoparticles with SHINERS. Platinum-group metal nanoparticles (Pd, Pt, Rh and Ru) with controlled morphology were then prepared by colloidal synthesis. These catalyst nanoparticles must be assembled on the silica shell of SHINs to obtain the desired superstructures. This has proven to be a challenging task. Several ligand exchange methods were evaluated in order to replace the isolating capping agents from the colloidal catalyst nanoparticles with smaller ligands. After ligand exchange, self-assembly of catalyst nanoparticles on Au@SiO₂ SHINs should take place, driven by electrostatic interaction. Of the methods evaluated, ligand exchange with NOBF₄ has proven to be the best for this purpose. This method resulted in successful assembly of colloidal nanoparticles on SHINs.

Platinum and ruthenium superstructures were treated with UV/Ozone and reduced, after which CO adsorption was observed in SHINERS. This indicates that even though assembly on the SHINs was not optimal or reproducible, these superstructures can be applied to study surface reactions. For Rh superstructures, the Raman signal was too weak to observe CO adsorption signals in SHINERS, but successful detection of CO adsorption on Au@Rh core-shell nanoparticles indicated that this can be achieved. In conclusion, the superstructures that were developed in this work can be applied to study surface reactions with SHINERS.

It is thought that the Raman signal intensity provided by the superstructures will become even stronger after optimisation of the assembly process, leading to a better ability to detect species *in situ*. Additionally, SHINERS can be applied to study structure-sensitive reactions by preparing superstructures for catalyst nanoparticles with varying morphology. Therefore, the developed superstructures show great promise for application to study heterogeneous catalysis.

Abbreviations

APTMS	(3-Aminopropyl)trimethoxysilane
BD	1,4-Butanediol
CARS	Coherent anti-Stokes Raman spectroscopy
DEA	Diethylamine
EDX	Energy dispersive X-ray spectroscopy
\mathbf{EF}	Enhancement factor
FA	Formamide
FTIR	Fourier-transform infrared spectroscopy
HAADF	High-angle annular dark-field
IR	Infrared
LSP	Localised surface plasmon
LSPR	Localised surface plasmon resonance
MPTMS	(3-Mercaptopropyl)trimethoxysilane
NP	Nanoparticle
OA	Oleic acid
OAm	Oleylamine
PGMs	Platinum-group metals
Rh6G	Rhodamine 6G
SERS	Surface-enhanced Raman spectroscopy
SHIN	Shell-isolated nanoparticle
SHINERS	Shell-isolated nanoparticle-enhanced Raman spectroscopy
SPP	Surface-plasmon polariton
STEM	Scanning transmission electron microscopy
TBA	tert-Butylamine
TEM	Transmission electron microscopy
TTAB	Trimethyl(tetradecyl)ammonium bromide
PVP	Poly(N-vinyl-2-pyrrolidone)
NMP	N-Methyl-2-pyrrolidone

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1. Introduction

1.1 Aim of the Study

The field of catalysis is of critical importance in society, for example in green chemistry and environmental pollution control.^[1,2] Approximately 85 to 90% of the products produced in industry require catalytic processes, including transportation fuels, bulk chemicals and fine chemicals.^[2] Catalysis is the key to sustainable chemistry, it often enables waste minimisation and optimal conversion of resources. A catalyst provides an alternative reaction pathway with a lower activation energy than the uncatalysed reaction, effectively increasing the reaction rate without being consumed in the process.^[1–3] Heterogeneous catalysis involves a catalyst in a different phase than the substrates, it refers most commonly to a solid catalyst and liquid or gas phase reagents.^[4] Heterogeneous systems offer the advantage of facile catalyst separation.^[1–4] A chemical transformation with a heterogeneous catalyst typically starts with adsorption of the reagents on the catalyst surface, followed by reaction of adsorbed species, and finally desorption of the products, liberating adsorption sites on the catalyst surface.^[1–4]

Palladium, platinum, iridium, rhodium, ruthenium and osmium belong to the platinumgroup metals (PGMs).^[5,6] These precious transition metals are of great importance in the field of catalysis due to their excellent performance in a wide range of reactions, including CO oxidation,^[5,7–11] reduction of NO_x ,^[12–14] hydrogenation^[15] and ethanol steam reforming.^[16] An important application for the platinum-group metals in modern society is in three-way catalysts (TWC), which are used to remove NO_x , CO and unburnt hydrocarbons from automotive exhaust.^[12,17]

As mentioned above, heterogeneous catalytic reactions typically take place at the catalyst surface. For this reason, solid catalysts are often applied in the form of nanoparticles.^[1] The amount of rare noble metal catalyst that is required can be minimised by reducing the particle size: the significant increase of the surface to volume ratio ensures a high activity per gram.^[18] However, catalyst properties such as reactivity and selectivity can be considerably affected by this decrease in the particle size.^[19] In addition to changes in particle size, changes in the nanoparticle shape may affect catalytic properties.^[20] This effect of morphology on catalytic properties is referred to as structure sensitivity. Understanding structure sensitivity is an important step in the optimisation of catalyst activity and selectivity.

Structure-sensitive surface reactions over platinum-group metal nanoparticles can be studied with Raman spectroscopy. In this technique, energy differences between vibrational energy levels are measured through the inelastic scattering of photons.^[3,21] An essential advantage of Raman spectroscopy is the fact that it is well-suited for *in situ* study of catalytic reactions.^[22] Additionally, Raman spectroscopy is useful for the detection of metal oxide vibrations in the lower wavenumber region.^[3,23] Therefore, Raman spectroscopy provides information about intermediates and other surface structures present under reaction conditions. In shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), the Raman signal is locally enhanced by the presence of plasmonic metal nanoparticles (e.g. gold or silver).^[24] The delocalised conduction electrons of these plasmonic nanostructures can be resonantly excited by incident light, causing an increase in electric field strength near the surface of these structures.^[25] Due to the local nature of this effect, SHINERS is well-suited to detect surface structures and adsorbates.^[26,27] The signal-enhancing nanoparticles are isolated by an ultrathin shell to improve thermal stability and reduce plasmon-driven side reactions.^[27–31] The shell can function as a support for catalyst nanoparticles.

The catalyst nanoparticle morphology can be controlled through colloidal synthesis. With this approach, shape control is achieved through preferential chemisorption of surface capping agents, among other things.^[18,32,33] For example, rhodium nanoparticles have been prepared in several shapes, including spherical particles, ^[20,34–36] tetrahedra, ^[34] cubes, ^[35] multipods, ^[36] icosahedra, ^[20] triangular plates, ^[20] and octahedra. ^[20] Colloidal synthesis of catalyst nanoparticles can be combined with SHINERS, allowing application of this technique to study structure-sensitive reactions. Understanding the mechanism of a surface reaction enables the optimisation of the performance of catalytic materials through rational design.^[31]

The aim of this project is to prepare superstructures consisting of shell-isolated nanoparticles (SHINs) with colloidal platinum-group nanoparticles anchored on the shell. The successful preparation of these superstructures enables *in situ* study of structure-sensitive reactions using shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).



1.2 Approach

Figure 1.1: Schematic of the synthesis process of colloidal nanoparticles supported on SHINs for testing with SHINERS.

In order to study structure sensitivity with SHINERS, superstructures consisting of colloidal platinum-group metal nanoparticles supported on silica-coated gold nanoparticles (Au@SiO₂) were developed. The preparation of these superstructures is schematically represented in Figure 1.1. A seeded growth method is applied in order to synthesise monodisperse gold nanoparticles that are required for the enhancement of the signal intensity in Raman spectroscopy.^[27,37] A silica shell was then introduced to isolate the gold nanoparticles, improving their thermal stability and reducing side reactions on the gold surface.^[27,30] The resulting Au@SiO₂ nanoparticles are referred to as shell-isolated nanoparticles or SHINs, which function as a support material for catalysts. Colloidal platinum-group catalyst nanoparticles with a diameter below 5 nm were subsequently synthesised by employing capping agents such as polyvinylpyrrolidone (PVP). These capping agents provide a barrier around each particle, thus stabilising the catalyst particles in solution.^[38] However, this barrier also prevents assembly of the catalyst nanoparticles on SHINs. In order to prepare the desired superstructures, different ligand exchange methods have been evaluated. The NP/SHINs structures were then applied to study structure-sensitive reactions with SHINERS. CO oxidation was applied as a model reaction.

2. Theoretical Background and Techniques

2.1 Vibrational Spectroscopy for In Situ Analysis

Optimisation of catalytic materials is essential in green chemistry, because it allows effective use of resources and minimisation of waste.^[1–3] Knowledge of the mechanism behind surface reactions and the local surface structure of the catalyst is invaluable in this process, allowing rational catalyst design to improve the activity, selectivity and stability.^[21,22,31] Many different methods are employed for the characterisation of catalytic materials for this purpose, including vibrational spectroscopy techniques such as infrared (IR) and Raman spectroscopy.^[39,40] IR and Raman spectroscopy are two complementary techniques that can be applied *in situ* to probe the energy of molecular vibrations under working conditions, thereby allowing the identification of chemical species present during reaction.^[3,23,41]



Figure 2.1: Schematic energy level diagram of (a) IR absorption, (b) Rayleigh scattering, (c) Stokes Raman scattering and (d) anti-Stokes Raman scattering. Adapted from ref 42.

Both IR and Raman spectroscopy are applied to characterise compounds by identifying the type of chemical bonds that are present. In IR spectroscopy, a sample is irradiated with infrared light, and the variation of absorbance is measured as a function of the wavenumber. The absorption of photons causes the excitation of molecular vibrations in the sample (Figure 2.1).^[3] The frequency of molecular vibrations depends on the bonding and geometry of the probe molecule. Therefore, the signals observed in IR allow identification of the nature of chemical bonds in a sample.^[43] When a sample is irradiated with light, the majority of the photons are transmitted without any changes, but photons can also be scattered by the sample. In the process of scattering, monochromatic light with frequency ν_0 hits the sample, causing the excitation of a molecule an excitation to an unstable virtual state. The molecule then relaxes back to a real, lower energy state, emitting a photon with frequency ν_1 .^[3,21] A fraction of approximately 0.1% of the photons is scattering:

the virtual state collapses back to the initial state.^[44] An even smaller fraction (1 photon in 10^6 to 10^7) of the incident light is scattered inelastically (Raman scattering), with a different frequency.^[44] In inelastic scattering, energy is transferred from the photon to the molecule or vice versa, causing the photon to be scattered with lower (Stokes scattering) or higher energy (anti-Stokes scattering) than the incident light. Anti-Stokes scattering is very rare, as the molecule must already be in an excited vibrational state in order for this process to occur. The energy transfer occurs at certain energy values corresponding to the vibrational energies of the analyte.^[44] These principles are schematically illustrated in Figure 2.1.

Raman spectroscopy is based on inelastic scattering.^[3,21,44] In this technique, a sample is irradiated with visible laser light, and molecules scatter the light with a different frequency. The shift in frequency is depends on the vibrational frequencies of the scattering molecule. Therefore, Raman spectroscopy provides information on the structure and molecular composition of a sample.^[3,21,44] As mentioned before, infrared and Raman spectroscopy are complementary techniques. In both of these techniques, not all molecular vibrations can be observed. Only molecular vibrations that involve a change in dipole moment can absorb infrared light and are therefore IR active. In contrast, vibrations that correspond to a change in polarisability will be Raman active.^[3,44]

Advantages of Raman spectroscopy with respect to IR spectroscopy include negligible sample preparation and versatile operational conditions, in addition to the fact that IR spectroscopy is not applicable in aqueous systems due to strong water absorption.^[29] The gas phase signals only interfere weakly with the spectra of adsorbed molecules in Raman spectroscopy, and many widely used support materials such as silica and alumina are weak Raman scatterers.^[45] These properties contribute to the fact that Raman spectroscopy is highly suitable for *in situ* measurements.^[3,21] A downside of Raman spectroscopy, fluorescence can cause a strong spectral background, which decreases the signal/noise ratio for Raman scattering.^[3,44] This can fortunately be avoided by using a different excitation wavelength^[3,44,45] Additionally, Raman scattering is an inherently weak process due to small Raman scattering cross-sections of analyte molecules.^[45] The sensitivity of Raman spectroscopy can be improved by applying resonance Raman,^[46,47] coherent anti-Stokes Raman spectroscopy (CARS)^[48] or surface-enhanced Raman spectroscopy (SERS).^[49] The main advantage of SERS in comparison to these other techniques is its strongly localised sensitivity, which makes it a powerful tool to study surface species.^[25,50,51]

2.2 Surface-Enhanced Raman Spectroscopy

Surface-enhanced Raman spectroscopy (SERS) is a powerful, non-destructive tool that can provide high sensitivity to the level of single-molecule detection.^[27] SERS is a technique that employs metallic nanostructures to enhance the Raman signal intensity locally by several orders of magnitude.^[52] Gold and silver are most often applied as nanostructured substrates for SERS, because collective oscillations of the surface conduction electrons can be excited in the visible region of the electromagnetic spectrum for these metals.^[53] This effect is defined as a surface plasmon. Two distinct types of surface plasmons are distinguished: surface-plasmon polaritons (SPPs), which propagate along the metal surface as a longitudinal wave, and localised surface plasmons (LSPs), local oscillations of conduction electrons in the metal nanostructure.^[52] LSPs of a metal nanostructure can be resonantly excited by an external oscillating electric field (e.g. laser light) with a frequency that matches the resonant frequency of the plasmon, resulting in a charge separation (Figure 2.2a).^[25] The magnitude of the induced dipole depends on the incident electric field strength and on the polarisability of the metal nanostructure.^[51] The induced dipole will then resonate with the same frequency as the incident light, a phenomenon that is called localised surface plasmon resonance (LSPR).^[25] This results in the generation of a strong and localised electric field near the plasmonic nanostructure.^[54]

As mentioned above, gold and silver are most often applied as substrates in SERS. Plasmon absorption peaks are located in the visible region of the spectrum for colloidal gold, silver and copper, indicating that plasmons can be excited using visible light for these metals.^[53] Implementing gold or silver for the enhancement of the Raman signal offers different advantages. Silver is plasmonically more active than gold and will therefore result in larger enhancement factors.^[25,55] On the other hand, gold is chemically more inert and is often preferred for applications in which the chemical stability is of the greatest importance.^[25,31,53]

The intensity of Raman scattering depends on the molecular polarisability of a molecule (α) and the electric field (E).^[44] Due to a stronger local electric field, a dipole of greater magnitude is induced in the analyte molecules in the vicinity of the SERS substrate. This larger induced dipole results in stronger Raman scattering.^[25] Raman scattering scales with the electric field approximately as E⁴.^[54] This indicates that moderate increases of the local electric field will result in enormous enhancement factors (EFs) for Raman scattering.^[25] For instance, an increase in electric field by a factor 100 results in an intensity increase of 10⁸. The increased signal strength in SERS with respect to regular Raman spectroscopy can therefore be attributed to the very high local electric fields generated by metal nanostructures.^[25,44] Average enhancement factors above 10⁶ have been obtained, depending on the properties of the SERS substrate and the excitation laser.^[25,50,51]



Figure 2.2: (a) Electromagnetic enhancement in surface enhanced Raman spectroscopy (SERS). Excitation of a localised surface plasmon resonance (LSPR) in a gold nanoparticle with radiation of frequency ω_{inc} and incident electric field E_0 . Adapted from ref 25. (b) Distribution of the enhancement factor (EF) in the gap between two gold colloids. Adapted from ref 55.

The electric field strength of dipolar radiation scales with $E(r) \sim r^{-3}$, and the SERS intensity should therefore depend on the distance from the metal particle according to $I_{SERS} \sim r^{-12}$, as follows from the E^4 approximation.^[25,54] This indicates that the enhancement factor will decrease rapidly as the distance from the metal nanostructure is increased. Typically, strong enhancement factors are only obtained within 5 nm of the metal substrate.^[51] From this distance dependence, it can be concluded that SERS is a surface-sensitive technique, suitable for characterisation of surface species.^[25,31]

It was found that isolated metal nanoparticles do not exhibit very large EFs, typically on the order of 10^3 .^[25,56] The strongest Raman signal enhancement is obtained for so-called "hot spots" in the SERS substrates. Hot spots typically occur in spatially narrow regions, including nanotips, particle-substrate nanogaps and interparticle nanogaps.^[52,57,58] These sites show the strongest LSPR, resulting in EFs up to 10^8 .^[25,52,55] For example, arrays of plasmonic nanoparticles can be prepared with nanolithographic methods for application as SERS substrates.^[59,60] In these arrays, gap-mode plasmons can form in the junction between two metal nanoparticles when the particles are sufficiently closely spaced, resulting in high EFs (Figure 2.2b). However, these high EFs are strongly localised and decrease rapidly upon increasing the distance between the particles.^[55,61] The electric field is strongest when the two nanoparticles are in contact, and decreases as the interparticle spacing is increased. Dimers with surface-to-surface distances up to 15 nm show enhanced Raman signals in comparison to the corresponding monomers.^[61] It can therefore be concluded that a close spacing between supporting metal particles is beneficial for the generation of extremely high and spatially localised enhancement factors.

The probability of a molecule being in a hot spot is very low due to their highly localised nature. Even though only a small fraction of the analyte molecules is located in a hot spot, this small fraction accounts for a large contribution to the total Raman intensity.^[25] In a measurement of the molecule distribution, hot sites with enhancement factors $>10^9$, contained only 63 out of 10^6 molecules but contributed 24 % of the overall SERS intensity. In contrast, the coldest sites (EF $<10^5$) contained 61 % of all molecules, but contributed only 4% of the overall SERS intensity.^[62] This example illustrates the importance of hot spots in the enhancement of the signal intensity in SERS. The ideal SERS-substrate results in a high, spatially uniform EF, has a high stability and is facile to synthesise in a reproducible way.

2.3 Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy

Even though SERS is a promising technique for the study of heterogeneous catalysts, several hurdles must still be overcome. The plasmonic nanostructures that are applied for Raman signal enhancement are not inert: they can interfere with the catalytic reaction of interest.^[63,64] For instance, the strong electric field in the proximity of the SERS-substrate can activate chemical bonds to initiate a reaction.^[65] A second challenge is the limited stability of SERS-substrates at elevated temperatures.^[28,60]

In shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), the plasmonic nanoparticles that are applied to enhance the Raman signal are isolated with an ultrathin shell.^[24,29,66,67] The resulting structures are referred to as shell-isolated nanoparticles (SHINs). The shell ensures the thermal stability of the metal nanoparticles up to $500 \,^{\circ}C^{[28,30]}$ and reduces potentially disturbing photocatalytic side reactions between the plasmonic nanoparticle and molecules in the sample.^[29] However, it has been shown that the Raman enhancement is significantly decreased by the introduction of this coating due to the r⁻¹² dependence of the enhancement factor.^[24] Therefore, the oxide layer must be extremely thin (up to 2 nm) in order to obtain sufficiently strong enhancement of the Raman signal.^[25,31] Uniform shells of 1.5 nm proved to be sufficiently thick to eliminate photocatalytic side reactions while retaining sufficiently strong Raman signal enhancement.^[29] SHINERS is a more versatile technique than SERS, because it is applicable to substrates of any composition and surface morphology.^[27,67] The resulting shell-isolated nanoparticles (SHINs) can be applied as a support material for catalytically active metal nanoparticles, enabling the detection of Raman active surface species and adsorbates on these catalysts.^[26,68,69] This allows for monitoring of chemical reactions on the molecular level, and introduces the opportunity to elucidate or clarify reaction mechanisms.^[31,69]

SHINERS has previously been applied to study structure sensitivity in the hydrogenation of ethyl peruvate over $Pt\{hkl\}$ single-crystal electrodes.^[70] Differences were observed in the relative populations of two surface intermediates for the $Pt\{100\}$, $Pt\{110\}$, $Pt\{111\}$, $Pt\{321\}$ and $Pt\{721\}$ surfaces.^[70] This example indicates that SHINERS is a valuable technique in studies of structure-sensitive catalysis. By immobilising shape-controlled catalyst nanoparticles on SHINs, the effect of nanoparticle shape on catalyst performance can be studied with SHINERS. This in turn enables catalyst optimisation through rational design.

2.4 Structure Sensitivity

As mentioned previously, catalysts are often applied in the form of nanoparticles to maximise the surface-to-volume ratio.^[1,18] The reactivity of these nanoparticles is often affected by their size, especially when catalyst nanoparticle diameters are reduced below a certain size limit (typically on the order of 10 nm). This phenomenon is termed structure sensitivity.^[71–73] Three different classes of structure sensitive reactions are distinguished, in which the reaction rate per exposed metal surface atom is affected differently by a decrease in particle size (Figure 2.3).^[19] The activity per surface atom decreases with decreasing particle size in class I and increases with decreasing particle size in class II, while the rate of class III reactions is not affected by a change in particle size.^[19] Structure sensitivity is linked to the nature of the chemical substrate bond that is activated. A distinction is made between reactions concerning σ -bond activation (for example C-H bonds in methane), and reactions where molecular π -type bonds are formed or cleaved (e.g. in CO).^[19] Step-edge sites are required for activation of π -bonds: molecules are activated through multiple contact with surface atoms. These sites are geometrically not available below a particular particle size limit, therefore the rate per exposed metal surface atom will decrease with decreasing particle size.^[19] This is defined as a class I structure sensitive reaction (Figure 2.3). The rate may decrease uniformly as the particle size is reduced (trend Ia) or show a maximum as shown by trend Ib.

The activity and selectivity of heterogeneous catalysts in structure sensitive reactions are largely determined by the surface atom arrangement, and thus by the type of crystallographic planes that are exposed. ^[74,75] This indicates that nanoparticle shape is of crucial importance in structure-sensitive reactions. ^[18,19] For instance, the activity in the oxygen reduction reaction over platinum nanoparticles has been shown to be significantly dependent on the crystallographic orientation of the Pt surface. ^[76,77] Furthermore, comparison of the Rh{100} and Rh{111} crystallographic planes has revealed that CO oxidation over these surfaces is structure sensitive at low coverage: the surface reaction is faster on Rh{100} than on Rh{111}. ^[78] Similarly, it was shown that Rh{110} is more reactive than Rh{111} in CO oxidation at elevated temperatures. ^[79] This is attributed to the fact that oxygen coverage increases at higher temperatures and oxygen binds more tightly to Rh{111} than to Rh{110}. This is expected to cause a difference in activation energy for the two facets, with a different reactivity as a result. ^[79] These examples serve to illustrate



Figure 2.3: The three different classes of structure sensitivity. Adapted from ref 19.

that different facets may result in different catalytic activity. Identification of the most reactive plane and synthesis of nanoparticles with mainly this plane exposed at the surface therefore allows for optimisation of catalyst activity. Additionally, the process of shape control may help to reduce the amount of scarce catalyst material that is required.^[18]

Colloidal synthesis is a convenient tool when it comes to catalyst preparation: it allows control of particle size,^[80,81] shape^[33,74] and composition.^[82,83] Control over these parameters enables the study of catalytic performance in relation to particle morphology. Multiple approaches are available to control the shape of nanoparticles in colloidal synthesis, including the use of capping agents,^[84,85] kinetic control,^[86,87] oxidative etching^[88,89] and electrochemical alternation.^[90,91]

If no shape control is exerted, nanocrystals will be formed in the shape with the lowest surface free energy, which is the sum of the products of the specific surface free energy and surface area for all facets. This is caused by the thermodynamic driving force to achieve minimisation of the total surface free energy during nanoparticle growth. ^[74,93] The nanoparticle shape with the lowest surface free energy can vary for different metals. When a surface capping agent is introduced into a precursor solution, the shape of the resulting nanoparticles will be altered by preferential adsorption of the capping agent onto a specific type of facet, selectively stabilising that facet by lowering its surface free energy. ^[84,85] Due to this stabilisation, the percentage of the nanoparticle surface composed of this facet will increase. It can thus be concluded that the use of capping agents is a suitable way to alter the nanoparticle shape. The possible capping agents to prepare noble metal nanoparticles include a wide variety of organic molecules, in addition to inorganic species like halide anions. ^[84,85,94,95]

The surface free energy of all facets therefore plays a key role in the nanoparticle shape that is obtained. It has been suggested to be more difficult to control the shape of Rh nanoparticles, due to the overall higher surface free energy compared to other platinumgroup metals.^[92] The number of reports on shape control is far lower for Rh than for



Figure 2.4: A comparison of the specific surface energies of different facets and the corresponding nanocrystal shape for Rh, Pt, Pd and Au. The shapes correspond to octahedral, trisoctahedron (TOH), trapezohedron (TPH), rhombic dodecahedron (RD), tetrahexahedron (THH) and cube, from left to right. Adapted from ref 92.

Pd, Pt and Au.^[20] Rhodium nanoparticles have previously only been prepared in a limited number of shapes, including tetrahedral,^[34] cubic,^[35] spherical,^[96] octahedral^[97] and concave nanocubes.^[98]

High-index facets typically show better catalytic activity than low-index facets because they have a higher density of step atoms with a low coordination number exposed at their surface. Unfortunately, these high-index facets also have a higher surface free energy and are consequently more difficult to obtain (Figure 2.4).^[92,99] By applying capping agents in colloidal synthesis, this thermodynamic limitation of surface energy minimisation can be overcome.^[100] This results in the possibility to prepare nanoparticles with a wide variety of shapes.

2.5 Ligand Exchange

Colloidal nanoparticles consist of an inorganic core stabilised by a layer of surface ligands.^[101] The surfactants attach to the nanoparticle and form an isolating capping layer, which shields the particle from the environment, passivates dangling bonds and controls kinetics of nucleation and growth during synthesis.^[101] Preferential adsorption onto a specific facet lowers the surface free energy of this facet, which affects the nanoparticle shape.^[18,35,84,85] However, the surfactants can block the access of reagents to the nanoparticle surface, which is detrimental to catalyst activity.^[38,102] The capping barrier also hinders deposition of the catalytic nanoparticles on a substrate material, which is often required to prevent aggregation during catalysis.^[102,103]

In order to study the performance of shape-controlled colloidal nanoparticles in heterogeneous catalysis with SHINERS, the catalyst nanoparticles must be immobilised on SHINs. This has been proven to be possible by functionalising the silica surface with thiol groups using (3-mercaptopropyl)trimethoxysilane (MPTMS). These thiol groups can capture the catalytic nanoparticles that are added in the next step, anchoring them by the formation of a covalent M-S bond.^[29] However, the MPTMS increases the separation between the signal-enhancing gold core and the catalyst surface. Raman signals from MPTMS may also interfere with analyte signals. One more downside of MPTMS is the fact that it contains a sulfur atom, and sulfur is commonly known to act as poison to metal catalysts.^[104] It is therefore desirable to assemble the catalyst nanoparticles directly on the Au $@SiO_2$ shell, by removing the capping agents from the catalyst surface. This is most often accomplished using thermal annealing treatment, ^[103,105] UV/ozone treatment ^[103,106,107] or acid/base solutions.^[103] However, these methods can result in changes in size, shape and composition. Application of UV/ozone treatment may result in partial oxidation of nanoparticle surface atoms and is therefore limited to materials that can withstand the strong oxidative environment.^[107] Thermal treatment can cause nanoparticle sintering and shape change, and acid/base treatment may leach out some metals in alloy nanoparticles.^[108] Ligand exchange treatments might offer improvement in this respect, because they do not alter the nanoparticle morphology. The bulky ligands required for synthesis are replaced with surfactants that are better suited for application.^[102,108] For instance, ligand exchange can enable phase transfer of nanoparticles from a nonpolar to a polar phase.^[109]



Figure 2.5: Schematic for the removal of oleylamine (OAm) or polyvinylpyrrolidone (PVP) ligands for several treatments.

After successful ligand exchange, the nanoparticle surface will be positively charged. In contrast, the silica shell of the SHINs is negatively charged at neutral pH, due to its point of zero charge at pH 2-4.^[110] Therefore, it is expected that self-assembly of the catalyst nanoparticles on Au@SiO₂ SHINs will be possible, driven by electrostatic interaction.^[26] Assembly of these superstructures enables the study of catalyst nanoparticles with SHIN-ERS. In this project, several different approaches have been evaluated for this purpose (Fig-

ure 2.5): acetic acid treatment, $^{[103,111-113]}$ ligand exchange with Na₂S, $^{[109]}$ NOBF₄, $^{[26,102]}$ NaBH₄ $^{[108,114]}$ and diethylamine $^{[115]}$ to replace oleylamine (OAm) and polyvinylpyrrolidone (PVP) ligands. The assembled superstructures can be tested with shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).

2.5.1 Na₂S Exchange

Oleylamine is a long-chain primary alkylamine and is regularly applied as a surfactant in colloidal synthesis.^[113,116] Oleylamine adheres to the nanoparticle surface through its amine group, providing steric stabilisation. In a good solvent (e.g. hexane), the hydrocarbon chains repel each other, keeping the nanoparticle in dispersion.^[117] Metal nanoparticles can also be stabilised by electrostatic interaction: charged ions stabilise the oppositely charged nanoparticle surface. The best solvents for effective electrostatic stabilisation have a high dielectric constant.^[117]

A ligand exchange strategy with inorganic ligands in formamide (FA) was introduced as a successful method to replace oleylamine ligands bound to the surface of metal nanoparticles by metal-free inorganic ligands.^[109] In order to achieve the ligand exchange, capped nanoparticles in a nonpolar solvent (toluene, hexane) are combined with a solution of the desired inorganic ligand in formamide (FA). This mixture forms a two-phase system with the nanoparticles and the inorganic ligand in separate phases. After magnetic stirring for 10 min, complete phase transfer of the NPs from the top phase to the bottom phase was observed, indicating successful ligand exchange.^[109] It was concluded that this ligand exchange method did not affect the nanoparticle morphology, since no changes were observed in the absorption and photoluminescence spectra after ligand exchange.^[109] In this work, Na₂S was applied as the metal-free inorganic ligand. A schematic of this ligand exchange approach is presented in Figure 2.5. A downside of this ligand exchange approach is the fact that sulfur is involved, which can act as poison to a metal catalyst.^[104]

2.5.2 Acetic Acid Treatment

A treatment with acetic acid was also reported to result in successful removal of oleylamine ligands.^[111,112] In this approach, acetic acid is added to the nanoparticle dispersion and the mixture is heated to 80 °C for 10 h. This treatment has previously been applied to colloidal PtRu alloy nanoparticles deposited on Vulcan carbon.^[111,112] Fourier-transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM) analysis showed that the oleylamine surfactants had been successfully removed without causing significant changes in particle size. In addition, the distribution of the particles on the support was still uniform after treatment, and the catalytic activity was significantly improved.^[111,112] Similar results were reported for platinum nanoparticles loaded on carbon black^[103] and for palladium nanoparticles supported on silica gel.^[113] The chemical explanation behind the success of this approach is the protonation of the amine group of oleylamine, resulting in a decreased affinity for the metal surface.^[38] This process is schematically represented in Figure 2.5

2.5.3 NOBF₄ Exchange

The exchange of organic ligands like oleylamine for small inorganic ligands can also be achieved by treatment with nitrosonium tetrafluoroborate (NOBF₄).^[102] Like Na₂S-exchange, this ligand exchange strategy can be applied to transfer colloidal nanoparticles

from a nonpolar to a polar phase. A solution of NOBF₄ in a polar solvent (e.g. acetonitrile) is added to a dispersion of OAm-protected nanoparticles, forming a two-phase system. The mixture is stirred for several minutes, until the nanoparticles have completely transferred to the polar layer.^[102] This ligand exchange procedure has been successfully applied to a variety of nanoparticles with different shapes, sizes and compositions.^[26,102] The particle morphology was preserved after ligand exchange with NOBF₄.^[102] Analysis with FTIR spectroscopy showed that 80–85% of the oleic acid ligands capping Fe₃O₄ nanoparticles was removed by the NOBF₄ treatment.^[102]

The suggested mechanism for this exchange is initiated with the rapid removal of NO⁺ cations through reduction by oxygen or water to form NO₂ or HNO₂, respectively. This is followed by protonation of the organic ligands, which facilitates desorption and promotes coordination of BF₄⁻ anions to the metal nanoparticle. It is suggested that polar solvent molecules also help to stabilise the nanoparticles. Ligand exchange with NOBF₄ is schematically illustrated in Figure 2.5.

2.5.4 NaBH₄ Exchange

Polyvinylpyrrolidone (PVP) is another surfactant that is widely applied in colloidal synthesis. PVP is a polymer that consists of a repeating hydrophilic pyrrolydone moiety and a hydrophobic alkyl chain.^[118] Like oleylamine, PVP provides steric stabilisation for metal nanoparticles, through repulsive forces between the hydrophobic carbon chains.^[117,118]

A method was developed to completely remove polyvinylpyrrolidone (PVP), organothiols and other adsorbates from the surface of metal nanoparticles at room temperature using sodium borohydride (NaBH₄).^[114] Computational and experimental studies have shown that hydrides generated by the hydrolysis of NaBH₄ compete with PVP adsorption.^[114] However, the sodium borohydride is decomposed after a certain period of time, allowing readsorption of PVP. It was found these readsorption issues can be overcome by the addition of *tert*-butylamine (TBA). The PVP that is desorbed from the nanoparticles is said to dissolve in the TBA, effectively preventing the re-adsorption of PVP.^[108]

This approach has been successfully applied to remove PVP capping agents from Au, Pt and Pt-Pd alloy nanoparticles without affecting the nanoparticle size, shape or crystallinity.^[108,114] A schematic of this ligand exchange method is presented in Figure 2.5.

2.5.5 DEA Exchange

A ligand exchange method with diethylamine (DEA) was reported to be suitable for the removal of both oleylamine and polyvinylpyrrolidone ligands.^[115] In this approach, an excess of diethylamine is added to an aqueous dispersion of colloidal nanoparticles, after which the mixture is kept static for 24 h.^[115] DEA can bind to surface atoms of the metal nanoparticle through the lone pair on the nitrogen atom, forming strong coordination bonds.^[115,119,120] The formation of these bonds is the driving force for the ligand exchange process, in combination with the high concentration of DEA. Based on ζ -potential measurements, it was suggested that diethylamine loses a proton upon adsorption, which would explain the negatively charged metal surface after ligand exchange.^[115]

After depositing the DEA-coated nanoparticles on a silicon wafer, the DEA can be removed by immersing the wafer in diluted acetic acid.^[115] Like oleylamine, the affinity of DEA for the metal surface is significantly decreased by protonation, causing it to detach from the metal surface. This results in nanoparticles with clean surfaces.

An advantage of diethylamine is the fact that it is a small molecule and a mild chemical: it does not cause surface oxidation or affect the surface characteristics of the metal nanoparticles.^[115,121] For this reason, the particle morphology should remain unchanged by this ligand exchange treatment.^[115] This has been confirmed by successful application of this ligand exchange strategy to PVP-capped gold nanospheres and nanoflowers, as well as Pt nanocubes capped by oleylamine.^[115]

2.6 CO Oxidation as a Model Reaction

After the assembly of superstructures, catalyst nanoparticles can be tested using SHIN-ERS. In order to assess the applicability of superstructures, CO oxidation is introduced as a model reaction. CO is produced in the incomplete combustion of hydrocarbons, for instance in the combustion of gasoline in motor vehicles.^[8] Three-way catalysts containing supported platinum-group metals (Pt, Pd, Ir or Rh) are applied to convert the toxic and harmful NO_x and CO automotive exhaust gases to CO₂, N₂ and O₂, gases that are less harmful to the environment.^[12,17,122] Due to its important role in the regulation of automotive emission, CO oxidation has been widely investigated in the past.^[8-10]



Figure 2.6: A schematic representation of catalytic oxidation of CO on a noble metal surface. Adapted from ref 3.

Catalytic oxidation of CO to form CO_2 occurs according to the following reaction equation: $CO + \frac{1}{2}O_2 \longrightarrow CO_2$. This reaction has been widely accepted to proceed according to the Langmuir-Hinshelwood mechanism, in which associative adsorption of CO and dissociative adsorption of O_2 onto the metal surface occurs, followed by reaction of the adsorbed species to form CO_2 (Figure 2.6).^[3] In this case, the rate-limiting step is the reaction of adsorbed surface species to form the adsorbed product. The role of the catalyst in this reaction includes concentration of reagents at the catalyst surface, thus ensuring a sufficiently high reaction rate. Noble metals such as Pt, Pd, Ir, Rh, Ru and Au are typically employed to catalyse the oxidation of CO. [8,9]

Information about CO oxidation under a variety of conditions is readily available, because CO oxidation is so important in automotive emission control. Additionally, CO_2 is the only product that is formed in the oxidation of CO.^[123] These two advantages make CO oxidation attractive as a model reaction for SHINERS.

2.7 Ultraviolet-Visible Spectroscopy

The localised surface plasmon resonance (LSPR) of gold nanoparticles occurs in the visible range of the electromagnetic spectrum, ^[53] and is strongly dependent on the nanoparticle size and shape. ^[25] Therefore, ultraviolet-visible (UV-vis) spectroscopy can be applied as a quick method to obtain an estimate for the gold nanoparticle size and concentration. ^[124] It is also possible to derive the degree of particle aggregation from the spectrum: aggregation will cause the appearance of a broad band at longer wavelengths (600–800 nm) paired with a decrease in surface plasmon resonance intensity. ^[125–127]

The location of this plasmon peak depends on the size of the nanoparticles.^[25] A fast method to calculate nanoparticle size and concentration from UV-vis spectra has been reported.^[124,128] For spherical particles with a diameter above 35 nm, the particle size is estimated from the wavelength at which the surface plasmon resonance peak occurs. This method is not accurate for smaller particles, a finding that was ascribed to the increasing ratio of surface atoms to bulk atoms.^[124] For particle diameters below 35 nm, an estimate for the diameter is obtained through the ratio of the absorbance at the surface plasmon resonance number of the absorbance at 450 nm (A_{SPR}/A₄₅₀).^[124]

3. Experimental Methods

3.1 Materials

3.1.1 Reagents

The following chemicals were used as received:

 Acetic acid, 99.8%, Acros Organics Acetonitrile, ≥ 99.5% Honeywell, Riedel-de-Haën Acetone, ≥99.9%, Merck (3-Aminopropyl)trimethoxysilane (APTMS), 97%, Sigma-Aldrich 1,4-Butanediol, 99%, Sigma-Aldrich <i>tert</i>-Butylamine (TBA), 99+%, Acros Organics Citric acid trisodium salt dihydrate (sodium citrate), 99%, Acros Organics Dichloromethane, ≥99.9%, Biosolve Diethylamine, ≥99.5%, Sigma-Aldrich Diethylether (stab./BHT) AR, Biosolve N.N-Dimethylformamide, ≥99.8%, Sigma-Aldrich Ethanol absolute,99.5%, Acros Organics Ethylene glycol, J.T. Baker Formamide, ≥98.0%, Fluka Analytical <i>n</i>-Hexane, 99+%, Acros Organics Hydrochloric acid fuming, 37%, Merck Hydroxylamine hydrochloride (NH₂OH· HCl), 98.0%, Sigma-Aldrich Methanol, ≥99.9%, Honeywell, Riedel-de-Haën Millipore water (18.2 MΩ cm at 25 °C) from a Millipore Direct-Q 3 UV water purification system Myristyltrimethylammonium bromide 	 Nitrosonium tetrafluoroborate (NOBF₄), 97%, Acros Organics N-Methyl-2-pyrrolidone (NMP), 99%, Bio- solve LTD Oleylamine (OAm), 70%, Sigma-Aldrich Palladium(II) chloride, 59% Pd, Acros Organ- ics Platinum(IV) chloride, 98%, Aldrich Chem- istry Polyvinylpyrrolidone (PVP), Sigma-Aldrich, average MW 40,000 2-Propanol, 99.5%, Acros Organics Pyridine, 99.8%, Sigma-Aldrich Rhodamine 6G, Sigma-Aldrich Rhodium(III) acetylacetonate, 97%, Acros Organics Rhodium(III) chloride hydrate, Rh 38.5- 45.5%, abcr Ruthenium(III) acetylacetonate, 97%, Aldrich Sodium borohydride (NaBH₄), ≥98.0%, Sigma-Aldrich Sodium hydroxide, ≥99%, Merck Sodium silicate, ≥10% NaOH basis, ≥27% SiO₂ basis, Sigma-Aldrich Tetrachloroaurate(III) trihydrate (HAuCl₄ · 3H₂O), ACS 99.99%, Alfa Aesar Toluene, 99+%, Acros Organics
· Myristyltrimethylammonium bromide $(TTAB), \geq 99\%$, Sigma-Aldrich	- Toluene, 99+%, Acros Organics

3.1.2 Measurement Protocols and Equipment

Transmission electron microscopy (TEM) images were recorded using a FEI Tecnai 12 Icor TEM operating at $120 \,\mathrm{kV}$ and a Tecnai 20 TEM operating at $200 \,\mathrm{kV}$. A FEI Talos F200X Scanning Transmission Electron Microscope operating at $200 \,\mathrm{kV}$ and equipped with Energy Dispersive X-ray Spectroscopy signal detection was employed for elemental mapping. Samples for TEM and EDX studies were prepared by drop-casting a colloidal dispersion on a carbon-coated copper grid, which were left to dry in air.

A Cary 50 Conc UV-Visible Spectrophotometer was used to measure UV-visible spectra for dispersions of gold nanoparticles and SHINs.

Raman spectra were obtained by using a Renishaw in Via Raman Microscope with a $785\,\rm nm$ laser, $1200\,\rm l\,mm^{-1}$ grating, 20 and 50 x objectives with NA 0.4 and 0.75, respectively, and WiRE software. Raman samples were prepared by drop-casting sample onto silicon wafer and drying under vacuum. A BioForce Nanosciences UV/Ozone ProCleaner[™]Plus was used for UV/Ozone treatment.

An IKA RCT Classic Safety Control hot plate magnetic stirrer coupled with VWR VT-5 electronic contact thermometer was used for synthesis. Samples were washed by centrifugation using a Hettich Rotina 380R centrifuge followed by redispersion using a Bransonic Ultrasonic Cleaner 2510.

3.2 Synthesis of Shell-Isolated Nanoparticles

3.2.1 Au NPs

In a 250 mL triple-neck round bottom flask connected to a reflux condenser, 30 mL Millipore water was heated to 120 °C using an oil bath. When the water had reached 120 °C, 0.3 mL of an aqueous 25.6 mM chloroauric acid (HAuCl₄ · 3H₂O) solution was rapidly added, immediately followed by the addition of 0.9 mL 39.5 mM aqueous sodium citrate solution. This mixture was refluxed for 10 min, during which the colour changed from yellow to red, and was then cooled to room temperature.^[37]

These seeds were subsequently used for the preparation of larger gold nanoparticles. 112 mL Millipore water was placed in a 250 mL triple-neck round bottom flask, and 2 mL 39.5 mM sodium citrate solution was added while stirring at high speed, followed by addition of 0.9 mL of Au seed solution. After this, 30 cycles of first adding 78 μ L 12 mM hydroxylamine hydrochloride and then 53 μ L 25.6 mM chloroauric acid (one droplet every 10 s) were completed.^[27]

3.2.2 Au@SiO₂

15 mL of the colloidal Au suspension was placed in a 20 mL glass vial, and 0.15 mL 1 mM (3-aminopropyl)trimethoxysilane (APTMS) solution was added very slowly (one droplet every 10 s) while stirring. The mixture was left to stir for 15–20 min. Subsequently, 1.2 mL 0.54 wt% sodium silicate solution (acidified to pH=10.8 with 0.01 M HCl) was added and the mixture was stirred for 3 min at room temperature. The sample was then heated to 90 °C using a water bath, and was kept at this temperature for 1 h. The sample was quickly cooled to room temperature with cold water from the tap to slow the reaction. The SHINs were then collected by centrifugation at 4000 rpm for 10 min, and washed with 15 mL Millipore water three times. The SHINs were finally dispersed in 5 mL Millipore water.^[27]

3.2.3 Au@Rh Core-Shell Nanoparticles

 $0.5\,\mathrm{mL}$ 31 mM sodium citrate solution and $1\,\mathrm{mL}$ $0.75\,\mathrm{mM}$ RhCl₃ solution were added to $15\,\mathrm{mL}$ as-prepared gold nanoparticle sol. This mixture was refluxed for 3 h, then cooled to room temperature and centrifuged at 4000 rpm for 5 min. The supernatant was removed, and the precipitate was washed two times with 5 mL Millipore water. The nanoparticles were dispersed in 2 mL Millipore water. ^[58]

3.3 Metal Precursor Impregnation of SHINs

SHINs were impregnated with palladium, platinum, rhodium and ruthenium precursors, by mixing 0.3 mL SHINs with 60 μ L 2 mM rhodium(III) chloride hydrate (RhCl₃), ruthenium(III) acetylacetonate (Ru(acac)₃), hexachloroplatinic(IV) acid hydrate, (H₂PtCl₆) or palladium(II) chloride (PdCl₂). Hydrochloric acid (HCl) was added to the palladium precursor solution in order to dissolve the PdCl₂ powder. For PdCl₂, additional samples were prepared with different precursor concentrations by mixing 15 μ L, 30 μ L and 120 μ L 2 mM PdCl₂ solution with 0.3 mL SHINs.

3.4 Colloidal Synthesis of Platinum Group Metal Nanoparticles

3.4.1 Hot Injection Method

Spherical rhodium nanoparticles (5 nm) protected by oleylamine were prepared by a hot injection method. ^[34] A solution of 0.05 g rhodium(III) acetylacetonate in 4 mL oleylamine (31 mM) was rapidly injected into 6 mL oleylamine at 250 °C while stirring. The solution colour changed from yellow to black within 1 min. The reaction mixture was then kept at 250 °C for 1 h, after which it was cooled to room temperature and added to 25 mL methanol, which caused immediate formation of black precipitates. The rhodium nanoparticles were collected by centrifugation at 4000 rpm for 3 min and washed twice with 25 mL methanol. The nanoparticles were then dispersed in 10 mL hexane.

3.4.2 PH-Controlled Polyol Method

Small PVP-capped spherical rhodium nanoparticles (1-2 nm) were synthesised by a pHcontrolled polyol method.^[129] 1.04 mL 38 mM RhCl₃ solution was placed under vacuum in a Schlenk flask and flushed with nitrogen several times. After 30 min, a mixture of 53 mg PVP (average MW = 40,000), 15 µL 15.6 M NaOH solution and 10 mL ethylene glycol was added under nitrogen atmosphere. After stirring for 5 min, the solution was refluxed at 130 °C for 1 h. 50 mL acetone was added and the mixture was centrifuged at 4200 rpm for 5 min. The product was washed by discarding the supernatant, redispersing in 4 mL 2-propanol with ultrasonication and again adding 30 mL and centrifuging at 4200 rpm for 5 min. The final product was dispersed in 50 mL ethanol.

3.4.3 Seedless Polyol Method

PVP-stabilised platinum-group metal nanoparticles were prepared by a seedless polyol method.^[35,130] The synthetic details for the different samples are presented in Table 3.1 The metal precursor, trimethyl(tetradecyl)ammonium bromide (TTAB) and polyvinylpyrrolidone (PVP, average MW = 40,000) were dissolved in 20 mL ethylene glycol (EG) or 1,4-butanediol (BD). For ruthenium, no TTAB was used.^[130] This solution was transferred to a Schlenk flask and heated to the evacuation temperature. The reaction mixture was evacuated under magnetic stirring for 20 min to remove oxygen and water. During this process, the solution colour changed to black, and some foam was formed when switching from N₂ atmosphere to vacuum, indicating the evaporation of water. The flask was then heated to the reaction temperature under N₂ atmosphere. This temperature using cold water, after which the product was divided over four 50 mL centrifuge tubes, and

 $35 \,\mathrm{mL}$ acetone was added to each tube. The black product was collected by centrifugation for 10 min at 4000 rpm, discarding the clear supernatant. For palladium, platinum and ruthenium, the nanoparticles in each centrifuge tube were washed three times by redispersing in 1 mL ethanol with ultrasonication followed by the addition of 10 mL hexane and centrifugation at 4000 rpm for 10 min to precipitate the nanoparticles. The product was combined and dispersed in 10 mL ethanol. For rhodium, the nanoparticles in each centrifuge tube were washed twice times by redispersing in 3 mL 2-propanol with ultrasonication followed by the addition of 17 mL diethylether and centrifugation at 4200 rpm for 2 min. The product was combined and dispersed in 16 mL 2-propanol.

	Pd	\mathbf{Pt}	Rh		Ru	
Particle size (nm)	5.0 ± 1.9	5.4 ± 0.8	3.8 ± 0.5	2.6 ± 0.3	2.9 ± 0.4	4.2 ± 1.2
Precursor	PdCl_2	$PtCl_4$	RhCl_3	$\operatorname{Ru}(\operatorname{acac})_3$	$\mathrm{Ru}(\mathrm{acac})_3$	$Ru(acac)_3$
Precursor concen- tration (mM)	2.65	2.96	9.68	2.65	4.93	10.3
TTAB concentra- tion (mM)	36.9	37.7	48.2	-	-	-
PVP concentra- tion (mM)	49.7	50.4	196	53.7	53.0	100
Solvent	EG	\mathbf{EG}	\mathbf{EG}	\mathbf{EG}	EG	BD
Precursor solu- tion colour	Orange	Yellow	Red	Red	Red	Red
Evacuation temperature (°C)	80	80	80	80	80	140
Reaction temper- ature (°C)	140	180	185	180	180	215
Reaction time (h)	1	1	1.5	2	2	2

Table 3.1: Experimental data on the preparation of platinum group metal nanoparticles stabilised by PVP.

3.5 Assembly of Catalyst Nanoparticles on SHINs

3.5.1 Ligand Exchange with Na₂S

A ligand exchange with Na₂S was applied to spherical rhodium nanoparticles capped with oleylamine.^[109] A solution of 0.6 g Na₂S $\cdot 9\text{H}_2\text{O}$ in 50 mL formamide (0.05 mM) was prepared in a 50 mL volumetric flask. This mixture was placed in an ultrasonication bath for 2 h to dissolve all Na₂S. Subsequently, 1 mL rhodium nanoparticle dispersion in hexane was mixed with 1 mL of the Na₂S solution, forming a two-phase system. The resulting mixture was stirred at 1100 rpm for 3 h, after which the top phase had turned from dark black to colourless, while the bottom phase remained yellow and the black particles were on the glass and in between the two phases. The sample was centrifuged at 5000 rpm for 5 min, and the clear, colourless top layer was removed as much as possible using a pipette. Then, 2 mL toluene was added and the mixture was centrifuged at 5000 rpm for 5 min. This resulted again in the formation of two phases, with the rhodium nanoparticles mostly precipitated. The two clear phases were removed, and 1 mL formamide was added to redisperse the nanoparticles.

3.5.2 Acetic Acid Treatment

An acetic acid treatment was applied to the spherical rhodium nanoparticles protected by oleylamine ligands.^[111,112] First, 3 mL of the rhodium spheres were centrifuged at 4000 rpm for 5 min. The clear, colourless supernatant was discarded, and 1.5 mL acetic acid was added. The nanoparticles were dispersed using the ultrasonication bath for 10 min, followed by heating to 80 °C for 16 h while stirring at 500 rpm. The nanoparticles were collected by centrifugation at 4000 rpm for 10 min, washed 3 times with 2 mL ethanol, and dispersed in 1.5 mL 2-propanol.

3.5.3 Ligand Exchange with NaBH₄

NaBH₄/tert-butylamine (TBA) treatment was applied to the rhodium nanocubes and the palladium, platinum and ruthenium nanoparticles.^[108] To precipitate the nanoparticles, 7 mL hexane and 7 mL toluene were added to 1 mL NP dispersion, followed by centrifugation at 11,000 rpm for 10 min. The supernatant was removed and the nanoparticles were redispersed in 1 mL Millipore water by ultrasonication. This dispersion was combined with a solution of 0.75 mg NaBH₄ in 4 mL tert-butylamine, and the resulting mixture was placed in the ultrasonication bath for 30 min. The nanoparticles were retrieved by centrifugation at 11,000 rpm for 10 min and washed three times by redispersing in 1 mL 1:1 acetone/ethanol by ultrasonication, followed by addition of 13 mL 1:1 hexane/toluene and centrifugation for 10 min at 11,000 rpm. The product was finally dispersed in 1 mL 1:1 acetone/ethanol.

 $100\,\mu\mathrm{L}$ of the sample was diluted 10 times, and $50\,\mu\mathrm{L}$ of the diluted solution was added to $0.25\,\mathrm{mL}$ SHINs combined with $0.25\,\mathrm{mL}$ 2-propanol. This mixture was placed in the ultrasonication bath for 1 h and kept static overnight, after which the sample was centrifuged at 4000 rpm for 10 min to remove nanoparticles that were not assembled on the SHINs. The supernatant was removed and the precipitate was redispersed in $0.5\,\mathrm{mL}$ Millipore water.

3.5.4 Ligand Exchange with Diethylamine (DEA)

A diethylamine (DEA) ligand exchange method was applied to rhodium nanocubes and palladium, platinum and 2.9 nm ruthenium nanoparticles capped with PVP. The nanoparticles in 0.5 mL of these colloidal dispersions were precipitated through the addition of 5 mL hexane, followed by centrifugation at 11,000 rpm for 15 min. The clear, colourless supernatant was removed, and the nanoparticles were redispersed in 0.5 mL Millipore water by applying ultrasonication for 15 min. After the nanoparticles had been redispersed, 15 μ L diethylamine (DEA) was added. The samples were sonicated for 30 seconds and kept static at room temperature for 24 h. The nanoparticles were collected by centrifugation at 11,000 rpm for 60 min. The brown/yellow supernatant was removed, 0.5 mL ethanol was added and the samples were placed in the ultrasonication for 1.5 h. The DEA-exchanged nanoparticles were washed by adding 5 mL hexane, centrifuging for 10 min at 11,000 rpm and redispersing in 0.5 mL Millipore water by ultrasonication for 1 h. Dilutions of the samples were prepared as described in Table 3.2. Since the concentration of these undiluted sample were applied for the different metals in order to obtain similar dilution concentrations and

solution colours. To assemble the DEA-exchanged nanoparticles on SHINs, 100μ L of the diluted samples were mixed with 0.5 mL SHINs. This mixture was placed in the ultrasonication bath for 1 h and kept static overnight. Subsequently, 0.3 mL of each sample was centrifuged at 11,000 rpm for 10 min and redispersed in 0.3 mL Millipore water in order to remove nanoparticles not assembled on SHINs.^[115]

	Pd	Pt	Rh	Ru
Undiluted sample (μ L) H ₂ O (mL)	$\begin{array}{c} 300 \\ 0.5 \end{array}$	$\begin{array}{c} 100 \\ 0.5 \end{array}$	$\begin{array}{c} 100 \\ 0.5 \end{array}$	$50\\0.5$

Table 3.2: Preparation of dilutions for the DEA-exchanged nanoparticles.

3.5.5 Ligand Exchange with Nitrosonium Tetrafluoroborate (NOBF₄)

For PVP-capped nanoparticles, 0.9 mL of a 10.9 mM NOBF₄ solution in acetonitrile was added to 0.1 mL colloidal NP dispersion, and the mixture was placed in the ultrasonication bath for 1 h, then kept static overnight. 4 mL 1:1 hexane/toluene was added and the mixture was centrifuged at 4000 rpm for 5 min. The clear, colourless supernatant was removed and 1 mL acetonitrile was added to redisperse the ligand-exchanged nanoparticles. The resulting dispersion was diluted 10 times with acetonitrile, and 0.5 mL of the diluted dispersion was mixed with 0.25 mL SHINs and 0.25 mL 2-propanol. This mixture was placed in the ultrasonication bath for 1 h, then kept static overnight. The nanoparticles not assembled on SHINs were removed by centrifugation at 4000 rpm for 10 min, after which the colourless supernatant was removed and the precipitate was redispersed in 0.1 mL Millipore water.^[102]

For oleylamine-capped nanoparticles, $2 \text{ mL } 10 \text{ mM } \text{NOBF}_4$ solution in acetonitrile was added to 2 mL NP dispersion in hexane. This lead to the formation of a two-phase system: a black hexane layer containing the nanoparticles on top of a clear and colourless acetonitrile layer with NOBF₄. The mixture was placed in the ultrasonication bath for 30 min, after which the nanoparticles were still in the top phase. The two layers were merged by the addition of 2 mL toluene, after which $2 \text{ mL } 10 \text{ mM } \text{ NOBF}_4$ solution was added. The sample was shaken well, then kept static for 15 min. The mixture was centrifuged at 4000 rpm for 10 min. The clear supernatant was removed, and the black precipitate was redispersed in 1 mL acetonitrile by ultrasonication. The sample was washed once by adding 8 mL 1:1 hexane/toluene, sonicating at 4000 rpm for 10 min, removing the supernatant and redispersing the precipitate in 1 mL acetonitrile. A mixture of 1 mL SHINs and 100 µL Rh dispersion was prepared, and kept static for $1 \text{ h.}^{[102]}$

3.6 SHINERS

3.6.1 Preparation of Raman Samples

Silicon wafer was cut into squares of 5 mm by 5 mm. The wafers were cleaned by immersing them in ethanol and sonicating for 15 min. The pieces were then washed with ethanol two times and placed in an oven at 90 °C to dry. To prepare Raman samples, 15 μ L of a sample was drop-cast on a clean piece of silicon wafer and dried under vacuum.

3.6.2 SHINs Pinhole Test

The SHINs were subjected to a pinhole test using pyridine, by drying 15 µL of the SHIN sol (prepared as described in section 3.2) on a clean Si wafer under vacuum. Subsequently, 15 µL 10 mM pyridine solution was applied to the silicon wafer with SHINs and a quartz coverslip was placed on top. Raman spectra were then measured from 822 to 1195 cm^{-1} with a 50 x objective, 0.43 mW laser power, an exposure time of 1 s and 1 accumulation. Ten spectra are collected in this manner, after which their baseline is subtracted and the average spectrum is calculated. These averaged spectra are used to compare the extent of pinholes in the silica shell for different SHINs.^[27]

3.6.3 SHINs Enhancement Test

The effectiveness of the SHINs was tested by drying 15 µL of the SHIN sol on a clean silicon wafer and applying 15 µL 10^{-4} M aqueous rhodamine 6G (Rh6G) solution. A quartz coverslip is placed on top. Raman spectra are then measured from 1184 to $1533 \,\mathrm{cm^{-1}}$ with a 50 x objective, 0.43 mW laser power, an exposure time of 1 s and 1 accumulation. Ten spectra are collected in this manner, after which their baseline is subtracted and the average spectrum is calculated.^[27,131]

3.6.4 In Situ Measurements

Raman samples were prepared by drying $15 \,\mu\text{L}$ of the sample dispersion on a clean silicon wafer. Several samples were then subjected to UV/Ozone treatment overnight to remove contaminations. The silicon wafer was then placed in a Linkam cell, which was connected to a thermocouple, water cooling system and gas flow in- and output. The connected Linkam cell was then placed under the Renishaw inVia Raman microscope. Spectra were collected at several different spots on the sample under different temperatures and gas atmospheres (including Ar, H₂, O₂ and CO), using a 20 x objective. The scan range, laser power, exposure time and the number of accumulations were varied depending on the experiment.

4. Results and Discussion

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is applied to study CO oxidation over catalyst nanoparticles. This technique requires the preparation of shell-isolated nanoparticles (SHINs) consisting of a gold core and a silica shell to enhance the Raman signal, which are subsequently used to support colloidal catalyst nanoparticles. The synthesis process of the structures required for this technique is presented in Figure 4.1.



Figure 4.1: Schematic of the synthesis process of colloidal nanoparticles supported on SHINs for testing with SHINERS.

4.1 Synthesis of Shell-Isolated Nanoparticles

Shell-isolated nanoparticles (SHINs) consisting of a gold core with a thin silica shell are applied to enhance the Raman signal. A seeded growth method is employed for the synthesis of monodisperse gold nanoparticles. First, a seed solution of gold nanoparticles is prepared by reduction of the chloroauric acid (HAuCl₄·3H₂O) precursor, where sodium citrate acts both as a capping agent and a reducing agent.^[37]

These seeds were subsequently applied for seeded growth with hydroxylamine hydrochloride (NH₂OH · HCl) as a reducing agent, ^[27] to form larger Au nanoparticles of about 100 nm in diameter. The resulting Au particle size can be tuned by altering the concentration of the reducing agent, Au seeds, and the gold precursor (HAuCl₄). ^[27,37,132]

The gold nanoparticles were then coated with an ultrathin silica shell to improve their thermal stability and prevent Raman signal interference of the gold nanoparticles.^[27] In this method, (3-aminopropyl)trimethoxysilane (APTMS) is used to replace the ligands and to increase the susceptibility of the metal nanoparticle for a SiO₂ coating. Subsequently, sodium silicate is added as a silicon source. Heat (90 °C) is applied in order to increase the growth rate of a silica shell. The pH of the sodium silicate is a crucial parameter in this process. For high pH-values (e.g. pH > 11), the silica shell will remain very thin due

to dissolution by sodium hydroxide. However, if the pH is too low (e.g. pH = 8), growth occurs very rapidly, and the silica shell quickly becomes too thick.^[27]



Figure 4.2: (a) UV-visible spectra for 17.4 nm Au NPs, 97.5 nm Au NPs and 97.5 nm Au@1.7 nm SiO₂. The surface plasmon resonance peak occurs at 519 nm for the gold seeds, and at 567 nm for gold nanoparticles and SHINs. (b) TEM image of gold seeds, with an average particle size is 17.4 ± 1.2 nm. (c) TEM image of the final Au NPs, with an average diameter of 97.5 ± 9.7 nm.

UV-visible spectra were collected to estimate the particle size of the gold seeds, larger gold nanoparticles and SHINs (Figure 4.2a). All three samples have surface plasmon resonance in the visible wavelength region. It can be seen that the surface plasmon resonance peak is located at 519 nm for the seeds, and at 567 nm for the bare gold nanoparticles and the SHINs. The size of the seeds is estimated at 17 nm ($A_{SPR}/A_{450}=1.67$) and that of the Au NPs and SHINs at 99 nm.^[124] Additionally, the absence of a band at 600–800 nm indicates that there is no aggregation for these samples.^[125–127] It can be seen that there are no significant differences between the UV-vis spectra for the gold nanoparticles and the SHINs, aside from a slight red shift of the surface plasmon resonance for SHINs due to the addition of the sulface shell. It can thus be concluded that the silica shell does not significantly affect the surface plasmon resonance of the gold core. Similar results were obtained by Li *et al.*^[58]

In order to determine the particle size more accurately, Transmission Electron Microscopy (TEM) images were collected for Au seeds, Au NPs and SHINs. The resulting images for



Figure 4.3: TEM images of gold nanoparticles coated by a silica shell varying in thickness: (a) 1.7 nm, (b) 2.5 nm, (c) 3.1 nm. The scale bar in the inset is 5 nm.

the seeds and Au NPs are presented in Figures 4.2b and 4.2c. The seeds were spherical and 17.4 ± 1.2 nm in diameter, while the final Au NPs were 97.5 ± 9.7 nm in diameter (Figure 4.2c). It can thus be concluded that the particle sizes obtained via UV-vis and TEM match for both the seeds and the gold nanoparticles.

The thickness of the silica shell was varied between 1.7 and 3.1 nm by changing the heating time and the amount of sodium silicate that was added. The experimental data are summarised in Table 4.1 for three different silica shells, prepared according to section 3.2.2, varying only the heating time and the sodium silicate concentration. It can be concluded from this table that an increase in heating time and sodium silicate concentration results in thicker silica shells, in agreement with expectations and previous publications.^[27] By tuning these parameters, the shell properties can be optimised to produce a silica shell that is as thin as possible while still covering the gold nanoparticle homogeneously.

A uniform silica shell is required for optimal performance of the SHINs as SHINERSsubstrates for catalysts (Figure 4.4a). If the shell is too thin (<2 nm), it likely contains so-called "pinholes". These pinholes allow molecules in the solution or in the air to adsorb on the gold core (Figure 4.4b), which gives rise to strong Raman signals. These strong signals may interfere with the relatively weak signals from molecules adsorbed on the catalyst surface.^[27] The uniformity of the silica shell can be tested by applying pyridine as a probe molecule: pyridine can adsorb on the Au core (Figure 4.4c), causing strong Raman signals around 1010 and 1040 cm^{-1} .^[27,133] These bands correspond to the ring breathing mode and symmetric triangular ring deformation, respectively.^[127,134] Since

Table 4.1: Experimental data on the coating of gold nanoparticles with silica, and the resulting shell thickness.

Sodium silicate 0.54 wt% solution (mL)	Heating time (min)	SiO_2 shell thickness (nm)
1.0	20	1.7 ± 0.3
1.2	60	2.5 ± 0.4
1.4	120	3.1 ± 0.4



Figure 4.4: (a) Schematic of a shell-isolated nanoparticle that is homogeneously coated with a silica shell. (b) Schematic of a SHIN with pinholes. The blue shape represents pyridine adsorbed on the exposed gold surface. (c) Adsorption of pyridine on exposed Au surface. (d) Molecular structure of rhodamine 6G. (a-c) Adapted from ref 27.

pyridine does not strongly adsorb on silica, this signal will not be observed if the shell does not contain pinholes.^[27] In order to execute this test, $15 \,\mu\text{L} \, 10 \,\text{mM}$ pyridine is applied to a SHINs-coated silicon wafer. A quartz coverslip is placed on top to prevent evaporation of the solvent, and Raman spectra are recorded. By comparing the Raman intensities of the pyridine bands between SHINs and uncoated gold nanoparticles, the extent of pinholes in the different silica shells can be estimated.



Figure 4.5: Average Raman spectra for different tests performed on bare Au nanoparticles, and three different silica shells, obtained by baseline subtraction of ten spectra and calculating the average. (a) The pyridine pinhole test (822–1195 nm) and (b) the rhodamine 6G test (1184–1533 nm). All spectra were collected using 0.43 mW laser power, 1s exposure time and 1 accumulation. (c) Changes in intensity with increasing silica shell thickness for rhodamine 6G and pyridine bands.

The averaged Raman spectra for three different silica shells are presented in Figure 4.5a, and the relative pyridine band intensities are listed in Table 4.2. It can be seen that uncoated gold nanoparticles show the highest intensity, and therefore have the highest Au surface area exposed. The intensity decreases for both pyridine bands as the silica shell thickness is increased (0 nm > 1.7 nm > 2.5 nm > 3.1 nm), indicating a decrease in the amount of pinholes. The thinnest silica shell (1.7 nm) already shows a significant reduction

in intensity compared to uncoated Au NPs, which further decreases to less than 1% of the signal for uncoated Au NPs as the shell thickness is increased to 3.1 nm.

Additionally, it is important that the SHINs provide sufficiently strong Raman signal enhancement to detect surface species. SERS signals typically dissipate by r^{-10} to r^{-12} , as the separation between analyte and the Au surface (r) increases.^[25,31] It is therefore expected that an increase in silica shell thickness will result in a significant decrease in band intensity. The enhancement provided by the SHINs was tested by applying rhodamine 6G (Rh6G), a probe molecule with a large Raman scattering cross-section (Figure 4.4d): $15 \,\mu L \, 10^{-4} \,M$ Rh6G was applied to a SHIN-coated silicon wafer, and Raman spectra were recorded.^[27] Rhodamine 6G causes strong Raman signals around 1310 and $1360 \,\mathrm{cm}^{-1}$.^[131,135] These bands correspond to aromatic C-C stretching vibrations of Rh6G, more specifically to the in-plane xanthene ring breathing mode and the xanthene ring stretching vibration, respectively.^[131,135] An average of ten Raman spectra was calculated in order to compare the enhancement for different SHINs. The averaged Raman spectra are presented in Figure 4.5b, and the relative intensity of the rhodamine 6G bands for the different silica coating thickness can be found in Table 4.2. It can be seen that the uncoated gold nanoparticles show the highest intensity, and thus the strongest enhancement. This higher band intensity is caused by the smaller distance between the gold surface and the Rh6G molecules. For a shell of $1.7 \,\mathrm{nm}$, the average intensity drops by about 50%, and for shells of 2.5 and 3.1 nm, the resulting band intensity drops to approximately 15 and 10% of the signal for uncoated Au NPs, respectively. It can therefore be concluded that the enhancement factor provided by SHINs decreases significantly as the silica shell thickness is increased.

Table 4.2: Relative band intensities in the Raman spectra for the pyridine and rhodamine 6G tests that were applied to bare gold nanoparticles (97.5 nm in diameter) and gold nanoparticles coated with SiO_2 shells of 1.7, 2.5 and 3.1 nm thick.

SiO_2 shell thickness (nm)	Pyri	dine	Rhodamine 6G		
	$1015\mathrm{cm}^{-1}$	$1040\mathrm{cm}^{-1}$	$1310\mathrm{cm}^{-1}$	$1360\mathrm{cm}^{-1}$	
0	1.00	1.00	1.00	1.00	
1.7 ± 0.3	0.037	0.040	0.44	0.49	
2.5 ± 0.4	0.008	0.011	0.15	0.17	
3.1 ± 0.4	0.002	0.005	0.08	0.09	

For the application of SHINs to study surface reactions, it is crucial to maximise the enhancement and to minimise the extent of pinholes. Ideally, the silica shell should be ultrathin (around 1 nm) and uniform. Our results indicate that the Rh6G signal decreases more quickly than the pyridine signal. Introducing a silica shell of 1.7 nm results in a drop of the rhodamine 6G signal of about 50 % and a reduction of approximately 95 % in the pyridine signal. For the two thicker shells, the Rh6G signal is further reduced, while the pyridine signal does not decrease significantly. Therefore, the SHINs with a silica shell thickness of 1.7 ± 0.3 nm will likely show the best performance in SHINERS of these three different samples. The SHINs with thicker shells result in weaker Raman signal enhancement, and the signal may be too weak to detect surface species during catalysis.

4.2 Catalyst Nanoparticles

After SHINs were successfully prepared, the next step was the synthesis of colloidal catalyst nanoparticles that can be deposited on the SHINs. The colloidal synthesis of palladium, platinum, rhodium and ruthenium nanoparticles is described in this section.

4.2.1 Rhodium Nanoparticles



Figure 4.6: (a) TEM image of cubic rhodium nanoparticles with an average edge length of 3.8 ± 0.5 nm. (b) TEM image of Rh nanoparticles of approximately 1 nm in diameter, prepared by a pH controlled synthesis. (c) Molecular structure for trimethyl(tetradecyl)ammonium bromide (TTAB), and (d) polyvinylpyrrolidone (PVP).

Rhodium nanocubes stabilised by polyvinylpyrrolidone (PVP) were prepared through a seedless polyol method with trimethyl(tetradecyl)ammonium bromide (TTAB) as a structure-directing agent. It is thought that the Br⁻ ions from TTAB selectively stabilise the rhodium {100} facets, resulting in the formation of cubic particles.^[35] A TEM image of the as-prepared rhodium nanoparticles is shown in Figure 4.6a. It can be seen that the Rh NPs are monodisperse, cubic and have an edge length of 3.8 ± 0.5 nm. The particle size distribution is relatively narrow, with a standard deviation of 13%. It can therefore be concluded that relatively monodisperse rhodium nanocubes can be prepared by this method. These cubic nanoparticles allow the study of CO adsorption on this specific {100} facet.

In another synthesis, the pH of ethylene glycol was increased by NaOH. Elevated pH-values increase the reducing ability of ethylene glycol, which results in higher nucleation rates and smaller rhodium nanoparticles.^[129,136] A TEM image of the resulting rhodium particles is presented in Figure 4.6b. These nanoparticles were too small to properly visualise them using TEM and to obtain an average particle size.

Spherical rhodium nanoparticles protected by oleylamine were prepared by a hot injection method (Figure 4.7a). The nanoparticles are clustered in groups of about 50 nm in diameter, but single nanoparticles are well-defined and about 6 nm in diameter. It is thought that this clustering may have been caused by the presence of methanol in the mixture, or by contamination in the oleylamine. Therefore, the synthesis was repeated with a new bottle of oleylamine (Figure 4.7b). Using new oleylamine unfortunately did not result in the formation of isolated rhodium nanoparticles. However, it is observed that the clusters


Figure 4.7: (a) TEM image of spherical rhodium nanoparticles, protected by oleylamine ligands and dispersed in hexane. (b) TEM image of a second batch of spherical rhodium nanoparticles prepared with new oleylamine (c) Molecular structure for oleylamine (OAm) and (d) N-methyl-2-pyrrolidone (NMP).

have decreased in size to a diameter of 20 nm. The oleylamine therefore is expected to have an effect, but there must be other factors that cause the clustering. The spherical rhodium nanoparticles were washed with hexane/ethanol, and toluene/methanol. Unfortunately, this washing step did not result in the disintegration of the clusters.

In addition, the rhodium nanoparticles were centrifuged and redispersed in several solvents to test the stability of the dispersion. It is expected that these rhodium particles would be easiest to disperse in an apolar solvent, due to the apolar hydrocarbon chain of oley-lamine (Figure 4.7c).^[117] The rhodium nanoparticles precipitated within 24 h in hexane and toluene. The nanoparticles seemed to be more stable when dispersed in N-methyl-2-pyrrolidone (NMP, Figure 4.7d). This solution showed no precipitation whatsoever up to 8 days. However, TEM analysis showed that redispersion in hexane, tolueme or NMP did not result in resolution of the clusters. The difference in the rate of precipitation might simply be caused by the higher density and viscosity of NMP.^[137] These findings indicate that the clustering is irreversible.

4.2.2 Ruthenium Nanoparticles

Ruthenium nanoparticles were prepared by colloidal synthesis through polyol reduction of $\operatorname{Ru}(\operatorname{acac})_3$ in the presence of PVP. The polyol solvent (ethylene glycol or 1,4-butanediol) also functions as the reducing agent.^[130] A TEM image of the resulting nanoparticles is presented in Figure 4.8a, in which it can be seen that the particles are spherical and have a diameter of 2.9 ± 0.4 nm. The standard deviation in particle size is lower than 15% of the mean size. The ruthenium nanoparticle size can be tuned by varying the polyol solvent, reaction temperature and the ruthenium precursor concentration.^[130] Spherical ruthenium nanoparticles with an average diameter of 2.6 ± 0.3 nm were prepared by halving the Ru(acac)₃ concentration (Figure 4.8b). Additionally, doubling the precursor concentration, increasing the evacuation and final reaction temperature (140 and 215 °C, respectively), and by using 1,4-butanediol as a solvent instead of ethylene glycol resulted in particles with a diameter of 4.2 ± 1.2 nm (Figure 4.8c). Most of these particles are spherical, but triangular particles and irregularly shaped particles can also be observed.



Figure 4.8: (a) TEM image of 2.9 ± 0.4 nm Ru nanoparticles. (b) TEM image of 2.6 ± 0.3 nm Ru nanoparticles that were prepared by using a lower precursor concentration. (c) TEM image of Ru nanoparticles of 4.2 ± 1.2 nm, which were prepared by using a different solvent, higher temperatures and higher precursor concentration.

4.2.3 Palladium and Platinum Nanoparticles

Palladium nanoparticles were prepared following a similar procedure as for the rhodium nanocubes, which is based on a method published by Zhang *et al.*^[35] A TEM image of the resulting particles, with an average particle size of 5.0 ± 1.9 nm, is presented in Figure 4.9. The particle size histogram is presented in the inset. The majority of the particles is spherical with a diameter around 4 nm on average, but the sample also contains rod-like palladium nanoparticles of 8 nm long and 4 nm thick. The difference in size between the rods and the spherical particles is clearly represented by the bimodal particle size distribution in the particle size histogram. Because of the irregularities in shape, the standard deviation is 38 % when all counted particles are considered.



Figure 4.9: (a) TEM image of 5.0 ± 1.9 nm palladium nanoparticles with the corresponding particle size histogram in the inset, obtained by counting 418 Pd particles. (c) TEM image of platinum nanoparticles with an average diameter of 5.4 ± 0.8 nm.

Platinum nanoparticles were prepared following a similar method, only lowering the precursor concentrations in order to obtain small particles. The resulting particles were analysed using TEM, and it was found that the particles were spherical, with an average diameter of 5.4 ± 0.8 nm (Figure 4.9b). The addition of TTAB did not result in cubic palladium and platinum nanoparticles, in contradiction to previous reports.^[35] This indicates that the presence of Br^- ions from TTAB is not the only variable of importance in the formation of cubic particles. The precursor that is used, its concentration and the reaction temperature are thought to be major contributors in obtaining cubic particles. This seems plausible since cubic rhodium nanoparticles can also be prepared without the addition of TTAB, simply by increasing the reaction temperature.^[138] The adjustments to the precursor concentration for the preparation of our palladium and platinum nanoparticles might be the reason for the difference in nanoparticle shape. The surface energy is much higher for rhodium than for palladium and platinum.^[92] It is possible that the surface energy of $\{100\}$ facets is further reduced by the adsorption of Br⁻ for rhodium than for palladium and platinum. The surface energy plays a significant role in shape control, and this difference can therefore be the cause for the difference in shape for the different metals.

4.3 Assembly

The capping agents employed in colloidal synthesis allow control over the size and shape of nanoparticles, and prevent aggregation. However, these ligands additionally provide a barrier around the particles, blocking the surface atoms from the solvent. The limited access of reagents to the surface caused by the capping agents is detrimental to catalytic activity.^[108] Additionally, the barrier provided by PVP and oleylamine capping agents leads to difficulties in assembling the catalyst nanoparticles on the SHINs, a step that is required in order to obtain a sufficiently strong signal in SHINERS. The catalyst surface must be as close to the Au core as possible, since the SHINERS signal decreases exponentially upon moving away from the Au core.^[25,31] Therefore, the catalyst nanoparticles must be homogeneously deposited on the SHINs.

Assembly was unsuccessful without any treatment to remove the surfactants from the catalyst surface (Appendix A.1) and with thermal treatment (Appendix A.2). For this reason, several methods were employed to remove the capping ligands of the catalyst nanoparticles and deposit them on the SHINs:

- Ligand exchange with Na_2S in formamide^[109]
- Acetic acid treatment^[103,111–113]
- Ligand exchange with $NaBH_4$ and tert-butylamine^[108,114]
- Ligand exchange with diethylamine (DEA)^[115]
- Ligand exchange with NOBF₄ (by a phase transfer and a single layer method)^[102]

Conventional methods of removing the ligands from the nanoparticle surface, including extensive washing, heat treatment in an oxidative atmosphere, acid/base treatment and UV/Ozone treatment, often result in changes in size or shape of the metallic nanoparticles.^[102,108,109,114,115] Since the aim of this project is to study the effect of size and shape, it is crucial that control over these parameters is maintained, leaving the nanoparticle morphology unchanged by the ligand removal process.

In a set of experiments, the assembly of catalyst nanoparticles on SHINs was achieved by a $NOBF_4$ ligand exchange method. The following paragraphs describe the process of reaching this result.

4.3.1 Ligand Exchange with Sodium Sulfide (Na₂S)

A ligand exchange method with metal-free inorganic ligands was reported to result in successful removal of oleylamine capping agents from the surface of colloidal nanoparticles, enabling transfer to a polar solvent.^[109] This ligand exchange method was applied to our clustered spherical rhodium nanoparticles protected by oleylamine, described in section 4.2.1. S²⁻ was employed as the inorganic ligand to replace the oleylamine on the rhodium surface. 1 ml 0.05 M Na₂S in formamide was added to 1 mL NP dispersion (in toluene or hexane), forming a two-phase system, and stirred magnetically. A schematic of the ligand exchange with Na₂S is presented in Figure 4.10.



Figure 4.10: Schematic representation of the Na₂S ligand exchange method.



Figure 4.11: (a) Phase transfer of colloidal nanoparticles during the K_2S ligand exchange performed by Nag *et al.*, adapted from 109. (b) Na₂S ligand exchange of spherical rhodium nanoparticles.

The colour of the phases can be used as an indicator for the ligand exchange process. In our experiments, the formamide solution was yellow even before addition of the NP dispersion. This is likely caused by some contamination in the formamide, and can be solved by deionisation in future experiments.^[139] Nag *et al.* have shown that their CdSe colloidal dispersion undergoes complete transfer to the formamide phase after 10 minutes of stirring, indicating successful ligand exchange (Figure 4.11a). Our rhodium nanoparticles did not transfer to the formamide phase even after 3 hours, but seemed to move to the interface and the glass (Figure 4.11b). The formamide phase remained yellow in colour, while the toluene phase did change in colour from black to clear and colourless. The rhodium nanoparticles could no longer be dispersed in toluene or hexane, but transfer to formamide did not occur either. This indicates that the oleylamine was removed from the Rh surface (at

least partially), but the particles did not disperse in formamide phase. It is suspected that the reason for the failed ligand exchange is the clustering of the nanoparticles (Figure 4.7 and 4.7b). The close packing of nanoparticles may have prevented access of S^{2-} to the metal surface on the inside of these clusters.

4.3.2 Acetic Acid Treatment

Acetic acid washing has previously been successful in removing oleylamine ligands from the surface of colloidal nanoparticles without affecting their morphology.^[103,111–113] A schematic of this method is presented in Figure 4.12. The acetic acid first protonates the amine group of the oleylamine ligands, which lowers the affinity for the metal surface. Washing steps can then be completed to remove the protonated ligands.^[38] In previous research, colloidal nanoparticles were already deposited on a support before treatment with acetic acid, while our aim is to achieve assembly of the colloidal nanoparticles on SHINs by applying this method.^[103,111–113]



Figure 4.12: Schematic for the removal of oleylamine ligands through treatment with acetic acid.

The acetic acid treatment was applied to the oleylamine-capped rhodium nanoparticles (section 3.5.2). After treatment, the nanoparticles proved to be very unstable in isopropanol, precipitating within 24 h. For this reason, the nanoparticles were dispersed in *N*-methyl-2-pyrrolidone (NMP). The dispersion was more stable than in isopropanol, but some precipitation still occurred within a day. Additionally, TEM images (Figure 4.13) showed that aggregation of the nanoparticles had occurred. Therefore, these nanoparticles were not mixed with SHINs, and acetic acid treatment was concluded to be unsuitable to assemble nanoparticles on the silica shell of our SHINs.



Figure 4.13: TEM image of spherical rhodium nanoparticles after treatment with acetic acid.

4.3.3 Ligand Exchange with Sodium Borohydride (NaBH₄)

Application of a ligand exchange method with sodium borohydride (NaBH₄) and *tert*butylamine (TBA) has been reported to result in complete removal of polyvinylpyrrolidone (PVP), organothiols and other adsorbates from the surface of metal nanoparticles at room temperature, without affecting the nanoparticle size, shape and crystallinity.^[108,114] A schematic of this ligand exchange method is presented in Figure 4.14.



Figure 4.14: Schematic representation of the NaBH₄ ligand exchange method.



Figure 4.15: TEM images of the NaBH₄-exchanged colloidal nanoparticles after mixing with SHINs. (a) Pd, (b) Pt, (c) Rh and (d) Ru.

This method was applied to palladium, platinum, rhodium and ruthenium nanoparticles capped with PVP. The ligand-exchanged metal nanoparticles were subsequently mixed

with SHINs. TEM images of the resulting samples are shown in Figure 4.15. Unfortunately, it appears that this ligand exchange method does not result in assembly of the catalyst nanoparticles on the ultrathin silica coating of the SHINs. All four images show several clusters of metallic nanoparticles around the SHINs, instead of a homogeneous distribution of separate metal particles around the silica shell. The majority of the SHINs is not in contact with catalyst nanoparticles. These samples will likely not result in sufficient signal in Raman measurements due to the lack of intimacy between the catalyst nanoparticles and the signal-enhancing SHINs.

Several explanations for the failed assembly seem plausible. First of all, it is possible that the PVP was not successfully removed from the nanoparticles, leaving the barrier intact and causing assembly to be very difficult. However, this seems unlikely due to the aggregation of the nanoparticles. Secondly, the ligand exchange was successful, while the assembly was not effective due to electrostatic repulsion between the nanoparticles and the silica coating. In a neutral environment, silica is negatively charged, seen as the point of zero charge is pH 2-4.^[110] In the case of successful ligand exchange, the catalyst surface will be positively charged, stabilised by polar solvent molecules and hydrides. Self-assembly on the SHINs based on electrostatic interaction should be possible in this scenario. Zeta potential measurements might offer some clarification as to why the assembly was unsuccessful with this ligand exchange method.

4.3.4 Ligand Exchange with Diethylamine (DEA)

Another approach that has proven successful in the removal of oleylamine (OAm) and polyvinylpyrrolidone (PVP) capping agents from the nanoparticle surface, is ligand exchange with diethylamine (DEA).^[115] A schematic of this ligand exchange process is presented in Figure 4.16. An excess of diethylamine is added to an aqueous dispersion of colloidal nanoparticles, after which diethylamine can replace the original ligands. DEA binds to surface atoms of the metal nanoparticle through the lone pair on the nitrogen atom, forming strong coordination bonds.^[115,119,120] The DEA can subsequently be removed by protonation with acetic acid.^[115] As for oleylamine, the affinity of DEA for the metal surface is significantly lowered by protonation, causing it to detach more easily from the metal surface. After washing, this results in nanoparticles with a clean surface.



Figure 4.16: Schematic for the removal of PVP or oleylamine capping agents through ligand exchange with diethylamine (DEA).

This DEA ligand exchange method was applied to palladium, platinum, rhodium and ruthenium nanoparticles protected by PVP. After ligand exchange, the colloidal particles were diluted and mixed with SHINs. Figure 4.17 shows TEM images for the resulting samples. It can be seen in Figure 4.17b that the assembly of platinum nanoparticles on SHINs

has been achieved: the TEM image shows several SHINs with platinum nanoparticles anchored to them. Several separate platinum nanoparticles are also observed, indicating that more washing steps are required to remove all unbound platinum particles. Additionally, even though a number of platinum nanoparticles were successfully assembled on the SHINs, the distribution is not uniform: it can be seen that a significant fraction of the silica shell is not covered with nanoparticles, in addition to several nanoparticle clusters on the SHIN surface, where a monolayer coverage is desirable.



Figure 4.17: TEM images of metal nanoparticles anchored on SHINs. (a) Palladium, (b) platinum, (c) rhodium and (d) ruthenium particles of 2.9 nm. The samples were obtained by applying DEA ligand exchange to the PVP-capped nanoparticles.

For palladium, rhodium and ruthenium, the assembly was less successful (Figures 4.17a, 4.17c and 4.17d). At several locations, it seems that some nanoparticles have been attached to the silica shell, but a significant fraction of the silica surface is unoccupied. Additionally, the nanoparticles appear to be clustered, especially for ruthenium (Figure 4.17d). This clustering might prevent reagents from reaching the metal surface, which is expected to significantly affect the signal intensity in SHINERS. In order to reduce clustering, lower nanoparticle concentrations can be applied in the future.

In conclusion, the diethylamine ligand-exchange method has proven to be suitable to assemble metallic nanoparticles capped with PVP on SHINs, but assembly is not yet optimal. This can be improved by tuning the reaction conditions, for example metal NP and SHIN concentrations, increasing the mixing time and optimising the stirring method.

4.3.5 Ligand Exchange with Nitrosonium Tetrafluoroborate (NOBF₄)

A ligand exchange method involving nitrosonium tetrafluoroborate (NOBF₄) was applied to metal nanoparticles protected by oleylamine, in order to assemble them on SHINs.^[102] This ligand exchange process is schematically illustrated in Figure 4.18. This method allows transfer of the nanoparticles from an apolar solvent to a polar solvent (e.g. acetonitrile), which is achieved by replacing the original ligands with BF_4^- ions and polar solvent molecules.



Figure 4.18: Schematic representation of the $NOBF_4$ ligand exchange method. Adapted from 102.

First, this phase-transfer ligand exchange method was applied to our spherical rhodium nanoparticles protected by oleylamine ligands. After ligand exchange, these nanoparticles remain aggregated in clusters with a diameter of 20-50 nm. It is thought that this aggregation is causing the ligand exchange method to be ineffective. Several parameters were then changed. The first change involved immediately merging the acetonitrile and hexane phases into a single phase by adding toluene, a solvent that mixes with both of these solvents. Secondly, the nanoparticles were dispersed in NMP instead of hexane and single-phase ligand exchange was carried out while stirring at 800 rpm for 22 h. Finally, NOBF₄ phase transfer was attempted without merging the phases, magnetically stirring at 1100 rpm for 3 h instead of using the ultrasonic bath. All other parameters remained unchanged. Unfortunately, these efforts did not result in successful assembly on SHINs, which is again likely caused by the clustering of the nanoparticles.

Even though this ligand exchange method is only known to be successful in the removal of oleylamine capping agents, it was also applied to nanoparticles protected by PVP. After ligand exchange, the nanoparticles were washed three times with acetonitrile, and subsequently mixed with SHINs. This mixture was placed in an ultrasonic bath for an hour, and left static overnight. The sample was centrifuged to remove any nanoparticles that were not assembled on the SHINs and finally analysed with TEM. Application of the method exactly as described by Dong *et al.*^[102] proved to be unsuccessful in anchoring the nanoparticles on the SHINs (Appendix A.3). By varying parameters, it was found to be possible to assemble the catalyst nanoparticles on SHINs by using a large excess of the NOBF₄ solution. A volume ratio of 9:1 (3:1 for 2.6 ± 0.3 nm ruthenium nanoparticles, due to a lower concentration) was used instead of 1:1. The nanoparticles were diluted 10 times after ligand exchange and mixed with an equal volume of SHINs, twice diluted with 2-propanol. The results of this ligand exchange treatment are presented in Figure 4.19. It appears that this method was successful for the assembly of platinum, rhodium and ruthenium nanoparticles on SHINs.



Figure 4.19: TEM images of (a) palladium nanoparticles after ligand exchange with NOBF₄, without the addition of SHINs. Metal nanoparticles assembled on SHINs after NOBF₄ exchange: (b) platinum, (c) rhodium and (d, e, f) ruthenium particles with a diameter of 2.6 ± 0.3 nm, 2.9 ± 0.4 nm and 4.2 ± 1.2 nm, respectively.

The palladium mixture quickly turned yellow during the ligand exchange process, a colour resembling that of the PdCl₂ precursor solution. A TEM image of the ligand-exchanged palladium nanoparticles before the addition of SHINs is presented in Figure 4.19a. Several nanoparticles can still be observed, but aggregates have formed after treatment with NOBF₄. These observations confirm the significant alterations to the nanoparticles caused by the NOBF₄. Palladium is known to dissolve in nitric acid (HNO₃),^[140,141] and a similar environment might have been created by NO⁺ ions from NOBF₄. NO⁺ readily reacts with water, forming nitrous acid (HNO₂) and fluoroboric acid (HBF₄).^[102] Therefore, these observations were likely caused by dissolution of the nanoparticles. This method was also conducted with lower NOBF₄ concentration, which did not result in dissolution of the palladium nanoparticles, but assembly was far from optimal (Figure A.3a in Appendix A.3). It can therefore be concluded that this method is not suitable for the assembly of palladium nanoparticles on SHINs.

The TEM images in Figures 4.19b and 4.19c show the successful assembly of platinum and rhodium nanoparticles on SHINs, respectively. For platinum nanoparticles with a diameter of 5.4 ± 0.8 nm, the result is very promising. The nanoparticles are assembled on the SHINs in a homogeneous monolayer. For rhodium nanocubes with an edge length of 3.8 ± 0.5 nm, several nanoparticles have been attached to the SHINs, which have retained their cubic shape. Figures 4.19d to 4.19f show the assembly for ruthenium nanoparticles with three different diameters: 2.6, 2.9 and 4.2 nm. It can be seen that the assembly is not identical for the three samples. For the ruthenium particles with a diameter of 2.6 ± 0.3 nm and 4.2 ± 1.2 nm, a monolayer of the catalyst nanoparticles is assembled on the SHINs, whereas clusters can be observed for ruthenium nanoparticles of 2.9 ± 0.4 nm. It can therefore be concluded that the process of assembling catalyst nanoparticles on SHINs is not reproducible yet. Testing these samples with SHINERS will reveal whether the signal is strong enough to study surface reactions.

4.4 SHINERS

After successful assembly of catalyst nanoparticles on SHINs, shell-isolated nanoparticleenhanced Raman spectroscopy (SHINERS) was employed to study the samples. CO oxidation was applied as a model reaction.

4.4.1 SHINs Impregnated with Metal Precursors

SHINs were impregnated with a 0.33 mM solution of palladium, platinum, rhodium and ruthenium precursors, as described in section 3.3. The samples were dried on a single Si wafer and treated with UV/Ozone overnight for cleaning, causing partial oxidation of the metal precursors. This ensures identical treatment for all four metals. The sample was then placed in a Linkam cell and reduced at 150 °C under 40 mL min⁻¹ Ar and 10 mL min⁻¹ H₂, which causes the formation of metallic particles on the silica shell (Figure 4.20). This method allows the preparation of metallic nanoparticles on SHINs, although control over particle shape and size is limited. Raman spectra were recorded after UV/Ozone treatment and after reduction (Figures 4.21a and 4.21b).



Figure 4.20: Schematic of the structures formed by impregnation of SHINs with metal precursors, followed by UV/Ozone treatment and reduction to form metallic nanoparticles.

It can be seen in Figure 4.21a that the initial spectra contain several bands: at 300 and $500 \,\mathrm{cm}^{-1}$ for Pd, 330 and $550 \,\mathrm{cm}^{-1}$ for Pt, at 310 and $515 \,\mathrm{cm}^{-1}$ for Rh and at 280 and $400 \,\mathrm{cm}^{-1}$ for Ru. The lower frequency band of these two is assigned to the M-Cl stretching vibration of remaining metal precursor, whereas the higher frequency band is assigned to the M-O stretching vibration of adsorbed atomic oxygen. ^[142–144] These oxide species are formed during the UV/Ozone treatment. After reduction (Figure 4.21b), these M-Cl and M-O bands have (almost) entirely disappeared, which indicates the formation of metallic nanoparticles. Only the Pt/Au@SiO₂ shows a bump at 360 cm⁻¹, which likely originates from Pt-O species or some remaining Pt-Cl species from the precursor, in addition to two sharp peaks at 520 and 1000 cm⁻¹ originating from the silicon wafer substrate.

After reduction, the samples were exposed to CO atmosphere, resulting in the appearance of new bands at 360, 480 and $470 \,\mathrm{cm^{-1}}$ for Pd, Pt and Rh, respectively (Figure 4.21c). These bands are assigned to the M-C stretching vibration of terminal CO for Pt and Rh,

and of CO adsorbed to twofold bridging sites for Pd. $^{[142-144]}$ The corresponding bands for terminally adsorbed C-O stretching vibrations appeared at 2050 and 2020 cm⁻¹ for Pt and Rh, respectively. For Pd, the band for bridge-bound CO appeared at 1930 cm⁻¹. Only terminal CO adsorption is observed for Pt and Rh, while Pd shows only adsorption of CO in a bridged mode. For Ru, no new bands appear in the regions where CO adsorption is expected to become visible.

It can thus be concluded that it is possible for these samples to observe CO adsorption using SHINERS. It cannot be said with certainty why this method is unsuccessful for ruthenium, but it might be caused by the metal precursor that is applied. $Ru(acac)_3$ does not dissolve in water as well as $RuCl_3$ and other metal chloride precursors. This might also explain why the band assigned to the Ru-O stretching vibration is much less intense than the oxide band for the other metals.



Figure 4.21: Raman spectra for SHINs impregnated with $PdCl_2$, H_2PtCl_6 , $RhCl_3$ and $Ru(acac)_3$. (a) Before reduction, under Ar atmosphere (40 mL min⁻¹) at room temperature. (b) After reduction at 150 °C, under Ar (40 mL min⁻¹) and H_2 (10 mL min⁻¹) atmosphere. (c) Under Ar (40 mL min⁻¹) and CO (10 mL min⁻¹) atmosphere at 150 °C. All spectra were measured using 10 s exposure time. The laser power was 0.44 mW for (a), and 0.93 mW for (b) and (c). The intensity has been normalised, setting the highest intensity measured to 1.

The same method was carried out using different PdCl₂ precursor concentrations, to test the optimal precursor concentration. The measurements for a $PdCl_2$ concentration of $0.33 \,\mathrm{mM}$ were conducted on a different day than those for the other three samples, which were all dried on a single, large Si wafer to ensure identical experimental conditions. The reduction temperature for the 0.33 mM sample was 150 °C instead of 200 °C, and the laser power was 0.93 mW instead of 1.96 mW. Figure 4.22 shows SHINERS spectra of samples prepared with various PdCl₂ concentrations. The band assigned to bridged CO adsorption $(360 \,\mathrm{cm}^{-1})^{[142,144]}$ increases in intensity as the PdCl₂ concentration is increased from $0.095 \,\mathrm{mM}$ to $0.33 \,\mathrm{mM}$, but once the concentration is increased further to $0.57 \,\mathrm{mM}$, the intensity drops significantly. Additionally, the corresponding C-O band at $1930 \,\mathrm{cm}^{-1}$ is only visible for a $PdCl_2$ concentration of $0.33 \,\mathrm{mM}$. A possible explanation for this is the formation of metal particles in the hot spots during reduction. These sites provide the highest Raman signal enhancement. The presence of metal nanoparticles in these hot spots prevents analyte molecules from accessing these spots. This significantly lowers the overall enhancement. The increase of the Raman signal intensity up to 0.33 mM might be caused by the formation of specific sites on the Pd surface that favour CO adsorption. However, the lower temperature that was employed for the 0.33 mM sample might also play a role. From these results, it appears that 0.33 mM is the optimal concentration for impregnation of SHINs with PdCl₂. This concentration results in the highest CO adsorption signal.



Figure 4.22: Raman spectra of SHINs impregnated with different concentrations of PdCl₂, measured under Ar (40 mL min⁻¹) and CO (10 mL min⁻¹) atmosphere. All spectra were collected at 200 °C using 1.96 mW laser power and 10 s exposure time, only for a concentration of 0.33 mM the laser power was 0.93 mW and the temperature 150 °C. The intensity has been normalised to the highest measured intensity.

4.4.2 Rh/SHINs

Rhodium nanocubes with an edge length of 3.8 ± 0.5 nm were assembled on SHINs through NOBF₄ ligand exchange. This sample was tested for CO adsorption using SHINERS, in order to ascertain if this sample results in a sufficiently strong signal to follow surface reactions. For this sample, UV/Ozone treatment was not applied. Figure 4.23a presents spectra before reduction, after reduction at 200 °C and under CO atmosphere. All recorded spectra contained many bands between 1000–1600 cm⁻¹, indicating organic material that likely originates from remaining PVP and from contamination.^[144] No clear Rh-O band

was observed before reduction, and the signal was very low. A small bump at $495 \,\mathrm{cm}^{-1}$ is observed in the spectrum under CO atmosphere at 200 °C. The Rh-C stretch vibration of linear CO is expected in this region, ^[143,145,146] but it cannot be excluded that this band is caused by a contaminant instead of by adsorbed CO. It is expected that UV/Ozone treatment will result in improvement of the signal for this sample, removing organic contaminants as CO₂ and H₂O.



Figure 4.23: (a) Raman spectrum of rhodium nanocubes assembled on SHINs through NOBF₄ exchange under 40 mL min⁻¹ Ar at 25 °C, after reduction at 200 °C under 20 mL min⁻¹ H₂ and 40 mL min⁻¹ Ar, and under 20 mL min⁻¹ CO and 40 mL min⁻¹ Ar at 200 °C. (b) Raman spectra of 1 nm Rh NPs mixed with SHINs obtained before reduction, after reduction under 10 mL min⁻¹ H₂ and 40 mL min⁻¹ Ar at 100 °C. All spectra were collected using 0.93 mW laser power and 10 s exposure time. The intensity was normalised to the maximum intensity.

Spherical rhodium nanoparticles protected by PVP (approximately 1nm in diameter) were mixed with SHINs and dried on a clean silicon wafer. The sample was treated with UV/Ozone for 1 h and tested using SHINERS. Raman spectra obtained before and after reduction are presented in Figure 4.23b. The initial spectrum shows bands at 260 and $540 \,\mathrm{cm}^{-1}$, in addition to some bands indicating the presence of organic material between $1000-1600 \text{ cm}^{-1}$. When the temperature is increased and H₂ flow is applied, the intensity of the first two bands decreases. The band at $540 \,\mathrm{cm}^{-1}$ is assigned to the Rh-O stretch vibration.^[143,145] Both spectra also show a band at $260 \,\mathrm{cm}^{-1}$, for which assignment is less straightforward. This band is also observed for uncoated gold nanoparticles (Figure A.6), and a similar band is occasionally observed for SHINs after UV/Ozone treatment. It is possible that this band is caused by an Au-O stretching vibration. These oxides may have formed during UV/Ozone treatment due to the presence pinholes in the silica shell of the SHINs. After reduction, the sample was exposed to CO. Unfortunately, no CO adsorption signals were observed (Figure 4.23b). A plausible explanation seems to be the improper assembly of the rhodium nanoparticles on the SHINs, since no ligand exchange treatment was applied in this case. It is also possible that the PVP capping agents simply block CO from accessing the rhodium surface.

In conclusion, detection of CO oxidation has not been successful for our Rh/SHINs superstructures. The fact that the assembly of rhodium nanoparticles on SHINs is not uniform is thought to be the cause for the low signal intensity. Therefore, optimisation of the superstructure preparation offers the possibility to improve the signal in SHINERS.

4.4.3 Au@Rh Core-Shell Nanoparticles

Gold nanoparticles were coated by an ultrathin rhodium layer as described in section 3.2.3.^[58] This core-shell material is expected to be useful as a reference for SHINERS due to the close proximity of the Rh surface to the Au core, leading to high Raman signals of adsorbed molecules and surface species.^[25,31,58] The aim was to create a shell of 1–2 nm thick, to retain the high signal enhancement provided by the Au NPs, while forming a shell thick enough to draw conclusions about the bulk. A TEM image of the resulting sample is presented in Figure 4.24, in which it is difficult to discern a shell. For this reason, scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDX) was applied. A HAADF-STEM image of an Au NP with elemental maps for Au, Rh and C (Figures 4.25b, 4.25c and 4.25d, respectively) is presented in Figure 4.25. It can be seen that the rhodium is indeed located more around the Au NP, even though it might be as small particles instead of a shell. Additionally, a small amount of RhCl₃ might still be present. Since the elemental maps prove the presence of rhodium around the Au nanoparticle, this sample was subsequently tested with SERS.



Figure 4.24: TEM image of gold nanoparticles coated by a rhodium shell.^[58]

A droplet of the sample was dried on a clean silicon wafer and treated with UV/Ozone overnight. This sample was then analysed using SERS. A Raman spectrum was measured in air at room temperature. This spectrum (Figure 4.26a) shows a broad band at 530 cm⁻¹, which is assigned to the Rh-O stretch vibration of a rhodium oxide species.^[144–146] A weaker band is visible at 290 cm⁻¹, which is likely a second Rh-O stretch vibration of another form of adsorbed oxygen.^[146,147] The band at 290 cm⁻¹ can also be assigned to Rh-Cl stretch vibration of remaining RhCl₃ precursor,^[144] but this seems unlikely since the sample was washed twice before drying on the silicon wafer substrate.

Rh-O bands were expected since the sample was treated with UV-Ozone for 45 min before the measurements, forming (partially) oxidised rhodium species on the gold nanoparticles. Based on this initial spectrum, it can be seen that there is indeed rhodium present in the sample, which could not be seen from the TEM images. The sample was then placed in a Linkam cell and slowly heated to 100 °C under H₂ atmosphere to reduce the rhodium species (Figure 4.26a). The bands at 290 cm⁻¹ and 535 cm⁻¹ have entirely disappeared after reduction. The remaining two bands in this spectrum (515 and 985 cm⁻¹) originate



Figure 4.25: STEM-EDX images for the Au@Rh core-shell sample: (a) HAADF image and elemental maps for (b) Au, (c) Rh and (d) C.

from the Si wafer substrate. Subsequently, the sample was exposed to $10 \,\mathrm{mL}\,\mathrm{min}^{-1}$ CO flow (Figure 4.26b). Bands appeared at 390 and $1850 \,\mathrm{cm}^{-1}$, which are assigned to the Rh-C and C-O stretching vibrations of bridged CO adsorption on Rh, respectively. The bands at 470 and 2020 cm⁻¹ are assigned to the Rh-C stretch and C-O stretch vibrations of linearly adsorbed CO (Table 4.3). ^[143–146] It can thus be concluded that CO adsorption occurs in both linear and bridged mode for this Au@Rh core-shell sample.

Raman Shift (cm ⁻¹)	Assignment
390	Rh-C stretch (bridged)
470	Rh-C stretch (linear)
1850	C-O stretch (bridged)
2020	C-O stretch (linear)

Table 4.3: Band assignment for CO adsorbed on rhodium.



Figure 4.26: (a) Raman spectra for the Au@Rh sample under several different atmospheres. (b) Raman spectrum for the Au@Rh reference sample under CO atmosphere at 100 °C. All spectra were recorded at 100 °C using 0.43 mW laser power and 10 s exposure time. The spectra have been normalised to the maximum intensity. (c) Two different modes of CO adsorption.



Figure 4.27: (a) Raman intensity over time for the two bands at 390 cm^{-1} (Rh-CO, bridged) and 470 cm^{-1} (Rh-CO, linear). 5 mLmin^{-1} O₂ was applied after t=50 s. (b) Spectra recorded before (t=0 s) and after (t=241 s) O₂ was applied. All spectra were recorded at 100 °C using 0.43 mW laser power. The exposure time was 1 s.

After CO adsorption, the sample was exposed to an oxygen atmosphere (5 mL min^{-1}) . Spectra were recorded from 250 to 650 cm^{-1} with 1s exposure time, in order to track changes when changing from CO to O₂ atmosphere. The results of these measurements are displayed in Figures 4.27a and 4.27b. Figure 4.27a shows the changes in intensity of the bands at 390 and 470 cm⁻¹, assigned to the Rh-C stretching vibration of bridge-bound and linearly adsorbed CO, respectively. It can be seen that the band intensity stays constant for a few seconds after O_2 flow is initiated, which is caused by the time that is required for the O_2 to reach the sample. It can be seen that the intensity decreases for both modes of CO adsorption after exposure to oxygen. Figure 4.27b presents spectra under CO and O_2 , and shows the same results: the band intensity is much lower for t=241 s than for t=0 s, at both 390 and 470 cm⁻¹. These results suggest that adsorbed CO is disappearing from the rhodium surface, either by competitive adsorption of O_2 or by reaction with oxygen to form CO₂. By applying an argon atmosphere after CO adsorption, it can be ruled out that CO is not simply desorbed due to competitive adsorption of oxygen. After 241 s, the bands at 390 and 470 cm⁻¹ can still be distinguished, indicating that not all adsorbed CO has been removed from the Rh surface.

In conclusion, the Au@Rh core-shell structure can be applied to successfully detect CO adsorption using surface-enhanced Raman spectroscopy. Both terminally adsorbed CO and bridge bonded CO are observed for this material, which are slowly removed upon exposure to O_2 .

4.4.4 Ru/SHINs

Spherical ruthenium nanoparticles were prepared, varying the diameter: 2.9 ± 0.4 nm, 2.6 ± 0.3 nm and 4.2 ± 1.2 nm. All three samples were successfully assembled on SHINs through NOBF₄ ligand exchange. In order to optimise the preparation of the samples for SHINERS, different treatments were applied to a silicon wafer with dried 2.9 ± 0.4 nm Ru NPs assembled on SHINs. The sample was tested with SHINERS without treatment, after UV/Ozone treatment overnight and after heating to 200 °C in air for 3 h. These different treatments might result in a stronger SHINERS signal than the untreated sample, due to removal of capping agents and contaminants. Raman spectra for the differently treated 2.9 nm Ru NPs under Ar, Ar and H₂ and Ar and CO are presented in Figures 4.28a, 4.28b and 4.28c, respectively.

It can be seen that there are many differences between the spectra of the different samples. This suggests that sample preparation is a crucial factor in these measurements. The yellow spectrum (heat treatment) is very noisy, and has no well-defined peaks, only a broad band around $500 \,\mathrm{cm}^{-1}$, which likely originates from the Ru-O stretch vibration. ^[143,145] The spectrum for the untreated sample contains a band around $600 \,\mathrm{cm}^{-1}$ for Ru-O and some peaks between $1000 \,\mathrm{cm}^{-1}$ and $1500 \,\mathrm{cm}^{-1}$ that likely originate from organic molecules.^[144] For the UV/Ozone treated sample, the Ru-O band seems to have shifted to lower Raman shift, and there is an additional band around $300 \,\mathrm{cm}^{-1}$. This band might originate from Au-O species, as discussed above for Rh/SHINs. After reduction (Figure 4.28b), these peaks have mostly disappeared, indicating that they were indeed caused by metal oxides. A sharp peak has appeared at $380 \,\mathrm{cm}^{-1}$, with a shoulder at $340 \,\mathrm{cm}^{-1}$. Similar bands were observed for tris(bipyridine)ruthenium(II).^[148] These bands therefore likely originate from some kind of Ru-N species. The sharp peak around $1000 \,\mathrm{cm}^{-1}$ originates from the silicon wafer substrate. Additionally, the spectra for untreated and heat-treated ruthenium show a new peak around $750 \,\mathrm{cm}^{-1}$, and a broad band centered around $1400 \,\mathrm{cm}^{-1}$. This band is likely caused by some carbon-containing impurities, especially since it is not present for the UV/Ozone treated sample.



Figure 4.28: Raman spectra for 2.9 ± 0.4 nm Ru NPs assembled on SHINs, treated in different ways. (a) Under $40 \,\mathrm{mL}\,\mathrm{min^{-1}}$ Ar at room temperature, (b) under $40 \,\mathrm{mL}\,\mathrm{min^{-1}}$ Ar and $10 \,\mathrm{mL}\,\mathrm{min^{-1}}$ H₂ at 200 °C, and (c) under $40 \,\mathrm{mL}\,\mathrm{min^{-1}}$ Ar and $10 \,\mathrm{mL}\,\mathrm{min^{-1}}$ CO at 200 °C. All spectra were collected using 10 s exposure time. The laser power was 0.93 mW for the untreated and UV/Ozone treated sample, and 4.13 mW for the heated sample. All spectra have been normalised to the maximum intensity.

After reduction, the samples were exposed to $10 \,\mathrm{mL\,min^{-1}}$ CO. A band appeared at $480 \,\mathrm{cm^{-1}}$ for the UV/Ozone treated Ru NPs, originating from the Ru-C stretching vibration of linearly adsorbed CO.^[144,145] For the untreated and heat treated samples, this band is it is difficult to distinguish. The corresponding C-O stretching vibrations are expected from 1850 to $2050 \,\mathrm{cm^{-1}}$, and all three samples seem to have a very weak bump in this region.^[144,145] From these spectra, it can be concluded that the sample treated with UV/Ozone has the best Raman signal in this reaction. It is thought that this originates from the fact that impurities have been removed with UV/Ozone treatment. However, there are many other factors that influence the measurements. For example, differences in the spectra could also be explained by inhomogeneities in the sample and drying effects.



Figure 4.29: Raman spectra recorded for Ru nanoparticles with a diameter of 2.6 ± 0.3 nm, 2.9 ± 0.4 nm and 4.2 ± 1.2 nm. (a) under 40 mL min⁻¹ Ar at room temperature before reduction and (b) after reduction at 200 °C under 40 mL min⁻¹ Ar and 20 mL min⁻¹ H₂. (c) under CO atmosphere at 200 °C. (d) Zoom-in (250–650 cm⁻¹) of the CO adsorption spectra. All spectra were recorded with 0.93 mW laser power and 10 s exposure time. The recorded spectra were normalised for (a-c).

The effect of ruthenium particle size was studied by applying SHINERS to ruthenium nanoparticles of 2.6 ± 0.3 nm, 2.9 ± 0.4 nm and 4.2 ± 1.2 nm on SHINs. Raman samples were prepared by drying a droplet of the superstructure dispersion on a Si wafer, followed by UV/Ozone treatment overnight. The samples were then placed in a Linkam cell and reduced under 20 mL min⁻¹ H₂ at 200 °C. Spectra before and after reduction are presented in Figure 4.29 for each of the three Ru NP sizes. The peak positions again seem to vary between the three different samples before reduction. The spectrum for Ru NPs of 2.9 ± 0.4 nm is different from the other two particle sizes, with additional bands at 335 cm^{-1} and 560 cm^{-1} , and no band at 390 cm^{-1} . The spectra for Ru NPs of 2.6 ± 0.3 nm and 4.2 ± 1.2 nm are very similar. As descibed above, the band at 280 cm^{-1} is thought to originate from the SHINs (Au-O stretching vibration). The band at 560 cm^{-1} is assigned to the Ru-O stretch vibration, and the band at 390 cm^{-1} is likely another form of Ru-O. Figure 4.29b presents the spectra of the three samples after reduction under 40 mL min^{-1} Ar and 20 mL min^{-1} H₂ at $200 ^{\circ}$ C. The bands have disappeared, indicating reduction of

the ruthenium species. New bands have appeared at $340 \,\mathrm{cm}^{-1}$ and $380 \,\mathrm{cm}^{-1}$ for the two largest particle sizes, similar to the spectra above.

After reduction, the Ru NPs were exposed to $20 \,\mathrm{mL\,min^{-1}}$ CO at $200\,^{\circ}$ C. The resulting spectra are presented in Figures 4.29c and 4.29d. A weak band appeared at $475 \,\mathrm{cm^{-1}}$, which is assigned to the Ru-C stretch vibration of linearly adsorbed CO.^[144,145] However, only weak bumps are observed for the corresponding C-O stretch vibrations (around $2000 \,\mathrm{cm^{-1}}$). Figure 4.29d shows a zoom-in of these spectra under CO at $200\,^{\circ}$ C, in which the weak CO adsorption band can be distinguished more easily. It can be seen that the bands at $340 \,\mathrm{cm^{-1}}$ and $380 \,\mathrm{cm^{-1}}$ increase in intensity as the particle size is increased. A similar trend is difficult to distinguish for the CO adsorption band, the intensities seem to be comparable. In conclusion, no size-effects have been observed for CO adsorption with the current instrumentation.

4.4.5 Pt/SHINs

Spherical platinum nanoparticles with a diameter of 5.4 ± 0.8 nm have been successfully anchored on SHINs through ligand exchange with NOBF₄ and with diethylamine (DEA). These superstructures were then subjected to SHINERS to test whether surface structures and adsorbed species can be detected. A droplet of the colloidal NP dispersion was dried on a clean silicon wafer and treated with UV/Ozone overnight. Raman spectra were then collected under different atmospheres (Figure 4.30). The samples were first exposed to 40 mL min^{-1} Ar, for which spectra are presented in blue. It can be seen that spectra for both samples are very similar (Figures 4.30a and 4.30b). Both spectra show a band around 560 cm^{-1} , which is assigned to the Pt-O stretch vibration.^[143] This band is much weaker for the platinum nanoparticles assembled on SHINs by DEA ligand exchange than for the NOBF₄-exchanged platinum nanoparticles. This difference in intensity was expected because of the lower coverage of Pt NPs on the SiO₂ shell after DEA ligand exchange. Both spectra also show a band at 265 cm^{-1} , which likely originates from the SHINs (Au-O stretching vibration), as described above for Rh/SHINs and Pt/SHINs.



Figure 4.30: Raman spectra for platinum nanoparticles anchored on SHINs through (a) DEA ligand exchange, and (b) $NOBF_4$ ligand exchange. All spectra were collected using 0.93 mW laser power and 10 s exposure time. The intensity has been normalised to the maximum intensity.

The samples were then reduced at $150 \,^{\circ}$ C under $40 \,\mathrm{mL}\,\mathrm{min}^{-1}$ Ar and $10 \,\mathrm{mL}\,\mathrm{min}^{-1}$ H₂. The Pt-O stretch band has entirely disappeared for both samples, indicating that the platinum surface oxide was reduced to metallic Pt. The band at $265 \,\mathrm{cm}^{-1}$ has also disappeared after reduction for both samples, confirming that this band was caused by an oxide. Spectra after reduction only show a band around $2050 \,\mathrm{cm}^{-1}$, which might originate from the Pt-H stretch vibration.^[144] However, its intensity is quite high, and therefore it is more likely that this band originates from some kind of impurity. For DEA-exchanged platinum nanoparticles, the band is less pronounced. After reduction, the samples were exposed to $10 \,\mathrm{mL}\,\mathrm{min}^{-1}$ CO at $150 \,^{\circ}\mathrm{C}$ (Figure 4.30). A band appeared at $480 \,\mathrm{cm}^{-1}$, which is assigned to the Pt-C stretch vibration of terminally adsorbed CO.^[142,143] The corresponding C-O stretching vibration is expected at $2060 \,\mathrm{cm}^{-1}$, ^[142,143] but this signal is obscured by the band that was already present in this region under H₂ atmosphere.

For platinum nanoparticles assembled on SHINs through ligand exchange with NOBF₄, $10 \text{ mL min}^{-1} \text{ O}_2$ was applied to the sample after CO adsorption. Figure 4.31 shows a spectrum that was recorded under CO atmosphere and a spectrum recorded 200 s after O₂ flow was initiated. In addition to a clear linear CO adsorption band at 485 cm^{-1} , the spectrum under CO atmosphere contains a small bump at 390 cm⁻¹, which is where the Pt-C stretch vibration of bridge-bound CO is expected. ^[142,143] The band at 485 cm^{-1} , which originates from CO adsorbed in a linear mode, has disappeared entirely after exposure to O₂. The remaining band at 515 cm^{-1} originates from the silicon wafer substrate. The amount of linearly adsorbed CO decreases upon exposure to O₂, either by competitive adsorption or by oxidation to form CO₂.

Even though the platinum particles are quite large $(5.4 \pm 0.8 \text{ nm})$, CO adsorption can be observed using these superstructures. Only linear CO adsorption is clearly distinguished for both samples, but a band for bridged CO seems to be present as well, with a very low intensity. It is expected that decreasing the diameter of the platinum nanoparticles and improving the homogeneity of the assembly will result in a stronger signal. A stronger signal should allow reduction of the exposure time, allowing us to track changes in band intensity over time.



Figure 4.31: Raman spectra for Pt NPs anchored on SHINs through NOBF₄ exchange, under $10 \,\mathrm{mL\,min^{-1}}$ CO and 200s after switching to $10 \,\mathrm{mL\,min^{-1}}$ O₂. Both spectra were collected at 150 °C using 1.96 mW laser power and 10 s exposure time.

5. Conclusions

In this research, superstructures consisting of colloidal nanoparticles on $Au@SiO_2$ shellisolated nanoparticles (SHINs) were successfully prepared. These superstructures were applied to study catalytically active platinum-group metal nanoparticles with shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), using CO oxidation as a model reaction.

Plasmonic gold nanoparticles were synthesised by seeded growth, and coated with an ultrathin silica shell to produce SHINs. These SHINs were applied to enhance the signal intensity in Raman spectroscopy. Subsequently, platinum-group metal nanoparticles (Pd, Pt, Rh and Ru) with controlled morphology were prepared using colloidal synthesis. Several methods were then evaluated for the removal of the capping agents from the surface of these colloidal nanoparticles, which is necessary in order to assemble them on SHINs. Combining the catalyst nanoparticles and SHINs to form superstructures for SHINERS has proven to be challenging. However, ligand exchange with NOBF₄ has resulted in successful assembly of catalyst nanoparticles on the silica shell of the SHINs.

Pt/SHINs, Rh/SHINs and Ru/SHINs superstructures were tested for CO oxidation with SHINERS. Even though assembly on the SHINs was not optimal or reproducible, adsorption of CO was observed with SHINERS for Pt and Ru superstructures. For Rh superstructures, the signal was too weak to study surface reactions. However, CO adsorption was observed for Au@Rh core-shell nanoparticles, indicating that SHINERS can be applied to study CO oxidation over rhodium nanoparticles. In conclusion, the superstructures that were developed in this work can be applied to study surface reactions with SHINERS.

It is thought that the Raman signal intensity provided by the superstructures will become even stronger after optimisation of the assembly process, leading to a better ability to detect species *in situ*. Additionally, structure sensitivity can be studied using the superstructures by tuning the catalyst morphology in colloidal synthesis. Therefore, the developed superstructures show great promise for application to study heterogeneous catalysis.

6. Outlook

This project was focused on the preparation of superstructures consisting of colloidal catalyst nanoparticles deposited on $Au@SiO_2$ core-shell nanoparticles (SHINs), which can be applied to study surface reactions with SHINERS. Assembly of the colloidal nanoparticles on SHINs has been achieved, but the assembly was not yet optimal or reproducible for most samples. Future work includes the optimisation of the assembly on SHINs, in order to obtain a stronger signal in SHINERS. Several parameters are thought to influence the assembly, including the concentration of SHINs and catalyst nanoparticles, and the time that is allowed for self-assembly of ligand exchanged nanoparticles on the silica shell. Using a lower concentration for both the SHINs and the catalyst nanoparticles was found to result in better assembly on SHINs, especially for platinum. Unfortunately, the decreased concentrations resulted in difficulties in obtaining a sufficiently strong signal in SHINERS. A solution to this problem might be to prepare a larger quantity of assembled superstructures, and concentrate the sample by centrifugation after assembly.

Once the assembly process has been optimised, the size and shape of catalyst nanoparticles can be controlled in colloidal synthesis. This enables the study of structure sensitivity of catalytic reactions over these Pt-group metals. The type of crystallographic planes exposed at the surface (and therefore the nanoparticle shape) has a significant impact in structuresensitive reactions, and may affect the adsorbates, intermediates, products and surface structures that are observed in SHINERS. By correlating size and shape with observations from SHINERS, the performance of these nanoparticle catalysts can be optimised through rational design.

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Acknowledgements

Over the course of my master thesis, various people have provided their invaluable help to my project.

Lars van der Wal has helped me with STEM-EDX analysis for one of my samples. Unfortunately, the results were inconclusive, but I appreciate the time and effort he has spent trying to make it work.

I would like to thank Caterina Wondergem, Mark Slagter and Thomas van Swieten for the useful discussions about SHINERS and valuable comments they have provided on my work, which have especially helped me to interpret Raman spectra.

Finally, I wish to thank prof.dr.ir. Bert M. Weckhuysen, dr. Gareth Whiting and Thomas Hartman for their supervision in this project. I especially want to express my gratitude to my daily supervisor, Thomas Hartman, for his patience and support in all aspects of my research.

A. Appendix

A.1 Assembly without Ligand Exchange

In addition to the many ligand exchange strategies that have been applied in this research, catalyst nanoparticles were also mixed with SHINs without any treatment to remove the surfactants. The catalyst nanoparticle dispersions were diluted $10 \times$ for Ru and Pt, $15 \times$ for Pd, and $10 \times$ for Rh. A mixture of 0.25 mL SHINs, 0.25 mL Millipore water and 0.25 mL diluted catalyst dispersion was then prepared, and placed in an ultrasonication bath for 1 h. The samples were washed two times by centrifugation at 4000 rpm for $10 \min$ and redispersing in 0.75 mL Millipore water. TEM images of the resulting mixtures are presented in Figure A.1. It can be seen that assembly was unsuccessful using this method. For ruthenium, there seem to be nanoparticles attached to the silica shell, but this will not be enough to ensure a sufficiently strong Raman signal in SHINERS.



Figure A.1: TEM images of metal nanoparticles after mixing with SHINs and washing to remove nanoparticles that were not assembled on the SHINs. (a) 5.0 nm palladium nanoparticles, (b) 5.4 nm platinum nanoparticles, (c) 3.8 nm rhodium nanocubes and (d) 2.9 nm ruthenium particles.

A.2 Thermal Treatment

Rhodium nanocubes capped with PVP in 2-propanol were diluted 20 times, and 100 µL of the diluted rhodium nanoparticle dispersion was mixed with 1 mL SHINs (section 3.2). This mixture was heated to 90 °C and stirred at 700 rpm for 2 h at this temperature. After cooling to room temperature, 0.3 mL of the solution was centrifuged at 4000 rpm for 5 min. The supernatant was discarded and the precipitates were redispersed in 0.3 mL Millipore water.^[105,108]

Thermal treatment was applied to the cubic rhodium nanoparticles capped with PVP as a method to anchor them on the SHINs. Elevated temperatures result in the decomposition of PVP,^[105,108] allowing the assembly on the silica shell of the SHINs. However, the decomposition temperature of PVP ranges from 200 to 350 K in a 20 % O_2 /He atmosphere,^[105,108] while the thermal stability of SHINs is limited. For this reason, thermal treatment is carried out at 90 °C.



Figure A.2: (a) TEM image of the mixture of SHINs and cubic rhodium nanoparticles after heating to $90 \,^{\circ}$ C for 2 h, before centrifugation. (b) TEM image of the heated mixture of SHINs and rhodium nanocubes after centrifugation and redispersion.

Dispersed rhodium nanoparticles were mixed with SHINs and heated to $90 \,^{\circ}$ C for 2 h. Part of the sample was centrifuged and redispersed to remove rhodium nanoparticles that were not assembled on the SHINs. TEM images before and after centrifugation are shown in Figure A.2. It can be seen that the sample before centrifugation contained rhodium nanoparticles in the proximity of the SHINs, in addition to some (organic) material that likely results from the disintegration of PVP. This organic material indicates that the heat treatment was (partially) successful for removal of the PVP capping agents. Cubic nanoparticles were still observed after heat treatment and centrifugation (Figure A.2b), even though some of the rhodium nanoparticles appear to have become more spherical. Unfortunately, Figure A.2b also shows that there are barely any rhodium nanocubes left after centrifugation. It can therefore be concluded that this method is not successful in assembling the catalyst nanoparticles on SHINs. Several factors play a role in this process, including the heating temperature, duration of the treatment, stirring speed and particle concentrations. It is possible that treatment at an increase in temperature or treatment duration will result in a better assembly of the catalyst nanoparticles on the silica shell. However, the SHINs have limited thermal stability, therefore thermal treatment might not be an ideal method to achieve assembly on SHINs.

A.3 Ligand Exchange with Nitrosonium Tetrafluoroborate $(NOBF_4)$

NOBF₄ ligand exchange was performed for Pt, Pd, Rh and Ru NPs following the method described by Dong *et al.*,^[102] with a lower concentration than described in section 3.5.5 and section 4.3.5. For these samples, 6 mg NOBF₄ was dissolved in 5 mL acetonitrile. Subsequently, 1 mL of this 10 mM NOBF₄ solution was added to 1 mL as-prepared colloidal nanoparticle dispersion. Otherwise, the same method was used as for the successfully assembled nanoparticles (section 3.5.5). The resulting TEM images are presented in Figure A.3. The assembly was unsuccessful for palladium, platinum and rhodium, very few to no nanoparticles are bound to the SHINs. For ruthenium, the assembly is better, but not optimal.



Figure A.3: TEM images of metal nanoparticles treated with $NOBF_4$ and mixed with SHINs. (a) Palladium, (b) platinum, (c) rhodium and (d) ruthenium particles of 2.9 nm. The samples were obtained by applying $NOBF_4$ ligand exchange to the PVP-capped nanoparticles.

Additionally, the concentration of SHINs and catalyst nanoparticles during assembly was found to have a large impact on the result. Figure 4.19 shows images obtained by diluting the SHINs twice with 2-propanol, and mixing the 10 x diluted NP dispersion with a 1:1 volume ratio of SHINs and catalyst NPs. TEM images for assembly with lower concentrations of SHINs and catalyst nanoparticles are presented in Figure A.4. From these results, we can conclude that lowering the concentrations during assembly results in a more uniform distribution of catalyst nanoparticles on the silica shell.



Figure A.4: TEM images for superstructures prepared by assembly at higher concentration for SHINs and catalyst nanoparticles, for (a) platinum, (b) rhodium and (c) ruthenium.

For the ligand exchange with an increased volume of NOBF_4 solution in acetonitrile (9:1 instead of 1:1), TEM images were collected before and after the ligand exchange treatment. These TEM images are presented in Figure A.5. No significant changes in particle size or shape are observed.



Figure A.5: TEM images of (a) palladium nanoparticles after ligand exchange with NOBF₄, without the addition of SHINs. Metal nanoparticles assembled on SHINs after NOBF₄ exchange: (b) platinum, (c) rhodium and (d, e, f) ruthenium particles with a diameter of 2.6 ± 0.3 nm, 2.9 ± 0.4 nm and 4.2 ± 1.2 nm, respectively.

A.4 Raman Spectrum for Uncoated Gold

Raman spectra were also collected for uncoated gold nanoparticles, in order to be able to determine the origin of a repeatedly occurring band around $260 \,\mathrm{cm}^{-1}$. The resulting spectrum is presented in Figure A.6. It can be seen that this spectrum contains a strong band at $260 \,\mathrm{cm}^{-1}$, indicating that this peak originates from the gold nanoparticles. In Figure A.6, a spectrum is included for these same gold nanoparticles, coated with a silica shel of 1.7 nm. It can be seen that all bands have disappeared. It is likely that the appearance of a band around $260 \,\mathrm{cm}^{-1}$ for some samples is caused by UV/Ozone treatment.



Figure A.6: Raman spectra in air for uncoated gold nanoparticles with a diameter of 97.5 nm and SHINs produced by coating these gold nanoparticles with a silica shell of 1.7 nm thick.