

MULTI METALLIC NANO ALLOYS: UNDERSTANDING
THE STRUCTURE AND PROPERTIES OF NANO ALLOYS

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ABSTRACT

MULTI METALLIC NANO ALLOYS: UNDERSTANDING THE STRUCTURE AND PROPERTIES OF NANO ALLOYS

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Nanomaterials are this age's defining material. Understanding how they are structured is key to controlling the formation of nanomaterials and obtain the desired properties. Nanoalloys are a key subset in that they have many applications in catalysis, medicine, energy, and informatics. In this dissertation, two, three, and four, metallic nanoparticles are studied under an electron beam to understand their structure and pull-out information about how they are formed. Looking at how size changed the structure, Pt and Cu were alloyed into small nanoparticles of size less than 20 nm. As size decreases, Cu becomes more likely to move to interstitial positions in the Pt-Cu lattice structure. This was studied by theoretical and experimental techniques. To more understand how three metals change the crystal structure, Au-Cu-Pt nanoalloys were synthesized to study the effects of adding a third metal (Pt) to a well-known system (Au-Cu). It was found that the structure is different from what is expected and the Cu forms bonds with Au and Pt forming core shell like structures. Another structure characteristic of nanoalloys is the prevalence of twin boundaries. Twins play an important role in the stabilization of multi metallic nanoparticles. To better explain the structure of nanoparticles, kinetic vs thermal equilibrium needs to be explored. The role of entropy in the stabilization of multimetallic nanoparticles is discussed along with the importance of the Gibbs free energy. The structure of multimetallic nanoparticles tends to form decahedra and icosahedra shapes. These shapes are full of twin boundaries where there is periodic strain throughout. Nanoalloys are of great interest and can find use in many fields, understanding the structure is the key.

Copyright Statement

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This image was used from: Khanal S, Bhattarai N, McMaster D, Bahena D, Velazquez-Salazar JJ, Jose-Yacamán M. *Highly monodisperse multiple twinned AuCu-Pt trimetallic nanoparticles with high index surfaces*. Phys Chem Chem Phys. 2014 Aug 14;**16(30)**:16278-83. doi:

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Dedication

This dissertation is dedicated to my family for all their support, for my wonderful wife, my great parents, and my grandpa who inspired me to dream.

Chapter 1

1.1 Introduction

Humanity is defined by what we make. Throughout the ages, advancements have been heralded by the objects and materials created by society. Indeed, the eras that define human existence have been described by the materials made, from the Bronze Age and the Iron Age to what can now be described as the Nano Materials Age. New materials have been created by understanding how the atoms are arranged in the material.

One way to create new materials is to change the crystal structure of an element. For example, carbon in its natural form is graphite, but if the crystal structure is changed it becomes diamond. Understanding how the change in crystal structure affects the material is a powerful tool in designing materials. A material can also have no crystal form and in that case be amorphous, the classic example of an amorphous material is silicon glass. The crystal structure can be thought of in three main ways, one-dimensional, two-dimensional, and three-dimensional. These are often referred to as the sp^1 , sp^2 and sp^3 bonding hybridizations. Sticking with carbon as an example and from the nanoscale, the structure controls the type of material and the properties. Sp^3 bonding creates three-dimensional carbon known as diamonds. Sp^2 carbon is that of two-dimensional sheets, there have been some exotic materials such as fullerenes[1], graphene[2], and carbon nanotubes[3] created from understanding and utilizing two-dimensional carbon. One-dimensional carbon has been of great interest due to its unique properties and has led to many searching for viable methods of synthesis[4-7]. Often times these materials are formed by accident[8] or found in nature[9].

Another way to create new materials is to combine different elements. Iron is turned to steel with the addition of carbon. Gold can have its colors changed when other elements such as nickel (white gold) or copper (rose gold) are added. When multiple metals are added together to create a new material, the new metal is called an alloy. Alloys have been instrumental to the advancement of civilization and are found everywhere. Classic alloys comprise of a base metal with trace amounts of other metals; modern alloys, on the other hand, comprise of more equal compositions. Bimetallic alloys are the simplest alloy comprising of two metals, the composition of which can range from equal parts to only trace amounts of the second metal. But why stop at only two metals, by combining multiple metals, the properties can be changed or enhanced. Combining metals comes with its own challenges and trying to alloy dissimilar metals can be difficult. Combining multiple metals has led to research in alloying five or six metals to create High Entropy Alloys (HEA)[10]. Metals on the macroscopic scale, often referred to as bulk material, have been well studied for centuries. However, in the last century advancements in technology have allowed research to be conducted at the atomic scale.

1.2 Metallic Nanoparticles and Clusters

Nanostructures can be divided into three categories, nano microstructures (>100 nm), nanoparticles (<100 nm), and clusters (<2 nm). Nano microstructures often resemble bulk material and do not necessarily show different properties. Due to of this, they will not be discussed further. Nanoparticles are of much interest due to the small size, interesting structures and properties can arise that differ from the bulk equivalent. Clusters are different as they are formed by a finite and known number of atoms. They can be considered as a superatom with discrete energy levels[11, 12]. In the last decade advances in synthesis methods resulted in a new field known as “atomically precise clusters” indicating the control in the number of atoms. Those

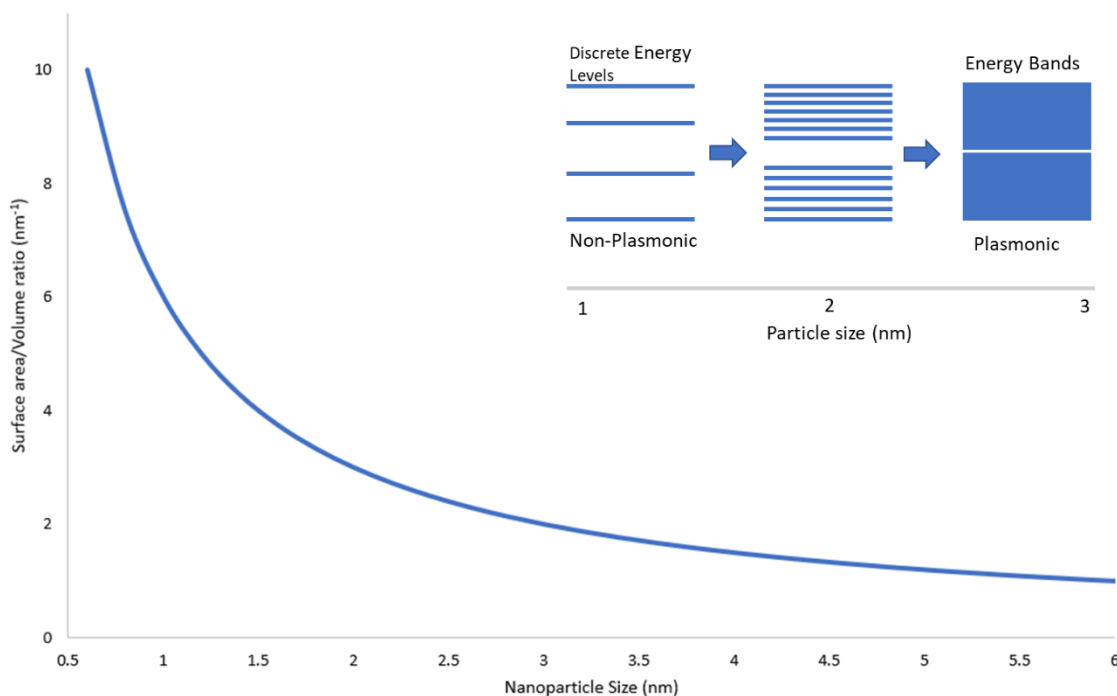


Figure 1-1: Plot of the surface area over volume for nanoparticles. Smaller particles have more surface effects due to size and that drops off like $3/r$. Inset shows as particle size increases from clusters to nanoparticles there is a change from discrete energy levels to energy bands.

cluster are stabilized by an organic molecule capping. They require ligands or another type of capping agent to remain stable. They differ from nanoparticles in that they do not show plasmonic resonance and their structure consist of a core followed by layers. The fact that clusters do not exhibit plasmonic resonance is due to their size and structure. Clusters have discrete energy levels, as they grow larger in size, these discrete energy levels turn to energy bands. This change is a way to distinguish clusters from nanoparticles; an illustration of this can be seen in the inset of **Figure 1.1**.

A reason that small particles like clusters and nanoparticles have unique properties could be due to the ratio of surface atoms compared to total number of atoms. This surface to bulk ratio can be seen in **Figure 1.1**. As the size of the particle increases, the contribution of the surface atoms to the properties decreases.

1.3 Nanoalloys

When multiple metals are combined in nanoparticles, the structure can change dramatically. The synthesis process plays a key role in the structure of nanoalloys. When the particles are forming, they will move towards an equilibrium point. But during this process, they will find kinetically stable regions and if particle synthesis is stopped, the resulting are kinetically stable particles. This leads to unique structures in nanoparticles such as core shell structures and twinned boundaries. These unique structures can produce desired properties or even limit the number of precise metals needed to achieve specific characteristics.

Kinetically stable particles are interesting as they will change structure if sufficient energy is introduced. Along with not being thermodynamically stable, there is also a strain introduced on the particles during formation. This strain is minimized in a kinetically stable region controlling the structure and can be observed through a technique called Geometric Phase Analysis (GPA). In this, an atomic resolution image of a particle is obtained and used to gain information about the lattice spacing. When done to nanoalloys, periodic tension and compression is observed. This is a way for the particles to relieve stress. This is a kinetically stable particle, if the particle is heated, then these regions will disappear, and particles will begin to coalesce and do not represent the previous state.

Chapter 2 Methods

2.1 Nanoparticle synthesis

There are many ways to grow nanoparticles, one of the common and fairly easy methods is the chemical reduction method. This method uses metals salts and a suitable solvent heated using a radiative heat source. This method can be done in two ways, simultaneous reduction of the metal salts or by successive reduction of the metal salts. The simultaneous method involves mixing all the precursors in at close to the same time. The solvent will dissolve the metal salts while a stabilizing ligand helps control the growth of the metallic nanoparticles. This method often results in an alloyed particle. The second method, successive reduction, a metal salt is dissolved first and then followed by the other desired metals. This method can be used to for seed particles that the following metals can grow around. This method often results in core-shell particles. Oleylamine ($C_{18}H_{35}NH_2$) has been a reliable solvent and coordinating agent for the growth of nanoalloys using this method. Oleic acid ($C_{18}H_{34}O_2$) is also used as a reducing agent.

Another way to synthesize nanoparticles is to use microwave radiation. The microwave produces high frequency electric field, typically range from 300 MHz to 300 GHz, that will heat the sample. 2.45 GHz is a commonly used frequency. In this method, the material and the microwaves interaction can be tuned based on the dipole interactions, conducting ions, and the oscillating electric field of the microwave[13, 14]. This is tuned to minimize the needed energy for the desired reaction to occur. This allows for a reduction in the reaction time and improvement in synthesis purity. This method cuts down on unwanted side reactions, provides rapid uniform heating, and narrow particle size distribution. Ethylene glycol ($C_2H_6O_2$) and polyvinylpyrrolidone ($C_{18}H_{34}O_2$) are commonly used for metallic nanoparticles.

A final method discussed here, though there are many other methods, is the seed growth method. This method can be similar to either of the previous methods but here, a seed nanoparticle is grown and then used in another reaction to promote specific growth. This method allows for control over the shape, size, and other morphologies such as stars, triangles, antenna, polyhedral, and more. This method separates the nucleation and growth stages of the nanoparticle which is how the size and shape can be well controlled.

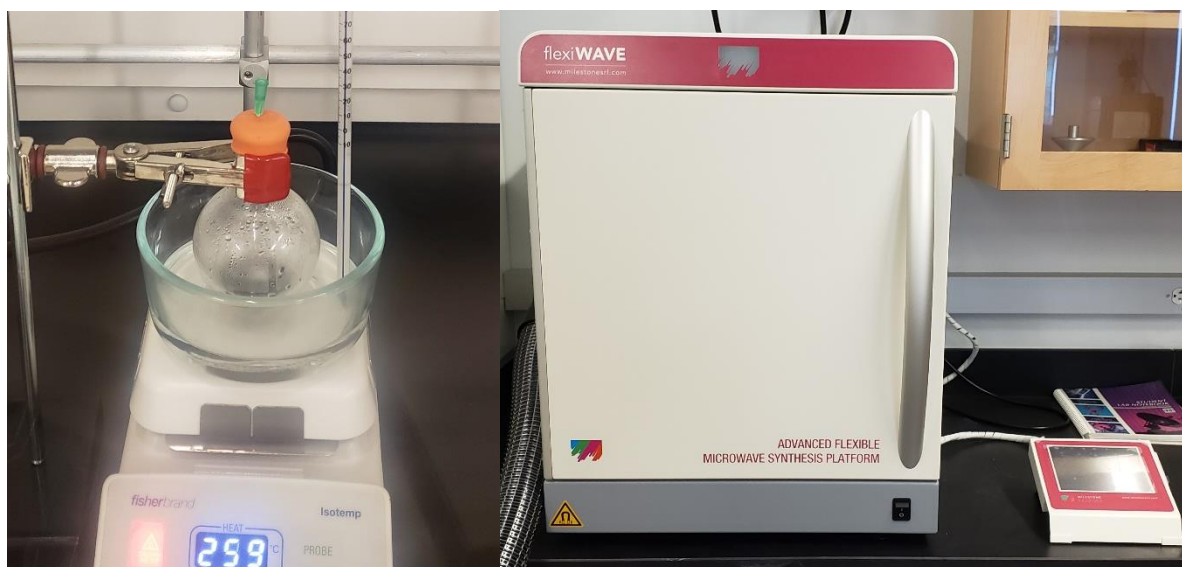


Figure 2-1: Pictures showing chemical reduction method on a hot plate (left) and a microwave system (right) for synthesizing nanoparticles.

2.2 Electron Microscopy

Microscopy has the goal to obtain images that can be analyzed, and information gathered. Using electrons as the illumination source has some great advantages in that the resolution is vastly increased compared to light microscopy. Due to the wavelike behavior of electrons, a wavelength can be calculated, and a theoretical resolution can be figured out by the following equation,

$$\lambda = \frac{h}{\sqrt{2m_0eV\left(1 + \frac{eV}{2m_0c^2}\right)}} \quad (2-1)$$

For an accelerating voltage of 200 kV, the wavelength is approximately 0.002 nm. This is far better than visible light (400 nm) and better than X-rays (0.15 nm). This theoretical limit has not been achieved due to practical constraints such as aberrations created in the magnetic lenses.

Aberrations such as spherical, coma, chromatic, and astigmatism are the limiting factors to the resolution. Electron microscopes have changed over the decades and have become more sophisticated and atomic resolution is becoming increasingly better. Currently, advanced scanning electron microscopes have been reported with resolution better than 0.05 nm[15].

Figure 2.2 shows a couple different electron microscopes, from an older JEOL with the control attached to the microscope, to newer microscopes that are controlled at a workstation away from the column to keep vibrations down.

An electron does not behave the same as a photon and therefore lens made of a medium will not work in an electron microscope. A high vacuum is also needed so that the electrons can move freely without interacting with unwanted material such as air molecules or dust. However, electrons do respond to an electromagnetic field, therefore, the lens used in electron microscopes



Figure 2-2: Images of different types of transmission electron microscopes. From left to right: JEOL Jem, JEOL NEOARM, Talos F200i. The JEOL Jem uses a heated filament type gun and is controlled at the microscope. Both the newer NEOARM and F200i use cold field emission guns and are controlled remotely.

are magnetic lens. There are a couple lens groups used in an electron microscopic, they are called the condenser lens, the objective lens, and the projector lens. Each of these lenses can contain multiple lens.

The gun is the most important part of an electron microscope. Originally the emission source was thermionic emitter from a tungsten or lanthanum hexaboride (LaB_6) filament that was heated to entice electron off. Those these are still in use, there are much better electron gun available. High resolution S/TEM use a Schottky electron source or a cold field emission source due to increased brightness and better coherence[16]. Cold field emission guns use nanometer sized point under a high magnetic field to pull electrons off with no heating element. The tip size is usually around 10-20 nm in diameter. Due to the probes small size, any contaminates will greatly decrease the efficiency of the electron gun.

The electrons are controlled by magnetic lenses. In light microscope, concave and convex lenses of different materials are used to limit aberrations. However, magnetic lenses can only act like a convex lens making it hard to control aberrations. This is the main reason that electron microscopes have not reached the theoretical limits of resolution. The lens is made up of a coil of wires with an iron shroud to create the magnetic field. In the center, a pole piece contained the electric field to form the area that interacts with the electrons, an illustration of this can be seen in **Figure 2.3**.

Different imaging techniques can be used to gain information about the nanoparticles.

Figure 2.4 The electron can either pass through the sample with no interaction or they can scatter either elastically or inelastically. Elastic scattering conserves the kinetic energy of the electrons. This type of scattering occurs due to the interaction with the nucleus of the sample's atoms. This scattering is used for backscatter detectors, diffraction, and high angle detectors.

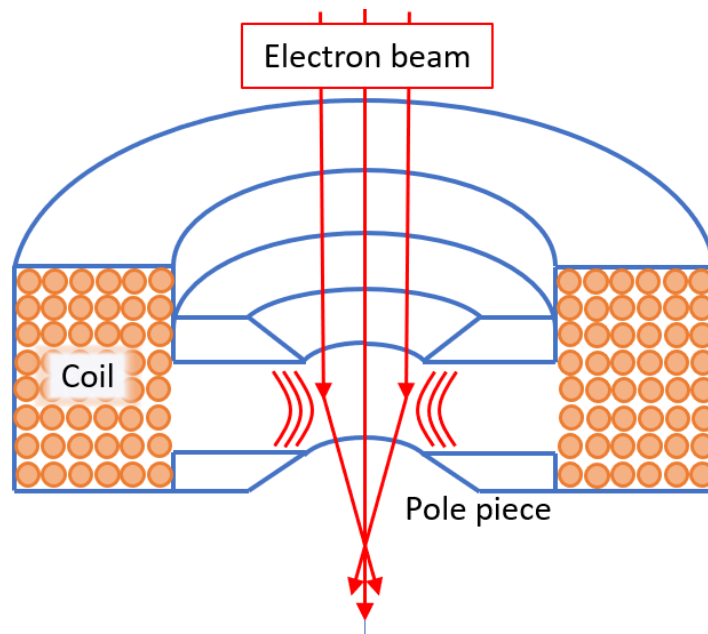


Figure 2-3: Illustration of an electromagnetic lens for electron microscopes. Coils create the magnetic field that is then confined to the pole piece that bends the electrons.

Inelastic scattering does not conserve kinetic energy and results in some energy transfer. That energy transfer can be used to determine the composition of the sample, either through Energy X-ray Dispersive Spectroscopy (EDS) or Electron Energy Loss Spectroscopy (EELS).

Image detection for TEM is formed at the image plane, for STEM the detectors are placed at the back focal plane, as seen in **Figure 2.4**. Diffraction images are also obtained at the back focal plane. Back scatter, secondary electron, and EDS detectors are all above the sample, while an EELS detector sits below and looks at how the sample affects the incident beam. Electron diffraction is a method to determine the crystal structure of a material. This is an advantage as the specimen does not need to be a single crystal and can be done selectively over a sample's regions.

One of the disadvantages of transmission electron microscopes is that the sample size needs to be thin, <100 nm, this often requires the cutting of a sample which adds difficulty to preparation. Thickness does vary depending on the material, as heavier elements transmit less

electrons. The electron beam can also cause damage to the sample, especially when there are capping ligands or other beam sensitive materials such as organic materials. The beam can

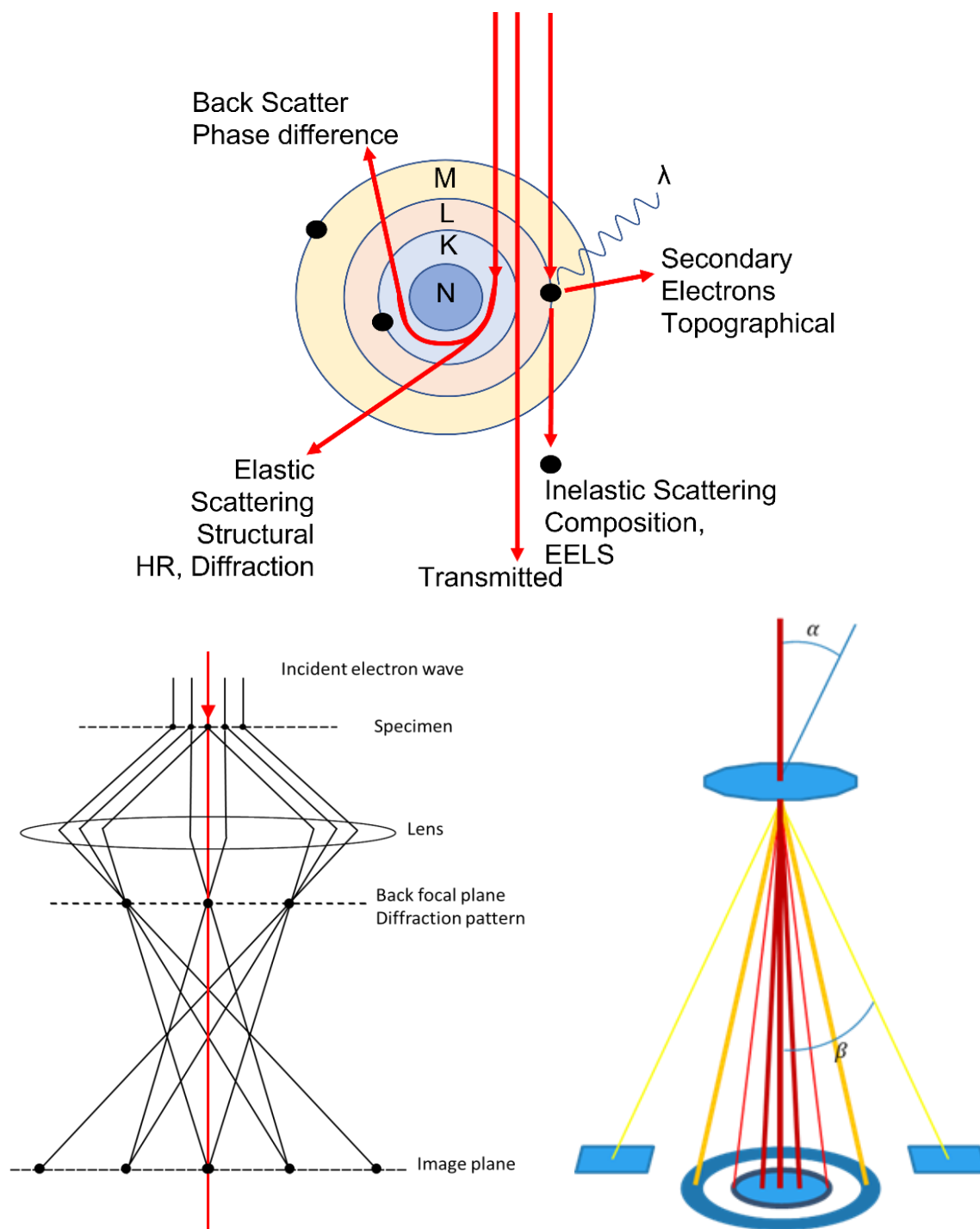


Figure 2-4: Illustrations (upper) showing possible electron pathways when they interact with the sample. In TEM mode (bottom left) the path of the electron to create the image and in STEM mode (bottom right) the location of the detectors.

transfer a fair amount of energy into the sample thus changing the morphology or destroying it all together.

2.3 Raman Spectroscopy

Raman Spectroscopy is a powerful tool in obtaining information about a specimen. When a monochromatic light source interacts with molecules, there are a few different interactions that occur. By far the most common interactions is Rayleigh scattering, this is filtered out. The next reaction, one that happens far less, is Raman scattering. This can happen either as Stokes or anti Stokes. This can be seen in **Figure 2.5**. This is where information about the sample is obtained. When the light interacts with the sample, there are small vibrational modes that occur, these vibrational modes are inherent to the elements and bonding in the sample. These molecular vibrations, or phonons, cause a shift in the photon's frequency either up or down. This creates a spectrum that can be used to gain information about the sample.

The signal produced during Raman Spectroscopy is very low. To enhance the signal,

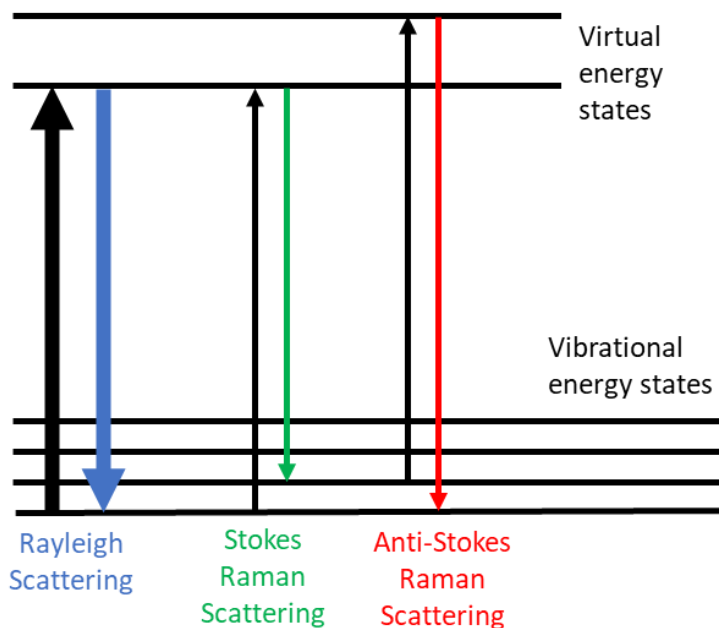


Figure 2-5: Diagram showing Rayleigh scattering and Raman scattering.

special surfaces can be used that will increase the signal 10^{10} or 10^{11} times. This technic is called

Surface Enhanced Raman Spectroscopy or SERS. This uses a special surface or sometime nanoparticles to create a surface plasmon that generates an enhanced signal. Various types of nanoparticles have been used to enhance the signal such as Ag nanorods or Au–Cu nanostars. A complementary technique to SERS is Tip Enhanced Raman Spectroscopy (TERS) which uses a fine tip containing a material to enhance the Raman signal, this can be used to control where the enhancement occurs across different regions of the sample.

2.4 X-ray diffraction (XRD)

X-ray diffraction is a power technique that can be used to example the atomic structure of a material using x-ray radiation. The x-ray source will play a role in the resolution and interpretation of the spectra, a typical XRD uses Cu K α ($\lambda = 1.54056 \text{ \AA}$) as the source. The crystal size from the spectra can be found by using the Scherrer equation,

$$T = \frac{k\lambda}{\beta \cos \theta} \quad (2.2)$$

where k is the shape factor (typically 0.95), λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle. X-ray diffraction is a great

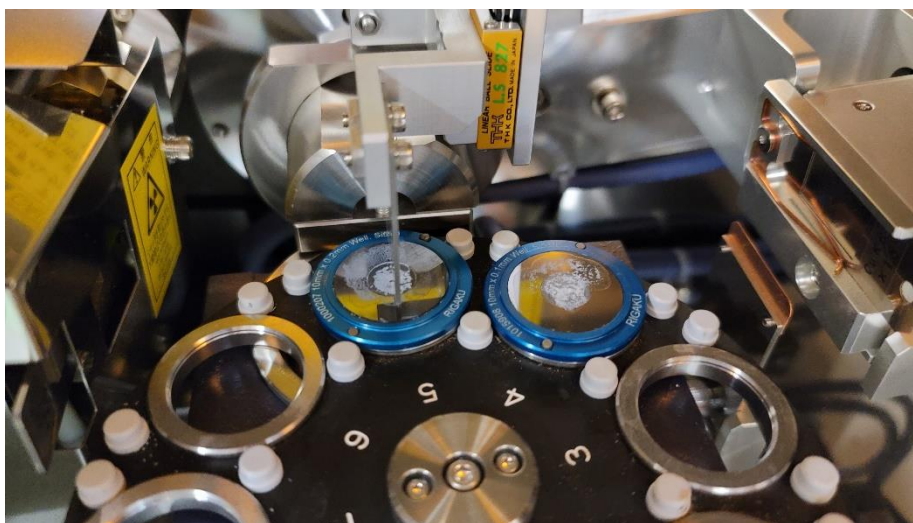


Figure 2-6: Inside of an XRD with two samples loaded. The samples can be rotated while the x-ray source and detector can scan through an angle of 90 degrees.

tool in discovering the crystal structure and atomic bond lengths of a material. **Figure 2.6** shows sample holders in an XRD ready to be sampled. This technique requires the sample to be in a powder form and the material to have the same crystal structure.

2.5 Geometric Phase Analysis (GPA)

GPA analysis uses high resolution images of nanoparticles to measure the interplanar distances, look at strain in the particle, and show any displacement of atoms within the structure. This method transforms the image using Fourier transforms to create an artificial diffraction pattern. This reciprocal space image is used to show periodic compression, expansion within the particle. This analysis is performed through Digital Micrograph by Gatan using a GPA script written for the software.

2.6 Ultraviolet Visible (UV-Vis) Spectroscopy

A technique that looks at the absorption spectra of a sample. The sample is subject to a spectrum of near-infrared and visible to near-ultraviolet radiation to determine at which wavelengths the sample is absorbent. This is helpful in examining the absorption peaks of metallic nanoparticles as the peaks can shift due to size, compositions, or structural changes. This is often used with other tools to gain excitation and emission spectra. This technique is useful for small particles such as clusters. However, nanoparticles do not show sharp absorption peaks due to the plasmonic resonance inherent in metals.

Chapter 3 Pt-Cu

This chapter is based on the published article ref[17].

Platinum is a rare earth element. It is used widely in catalysis and currently the only viable element for hydrogen fuel cell catalysis. However, it is expensive and not abundant. Therefore, it is important to reduce the needed amount of Pt for catalysis applications. In order to accomplish this a more abundant metal, such as copper, can be alloyed with the Pt. Copper is abundant and Pt-Cu system displays total miscibility over all its composition range[17]. Theoretical work was performed by the Guisbiers group of which predicted that as the Pt-Cu nanoparticles decreased in size, the copper atoms in the nanoparticle would move from a substitutional lattice position to an interstitial lattice position. To confirm the theoretical calculations, Pt-Cu were synthesized via wet chemistry methods[18-20].

3.1 Methods

The chemicals used for this synthesis were platinum (IV) chloride, copper (II) chloride, oleylamine ($C_{18}H_{35}NH_2$), 1-dodecanethiol ($C_{12}H_{26}S$), and hydrochloric acid. Both metal precursors were prepared in aqueous solutions at 0.1M concentration. The platinum (IV) chloride was dissolved in 1 M hydrochloric acid and heated to 100 °C until any water was evaporated. 5 ml of oleylamine was then added to the Pt solution. 0.1 M copper chloride in ethanol was then added to the solution. The solution was heated to 250 °C for two hours. A color change was seen from a yellow to a deep red color. At this point, 10 μ l of 1-dodecanethiol was added. After about one hour, the solution was finished, and the color changed to a dark brown.

Characterization of the Cu-Pt nanoparticles was carried out with a NION Scanning Transmission Electron Microscope (STEM) and was operated at 80 keV. The nanoparticles were

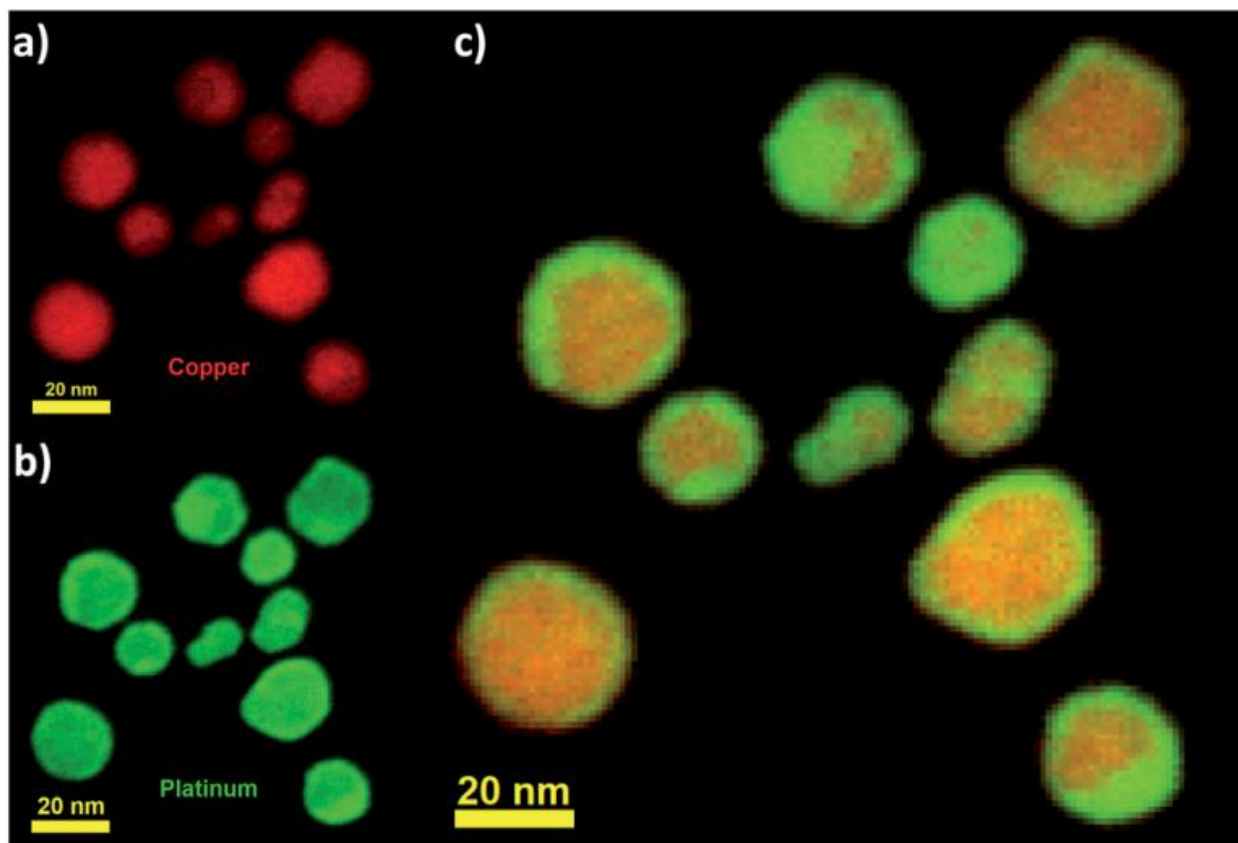


Figure 3-1: Chemical mapping of several Cu–Pt nanoparticles acquired using EELS. (a) 2D STEM-EELS map showing the Cu element, (b) 2D STEM-EELS map showing the Pt element and (c) 2D STEM-EELS map showing the overlay of Cu and Pt elements.

prepared on holey carbon TEM grids via drop casting. Chemical analysis was performed using Electron Energy Loss Spectroscopy (EELS). The particles were well dispersed on the grid and ranged in size from about 5 nm to about 25 nm. The EELS analysis, seen in **Figure 3.1**, show that both Pt and Cu are found in the particles. It is interesting to note that the central region of the particles composes mostly of copper while the surface regions of the particles are largely platinum. The larger particles show the two distinct regions more clearly while the small particles show less distinct regions and appear to be more mixed between the two elements.

3.2 Discussion

These nanoparticles are an interesting case in that from electron microscopy images, they appear to be plate like particles. **Figure 3.2** shows a particle oriented such that clear atomic

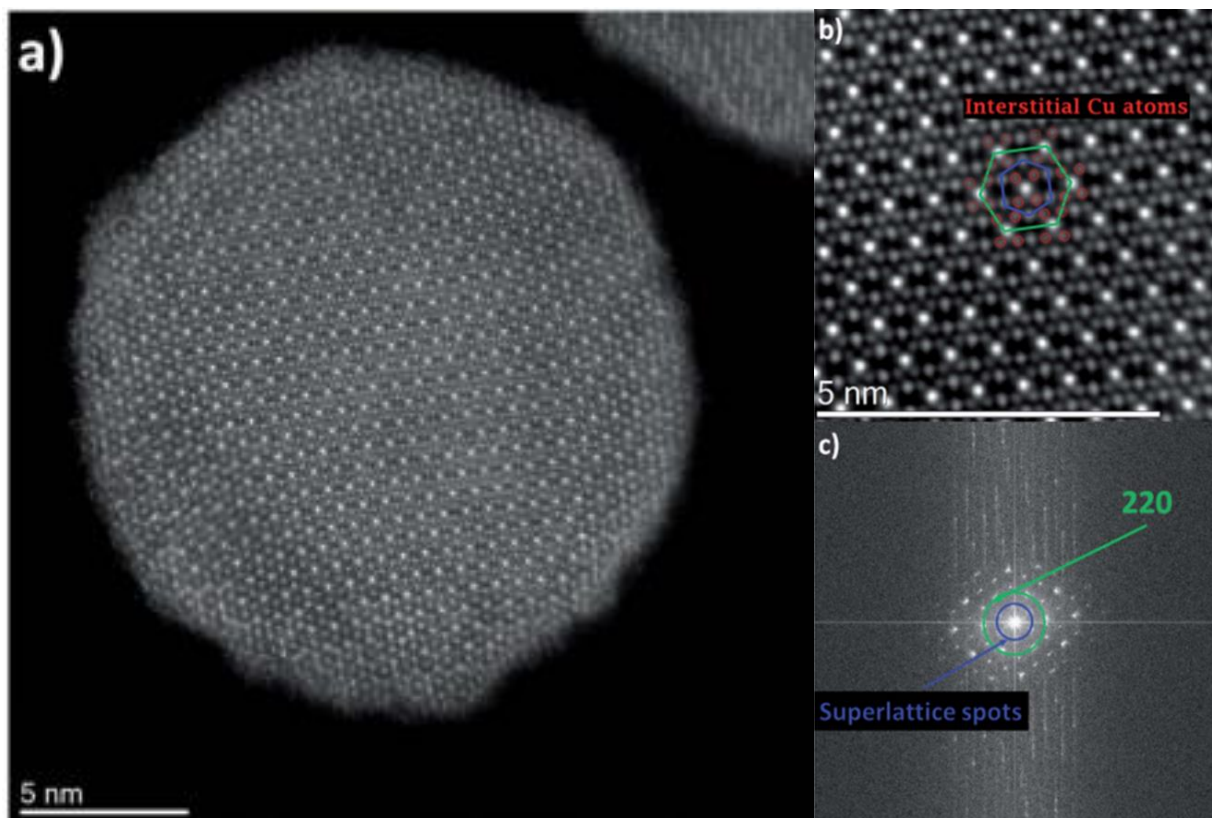


Figure 3-2: a) HAADF-STEM image of a Cu–Pt nanoparticle having a size around 20 nm. Bright spots represent Pt, while the weak spots represent Cu. (b) Zoomed-in image of the core of the nanoparticle shown in (a). The green hexagon connects the Pt atoms. The blue hexagon connects Cu atoms together. The red circles indicate the Cu atoms, which are in interstitial positions. (c) FFT pattern of the nanoparticle shown in (a).

resolution was achieved. **Figure 3.2 a)** shows a HAADF image where the entire structure is visible. In the image two distinct areas are seen, the interior is Cu-Pt superlattice and the outer shell. These two regions correspond well with the EELS with a Cu-Pt core and a Pt shell. **Figure 3.2 b)** shows a zoomed in image of the central area of the particle. In this image, the more intense spots correspond to Pt while the less intense spots correspond to Cu. This particle is structured in a superlattice made of intercalated layers of Pt and Cu in an FCC structure. The Fast Fourier Transform (FFT) of the particle in **Figure 3.2 a)** can be seen in **figure 3.2 c)**. The FFT reveals the superlattice and that the particle is oriented in the (220) direction. Taking a closer look at the distance between the bright spots is 0.675 nm. This corresponds to the distance

between two Pt atoms. Due to orientation, this value needs to be divided by two (0.388 nm) to get the distance between two Pt planes in the superlattice.

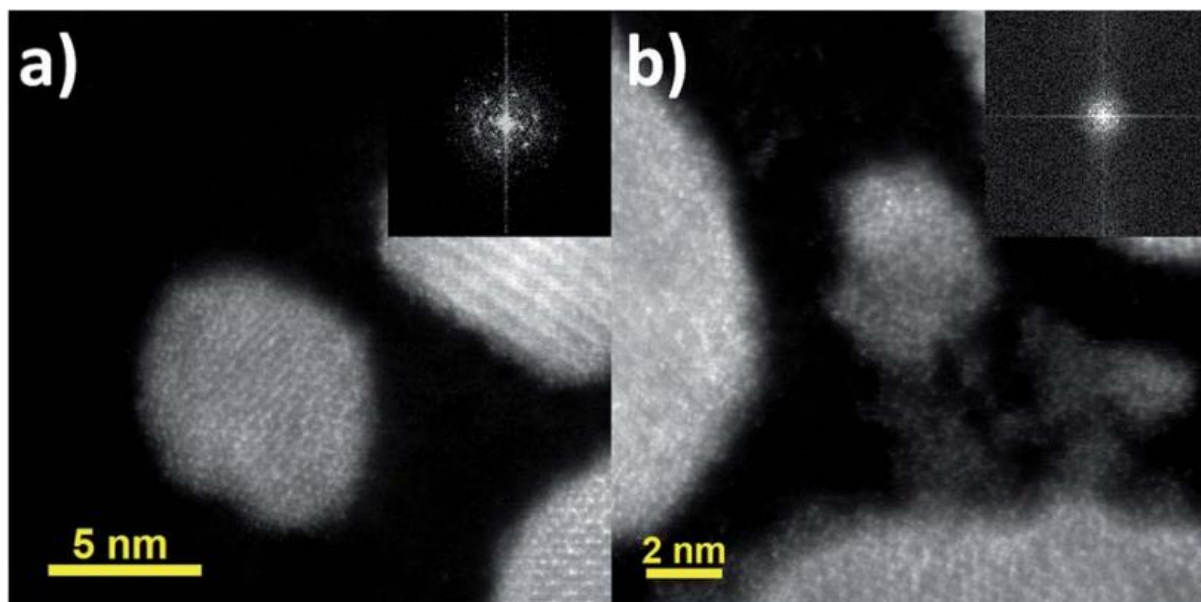


Figure 3-3: a) TEM image of a Cu–Pt nanoparticle having a diameter around ~ 7.6 nm. (b) TEM image of a Cu–Pt nanoparticle having a diameter around ~ 3.8 nm. In both images, the corresponding FFT of the particle is shown in the upper right corner as inset.

Other particles were observed ranging from ~ 2 to ~ 20 nm and similar structures were observed. The smallest particles, due to small size, were a challenge to get high resolution images. However, some information was still gathered such as the Fast Fourier Transform (FFT). A particle around 7.6 nm was imaged and its FFT was obtained in **Figure 3.3 a)**. The FFT pattern shows similar structure as the larger particles. A smaller particle of around 3.8 nm and its FFT are shown in **Figure 3.3 b)**; in this particle, a similar structure is confirmed by the two diffraction rings. This leads to some interesting conclusions. The theory predicts that the transition will occur in small composition ranges of above 90 %, but here it has been observed at a much larger composition range. **Figure 3.4** shows a theoretical nano-phase diagram for spherical Cu-Pt. In this diagram, the transition where Cu becomes interstitial occupies a larger compositional range as the size of the particle decreases. It is also important to recognize that these modes describe the thermodynamics of the system at equilibrium.

3.3 Theoretical Calculations

Several models (ideal, regular, and sub-regular) have been developed to predict theoretically any phase diagram. All those models rely on minimizing the Gibbs free energy of the system. The ideal solution model assumes that the solid solution is completely miscible i.e., not having a miscibility gap, resulting in the classical lens-shape phase diagram. This model is too simple to simulate a binary alloy with ordered phases such as Cu–Pt. By considering explicitly the chemical interaction between Cu and Pt within the solid solution, a composition-dependent mixing term is added to the Gibbs free energy, resulting in the so-called regular solution model. However, this addition is not sufficient to accurately describe the Cu–Pt phase diagram[21]. In order to describe the Cu–Pt system, the mixing enthalpy needs to be temperature–composition-dependent which falls under the sub-regular solution model[21]. In the sub-regular model, the Gibbs free energy of a non-ideal binary system such as Cu–Pt is represented by[22, 23]:

$$G = \sum_{i=1}^2 x_i G_i^0 + RT \sum_{i=1}^2 x_i \ln x_i + G_m \quad (3.2)$$

where x_i is the molar concentration of the constituents i ($i=1$ represents Cu and $i=2$ represents Pt) in solution, R is the molar gas constant, T is the temperature, and G_i^0 is the Gibbs free energy of the pure element i . G_m is the mixing Gibbs energy describing the interactions between the chemical elements in solution, which is represented by the Redlich–Kister polynomial[22, 24]:

$$G_m = x_1 x_2 \sum_{k=0}^n {}^k L_{12} (x_1 - x_2)^k \quad (3.3)$$

where the k^{th} order Redlich–Kister parameters, ${}^k L_{12}$, are represented by ${}^k A + {}^k B T$, where ${}^k A$ and ${}^k B$ are constants[25]. Experimentally, the bulk binary phase diagram of Cu–Pt does not display

any miscibility gap. But since Cu–Pt does not break any Hume-Rothery rules as mentioned in ref.[26] it makes perfect sense that Cu–Pt does not display any miscibility gap in its binary phase diagram. Moreover, the Cu–Pt system has several ordered structures appearing at low temperature and low platinum concentration namely the L11 and L12 ordered structures[21]. As a note, the Hume-Rothery rules are used to determine whether a binary system would form a miscible solid solution (negative mixing enthalpy). But those rules do not inform which model (regular or sub-regular) is the best to calculate the binary phase diagram. However, the sub-regular solution model is in good agreement with all the available experimental data, while the regular solution model from ref.[26] does not at all the available experimental data very well, except below 20% platinum weight composition. Above 20% platinum weight composition, the solidus–liquidus curves predicted by the regular solution model vastly underestimate the

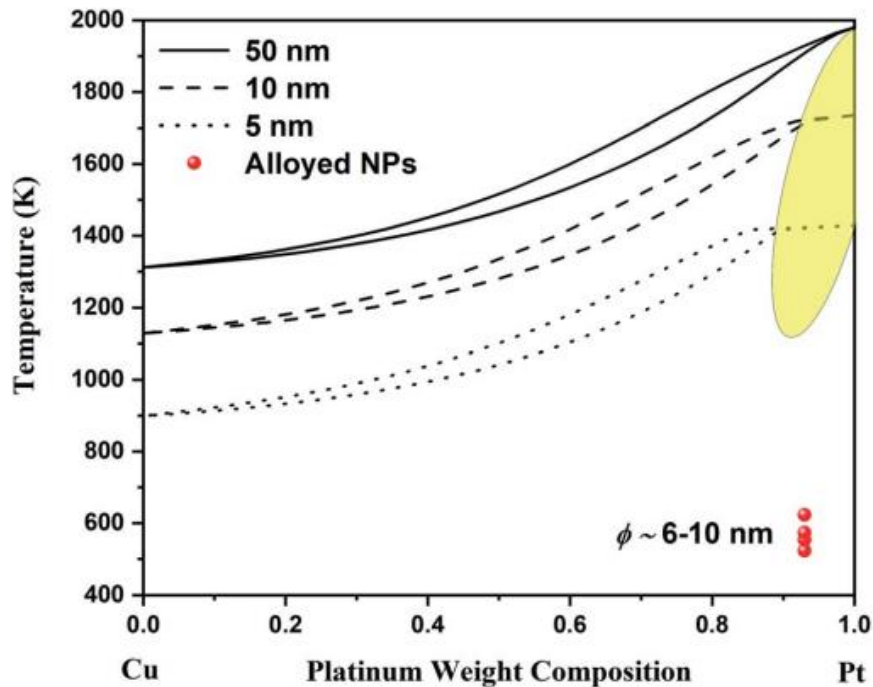


Figure 3-4: Nano-phase diagram for spherical Cu–Pt nanoparticles having a diameter of 50, 10 and 5 nm. The solidus–liquidus curves are obtained by using a sub-regular model. The experimental data come from Belenov et al. The experimental data points symbolize alloyed Cu–Pt nanoparticles after undergoing a thermal treatment. The diameter of the nanoparticles ranged between ~6 and ~10 nm. The yellow region indicates the region where the interstitial Cu–Pt alloy is expected.

experimental data points provided by ref[21, 27, 28]. Indeed, with respect to chemical composition, a sub-regular model is more adequate when the mixing enthalpy of the alloy is non-symmetrical with respect to the chemical composition at 50%, while the regular solution model is preferred when the mixing enthalpy is symmetrical with respect to the chemical composition at 50%[25]. At the nanoscale, Cu–Pt alloys experience size effects just as any other material[29]. Therefore, the nanophase diagram for a Cu–Pt spherical nanoparticle was predicted by using nano thermodynamic concepts; see **Figure 3.4**.

It is clear from **Figure 3.4** that the Cu–Pt phase diagram is shifted towards lower temperature as the size is reduced. Furthermore, the liquid–solid region (i.e. region between the solidus and liquidus curves) increases as the size reduces due to the size effect on the Gibbs free

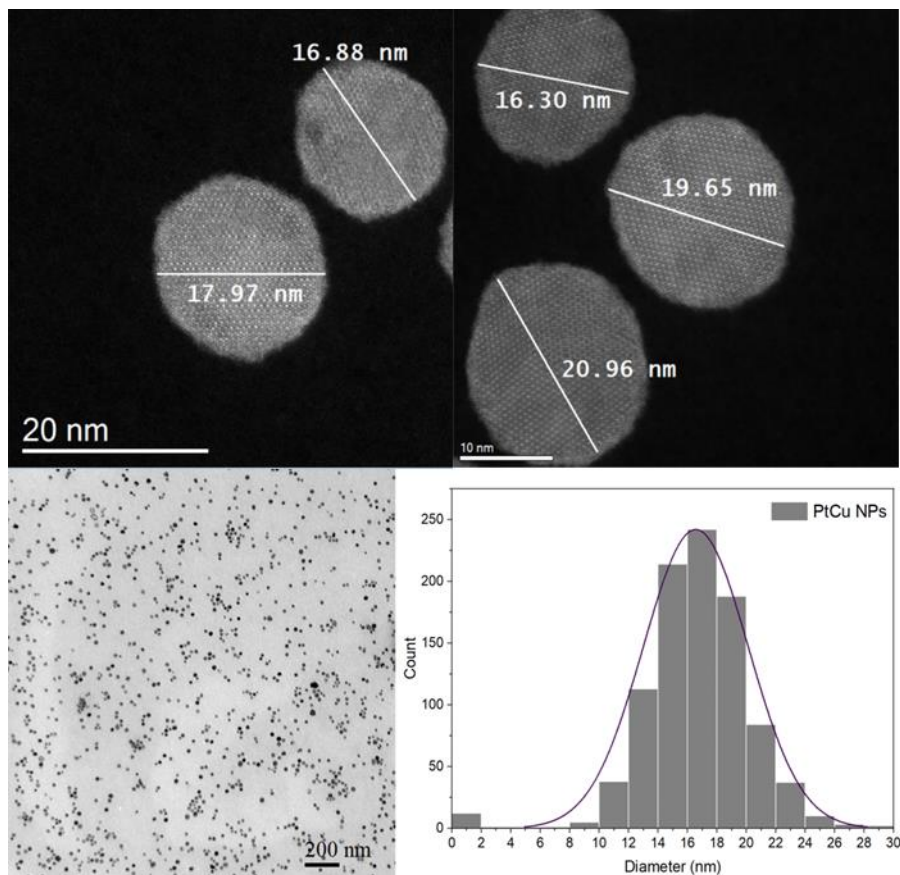


Figure 3-5: Four different particles (top) showing the average size. Low mag area (bottom left) showing many particles and how they are well dispersed along with the size distribution (bottom right) of the particles in that image. The particles fall within a range of about 8 nm to 28 nm in size with the majority around 17 nm.

energy of mixing. It is interesting to note that at small sizes of ~ 5 nm, the Cu–Pt alloyed nanoparticle with a platinum weight composition larger than 90% behaves like a pure Pt nanoparticle. Indeed, congruency occurs in that chemical composition range. Cu atoms seem to occupy interstitial positions within the crystalline structure made of Pt atoms until the chemical composition of Pt drops below the 90% platinum weight composition. This behavior could be explained by Cu–Pt being a substitutional solid solution within 0–90% platinum weight composition and becoming an interstitial solid solution above 90% platinum weight composition due to the size difference between Cu and Pt atoms. Since, the Gibbs free energy of mixing for Cu–Pt is negative at the bulk scale, the Gibbs free energy of mixing at the nanoscale will also be negative; see ref[22, 30]. This is supported by Monte Carlo simulations completed in ref[31]. Consequently, the binary phase diagram of Cu–Pt will not display any miscibility gap at the nanoscale, meaning that the formation of alloyed Cu–Pt nanoparticles is possible for any chemical composition. Experimentally, the synthesis of alloyed Cu–Pt nanoparticles with sizes around 3 nm and around 4–15 nm was successfully achieved by Khanal et al.[18] and Peng et al.[19], respectively. Furthermore, Belenov et al.[20] demonstrated that Cu–Pt nanoparticles with sizes between ~ 6 and ~ 10 nm formed a solid solution (i.e. an alloy) at ~ 523 – 623 K. Those results are well in agreement with our predicted nano-phase diagram displayed in **Figure 3.4** as the experimental data points are within the solid region of the phase diagram.

3.4 Conclusion

The synthesis of nanoparticles may not always allow the system to reach thermal equilibrium but may rather be in a kinetically stable state. This may cause a discrepancy between theoretical predictions and experimental observations. Though here, both theory and experiment agree that Cu–Pt nano alloys will have substitutional-interstitial structure transition below around

20 nm and in a composition range up to about 50%. The theoretical framework used here could be used as a predictive tool to identify structural phase transitions in binary nano alloys. This discovery is particularly interesting for its potential in future applications where the amount of platinum is reduced while preserving the thermal and catalytic properties of pure platinum.

Chapter 4 A Case for Au-Cu-Pt Nano Alloy

Nanoalloys allow the enhancement and tunability of properties and applications that monometallic nanoparticles cannot do alone. When adding more metals to a nanoparticle, the atomic structure must change to accommodate the new element. It is even more pronounced when the three elements are combined. Gold nanoparticles tend to create core-shell nanoparticles when combined with another metal. When platinum is introduced to gold-copper nanoparticles, the gold and copper combine to form a core with a shell comprised of mostly platinum. There are different crystal orientations seen in the different regions of the nanoparticles. Platinum on the surface could lead to enhanced catalysis properties of these Au-Cu-Pt nanoparticles.

4.1 Methods

These particles were synthesized using wet chemistry method[32]. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), copper (I) acetate (CuCO_2CH_3), and chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) were used for as the metal precursors. Oleylamine was used as the solvent, reducing agent, and stabilizer during the synthesis process. Ethanol and hexane were used to clean the particles after initial synthesis, they were then dispersed in toluene.

First, gold nanoparticles were synthesized to use as seeds for the formation of an Au-Cu bimetallic NP. The solution was 0.023 M of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 mL of oleylamine. It was heated to 110 °C and under magnetic stirring in a fume hood under room atmosphere, pressure and temperature. After two hours, 0.19 M of CuCO_2CH_3 in 2.5 mL of oleylamine was added drop by drop to the solution. The temperature was then raised to 280 °C and kept there under rapid stirring for an hour. The temperature was lowered to 240 °C and 0.029 M of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$

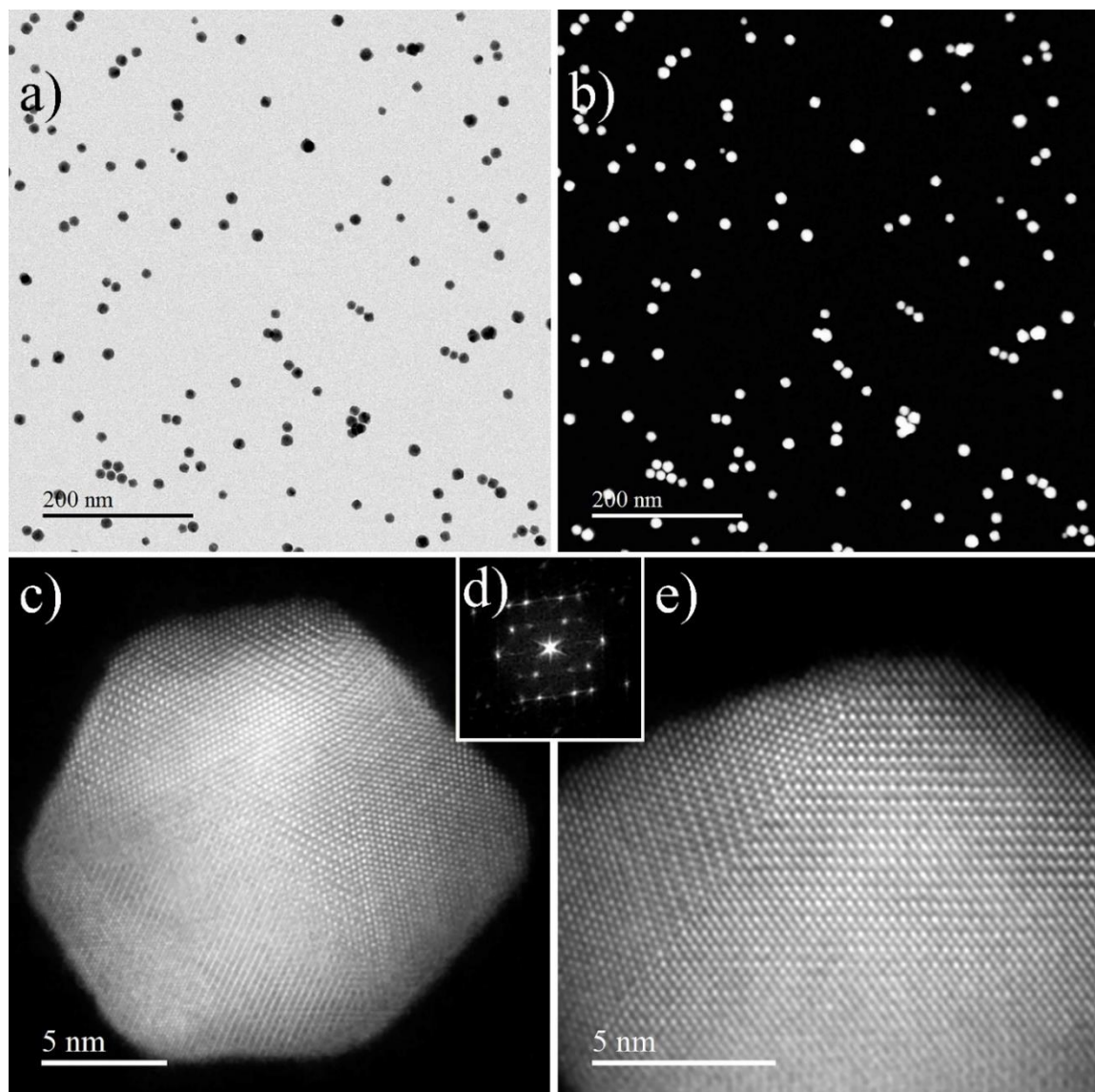


Figure 4-1: Typical images of the Au-Cu-Pt nanoparticles a) Low magnification bright field image and b) low magnification dark field image. c) STEM-HAADF image of a nanoparticle and its corresponding FFT in d). e) High magnification STEM-HAADF image showing the superlattice formed on top of the decahedral facets of the core.

in 2.5 mL of oleylamine was added drop by drop. This mixture was held for an hour before the solution was allowed to cool to room temperature. The solution was then dispersed in an ethanol/hexane solution (70/30) and centrifuged to remove any free ligands.

Transmission electron microscopy was used to determine the characteristics of the NPs. The solution was drop casted onto a nickel carbon coated TEM grid. The transmission electron microscope was operated at 200 keV in scanning mode (STEM). The microscope had Cs-

corrector with a point resolution of 0.19 nm. The probe size was 0.09 nm with a probe current of 22 pA. Both bright field and dark field images were obtained. Bright field images were collected using a semi-angle of 11 mrad. Dark field images were collected at a semi-angle of 50 to 180 mrad. This satisfies the conditions to meet HAADF imaging requirements and eliminates contributions of un-scattered and low angle scattered electrons. Electron dispersive X-ray spectroscopy (EDS) was obtained using a probe size of 0.13 nm and a probe current of 86 pA.

4.2 Results

The Au-Cu-Pt NPs were well dispersed and uniform in size, as can be seen in **Figure 4.1**. The particles range from about 15 to 20 nm in size and have either twinned polyhedron or asymmetrical decahedral structures. Figure 4.1 c) shows an individual particle with an increased magnification in e) showing the surface edge and a twin boundary. An FFT of Figure 4.1 c) shows spots corresponding to a superlattice.

Energy dispersive x-ray spectroscopy (EDS) was used to confirm the three elements alloyed within the particle. The analysis can be seen in **Figure 4.2** and confirms the presence of all three elements. The elemental map shows that Au is concentrated in the central region of the

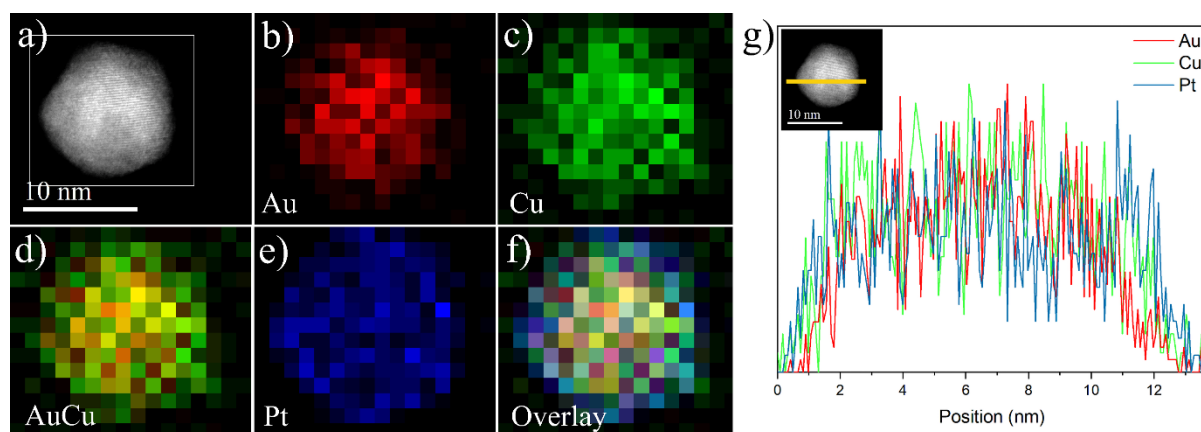


Figure 4-2: EDS analysis of the Au-Cu-Pt nanoparticles a) STEM-HAADF image b) map of gold c) map of copper d) superposition of Au and Cu e) Pt map f) superposition of the three elements. g) linear map of composition along a line indicated on the inset. Note that the Pt is depleted from the core and more prominent on the surface.

particle, while Cu is well dispersed. Pt is mostly concentrated around the surface of the particle. The line spectra indicates that the surface contains mostly Pt, and the core region contains mostly Au. While Cu is found throughout the particle, it lessens around the surface and does not seem to concentrate in any particular region.

During analysis, some particles were found oriented in the (110) direction with respect to the electron beam. This corresponds to the five-fold symmetry on the NPs[33]. STEM HAADF images were taken, and the five-fold symmetry of the particles can be seen. **Figure 4.3** shows the HAADF image along with EDS maps. In Figure 4.3 b), an FFT of the image that shows the superlattice. Using this FFT, taking only the spots corresponding to the superlattice, shows an image shown in image **Figure 4.3 c)**. Excluding the superlattice spots, an image is formed and shown in image **Figure 4.3 d)**. From this, three regions can be identified from the NP, the decahedral core, the surface region, and the superlattice. The superlattice region can be identified as $\text{Au}_2\text{Cu}_{1.9}\text{Pt}_{0.1}$ as reported by Kogachi[34]. That region corresponds to a tetragonal structure with space group $P4/mmm$ and parameters $a = 3.948 \text{ \AA}$, $b = 3.948 \text{ \AA}$, and $c = 3.72 \text{ \AA}$. The structure of the superlattice can be seen in **Figure 4.4** along with several crystal structures in different orientations. The central part corresponds to a decahedral twinned structure with a five-fold array of tetrahedra[35, 36]. The surface of the NP differs due to the Pt. The Pt along the surface is composed of two or three layers in an FCC structure along the (110) direction. Taking a closer look at **Figure 4.3 a)**, faceting can be seen forming a stepped surface. This reconstruction is the missing row 2×1 reconstruction of the Pt (1100) facets[37]. This well-known reconstruction is induced by the strain that is present in the particle[38, 39].

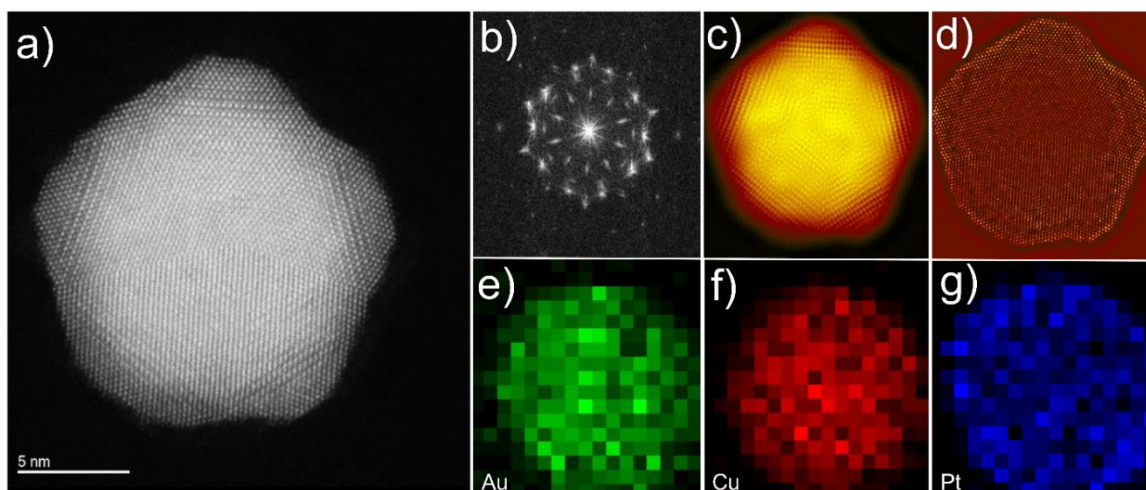


Figure 4-3: Image of an Au-Cu-Pt nanoparticle with decahedral shape oriented along the $\langle 110 \rangle$ direction a) STEM-HAADF, b) the FTT showing superlattice spots (indicated by arrows), c) image formed by using the superlattice spots showing how the superlattice is formed around the center. d) Image of the particle excluding all the superlattice spots. Note that the surface structure is different and more visible in the image. Corresponding EDS maps of e) Au, f) Cu and g) Pt. This image was used from: Khanal S, Bhattarai N, McMaster D, Bahena D, Velazquez-Salazar JJ, Jose-Yacamán M. *Highly monodisperse multiple twinned AuCu-Pt trimetallic nanoparticles with high index surfaces*. *Phys Chem Chem Phys*. 2014 Aug 14;**16**(30):16278-83. doi: 10.1039/c4cp02208d. PMID: 24975090; PMCID: PMC4128576.

Twin boundaries promote crystal growth[40, 41]. They play a similar role to nanocrystals as screw dislocations play in bulk crystals as shown by the work done by Fank, Burton, and Cabrera[42]. When Pt is added to the Au-Cu NP, there is a change in the structure. The core region is a decahedral structure which is often seen in Au and Au-X alloys. When the Pt is absent, an AuCu₃ superlattice is formed. AuCu₃ is normally the most stable phase as shown by Ferrando[43]. When the Pt is introduced, a distortion is created that results in a tetragonal phase where Pt atoms substitute Au atoms. The lattice misfit between Pt and Au is 3.6% which is enough to produce a distortion in the low concentration of Pt atoms, which is about 3%. A second phase grows on top of the decahedral core and is tetragonal structure where Pt substitutes Au atoms. This phase is only formed near the particle edges. The last few layers comprise of Pt and are an FCC phase with (110) and (100) orientations. The (110) surface is a reconstruction with a 2x1 structure[39] in which a row of atoms is missing and the (100) facets are reconstructed with a 5x1 structure[44]. This is the result of the nanoparticle revealing stress. It is

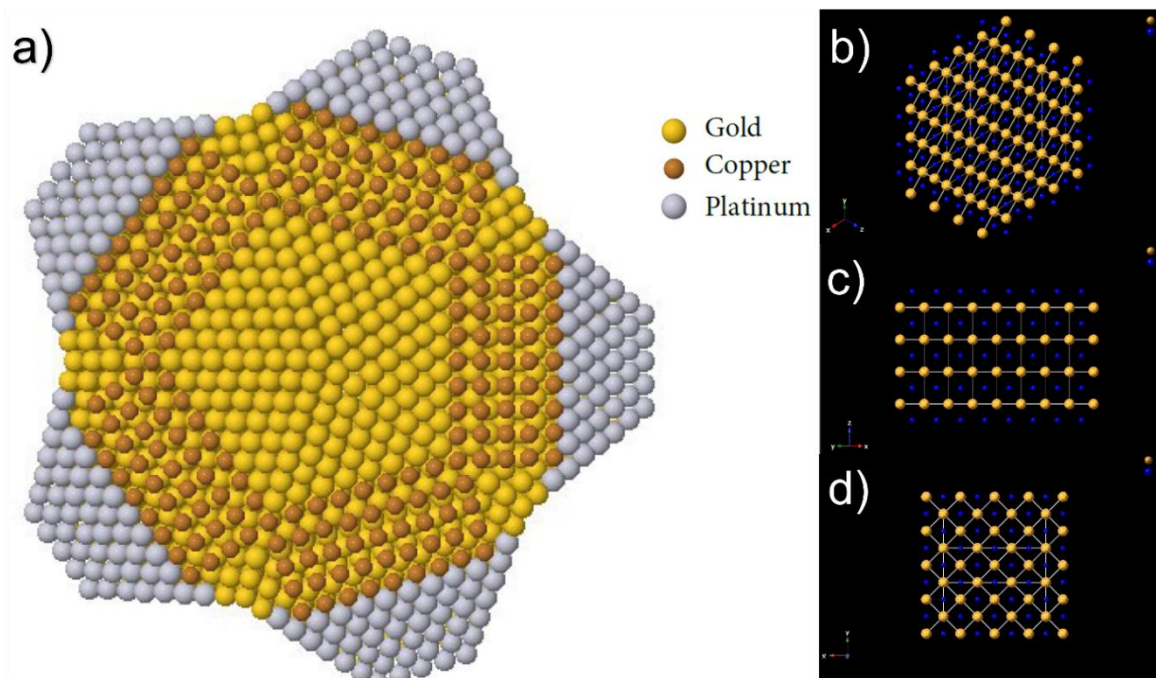


Figure 4-4: Model of the Au₂Cu_{1.9}Pt_{0.1} nanoparticle structure a) model of the 3 layers forming the nanoparticle. The lattice projection along <111>, <110> and <011> are shown in b) c) and d) respectively.

interesting to note that the surface is kinked. This leads to the expectation that these nanoparticles will have high catalytic activity[45]. This could be a good candidate to reduce the amount of Pt in catalytic reactions while keeping efficiency.

The quest for shape control in NPs is one of the most important challenges in the field of nano alloys[46]. The modified Hume-Rothery rules have been successful in predicting the structure and composition of bulk alloys[47]. However, the case for predicting nanoalloys is more complicated. The many different methods used to fabricate nanoparticles is one of the many challenges. For these Au-Cu-Pt NPs, the method used was a sequential reduction from precursor salts. Au nanoparticles were synthesized as seed particles and then Cu was added followed by Pt. The results were a decahedral NP that contains three different phases. This method has the advantage of having the Pt mostly near the surface. Other methods result in nano stars[48, 49], nano cubes[50], nano rods[51], and concave shapes[52]. Molecular dynamics simulations of Au-Cu-Pt have predicted core-shell structures[53] where Au is the core with a Cu-

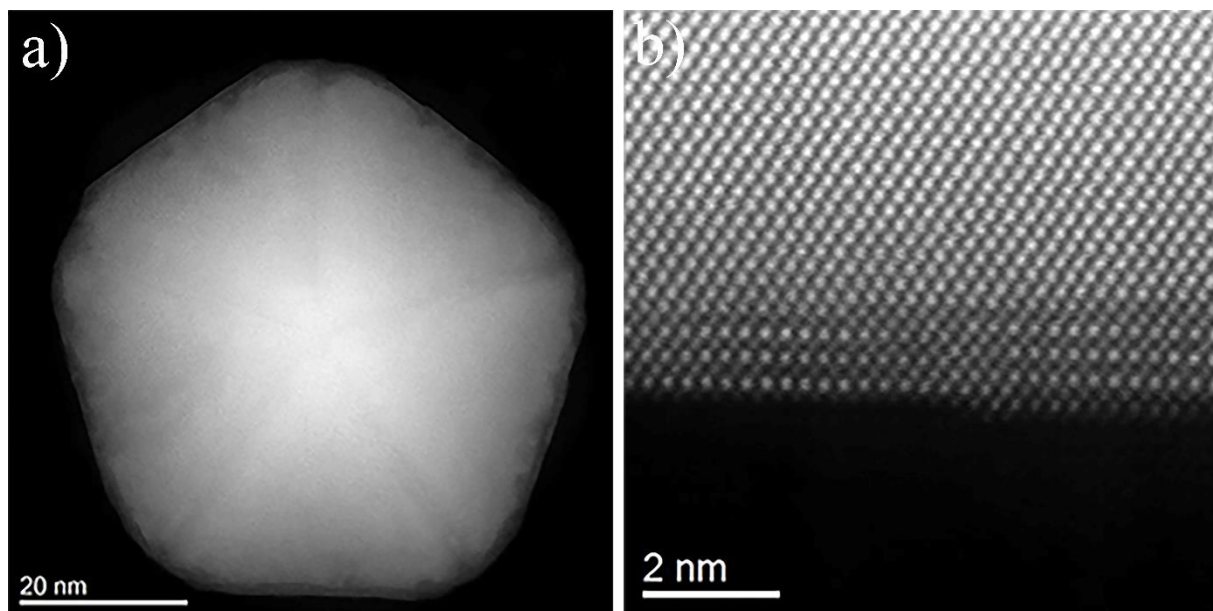


Figure 4-5: Image of a decahedral Au/Cu nanoparticle showing a) low mag STEM-HAADF image b) STEM-HAADF image showing the AuCu₃ phase at the edges of the nanoparticle.

Pt shell. The particles synthesized here indicated that the core is an Au-Cu composition where the Cu atoms can diffuse into the initial Au core. Pt then diffuses into the second shell to form a tetragonal structure, followed by an outer Pt shell. The three layered structure can be understood as a multicell structure with symmetry breaks as discussed by Ferrando[54]. Looking at an Au-Cu particle, there is also a superlattice formed but only on the facets, as seen in **Figure 4.5**. This superlattice corresponds to an AuCu₃ phase. For these particles, they were fabricated similarly to the Au-Cu-Pt particles and were grown at 280 °C. At this temperature, the Cu diffusion is limited and the superlattice is formed only on the surface of the facets of the Au.

4.3 Conclusion

The addition of a third metal results in an added complexity to a nanoparticle structure. With the Au-Cu-Pt NP, three regions within the nanoparticle are formed. The central region is mostly gold in a decahedra structure with a few copper atoms dispersed within. The second layer is a tetragonal superlattice of Au₂Cu_{1.9}Pt_{0.1} which is different from AuCu₃ due to the strain added by the addition of Pt. The third and final layer is mostly Pt and shows steps which correspond to

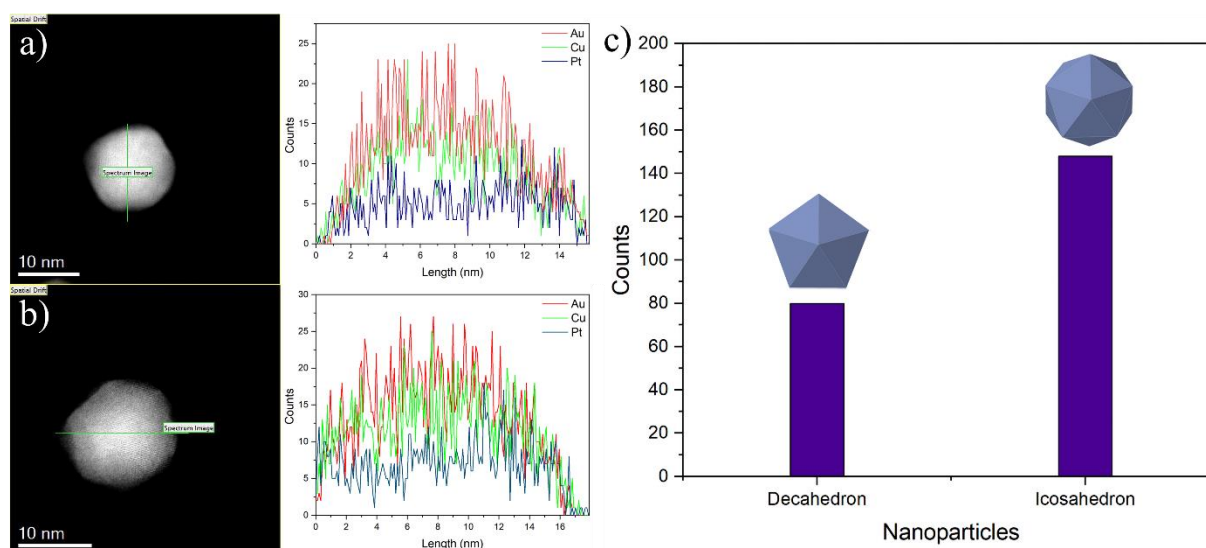


Figure 4-6: Image of a) decahedron and b) icosahedron particles with their corresponding EDS line scan. c) shows the distribution of the particles shapes over a large area, note that the icosahedron particles are more common.

surface reconstruction. These particles are expected to be catalytically active due to the large number of kinks and terraces on the surface. This is a way to optimize the catalytic performance of small particles and using a small amount of Pt. These nanoparticles show that further research, both experimental and theoretical, is needed to understand multimetallic nanoalloys as there is still much to be learned. What we learn from Au-Cu-Pt nanoalloys are that the addition of a third metal is a way to create new properties.

Chapter 5 The role of twinning in multi metallic nano alloys

This chapter is based on the published article ref [55]

In this chapter, metallic nanostructures will be discussed. The nanostructures in this chapter will be differentiated between clusters, nanoparticles, and nano-microstructures. At the nano scale, nanoalloys are expected to produce a rich variety of new materials. In contrast with the bulk alloys, the rules of alloying are not well established at the nano scale. The results indicate that twins are a key element of the growth. This results in the formation of multi twinned structures with five-fold symmetry. We conclude that twins at the nanoscale play the same role in crystal growth than screw dislocations do on the bulk.

5.1 Introduction

Fabrication of metallic alloys have been in the center of human civilization. Indeed, we name civilization eras after the materials and alloys that we were able to fabricate. In the last decades, great advances have been made in fabricating bulk alloys including: High entropy alloys[10], Quasicrystals[56], and different kinds of intermetallic alloys. These alloys have important applications in metallurgy[57], catalysis[58], electronics[59] among other fields. It is well established that we can predict the alloys' structure using a modern version of the Hume - Rothery[47, 60, 61] rules. However, when pricing alloys at the nano scale, problems become more complicated. It is well known that adding a second metal to a nanoparticle or nanostructure results in a dramatic change in the properties. A dramatic example was seen in the 70's when Exxon Pt-Re catalyst resulted in the elimination of lead from gasoline[62] and the introduction of catalytic converters to control car emissions based on Pt-Ru plus Pd[58, 63]. Adding metals to an

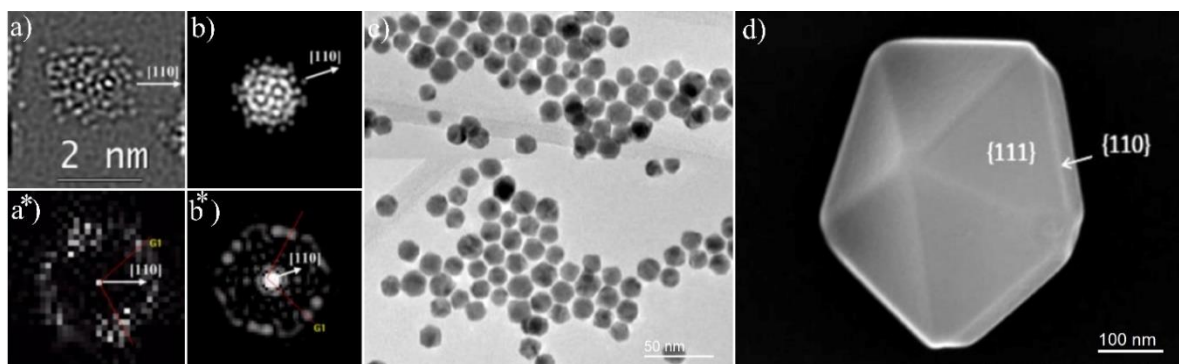


Figure 5-1: Representation of (a-b) clusters of few atoms with (a*-b*) showing FFT and orientation, (c) showing several nanoparticles and (d) a microstructure.

alloy signify new property will arise. Despite extensive research in the last two decades, the full control of the synthesis of multimetallic nanostructures is far from being achieved. Therefore, much work is done in synthesizing nanoalloys using different techniques to understand the controlling mechanisms[64]. Synthesis techniques from physical methods to various chemical reduction methods including green chemistry methods[65]. Understanding the core mechanisms of nanoalloys will allow for better synthesis techniques, prediction of properties and implications of the applications of nanoalloys. In this paper, we will discuss some research avenues that can be explored to achieve control of nanoalloys[66].

5.2 Clusters, nanoparticles, and microstructures

A first important definition is the scope of the nanoalloys to be studied. Using the number of atoms, we can divide nanostructures in three groups: clusters, nanoparticles, and nano microstructures. Figure 5-1 illustrates those cases.

The first category corresponds to clusters. Cluster are formed by a finite and known number of atoms and require a capping agent in order to be stable. Important advances have been made in their controlled synthesis[67-69] and theoretical understanding of their properties[12, 70]. A defining characteristic of clusters is the lack of plasmonic resonances. To understand clusters, they have been thought of as superatoms, which can be described by the “jellium”

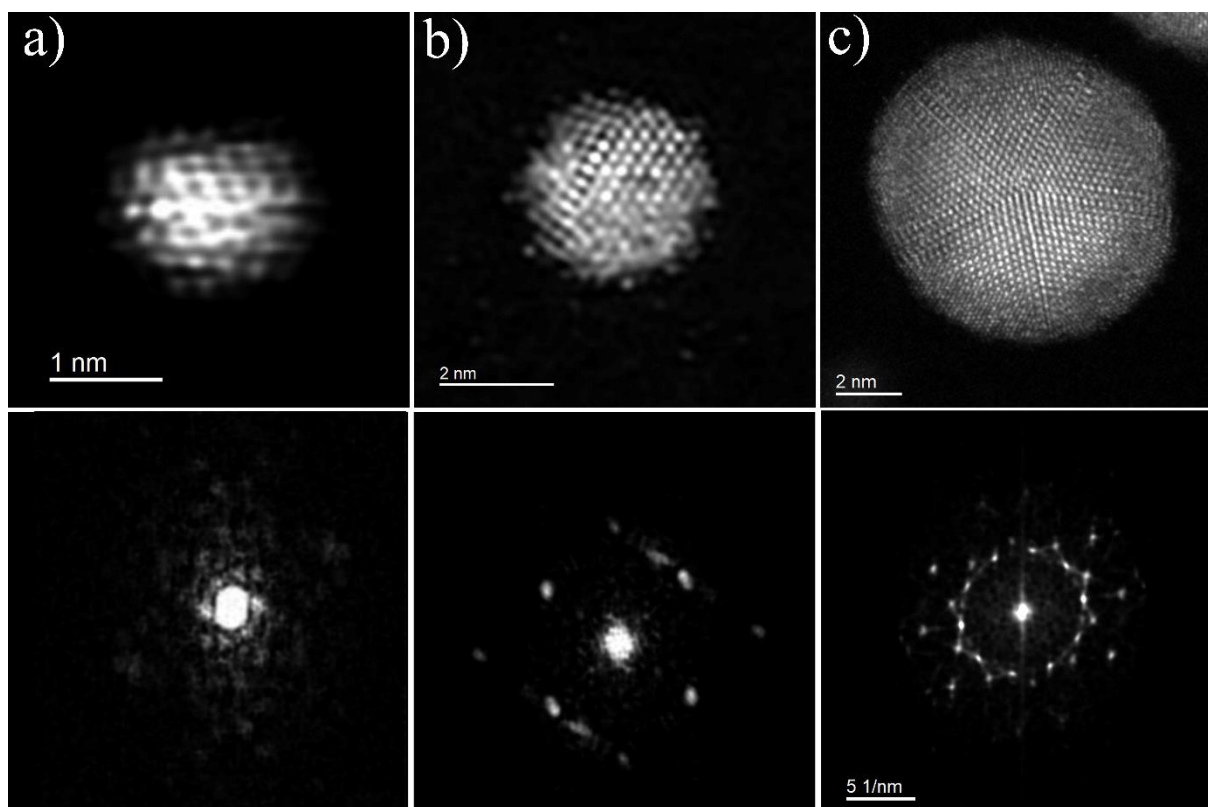


Figure 5-2: Images and FFT of Au-Ag nanostructures at different sizes. (a) is cluster of 1.8 nm showing diffuse spots indicating disorder on the atomic arrangement. (b) is a 2.2 nm cluster with a decahedral shape showing a more ordered structure. (c) is a nanoparticle of >5nm showing much more defined diffraction spots.

model of electrons confined within a spherically symmetric potential well of the metal core. If the number of free electrons falls in the “magic” number series of 2, 8, 18, 20, 34, 58, ..., the cluster shows high stability[71]. These clusters can have free electrons but cannot be considered metals. When analyzed under an electron microscope they show a diffraction pattern that cannot be explained by the Bragg law[72]. There has been success in producing bimetallic clusters of Au/Pd[73] and Au/Ag[74]. The second group are the nanoparticles which show strong plasmonic effects and very well-defined diffraction patterns.

Finally, nano/microstructures are more closely related to the bulk and do not necessarily show different properties. The size which defines each case is not totally defined. However, we can establish that clusters are <2 nm, nanoparticles are between 2-50 nm and nano/microstructure

will be between 50 nm to around a micrometer in size. The latter structures are very relevant for fields such as powder metallurgy. The electron diffraction pattern is a very good indicator of the nanostructure type. Figure 5-2 shows HAADF images of nanostructures of different sizes. As can be seen in the figure, as size increases the diffraction pattern is more defined and shows less diffuse scattering.

5.3 Bimetallic Clusters

The bimetallic cluster synthesis is a rapidly developing field with many new alloys being fabricated[75]. In this paper, we will report the general trends that we have observed in several alloys. A more detailed account will be given in a forthcoming publication. A very interesting bimetallic alloy is the Au-Pd of which has many applications[76]. We analyzed Au-Pd prepared following the methods of Negishi et al.[77]. According to Tofanelli et al.[78] this cluster has an icosahedral structure with the Pd atoms at the center. We have examined Au-Pd clusters using low dose HADDF-STEM microscopy[79] to minimize radiation damage. Figure 5-3 show the results. We basically observe fcc-like and fivefold icosahedral type despite the low electron dose ($\sim 1000 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$) used in obtaining the images. The results still might be affected by the electron radiation which introduces structural rearrangements[72]. This is also suggested by the fact that some particles in Figure 5-3a show coalescence. Nevertheless, the data indicate a strong preference to single and cyclic twinned structures.

One important result is that the clusters show an important degree of disorder. This can be made apparent by filtering the HAADF-STEM images as seen in Figure 5-4. Figure 5-4a and b shows the image and the FFT of two fcc-like Au-Pd clusters. The filtered image of the periodic portion is shown in 4c, and the image formed by using the diffuse scattering is shown in 4d. The considerable amount of diffuse scattering is due to internal disorder which might be caused, at

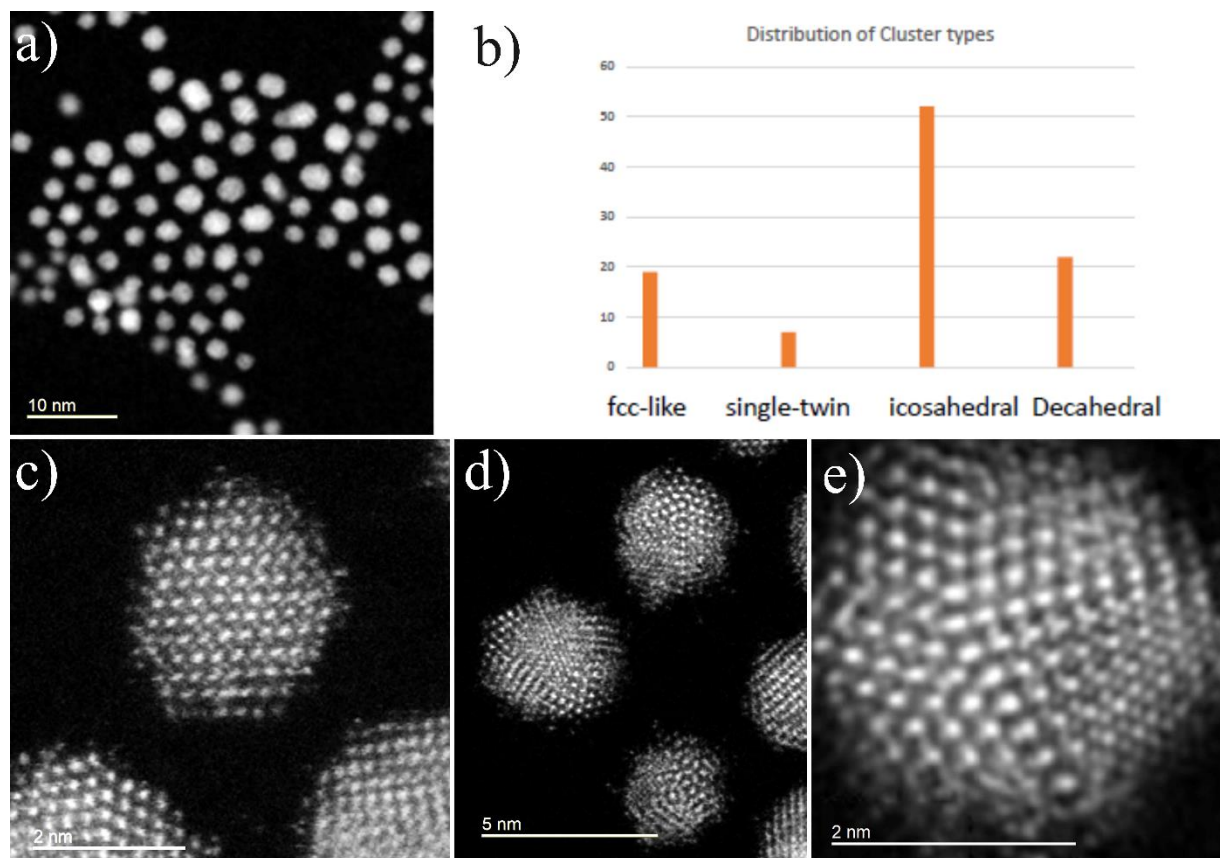


Figure 5-3: Images of Au-Pd clusters (a) low mag HAADF-STEM image, (b) distribution of structures of the clusters, (c) HAADF-STEM image of fcc-like cluster, (d) Icosahedral clusters, and (e) Decahedral cluster.

least partially, by the fact that the size of the cluster does not allow for fully coherent Bragg diffraction to happen. Figure 5-4a also shows some degree of surface disorder. We consider that disorder in the cluster might be a strong indicator that a band structure is still not formed, and the cluster might still be consider a “superatom [12, 71]. Other examples of clusters are Pt-Cu[80], Au-Co[81] and Au-Cu[82].

5.4 Bimetallic Nanoparticles

When bimetallic particles are prepared by wet chemistry methods, the two metal salts are reduced simultaneously. However, the rate of reduction is different in most cases producing core-shell types of structures. However, the core shell is not stable and annealing results in an intermetallic. We have prepared Au-Pd, Au-Cu and Pt-Pd core shell structures. A very

interesting case is the Au-Pd nanoparticles[83]. Core shell structures can also be fabricated in a more controlled way by the seed methods developed by the Murphy group[46, 84]. Several structures are formed: a) Cubes, b) Pyramids and c) Tetrahedral corresponding to (100), (110) and (111). These structures are shown in Figure 5-5. EDX analysis shows that the core is mostly Pd, and the shell is mainly Au. There is a mismatch between the lattice parameter of 4.7% which results in interface strain between the core and the shell [85]. This strain can be observed on the

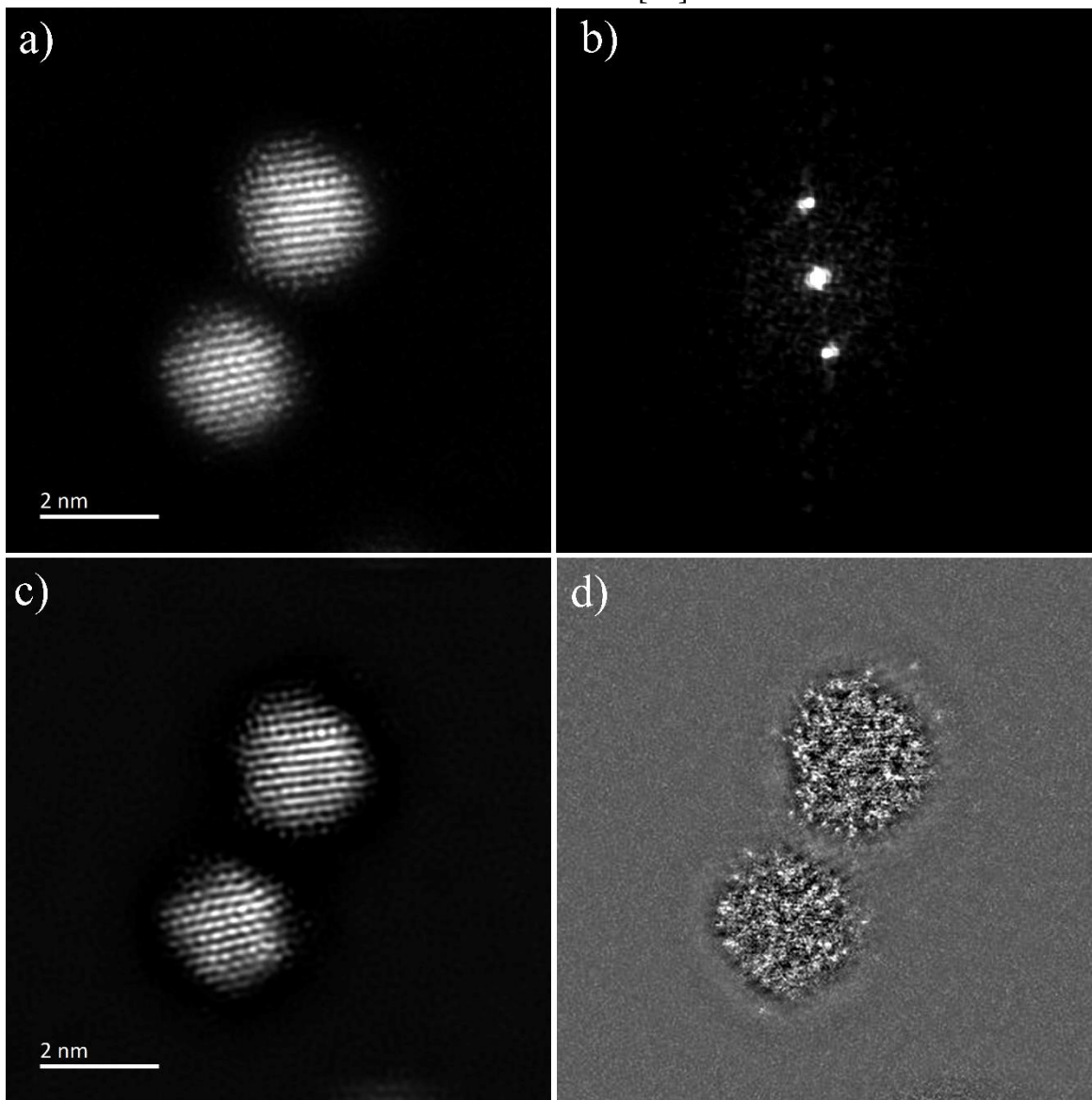


Figure 5-4: Sequence of images showing that bimetallic clusters have some internal disorder. (a) HAADF-STEM image with (b) corresponding FFT. (c) image produced by eliminating all the diffuse scattering showing periodic structure. (d) inverse FFT image of the disorder on the cluster forming by include only the diffuse scattering.

weak beam dark field images (Figure 5-5h&i). The weak beam image of the $\langle 100 \rangle$ nanoparticles shows thickness fringes that confirm the cubic shape[86, 87]. However, it is remarkable that the nanoparticles are single crystalline indicating an epitaxial growth. The strain mismatch is concentrated around the core. For a fcc crystal, cubic shape does not correspond to a low surface energy. The cubic shape is the result of the growth kinetics. Strain is produced on the surface of the nanoparticle. To produce stability, the resulting (100) facet become concave as demonstrated by tomographic data[83].

It should be noted that the core-shell structure is not stable. This can be demonstrated by an annealing experiment in the TEM. We follow the methods described in a previous publication[88]. After heating, the core-shell structure disappears, and the nanoparticle becomes a regular alloy. The stress at the core shell interface is relieved during the heating.

5.5 Trimetallic nanoparticles

By adding a third metal, the structure of the nanoparticles changes dramatically. The result depends heavily on the preparation method. If wet chemistry synthesis is used, the rate of reduction of each metal salt is a key factor. However, in general, there is a greater tendency to form twinned polyhedral structures. In cases such as Ag-Pt-Pd, the great majority of the nanoparticles are twinned. Figure 5-6 shows some of the observed shapes and the corresponding FFT patterns. The particles are still single crystals but contain several twins and are icosahedral, decahedral or single twinned as seen in Figure 5-6a, b and c. The EDS analysis shows that the metals are dispersed though the nanoparticle in a more or less random pattern. However, there is a slight increase in the Ag concentration at the surface (Fig 6g and h).

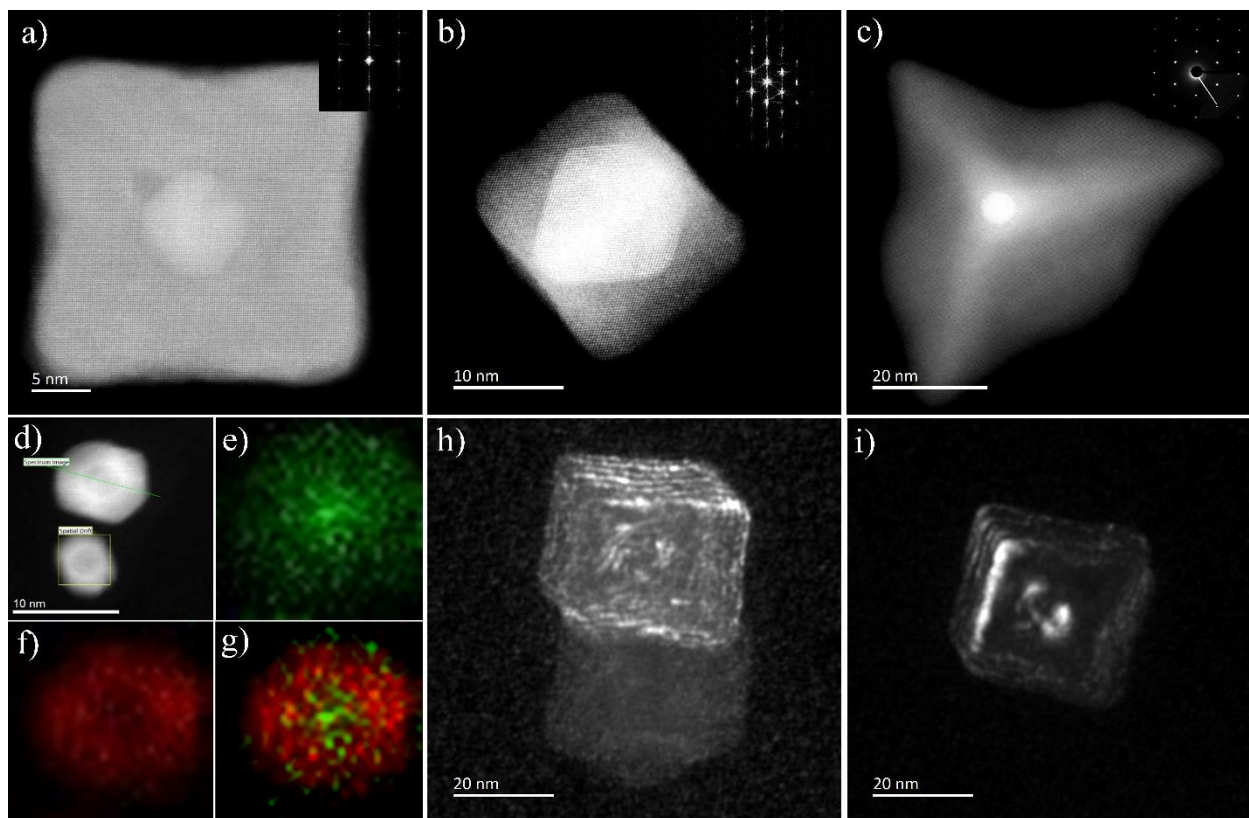


Figure 5-5: Au-Pd core shell alloy showing different shapes (a) cubic, (b) pyramidal and (c) tetrahedral. In each case the diffraction pattern is shown. In image (d) a microanalysis of a particle can be seen with (e) showing contribution of Pd and (f) showing contribution of Au. The Pd is the core of the nanoparticle with Au as the shell. This is due to the synthesis process of starting with a seed of Pd and then adding Au. (g) Shows the composition map illustrating a core shell structure. (h) and (i) are showing the strain on the particle.

5.6 Larger nanoparticles

As the size increases the tendency of twinned structures continues. Even if we add metal components, the trend remains. For example, a particle made of Au-Cu-Pd-Ni with a size ~ 0.1 micrometer is shown in Figure 5-7a. The FFT (Figure 5-7b) shows that the particle has pseudo five-fold symmetry. It is remarkable that the particle twinned into a single crystal. To take a closer look, an increased magnification image of the center, Figure 5-7c, shows stacking faults around the center of the particle.

5.7 Discussion

The analysis of typical nanostructures from clusters to micro particles has been presented. A common feature is the presence of twins. Since the nanostructures have not been subjected to any deformation, the twins should be the result of the growth process. During crystal growth, faceted interfaces may be perturbed by defects, leading to a rich variety of growth forms. One such defect is the coherent $\Sigma 3$ ([89] twin boundary, which is widely known to catalyze crystal growth. The twin mediated crystal growth was proposed for Germanium dendrites back in the 60's[90, 91]. Strong experimental evidence was provided more than 50 years after by the Voorhees group[41, 92]. This model, known as the VHS model, assumes that the nucleation of new layers during crystal growth starts at the intersection of a $\Sigma 3$ twin plane with a (111) facet. This model was extended by van de Waal[40]. The latter model known as cross twinned model can explain cyclic twinned structures produced during growth. Clusters and nanoparticles are produced by nucleation of metal atoms formed by the reduction of the metal salt solution. After a nucleus is formed, atoms are incorporated to grow the nanoparticle. The formation of twins favors the growth of the nanoparticle. If cross twinning is present during growth, non-parallel twin lamellas will be formed[92]. Intersecting twin lamellae, which are crossed, will result in regions with five-fold symmetry. That explains why decahedral, icosahedral and cyclic twinned polyhedral are so easily formed. If two metals are present, we can consider a similar situation to epitaxial growth because lattice mismatch interface dislocations are produced. However, in a cluster or nanoparticle the size is less than the dislocation distance, and elastic strain is produced at the interface. Partial dislocations are nucleated on the interface that will eventually move to the surface and leave a twin boundary.

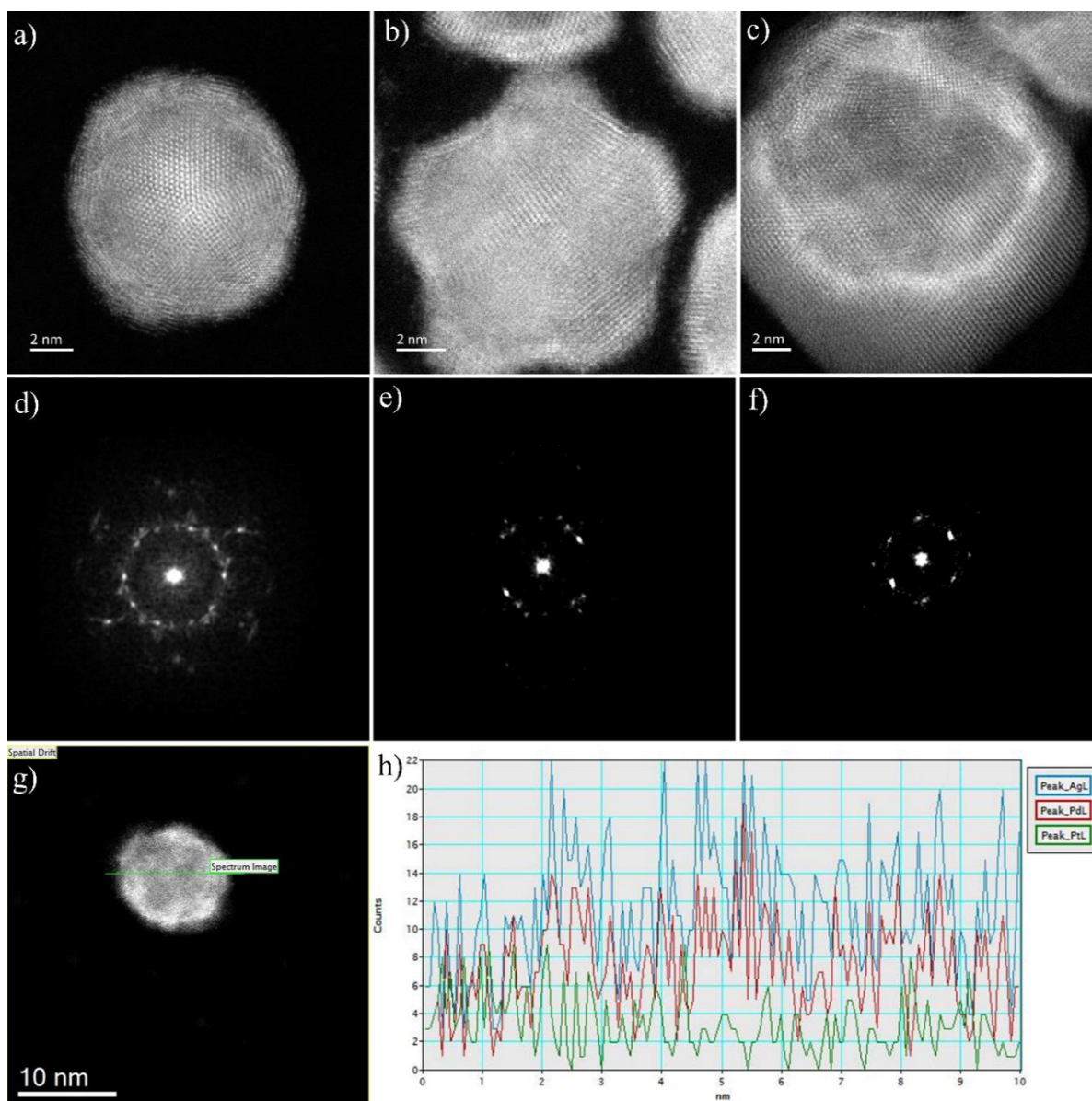


Figure 5-6: Image of a Ag-Pt-Pd nanoparticle. Different shapes are observed a) icosahedral, b) decahedral and c) single twinned. (d)-(f) show the corresponding FFT of the particle. The EDS is shown in (g) and (h) indicating the analysed nanoparticle and the distribution of elements across the particle.

On the other hand, it is likely that in clusters and nanoparticles non-conventional growth mechanisms are present. In Figures 6 and 7 we see that in trimetallic and multi metallics, the surface has a different structure from the bulk. This suggest the reverse growth mechanism discussed by Greer[93] in which growth starts at the surface. Another possibility is that nucleation seeds have icosahedral structure and the core grows with fivefold structure and recovers the normal structure as suggested by Kurkutuldu et al.[94].

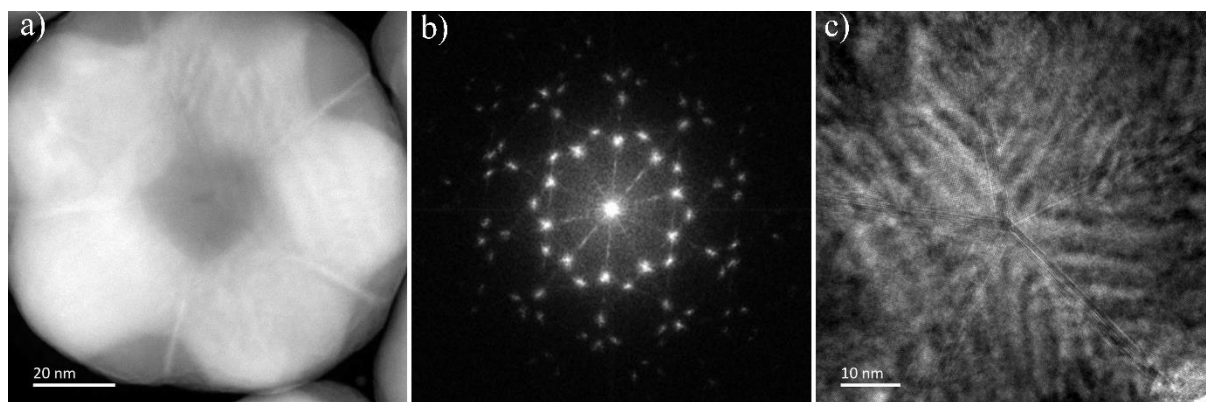


Figure 5-7: Image of a multimetallic micro particle Au-Cu-Pd-Ni showing a core shell structure (a) with fivefold symmetry as shown by the (b) FFT. An enlarged image of the center of the nanoparticle is shown in c) in which stacking faults can be observed.

5.8 Conclusion

In this paper we have shown that multimetallic alloys can produce a very rich variety of structures. The formation of growth twins is a key aspect of the growth of clusters and nanoparticles. We have also shown that twinning results in the formation of five-fold strained structures which are dominant. This opens a pathway to understand how to control the growth of multimetallic nanostructures. Finally, it was shown that core shell bimetallic structure is not stable and that under heating they disappear, thus an alloy is formed. The field of growth of multimetallic nanostructures is a path to fabricate new materials with improved properties. This is an exciting field with many avenues of research. With more research performed on the structure of nano alloys, both theoretical and experimental, not only will the field benefit from the discoveries, but applications that will better human technology will also arise.

Chapter 6 Nanoalloys of multiple components the road to advance the field, experimental and theoretical challenges

This chapter is based on the published article ref [95]

The field of nanoalloys has been advancing at rapid pace in the last two decades. Many new characterization methods and theoretical advances have produced a substantial knowledge of the nanoalloys properties and structure. Most of the work has been limited to binary alloys. A path forward for the field will be the study of nanoalloys with three or more metals. Adding new components will produce new properties and possibly more fabrication controls. In this paper, we will discuss the challenges that will arise in multi-metallic nanoalloys. We will show that Entropy and twin boundaries play a dominant role in multi-metallic alloys.

6.1 Introduction

Fabrication of bulk metallic alloys has been the center of human civilization and many key advances are the result of the discovery of new alloys. In the last century scientists realize that matter with size in the nanometer interval behave differently than the bulk. One historical discovery by Owaga, Ino, Alpress and Sanders was the discovery of gold nanoparticles with fivefold symmetry[96-98]. That trigger a wide research interest in monometallic nanoparticles in the following decades [35, 99-101]. Important theoretical advances were made to understand the monometallic nanoparticles [102-108]. In the last few decades researchers developed interest in bi- and multi-metallic alloys. In the field catalysis there is a well stablished use of bimetallic alloys[109]. There are two striking examples of the benefits of nanoalloys and the development of new properties. The first example was the introduction of the Exxon Pt-Re catalyst, in the

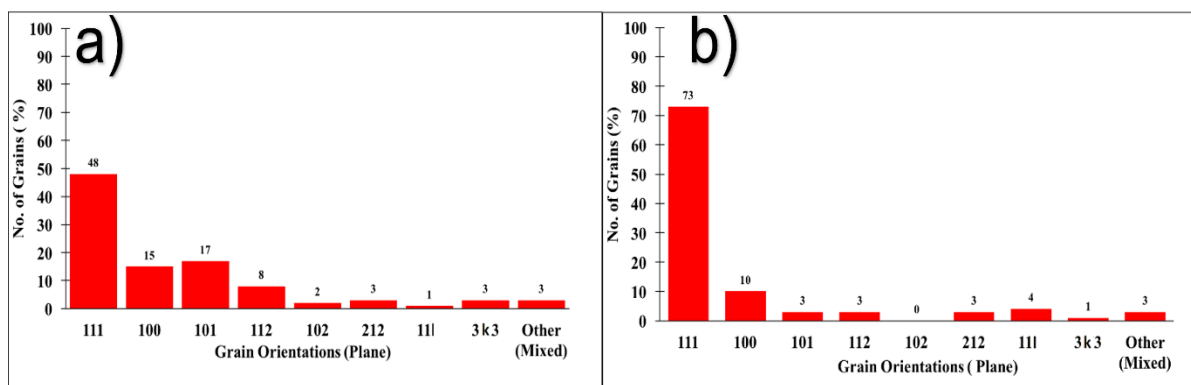


Figure 6-1: Distribution of grain orientations with respect to the electron beam. a) shows the distribution before and b) after an annealing of 300 °C for 3 hours. The percent of grain orientation in the (111) plane goes from 48% to 73%.

70's, which resulted in the elimination of lead from gasoline [62, 110]. The second example is the introduction of catalytic converters to control car emissions based on Pt-Ru plus Pd [58, 63]. These examples show that adding metals results in new properties. In the case of bulk alloys, an impressive advancement has been achieved by fabricating alloys containing up to six metals in equimolar concentrations. Those alloys named High Entropy Alloys (HEA) [10, 111-113] are already on the market and are very promising for applications involving corrosion resistance and high mechanical strength [114, 115].

An obvious path for advancing in the nanoalloys field, is to consider the fabrication of alloys containing several metals. In the field of catalysis, several trimetallic catalysts have been developed such as Ni-Mo-W and Ni-Co-Mo for hydrotreating [116], a Co-Au-Pd Catalyst for Hydrogen Generation from Formic Acid [117], Au-Ag-Pt for Methanol Electro-oxidation[118] and several others [119]. In the theoretical side, there have been a lot of advances on bimetallic systems, see for instance the references [12, 109, 120]. In contrast, the case of trimetallic, alloys only a few theoretical studies are available [121-124]. It is however clear that a full understanding of the physics behind the formation and structure of tri- and multi-metallic

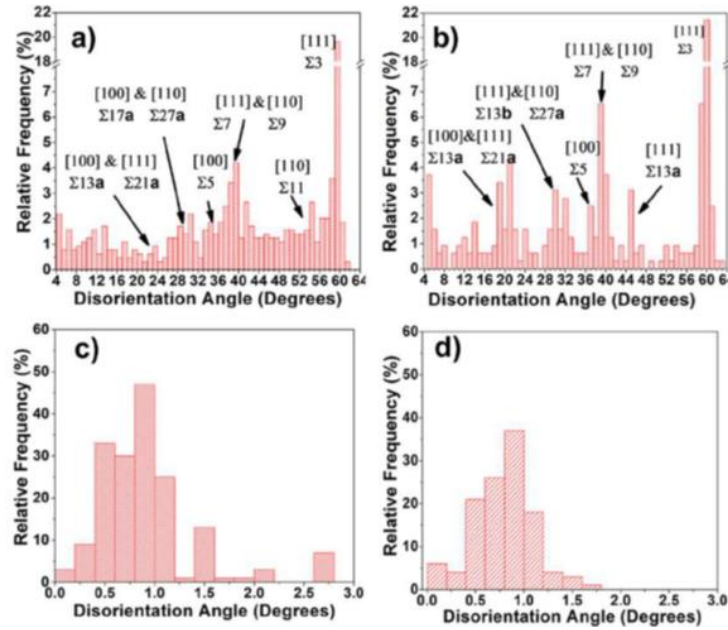


Figure 6-2: Distribution of the orientation of the Au grains. The grain rotation is expressed in terms of CSL and the Σ values. a) is before annealing and b) is after annealing. After annealing, more CSL boundaries are formed.

nanoalloys is still not fully understood. In the present paper we would like to discuss some of the most relevant phenomena that control multi-metallic alloys.

6.2 Kinetics vs Equilibrium

Nanoalloys can be nanoparticles or thin films. In both cases nuclei of few atoms are formed. When a critical size is reached, the nuclei start to grow by adding atoms to the seed. In principle, arriving atoms will tend to accommodate in minimum energy sites. Many times, the arrival of atoms to the nuclei occurs a rate such as the atoms do not have time to reach preferred sites. The growth becomes a competition of kinetics vs. equilibrium. One important aspect to consider when comparing theoretical calculations with experimental data is to determine if the observed nanoalloy structure is in an equilibrium state or is in a kinetically stabilize state. An example of this is an Au polycrystalline thin film grown in a NaCl surface at 100 °C. The sample was then heated in vacuum for 3 hours at 300 °C. We used precession methods to analyze the grains orientation using precession electron diffraction [125, 126]. Figure

6-1 shows the orientation of the grains with respect to the electron beam before and after annealing and the color plot of the orientation of the grains. As can be seen before annealing, there were several orientations including (111), (110), (100), (112) and several high index orientations. After the annealing the (111) orientation becomes prominent follow by the (100). The other low index orientations such as the (112) have been significantly reduced. It should be noted that some high index orientations are also reduced but have not completely disappeared.

A second experiment shows the relative disorientation of two grains i.e., the grain boundary structure. We express the results using the Coincidence Site Lattice method [127-129] designated by the symbol ΣN with the twin boundary corresponding to $\Sigma 3$. It is considered that CSL correspond to low energy boundaries. Figure 6-2 shows the behavior of the grain boundaries before and after the annealing. More CSL boundaries are produced by the annealing. A conclusion is that in the growth of thin films, kinetic stability is dominate. When thermal energy is provided energetically favorable structures begin to appear. However, it seems that kinetically stabilized structures remain even after some annealing.

6.3 The Role of Entropy

The Gibbs free energy of nanoalloy can be expressed following Calvo [130] as

$$G(N) = x_A \left[N\mu_A + \sigma_A N^{\frac{2}{3}} \right] + x_B \left[N\mu_B + \sigma_B N^{\frac{2}{3}} \right] + RT[x_A \ln x_A + x_B \ln x_B] \quad (6.1)$$

where x_A , μ_A and σ_A denote the molar fraction, chemical potential, and surface energy of element A, respectively. Which include the surface ($N^{2/3}$ terms). As we increase the number of metals in the alloy, we must add more terms to the entropy part. In terms of the Boltzmann approach, the entropy can be considered as

$$S = k \ln W \quad (6.2)$$

where W corresponds to the number of microstates. We have made a preliminary calculation of the possible number of arrays of three metals A, B and C at different concentrations for a 13 atom cubo octahedral cluster. From the total number of arrays, we consider only those which are different. The results are shown in Table 6-1. The Entropy becomes very important and perhaps dominant as the number of metals increase.

Table 6-1: Array for a Cubo Octahedral alloy of 13 atoms

Number of atoms	A	B	C	Number of arrays	Number of different arrays
13	1	1	11	156	5
13	1	2	10	858	21
13	2	1	10	858	21
13	1	3	9	2860	58
13	2	2	9	4290	81
13	3	1	9	2860	58
13	1	4	8	6435	103
13	2	3	8	12870	213
13	3	2	8	12870	213
13	4	1	8	6435	103
13	1	5	7	10296	143
13	2	4	7	25740	360
13	3	3	7	34320	506
13	4	2	7	25740	360
13	5	1	7	10296	143
13	1	6	6	12012	160
13	2	5	6	36036	475
13	3	4	6	60060	793
13	4	3	6	60060	793
13	5	2	6	36036	475
13	6	1	6	12012	160
13	1	7	5	10296	143
13	2	6	5	36036	475
13	3	5	5	72072	956
13	4	4	5	90090	1131
13	5	3	5	72072	956
13	6	2	5	36036	475
13	7	1	5	10296	143

A similar case are the homotopes that can be produced in an alloy isomer which differ only for swaps in the positions of atoms of different species[120, 131]. Some of these homotops may be symmetry equivalent, so that the number of inequivalent homotops is somewhat reduced. However, the resulting number is very large. That represents another way to see the entropy contribution. In the case of nanoparticles, the surface might have a different atomic array than the bulk which will result in additional surface entropy.

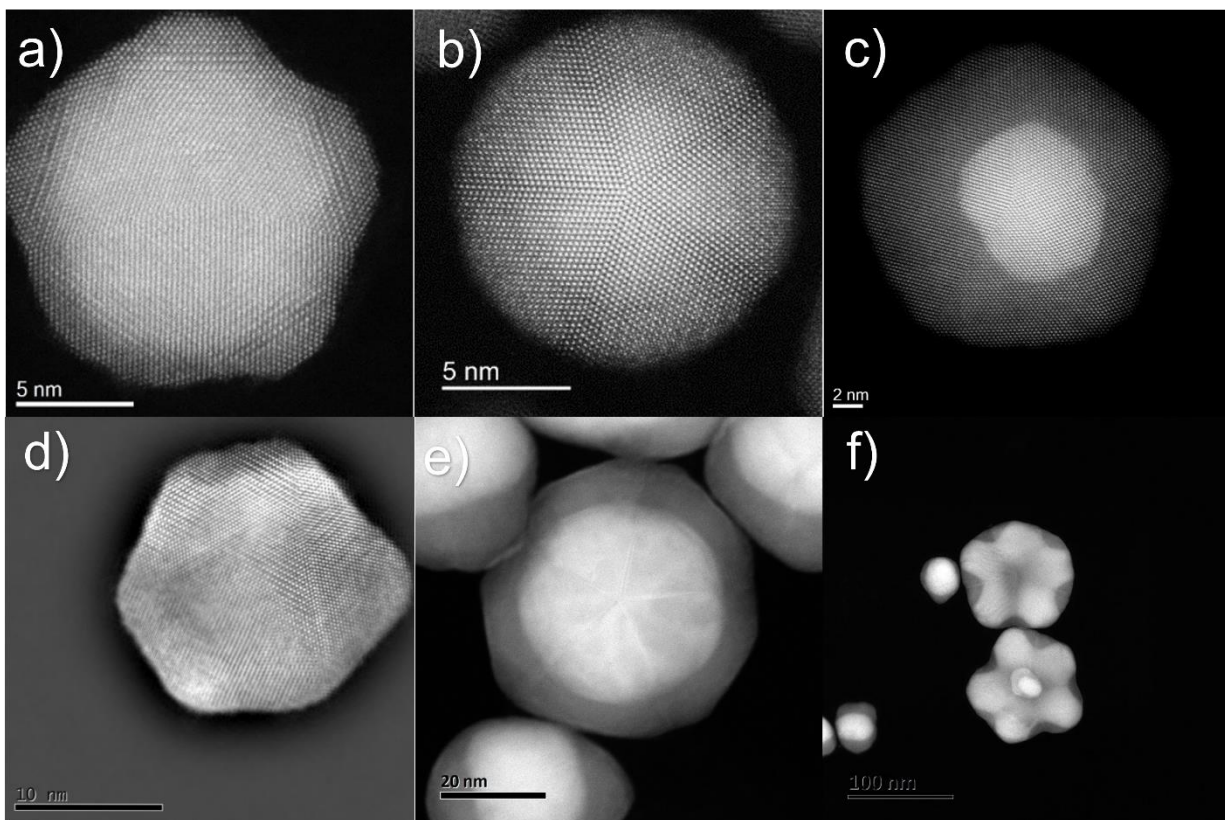


Figure 6-3: Examples of decahedral nanoparticles produced a) Au-Pt-Cu, b) Au-Ag, c) Pd-Au, d) Au-Pd-Cu, e) Au-Cu-Pd-Ni and f) Au-Cu-Pd-Ni-Co.

One of the challenges in this field is to calculate the entropy for multi-metallic alloys. Nowadays it is possible to obtain close, atom by atom, chemical analysis using EDS in an aberration corrected TEM. However, since every bright spot in a STEM-HAADF image represents the projection of an atom column, it is necessary to use atom counting methods to determine the number of atoms [132]. Combining these two methods it will be possible to determine experimentally the atomic combinations experimentally. That should encourage theoretical work to calculate the configurational entropy.

6.4 The Role of Twin Boundaries

It is well established that crystal growth of nanostructures is highly favored by twins [133]. Twin boundaries promote the growth by providing low energy sites for atoms [40]. We can expect that twins will always be present in nanoalloys. Strain due to different size atoms will result in the creation of partial dislocations. However, because of the size, partial dislocations can move to the surface. In their movement, they will leave stacking faults behind. Twin boundaries will result, bounded by two stacking faults. In addition, the mechanism known as cross twinning will induce fivefold structures [40, 134]. We have observed that as we produce nanoparticles with more metals, the number of multiple twinned, fivefold structures, with nearly decahedral shape, increase. An example of twins can be seen in Figure 6-3.

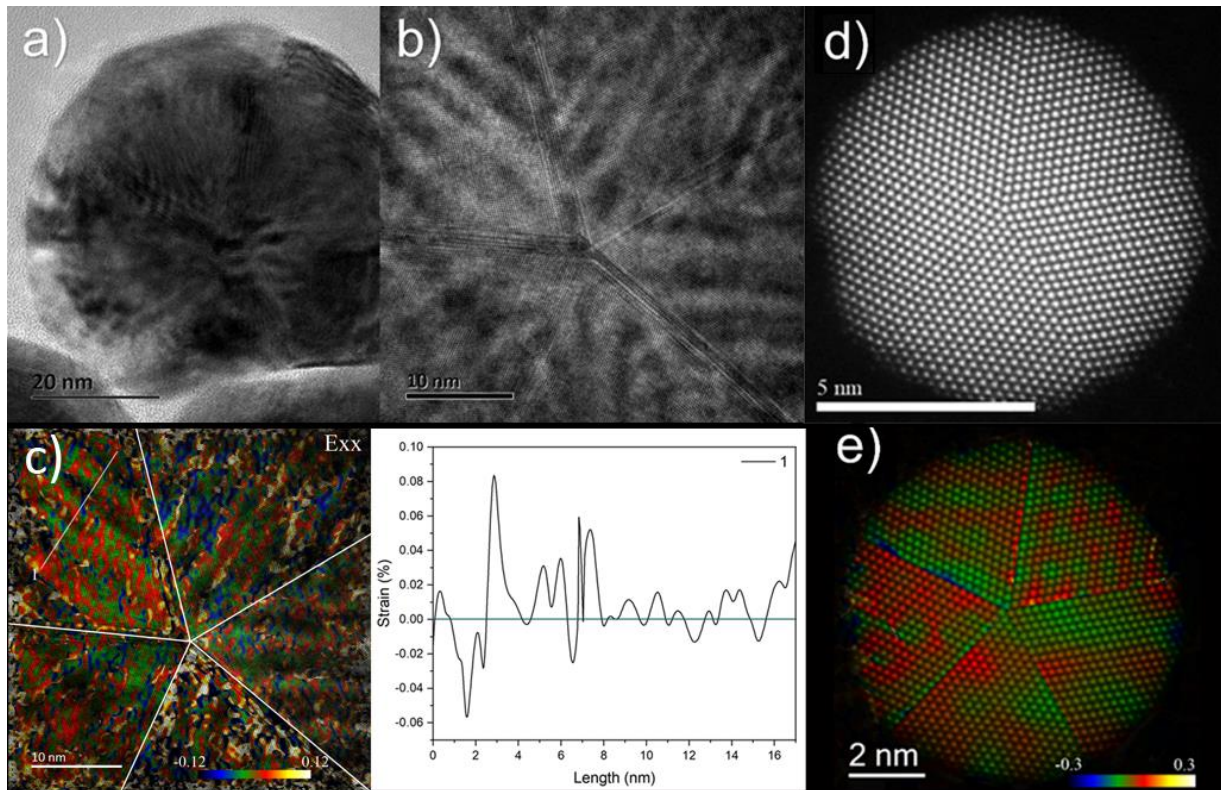


Figure 6-4: This figure shows the strain map of an Au-Pd-Ni-Cu nanoparticle a) bright field image with a b) magnified image of the center showing fivefold symmetry. c) is the strain map of the nanoparticle indicating alternative regions of tensile and compressive strain with the liner plot of the strain along line 1 indicated in image c). d) shows STEM-HAADF image of a gold nanoparticle with its corresponding strain map e) using GPA plot. The contrast of the pure metal and the alloy is very strong.

Of course, several other shapes are present such as single twinned and Janus structures. The presence of twins make the addition of an extra term to equation 1 as proposed by Patala et al. [135] with the form

$$\sim nA_t\gamma_t \quad (6.3)$$

where n is the number of twins, A_t is the area of twin boundary and γ_t is the surface free energy per unit area of twin boundary. From the TEM images it will be possible to calculate this contribution.

6.5 Role of the Strain

One of the most common assumptions is that in HEA alloys there is a strain due to the differences in atomic radii of the elements [113, 136],[137]. This is important to understanding the mechanical properties of HEA. On the other hand, Farkas and Caro [138, 139] have shown that the strain is small and practicably indistinguishable from diffuse thermal strain. However, in the case of nanoparticles, thin films and nano alloys there are a number of techniques available to determine the strain using aberration corrected microscopy and other techniques [140, 141]. A very popular method to map strain in HREM TEM images is the Geometric Phase Analysis (GPA) [142, 143]. We have measurements using GPA mapping of a number of multi-metallic nanoparticles. In Figure 6-4, we have shown a comparison of strain between a gold decahedral particle and a fivefold twinned Au-Pd-Ni-Cu particle.

The difference in both cases is very clear. As suggested in the references, it is necessary to introduce an additional term to the Gibbs Energy with the form:

$$\sim V W_v \quad (6.4)$$

where V is the volume of the particle and W_v is strain energy per unit volume produced on the particle by the atomic radius differences.

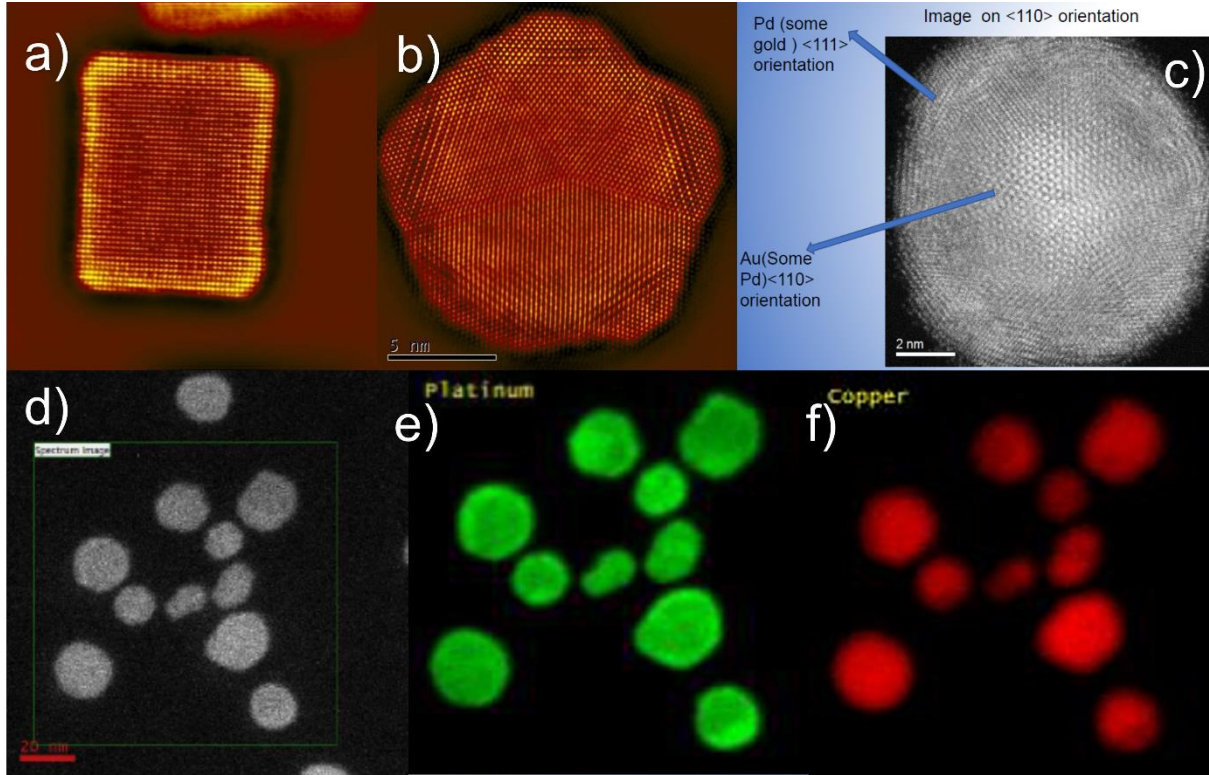


Figure 6-5: Images of nanoalloy particles that show how the surface is different. In the top left a) a Pt-Ni alloy. The image has been pseudo colored for clarity. In the middle b) an Au-Pt-Cu alloy showing a different surface structure. c) is an Au-Pd nanoparticles. The orientation and composition of the surface is different from the center of the particle. d)-f) shows an EELS microanalysis of Pt-Cu nanoparticles including the d) bright field image and the e) Pt and f) Cu maps. The size of the NPs in the platinum map seems larger than the Cu map, however, this is indicating a rich Pt surface.

Therefore, we can write the Gibbs Free Energy by adding the terms for the twins and the strain

as:

$$G(N) = x_A \left[N\mu_A + \sigma_A N^{\frac{2}{3}} \right] + x_B \left[N\mu_B + \sigma_B N^{\frac{2}{3}} \right] - RT[x_A \ln x_A + x_B \ln x_B] + V W_v + nA_t \gamma_t \quad (6.5)$$

6.6 The Surface Structure

After analyzing the structure of a multi-metallic nanoparticle, it becomes clear that the surface has an atomic array which is different from the interior of the particle. As the particle becomes larger, this effect becomes more pronounced. The surface might have a different

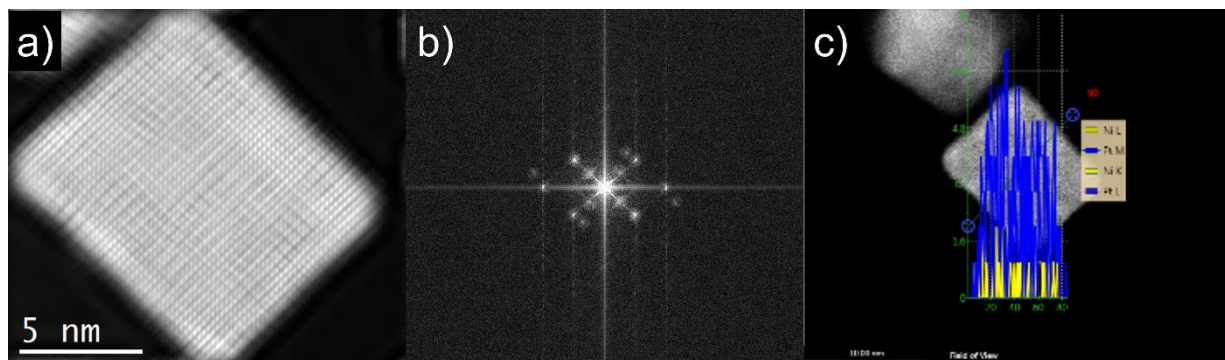


Figure 6-6: a) Filtered image of a Pt-Ni particle with the b) corresponding FFT and c) line EDS microanalysis. Different atomic arrays can be seen along the particle.

chemical composition by the segregation of a component. It is also possible that the surface might have a different crystallographic orientation or a different atomic array than that of the center. Examples of these effects are shown in Figure 6-5 for different alloys Pt-Ni, Au-Pt-Cu, Au-Pd and Pt-Cu.

6.7 The Electron per Atom Value

In the case of bulk alloys, the application of the Hume-Rothery rules leads to the use of the electron /atom value (e/a) [60, 144]. This value represents the number of itinerant electrons that can contribute to the formation of a metallic alloy. Calvo-Dolberg and Brown[47] have introduced a rule for predicting HEA. If we combine this with the knowledge of quasicrystal alloys [145, 146] we can express the prediction of the alloy structure based on e/a as:

- $e/a < 1.65$: fcc
- $1.65 < e/a < 2.05$: Complex phases Lave Phases, Intermetallic, quasicrystals and approximants
- $e/a > 2.05$: bcc

However, a question that arises whether this rule is valid for nanoalloys. This will depend on whether the nanoalloy has an overlapping energy band. One criteria that has been used is whether the nanoparticle shows plasmonic effects [147]. A small cluster of atoms is considered a

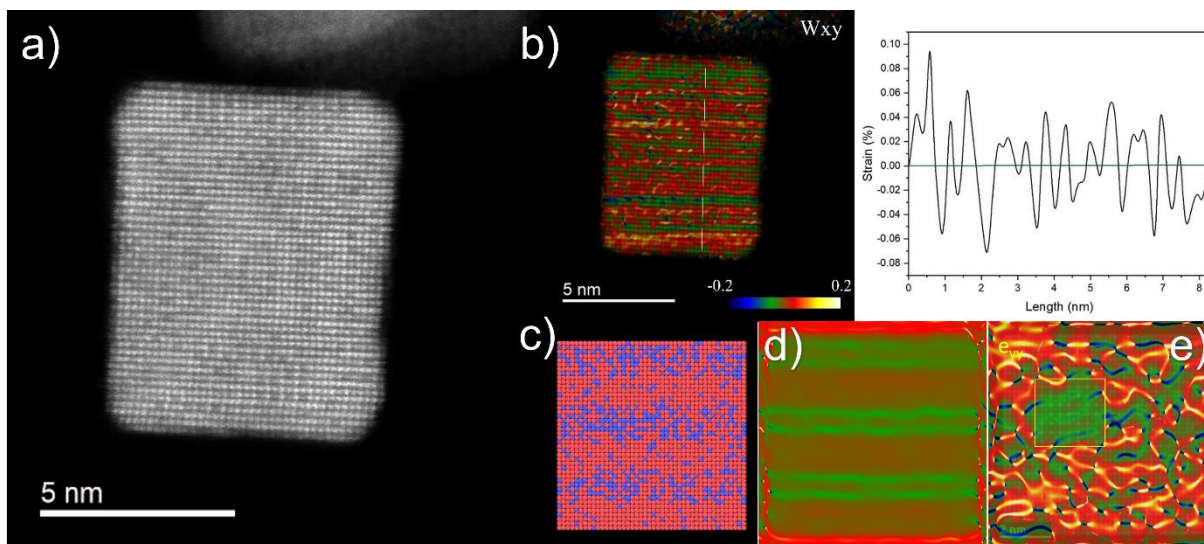


Figure 6-7: Analysis of a Pt-Ni alloy nanoparticle, a) HAADF-STEM image, b) GPA map of the image indicating periodic strain and plot of the strain along the vertical dash line indicated on the GPA image. c) shows a model of the distribution of Pt (red) and Ni (Blue) in order to simulate the nanoparticle, d) calculated GPA map resulting from the model and e) resulting GPA when the atomic distribution is random.

super atom [11]. However, at some point a transition from the molecular to the metallic electronic structure occurs [148]. In order to apply the e/a criteria the nanoparticle should be well into the metallic state.

6.8 More on Entropy

The role of the entropy in nanoalloys might be more important than originally assumed. Consider an alloy of Pt-Ni shown Figure 6-6a). This is a cubic superlattice with the average composition Pt_3Ni which is not commonly observed in bulk alloys and is determined by EDS. Figure 6-6 shows a HREM-STEM filtered image and the corresponding FFT. This image indicates that even though there is a superlattice the atom distribution is not the same along the nanoparticle. This is reflected in the FFT superlattice (100) spots which are spread out around a central point. If we apply the GPA method to find the strain distribution the result shown in Figure 6-7 indicates a periodic strain formed by regions of compressive and tensile strain in an almost periodic way.

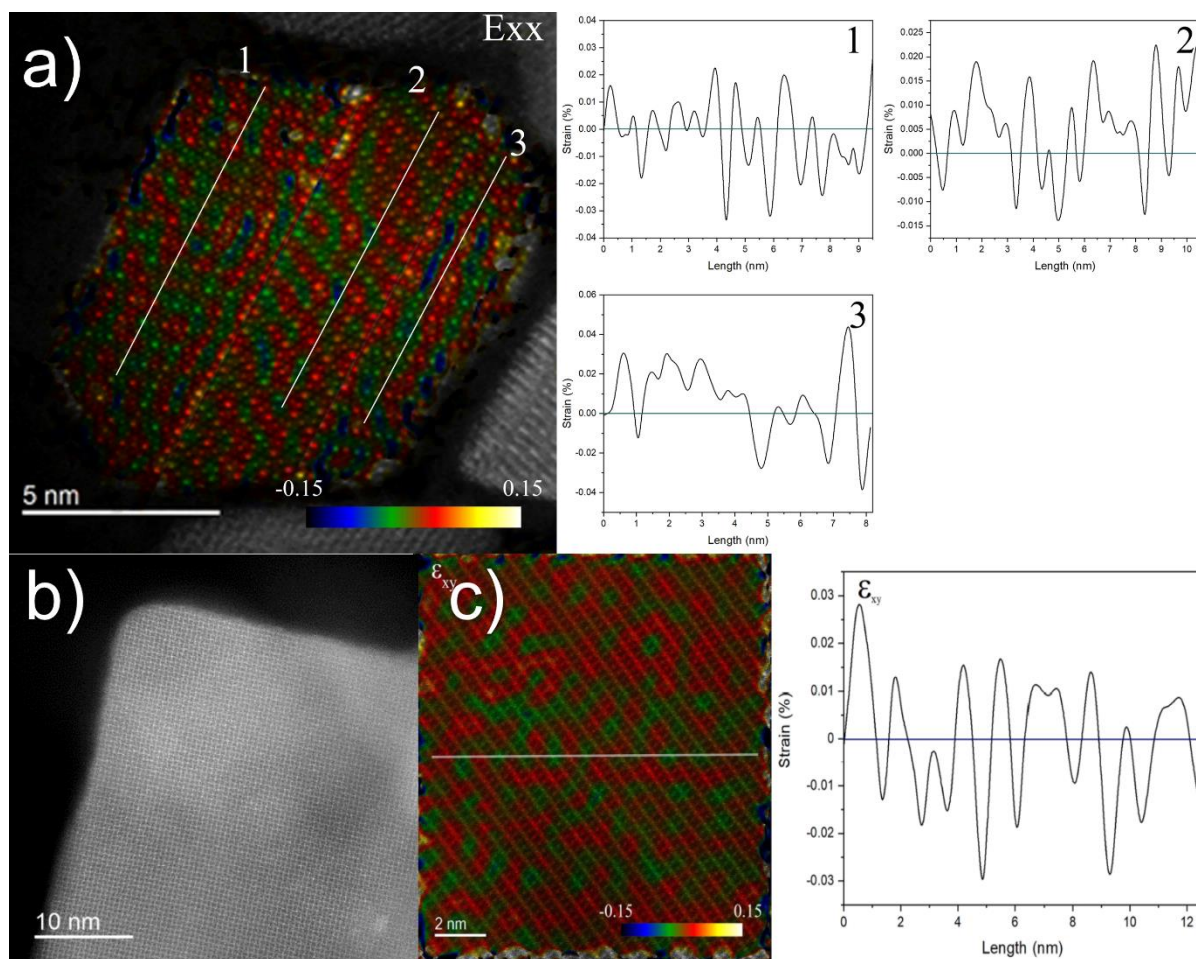


Figure 6-8: Two examples of periodic strain in nanoalloys. Top a) shows an Rh-Ni alloy GPA and its corresponding linear plots of the strain along the lines marked on the GPA. The bottom, b) & c) show a STEM-HAADF image of Al-Cu-Fe alloy with the GPA map c) and strain plot along a line indicated on the GPA.

We have performed some calculations of the strain. First, we build up a nanoparticle with a Pt_3Ni overall composition but made “strips” of varying concentration. Then we calculated the STEM-HAADF image and the GPA map. The results shown in Figure 6-7 indicate that this reproduces the experimental GPA. On the other hand, if we assume a random distribution of elements, the periodic strain cannot be reproduced.

We believe that the periodic strain comes from the fact that the growth of the nanoalloys is heavily influenced by maximizing the entropy. This is done by producing local variations in the composition. This appears to be the case in several other nanoalloys. Figure 6-8 shows an example of Rh-Ni and Al-Cu-Fe alloys respectively. In both cases the strain is periodic.

6.9 Conclusion

In advancing the nanoalloys field the introduction of multi-metallic alloys appears to be an important way forward. The metallurgy of bulk alloys has advanced dramatically in the last decade by the introducing of non-conventional alloys such as the high entropy alloy. We can foresee that the same trend will happen in nanoalloys. In this paper, we have discussed some of the important topics that should be addressed. Major issues are the role of entropy and of the twin boundaries (and other CSL boundaries). These seem to play a dominant role on determining the structure of nanoalloys. As we have shown both the entropy and the $\Sigma 3$ boundaries become more important as we increase the number of components and help to produce stable structures. However, in this field cooperation between theory and experiment is required. With the advances in artificial intelligence and machine learning techniques, time spent modeling these structures could be of worth, especially as the structures become more complex. We have now the instrumentation, analytical and theoretical methods needed for the advancement of the field.

Chapter 7 Decahedra and icosahedra everywhere: The anomalous crystallization of Au and other metals at the nanoscale

This chapter is based on the published article ref [149]

Throughout history objects with five-fold symmetry have been a popular topic of interest for artists, philosophers, and scientists. This may be because five-fold symmetry is very conspicuous in nature. In the case of crystals, five-fold rotational symmetry is mathematically forbidden, and macroscopic crystals exhibiting five-fold symmetry have never been shown to exist.

Nevertheless, in the nanoworld we often find nanoparticles with decahedral and icosahedral shapes that have an overall pseudo five-fold symmetry. These structures are observed at many



Figure 7-1: Examples of five-fold symmetry in nature. Three kinds of flowers with five leaves. Seashells with five-fold symmetry in growth.

length scales from 1 nm up to 1 μm . In this review we discuss several reasons for the stability of five-fold nanoparticles. These include the formation of twin boundaries, surface reconstruction faceting and other factors.

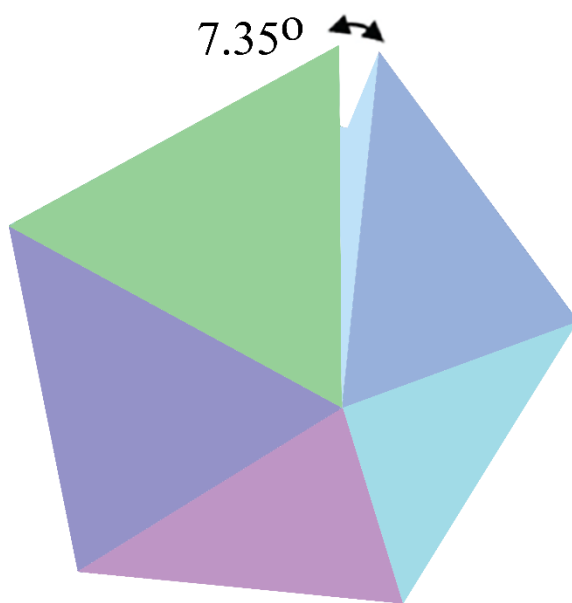


Figure 7-2: Image showing five-fold symmetry and the gap introduced due to the integer value of five not being allowed for rotational symmetry. Reprinted (adapted) with permission from Casillas et al., A New Mechanism of Stabilization of Large Decahedral Nanoparticles. *Journal of Physical Chemistry C*, 2012. **116**(15): p. 8844-8848. Copyright 2012 American Chemical Society.

7.1 Introduction

Objects with five-fold symmetry are very common in nature. We can see it in flowers, seashells and other objects[150] (as illustrated in **Figure 7-1**). It is known that in plants five-fold arrangements increase light harvesting and therefore photosynthesis[150]. In the case of classical crystals, it is established that in a bulk crystal the rotational symmetry $360/n$ can only have $n = 1, 2, 3, 4$ and 6 which results in repeatable rotation angle values. Five-fold symmetry, where $n=5$ is not allowed in classical crystals. We can explain this if the rotational symmetry reflects the shape of a polygon. We can fill the space with squares, triangles, and hexagons, but we cannot do it with pentagons. Suppose that we want to fabricate a decahedron from a pack of regular tetrahedra, and the rotation angle of the decahedron is 72° or $360^\circ/5$. The result is shown in **Figure**

7-2 and we end up with a gap. To close the gap strain on the tetrahedral units is necessary. It becomes clear that decahedral structures are not likely to be stable if crystal growth continues after their formation, and in bulk crystals, decahedral structures have been never observed. The discovery of quasicrystals indicates that true rotational five-fold symmetry can exist in a bulk solid however the price to pay is a lack of translational symmetry[56].

In the nanoworld however, decahedral structures are easily formed from sizes of a few nanometers up to several micrometers. Five-fold structures have been observed in different cases such as metals, alloys, semiconductors[151], carbon in fullerenes, diamond[3] and many other compounds. A large proportion of viruses have an icosahedral capsid[152-154]. In the case of carbon, the five-fold structure can be easily understood since all the atomic bonds are satisfied, but the case for metals is much more intriguing.

In this paper we will review the main mechanisms that explain the unanticipated stability of decahedral and icosahedral single metal nanoparticles. Decahedral and icosahedral structures formed at different sizes are shown in **Figure 7-3**. To study metal nanoparticles, transmission electron microscopy (TEM) has been a fundamental technique for understanding nanoparticle structure. Initially dark field images were used but the resolution of the TEM was limited[86, 98, 155]. An important advancement was the use of high-resolution machines in the late 70's[156]. The introduction of image and probe aberration correctors two decades ago produced a quantum change in our understanding of metallic nanoparticles. The generalized use of High Angle Annular Dark Field (HAADF) on the scanning transmission mode (STEM) increased our understanding of atomic positions and therefore strain.

The topic of five-fold symmetry in nanoparticles has created a very large field of interest by the scientific community. Marks has reported more than 60,000 papers in which the word

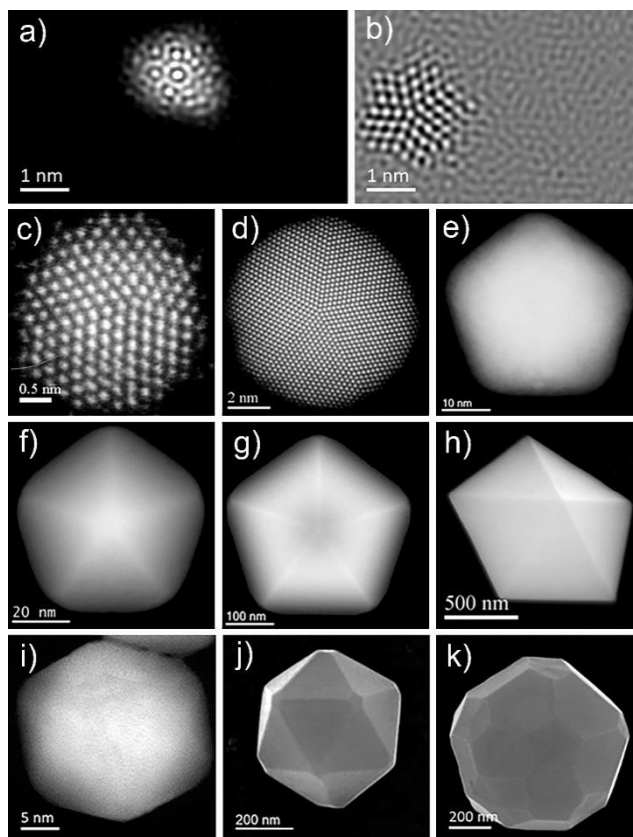


Figure 7-3: Examples of decahedral and icosahedral structures shown at different sizes. The five-fold symmetry can be seen in all the structures from the a) cluster size all the way to h) the microparticle size. Reprinted (adapted) with permission from Casillas et al., A New Mechanism of Stabilization of Large Decahedral Nanoparticles. *Journal of Physical Chemistry C*, 2012. **116**(15): p. 8844-8848. Copyright 2012 American Chemical Society.

nanoparticle appears[35]. If we narrow the search to papers containing the words decahedral and icosahedral more than 2,658 references appear. This clearly indicates the broad interest in this topic. Despite that extensive work, many problems remain. In this review, we will describe some of the interesting topics to be examined. We will discuss the nanoparticles as a function of size because as the number of atoms in the nanoparticle increases the properties change.

7.2 The case of clusters with a small number of atoms (size <2.5nm)

A first case of interest are clusters. The pioneering work of Farges on argon clusters[157] and the Borel group in metals[158, 159] showed that five-fold clusters can be produced in a molecular beam. Clusters often contain one or more kernels with five-fold symmetry. Examples

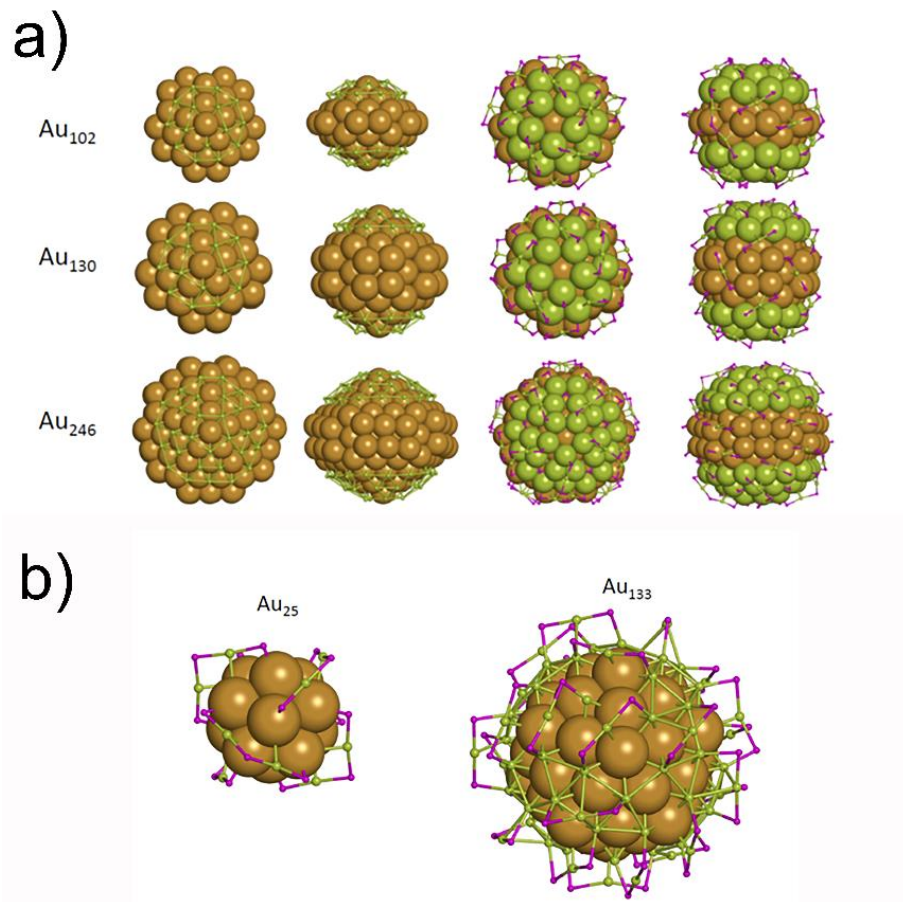


Figure 7-4: Here, several clusters of different atomic numbers are shown. In these clusters, there are areas that show five-fold symmetry.

of decahedral clusters are the experimental results for Au_{20} [160], Au_{103} , Au_{130} [161] and Au_{246} [162]. A selection of gold clusters is shown in **Figure 7-4**.

In addition, Rossi and Ferrando have predicted a large number of poly-decahedral clusters[163]. Examples of icosahedral clusters are Au_{25} [164], Au_{144} [165] and several others. A remarkable cluster is the predicted icosahedral cluster Au_{60} [166, 167] which connects metals with fullerenes. In addition, several icosahedral cluster cages have been predicted[168, 169]. Finding those clusters experimentally is one of the most attractive challenges for researchers in this field.

It should be noted that in clusters the number of atoms on the surface is an important fraction of the total atoms. For Instance, in a one shell icosahedron 12 of the 13 atoms will be on the surface. In a 3-shell icosahedron of 147 atoms, 92 will be on the surface. The latter cluster has a size of ~ 1.5 nm. In a 6-shell icosahedron of 923 atoms, 362 will be on the surface and will have a size of ~ 2.8 nm. The organic molecules on the surface bond strongly to the surface atoms and induce distortion which can propagate to the interior layers. Small strain can change the structure from FCC to decahedral. As noted by Bagley[170], if we assumed that each tetrahedron is distorted to a body centered orthorhombic lattice (BCO) all the tetrahedra will fit and no gap will be present. The lattice parameters of the BCO are $a=1$, $b=1.37$ and $c=1.05$ (in normalized units). This model was expanded by Yang[171] and Yacaman et al.[172, 173] and appears to be plausible for very small clusters. Barnard and Chen[174] have shown that the decahedral and FCC shapes are equally likely for small nanoparticles, if a decahedral nucleus is very likely. During the growth of clusters an initial rapid coarsening stage is produced where there is no shape-selectivity, but during which shapes with a combination of (111)[175, 176] and (100) facets deviate from the geometric ideals. So, a shape distribution like the one shown in **Figure 7-4** will be the most common case.

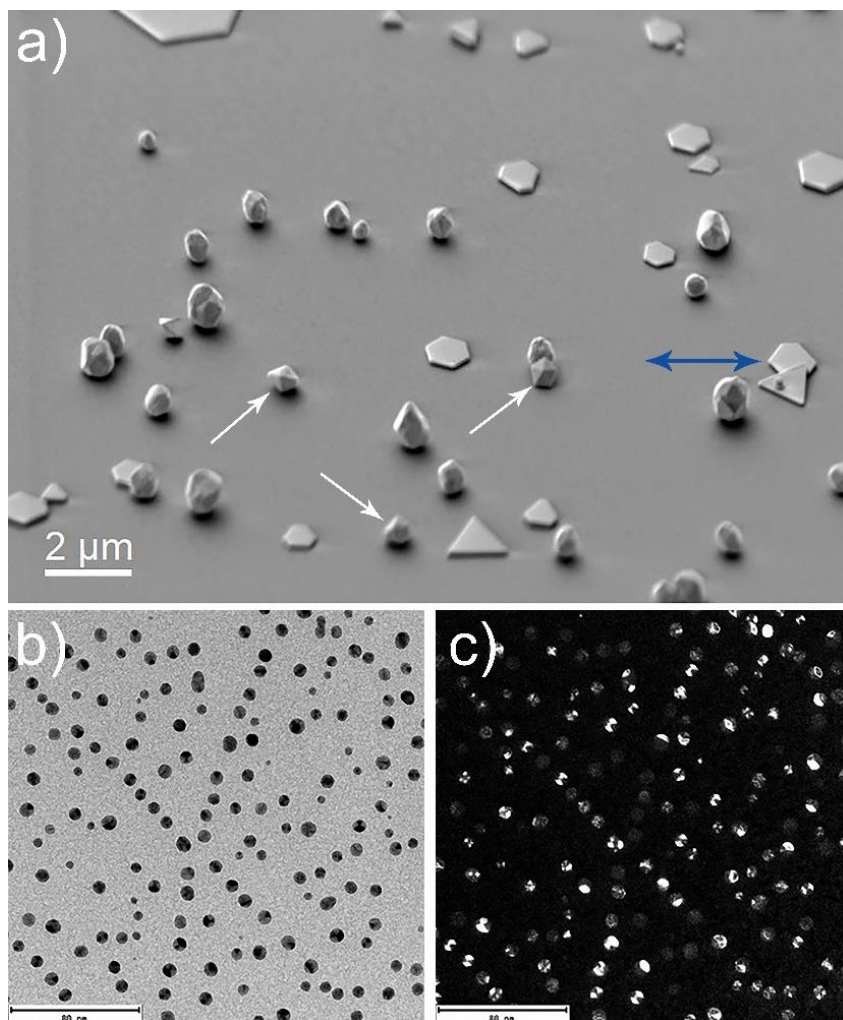


Figure 7-5: (a) SEM image showing the overall shape of micro-size particles. (b & c) Bright-field and dark-field images of Au nanoparticles. Dark-field imaging reveals their structure.

7.3 Nanoparticles with size >2.5 nm

The case of nanoparticles with a larger size it is very different than that of clusters. As the size increases the atoms in the interior become increasingly important. New mechanisms emerge to control the shape and equilibrium of nanoparticles. At first glance we expect the rules of crystallography will fully dominate the growth. Decahedral and icosahedral gold nanoparticles were first reported by Ino and Ogawa[98] and Alpress and Sanders[96]. Several calculations indicate that the decahedral and icosahedral nanoparticles are not stable beyond 2-3 nm in size[102, 103, 120, 177]. Nevertheless, when nanoparticles > 3 nm are prepared the decahedral

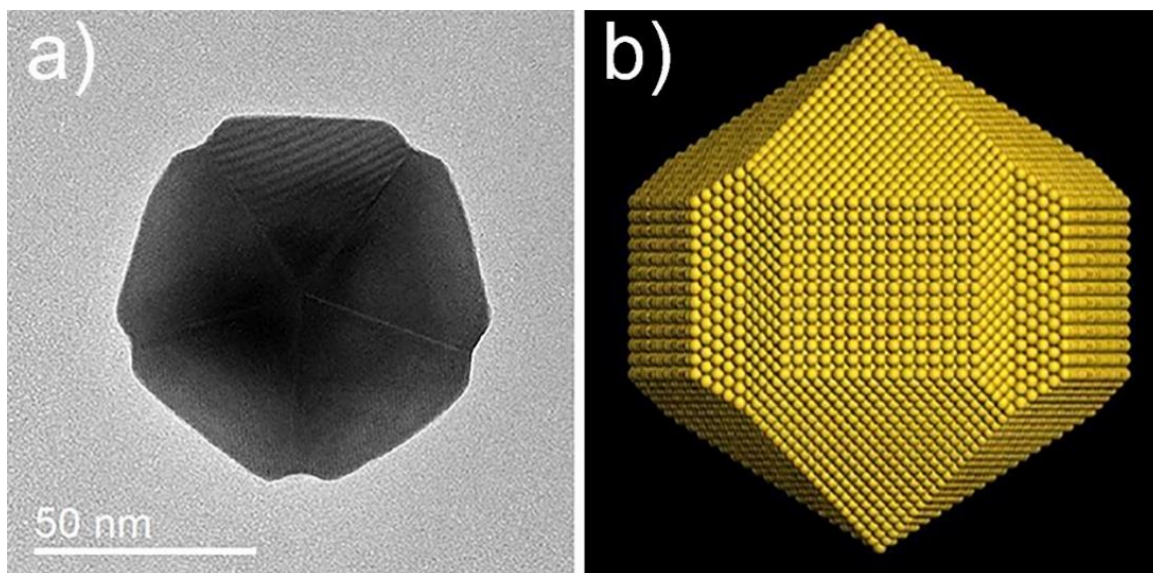


Figure 7-6: The Marks Decahedron showing the facets created in the particles. (a) Five-fold and (b) lateral views. Reprinted (adapted) with permission from Casillas et al., A New Mechanism of Stabilization of Large Decahedral Nanoparticles. *Journal of Physical Chemistry C*, 2012. **116**(15): p. 8844-8848. Copyright 2012 American Chemical Society.

and icosahedral shapes dominate. A typical sample of Au nanoparticles is shown in **Figure 7-5**. As can be seen, most nanoparticles have a decahedral shape (marked by arrows) or a polyhedral decahedron (double lines) or icosahedral (thick) arrow. A significant number are hexagonal or triangular platelets which are known to have twins parallel to the surface[178]. An examination of larger area shows that only 105 of the particles correspond to a non-twinned FCC structure. A similar result has been reported by Koga[179].

A question arises of how to explain the stability of five-fold symmetry in large particles. A first approach was reported by Ino[97] based on the minimization of the internal energy and application of the Wulff construction. This author predicted that (100) facets will develop into the decahedra. This structure is known as the Ino decahedra[105, 178].

A very important breakthrough was the work of Marks who introduced the twin boundaries contributions to the Gibbs free energy[180]. The result is that the particle will become faceted as shown in **Figure 7-6**. This structure was called “Marks Decahedron” by Landman[181, 182]. The name was widely accepted and is now a classical term in nanoparticles.

The theoretical aspect of the Marks decahedron was later expanded by Patala et al[135]. Several other similar nanoparticle truncations have been reported in the literature for decahedral particles[36, 179] and for icosahedral particles[183]. The stability of the Marks Decahedron is remarkable. We perform some nanoparticle heating using electron irradiation. In **Figure 7-7**, we show a decahedral nanoparticle grown by evaporation on a substrate. The particle has straight facets and most likely was kinetically stabilized. After heating with the e-beam the nanoparticle becomes a Marks Decahedron (that indicates that the MD corresponds to a lower energy configuration. This supports the idea that twins and faceting introduce stability on the five-fold nanoparticles.

It has been established that twins are favored in nanocrystal growth[90, 91]. The so called WHS theory (Wagner, Hamilton and Seidensticker) predicts that twins in nanocrystals play the same role that dislocations do in bulk crystal growth. During the crystal growth, atoms arriving from the gas (or liquid phase) will be deposited to the lowest energy (111) facets.

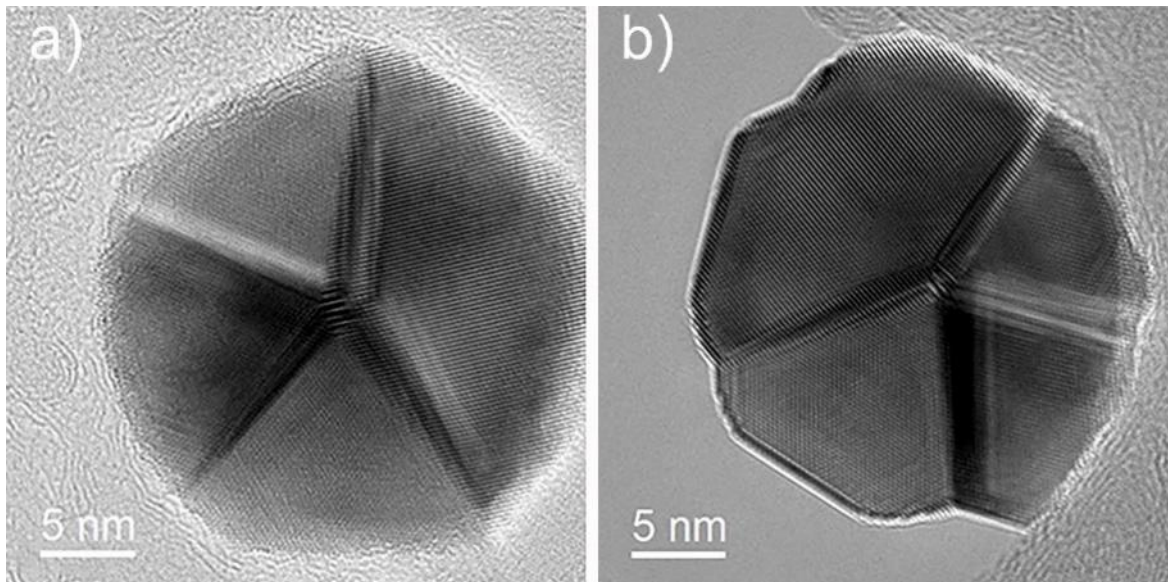


Figure 7-7: A particle grown on a substrate a) before electron heating. b) shows the particle after heating with the electron beam. The particle now shows facets and is a Marks Decahedron.

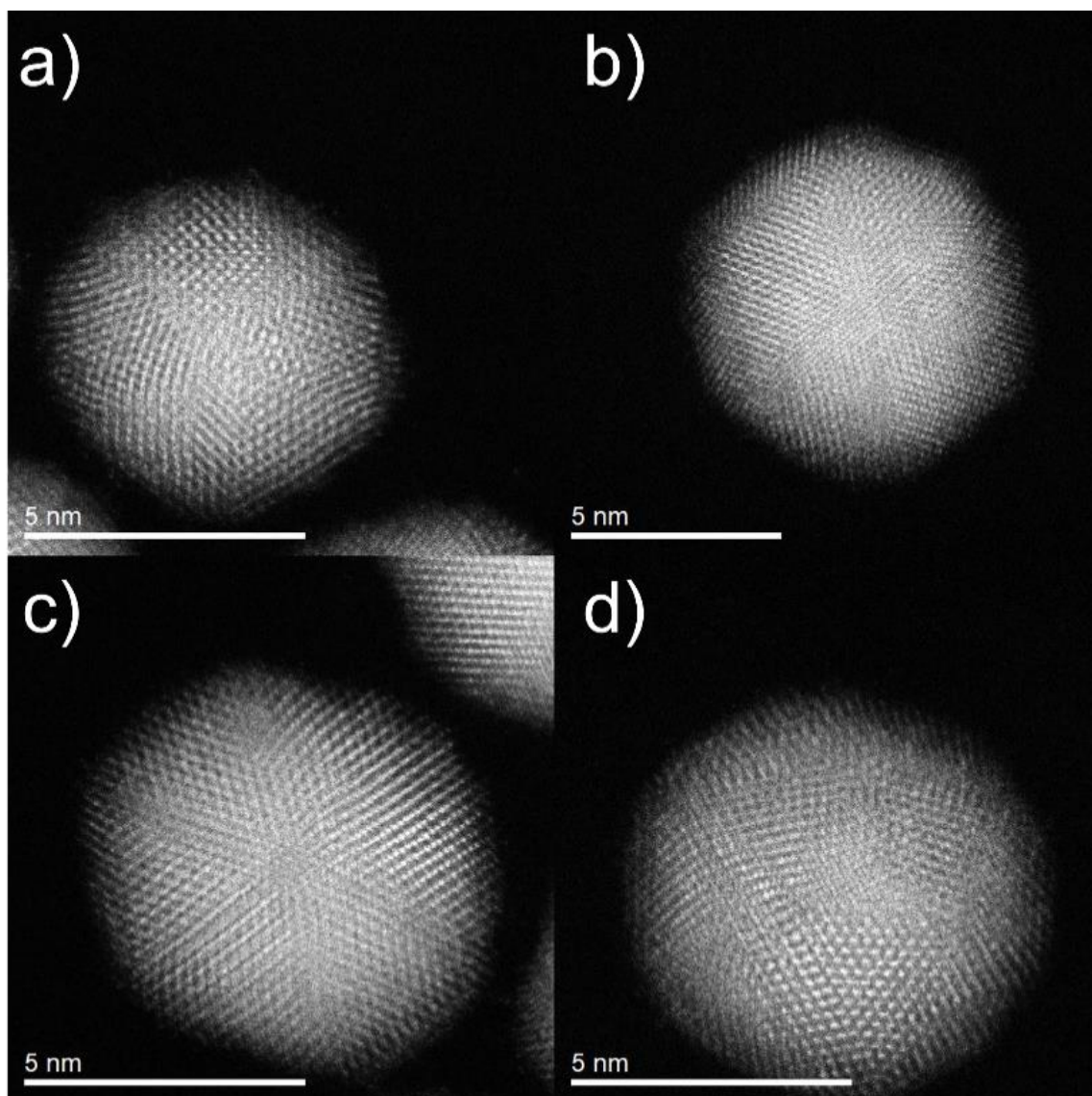


Figure 7-8: HAADF-STEM images of gold icosahedral nanoparticles in four different orientations. It can be observed that the near surface layers the atoms have a different stacking.

However, the chances to nucleate a new layer (111) in the correct or incorrect registry are the same. Thus, a completely random stacking sequence of close packed layers, for example ...BCABACABA ..., would seem to be more favorable than either ...ABCABC... (fcc) or ...ABABAB... (hcp). This is not what is observed. In the WHS model, a single twin is introduced which favors nucleation in 4-coordinated sites. A nucleated island will spread over the two faces forming the reentrant corner until it reaches the extensions of the adjoining faces. This type of growth results in thin hexagonal platelets with well developed (111) faces, as the ones observed

in **Figure 7-5**. Clearly, the reason for this is the absence of grooves and ridges on the (111) faces. In order to explain 3-growth it is necessary to assume a second twin lamella that intersects the (111) faces. This is the cross twin mechanism discovered by van der Waal[40]. Cross twinning leads directly to the formation of five-fold twins. Twins stabilize the nanoparticles, and along with surface faceting this might explain the prevalence of the five-fold shapes.

In addition, there is another possibility for growth of decahedral and icosahedral nanoparticles as reported by El Koraychy et al.[105] and Ma et al.[52] Decahedral and icosahedral nanoparticles can grow by coalescence of individual tetrahedra. This mechanism was first described by Balleto et al. for silver nanoclusters[184]. It is clear that for both mechanisms the decahedral and icosahedral particles are kinetically formed. Nevertheless, they are remarkably stable as we will show latter.

In the case of icosahedral particles an additional feature is observed in the layer stacking. As predicted by Settem and Kanjarla and Nelli and Ferrando[185, 186] the surface is reconstructed showing anti-Mackay stacking. We have systematically observed that in icosahedral particles the last few layers show a different stacking as shown in **Figure 7-8**. In the figure, four different nanoparticle orientations can be observed. In each case the near surface layers have a different stacking. In the icosahedral nanoparticles it is more difficult to obtain a low index plane that is aligned with the electron beam. Therefore, atomic resolution becomes more complicated to interpret. So, at this point we cannot fully corroborate that the stacking corresponds to anti-Mackay stacking. However, it seems difficult to explain the observed contrast with other mechanism. More research in this topic is needed.

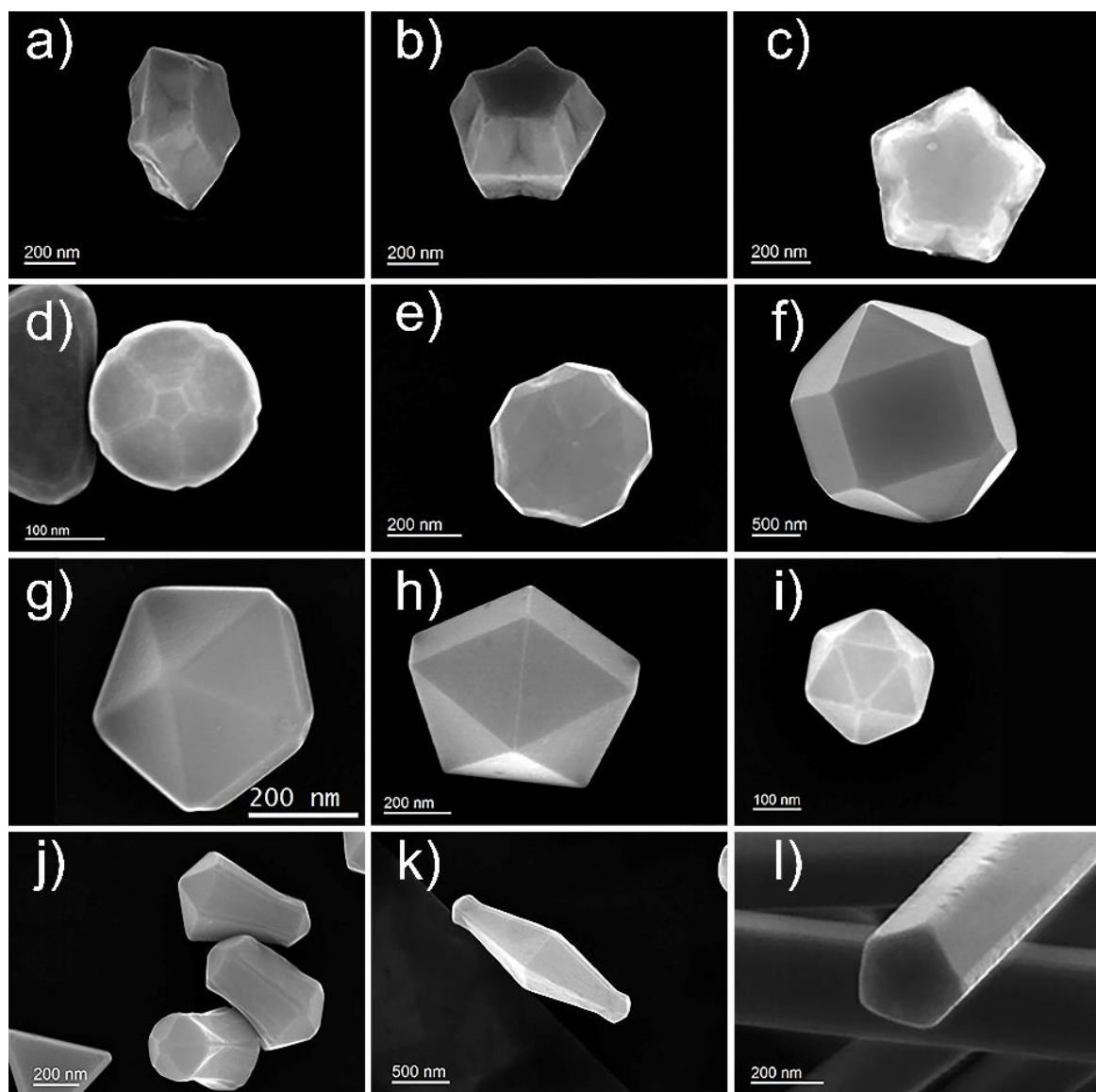


Figure 7-9: Various nanoparticles related to the decahedral and icosahedral shapes.

7.4 Nanoparticles with a size >100nm

As nanoparticles grow close to the micrometer range, several other polyhedral geometries begin to develop. A first group are the particles related to the decahedral and icosahedral geometry, some of these are shown in **Figure 7-9**. These structures include truncations of different types such as the Marks decahedron. However, there are additional geometries which produced shapes with even larger truncations. An interesting fact is that the Ino decahedra are observed frequently. If during the growth of the nanoparticle a surfactant is used to promote

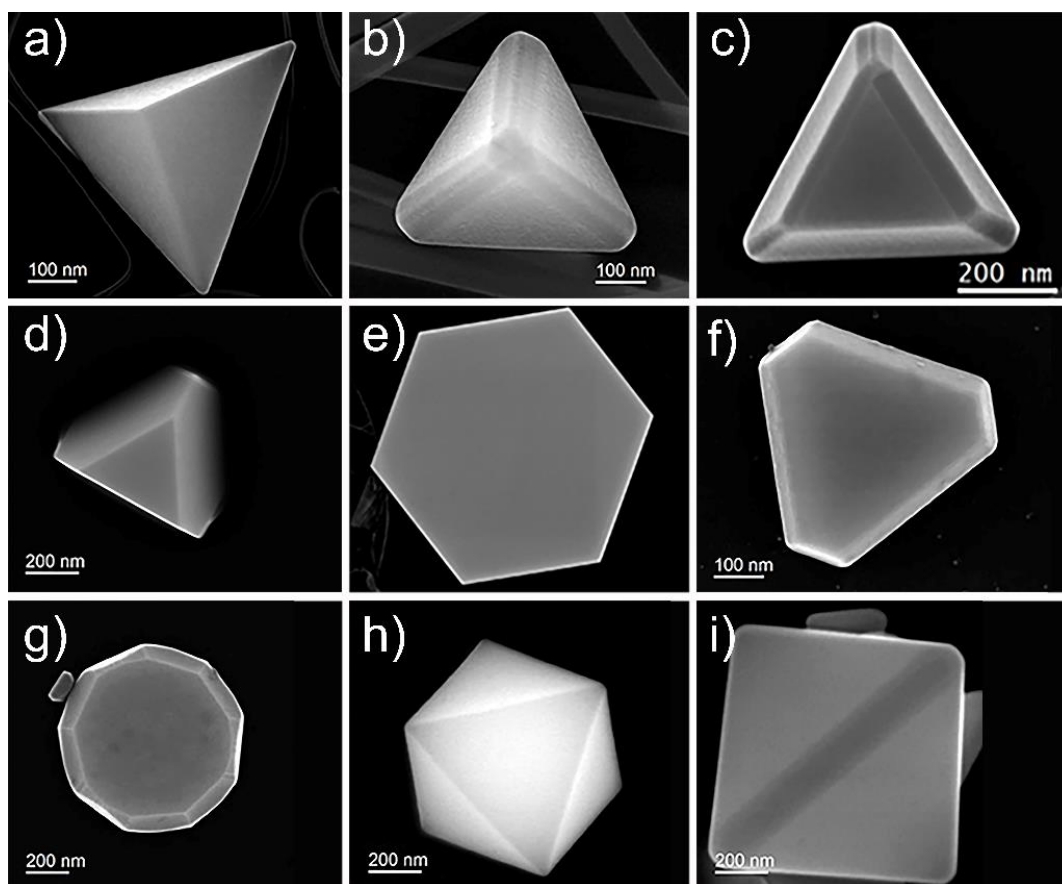


Figure 7-10: Micro-scale particles showing twin boundaries.

growth in a given direction, we see a myriad of elongated shapes which eventually lead to nanowires or nanorods. In the case of icosahedron, we can see the truncations described by Chui et al[187]. It should be mention that as demonstrated by Ma et al., decahedral and icosahedral nanoparticles can grow by coalescence of individual tetrahedra[134]. This can result in very large nanoparticles.

A second group of shapes are the ones corresponding to regular shapes shown in **Figure 7-10**. Most significant fact is that all the nanoparticles contain twins. An important portion of the observed nanoparticles have a hexagonal, triangular, tetrahedral, cubic and truncated platelets. All these particles have a twin parallel to the surface[188]. When looking at the particles in **Figure 7-9, a), b), and h)** the twin are going through the particle. In **c) through g)**, the twin in along the edge of the particle. The twin is diagonal through the particle in the case of the cubic

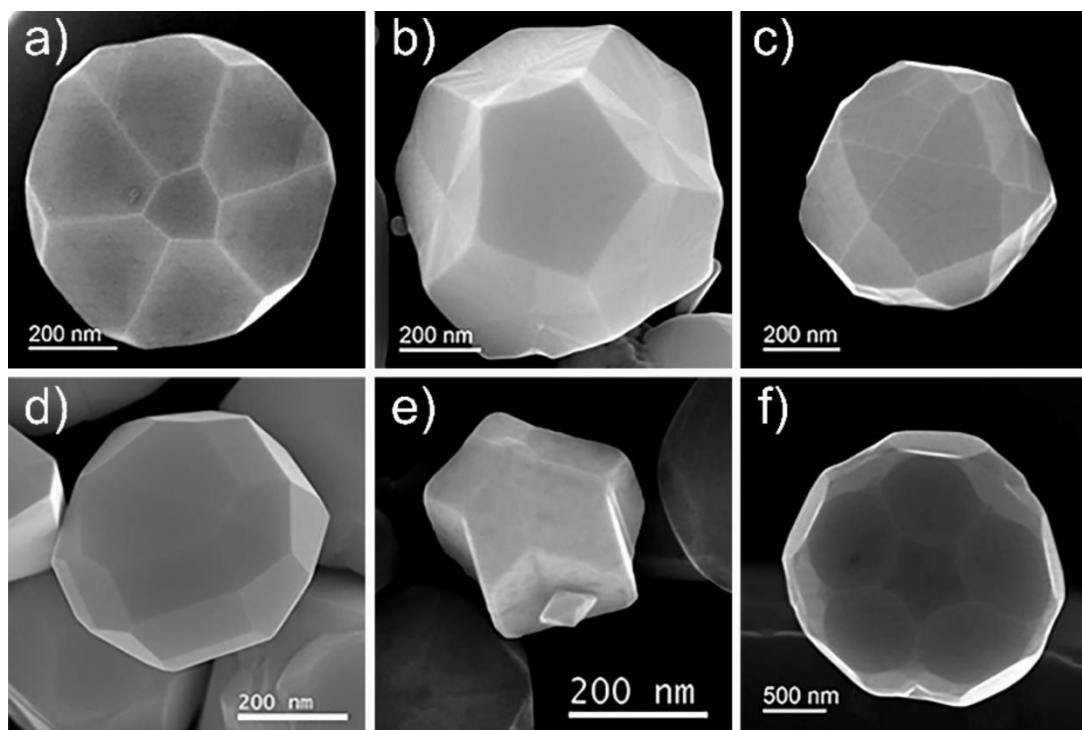


Figure 7-11: Various types of Johnson solids.

particle shown in **Figure 7-10 i**), which is a twin across the (110) direction. In addition, we have different polyhedral such as: Trapezoid rhombic dodecahedron, truncated triakis icosahedron, the elongated pentagonal pyramid, the rhombicosidodecahedron and others which are part of the Johnson Solids. Those are shown in **Figure 7-11**. The growth of these shapes were discussed by Mariscal et al.[189] and Niu and Xu[190] who showed that Johnson solids can be expected for larger particles.

If during the particle growth, we add a surfactant, such as PVP, that will promote unidirectional growth in some lattice directions we end with elongated structures such as the silver nanowires[178] or gold nano stars[51, 191, 192]. Some of these shapes are shown in **Figure 7-12**.

Gold particles were synthesized via the polyol method using ethylene glycol (EG) and PVP (0.208g) in EG (5 mL) at 280° C. The solution was withdrawn from the heat source and was cooled very rapidly in ice. Depending on the growth conditions, the particles can develop

multiple faceting and the surface formation of a Zig-Zag faceting pattern as they get larger, this is shown in **Figure 7-13**.

We were able to study some of these particles in an aberration corrected TEM. A decahedral particle was placed in such a way that the surface was perpendicular to the e-beam. The result is shown in **Figure 7-14 a)** and **b)** which shows the decahedron at low magnification. HAADF images using an aberration corrected instrument shows that the corners are faceted as expected in a Marks decahedron (**Figure 7-14 c)**. However, the surface between corners is formed by rounded promontories as shown in **Figure 7-14 d)**. High magnification is seen in **Figure 7-14 e)**. By using Cs-corrected STEM, it is possible to get atomic resolution imaging and determine the planes corresponding to these facets. The angle between the facets and the (001) planes is 14.8 degrees on average, while in a perfect crystal a (511) facet makes an angle of 15.79 degrees, with respect to a (001) plane. This is the best match; and the slight difference can be attributed to the rounded edges that connect the facets due to surface tension, as well as the internal strain existent in the lattice of the decahedron. The reason for this stability is that during synthesis fast cooling atoms of the nanoparticles do not have time to rearrange. This indicates that this is a kinetically driven shape. This is possible due to the stabilizing effect of the PVP; however, if removed, the facets will disappear. In this case, particles have rounded and smooth edges (**Figure 7-15**).

The result is a decahedron with no high index facets and very round contours at the twin boundaries. Hexagonal strings along the (110) orientation on the (001) terraces near the steps (**Figure 7-15b**) were observed, as well as strings along the (410) direction (**Figure 7-15c**). It has been proven that this reconstruction is more stable than the unreconstructed surfaces[7, 193]. This hexagonal reconstruction can take place by two different dislocations: dislocations formed

by 5 and 3 columns of atoms. These types of dislocations, as described by Pao et al.[194] refer to the “arc” formed by 5 columns of atoms as a dislocation of type I and the one formed by 3 columns of atoms as a dislocation of type II. Both dislocations occur due to the insertion of an

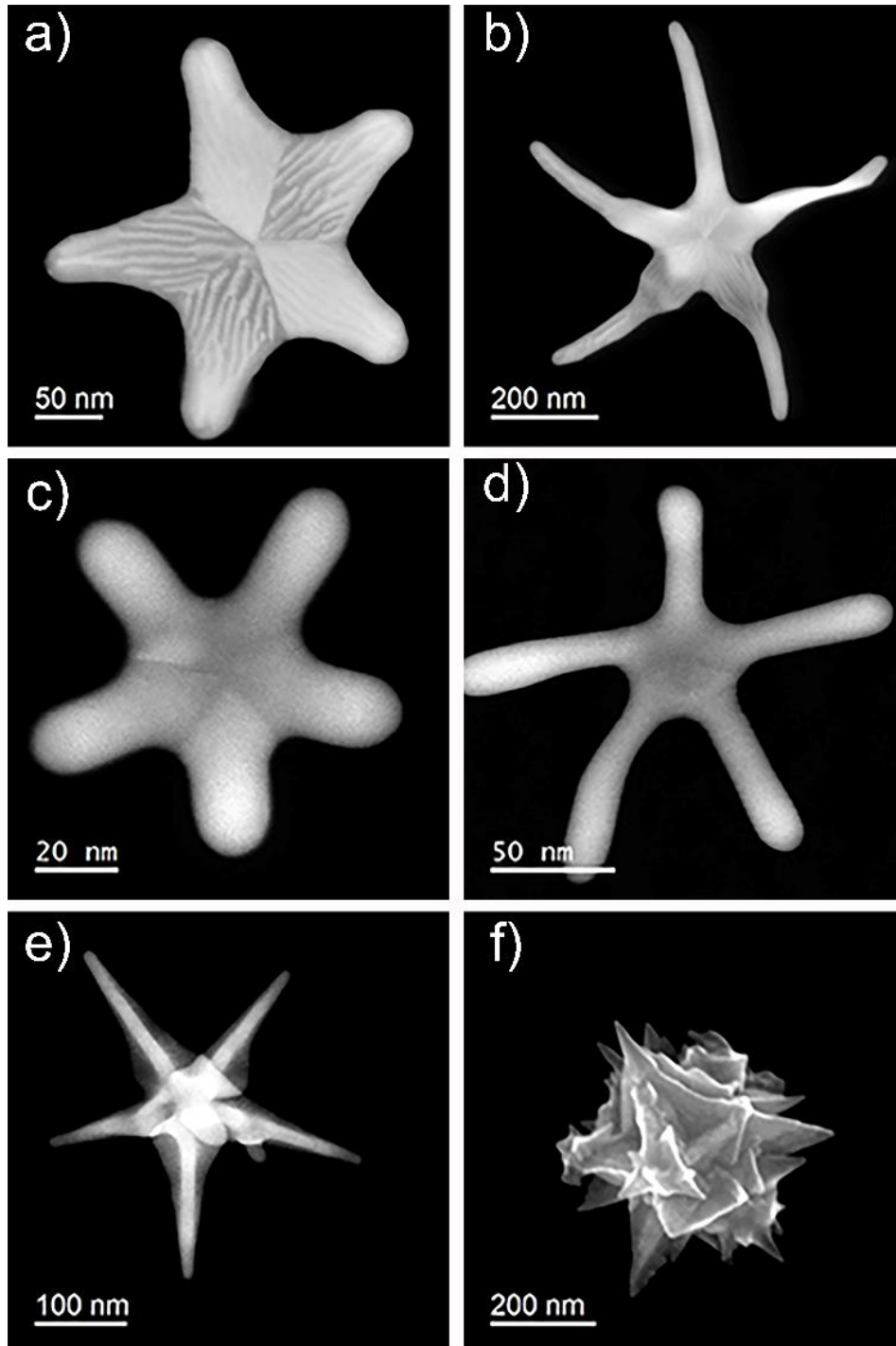


Figure 7-12: Different shapes can be obtained if during the growth process something is added to promote unidirectional growth.

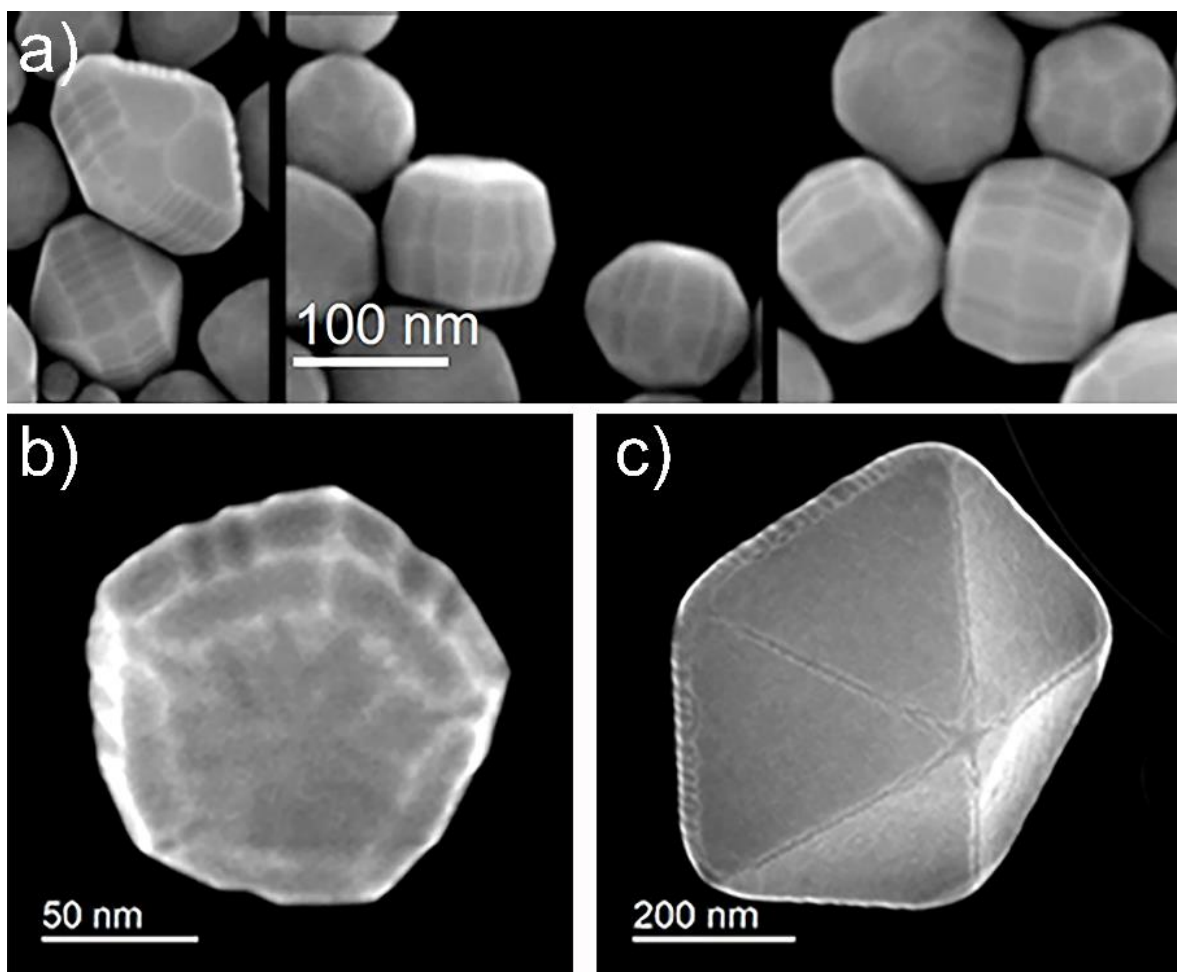


Figure 7-13: Gold nanoparticles that were cooled rapidly after synthesis in ice. The particles develop multiple facets and the formation of a Zig-Zag faceting pattern.

extra row of atoms to the (001) surface; however, they have different consequences in the stability of the surface. While type I dislocations increase the tensile strain, type II decrease it. On the other hand, they have the opposite effect on the surface energy, while type I dislocations decrease the surface energy, type II increase it. Formation of ridges and surface reconstruction is an additional factor to stabilize the nanoparticles as reported by Casillas et al[195].

7.5 Strain in decahedral nanoparticles

It is expected that decahedral particles will have strain to close the gap, produced by the packing of regular FCC tetrahedra's we mention above. In the case of clusters, there is an easy pathway to a distortion from FCC-BCO. However, for larger particles, in which the role of the

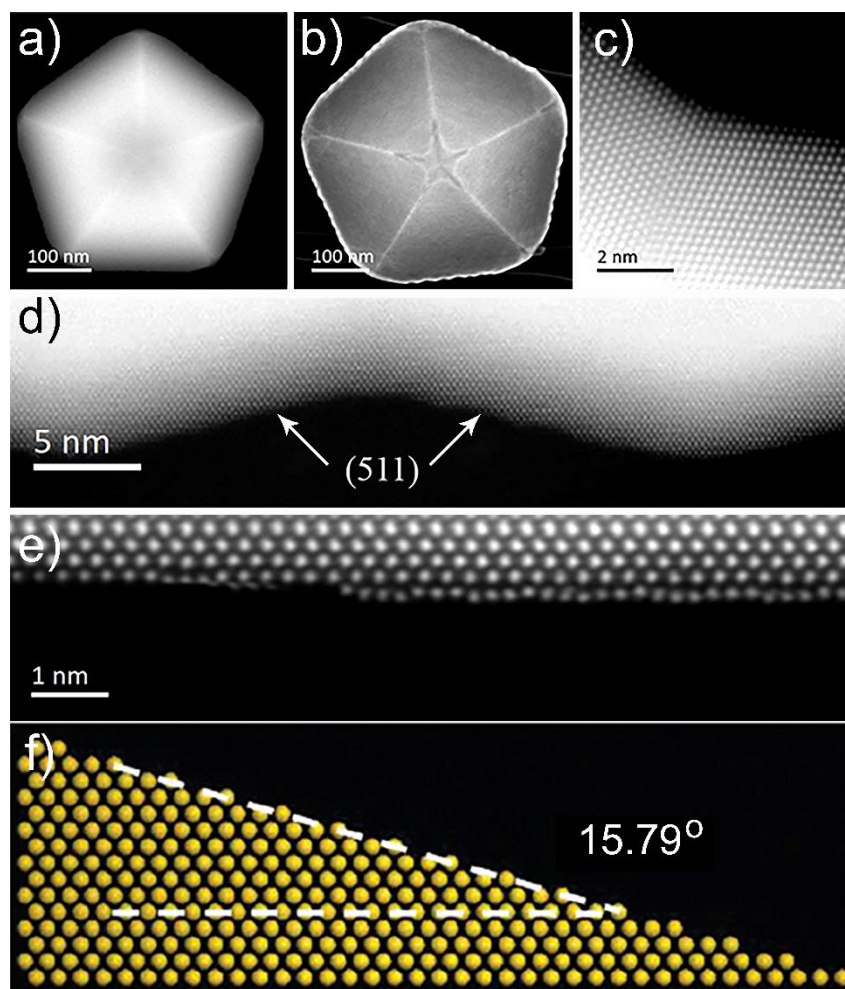


Figure 7-14: HAADF images of a gold nanoparticle that developed the zigzag pattern around the facet. The decahedral particle was oriented perpendicular to the e-beam. a) and b) show the decahedron at low mag. Marks decahedron (Figure 13 c). d) shows the corners are formed by rounded promontories. e) shows a high magnification of the edge of the particle. The angle between the facets and the (001) planes is 14.8-degree average while f) a perfect crystal (511) facet makes an angle of 15.79 degrees. Reprinted (adapted) with permission from Casillas et al., A New Mechanism of Stabilization of Large Decahedral Nanoparticles. *Journal of Physical Chemistry C*, 2012. **116**(15): p. 8844-8848. Copyright 2012 American Chemical Society.

surface is reduced, it does not seem a likely mechanism. Homogeneous strain in decahedral structures was first introduced by Ino[97] and de Witt[196]. Later more sophisticated models were introduced by the group of Romanov[197-199]. Theoretical work by Patala et al[135, 200] demonstrated the role of strain in stabilizing the shape. Experimental reports on strain in decahedral nanoparticles are contradictory. On one hand, some works support homogeneous

strain coupled with lattice bending[201]. On the other hand, some works support inhomogeneous strain[202].

To study this problem, we have used three different methods. The first one is the weak beam dark field method (WBDF). This method shows thickness fringes which can be used to study the shape of nanoparticles[86, 203]. The fringe contrast is also very sensitive to strain. In general fringes will be a superposition of thickness and bend contours. The use of Field Emission Gun Microscopes and CMOS cameras has allowed improved WBDF images. An example of WBDF images taking different diffraction spots to produce images of different sections of the decahedra, and these images are shown in **Figure 7-16**. The weak beam fringes are evenly spaced with a period equal to the extinction distance. However, if we measure the intensity variations along a thickness fringe, we can see intensity variations. Fringe space is modified by dynamical diffraction, however, variations of intensity along a fringe variation can only be due to strain. By tilting the sample in a slightly different direction we get the image of **Figure 7-16e**) in which stacking faults at the twin boundary are observed.

A second method is based on the analysis of a HAADF-STEM aberration corrected image. In this case the atomic columns on the image represent the true atomic positions. **Figure 7-17a**) shows a HAADF-STEM image of a decahedral particle. The FFT shows, **Figure 7-17b**), the overall five-fold symmetry (the pattern is indexed using FCC miller indexes). **Figure 7-17c**) shows the image formed using only the (111) spots and eliminating the rest. As can be seen, no strain distortion is present along the (111) planes. On the other hand, the image formed using only the spots of the (200) plane, **Figure 7-17d**), shows a very pronounced distortion. The center atomic array which is expected to be a perfect decahedron is heavily distorted.

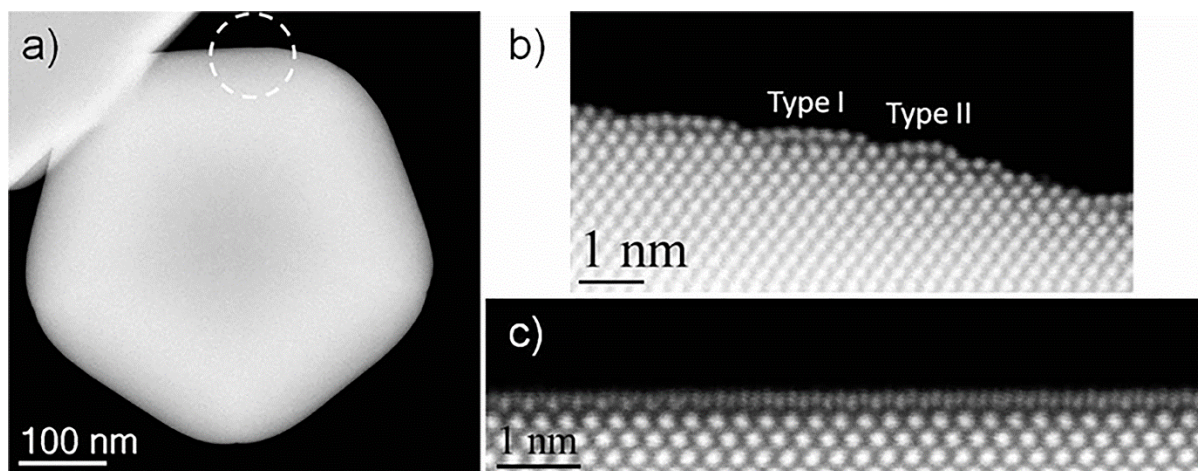


Figure 7-15: Showing a) a particle with rounded and smooth edges. b) shows hexagonal strings along the (110) orientation on the (001) terraces near the steps were observed, as well as c) strings along the (410) direction. Reprinted (adapted) with permission from Casillas et al., A New Mechanism of Stabilization of Large Decahedral Nanoparticles. *Journal of Physical Chemistry C*, 2012. **116**(15): p. 8844-8848. Copyright 2012 American Chemical Society.

A smaller particle is shown in **Figure 7--17e)** and **7-17f)** which is showing the same distortion. The incoherent twin boundaries are also apparent. The fact that the distortion appears only in the (200) planes was also reported by Peng et al[204]. A third method of measuring the strain is to apply the Geometrical Phase Analysis method[142, 143] to HAADF-STEM aberration corrected images. This method allows mapping of the strain on the image.

We have applied this method to decahedral particles. The result for the E_{xy} strain component is shown in **Figure 7-18 a)** and **b)** for two different nanoparticles. As can be seen, the strain is concentrated along the twin boundaries and on the surface regions. Our findings confirm the findings of Johnson et al[202] and the theoretical predictions of Patala et al.[135] which is the fact that the strain distribution follows the 2+2+1 pattern. That means that strain is distributed with two pairs of tetrahedra with the same strain and one with a different pattern. We conclude that the strain distribution in five-fold nanoparticles is more complicated than expected and might even be different for two particles of the same shape and size.

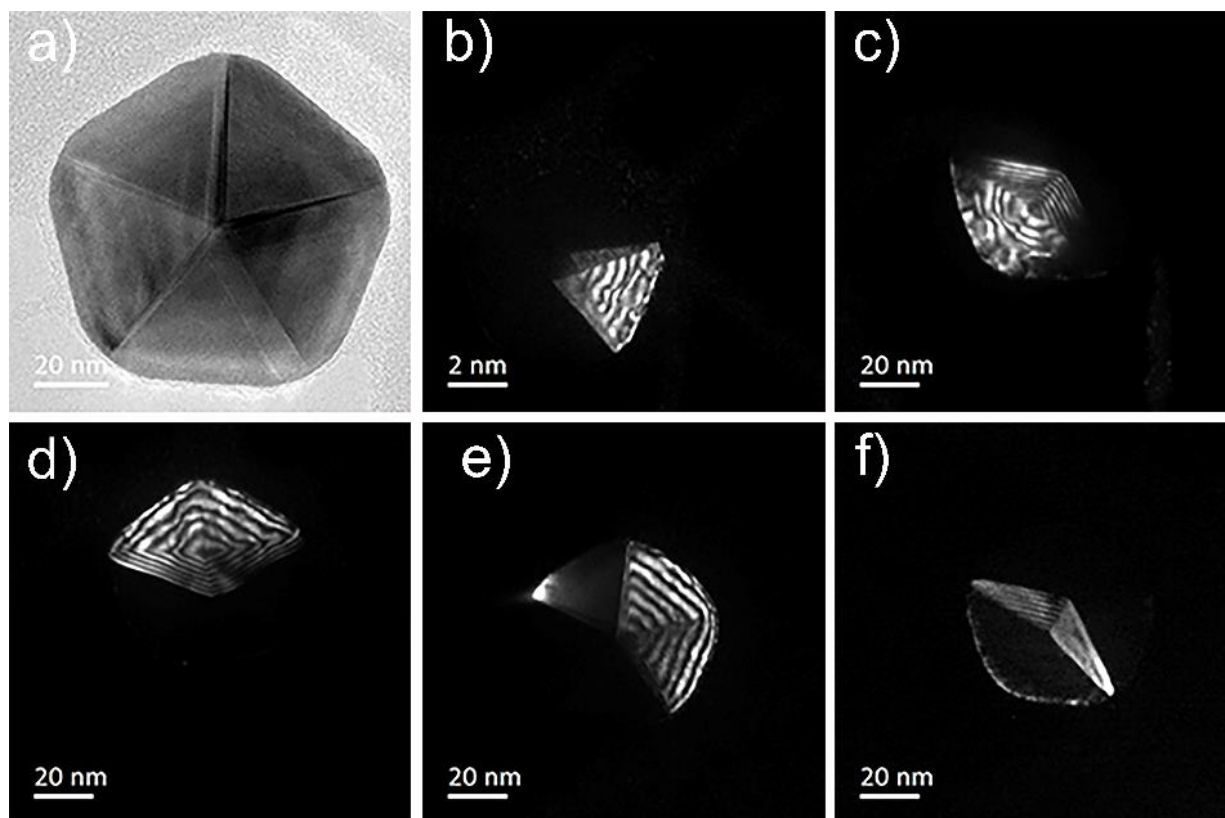


Figure 7-16: An example of Weak Beam Dark Field (WBDF) imaging. The weak beam fringes are evenly spaced with a period equal to the extinction distance. Fringe space is modified by dynamical diffraction, while variations in intensity along a fringe variation is due to strain. e) shows when the particle is tilted and the stacking faults at the twin boundary can be seen.

7.6 Other Metals and multimetallic nanoparticles

So far, we have only discussed the case of Au, however, other metals show a similar behavior. Decahedral and icosahedral structures have been reported for Pd[205, 206], Cu[175], In[207], Ag[208], Ge[209] and others[210]. In many cases the nanoparticles are grown on substrates.

The possibility of having decahedral nanoparticles increases significantly when two metals are present. Decahedral and icosahedral particles have been reported for Fe-Pt[211], Pt-Pd[212], Pt-Co[213], Au-Co and many others[81]. The theory of bimetallic alloys has been extensively reported in literature[43, 214-219]. It has been shown by Nelli et al.[218] that the evolution of bimetallic nanoparticles from initial core-shell configurations to their equilibrium

intermixed chemical ordering arises from a complex interplay between interdiffusion of atoms and shape rearrangements. Normally in synthesizing bimetallic nanoparticles the method of producing a seed and then depositing the second metal is used[46]. This results in a core shell structure. Even when the precursor salts are simultaneously reduced, the rate of formation of metal atoms is different for each salt and this also results in a core-shell structure. We have studied the case of Au-Cu[220], Au-Pd[83], Au-Ag[221] and other alloys[81]. When the core seed is decahedral (or icosahedral) the shell follows that structure. Examples are shown in **Figure 7-19**. In a) and b) there is an Au-Cu core shell structure and its EDS analysis. In c) we show an Ag-Au core shell. It is very important to note than in this case the shell (Ag) has an FCC packing. The same packing is shown in the case of Pt-Pd, as shown in d).

When elements with different atomic radii are present in a nanoparticle the internal strain increases dramatically. The subsequent structure is the result of the strain engineering in nano alloys as described by Nelli et al. and Front et al[218, 222].

The strain increases with the number of elements on the alloy. The net result is that decahedral and icosahedral shapes become even more prominent. **Figure 7-20** shows examples of from a five-metal nanoparticle (Au/Cu/Pd/Ni/Co) and a four-metal particle (Au/Cu/Co/Ni). Interestingly a core shell structure is formed with the decahedral core. The tendency to form core-shell is produced despite all the metal precursor salts are reduced simultaneously during the synthesis. In the case of multimetallic nanoparticles, the entropy makes a significant contribution to the Gibbs free energy. On the other hand, strain due to atomic radius differences becomes more significant. The particle shape will be determined by the minimization of the internal energy, including the contributions of strain and twins, and the maximization of entropy. At this

point there are still many unknowns in this area, and it represents a big challenge for researchers on nanoparticle physics.

7.7 Diffraction patterns of decahedral nanoparticles

Electron diffraction is a very powerful technique. It has become standard for researchers to use the FFT of a high-resolution micrograph as source of crystallographic data of nanoparticles. However, the FFT is not fully equal to the diffraction pattern and contains artifacts due the mathematical limitations. Electron diffraction contains more information specially about defects on structures. In recent years, the access of more coherent electron sources and aberration correction haves allowed the possibility of obtaining parallel beam diffraction with nanometric size[223-225]. These methods allow structural determination of nanoparticle facets[226]. We have applied nanobeam electron diffraction (or nano diffraction) to a decahedral particle. The whole particle shows overall five-fold symmetry. However, if we diffract individual tetrahedra, the patterns will resemble an FCC pattern in the (110) orientation. An example is shown in **Figure 7-21 a)**. The patterns were obtained avoiding the twin boundaries to avoid extra reflections. A similar figure for a Marks decahedron is shown in **Figure 7-21 b)**. The results indicate that particles have a pseudo five-fold symmetry resulting from the superposition of individual diffraction patterns. However, if we examined a nanobeam patter obtained from the whole particle we can see that the angle between (111) spots changes between reflections as shown in **Figure 7-21 c)**. As it can be seen in **Figure 7-21 c)** the angles follow a Zig-Zag pattern. The values of the larger and smaller angles are not exactly the same, but their summation equals 360° . Although the pattern in **Figure 7-21 c)** is slightly tilted away from the Laue condition, in which all the intensities are equal, the angular shift is far too long to be produced by tilting. The only possibility is strain produced to rotate the planes to close the gap. The (111) lattice

orientation distances deviate from the bulk value by $\pm 0.16\text{\AA}$ and again are different on every reflection because of the strain. A plot of the angles, due to the strain, of the diffraction pattern will be non-centrosymmetric as shown by Johnson et al[202]. This is consistent with the presence of phason distortion. Phasons are related to atomic displacements on the lattice and are commonly observed in non-periodic solids such as the quasicrystals[145]. One of the most characteristics of phason strain is the shift of diffraction spots in a zigzag along a line[227]. A possibility is that even though the individual tetrahedra are periodic crystals, the overall

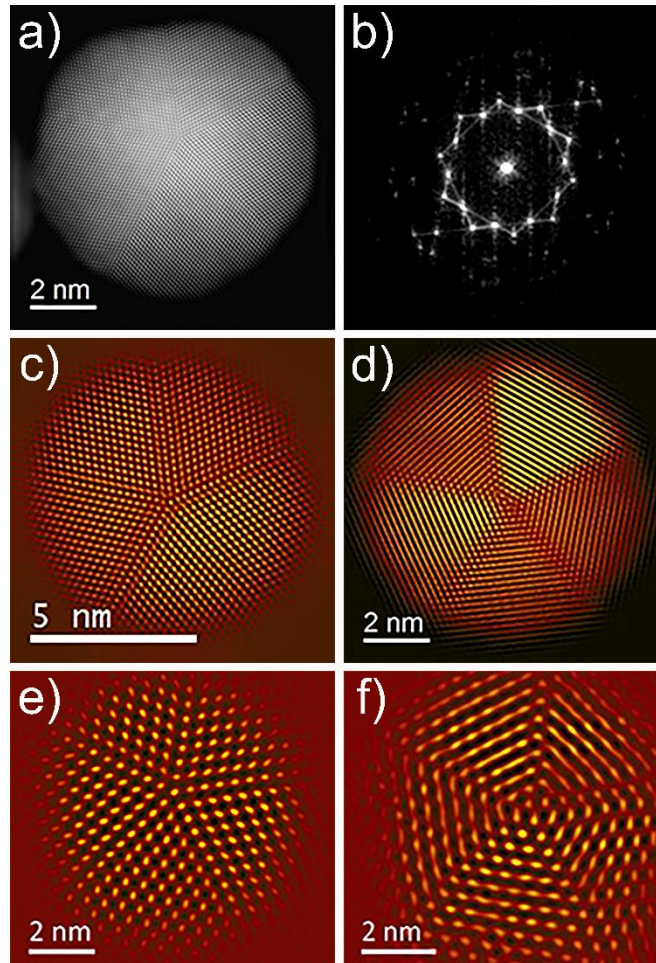


Figure 7-17: In this case the atomic columns on the image represent the true atomic positions. Figure 17a) shows a HAADF-STEM image of a decahedral particle. The FFT b) shows the overall five-fold symmetry. By showing only the spots corresponding to the (111) plane, c) no strain distortion is present. While looking at the (200) plane, d) there is a very pronounced distortion. The center atomic array which is expected to be a perfect decahedron is heavily distorted. In e) and f) a smaller particle is shown with the same distortion.

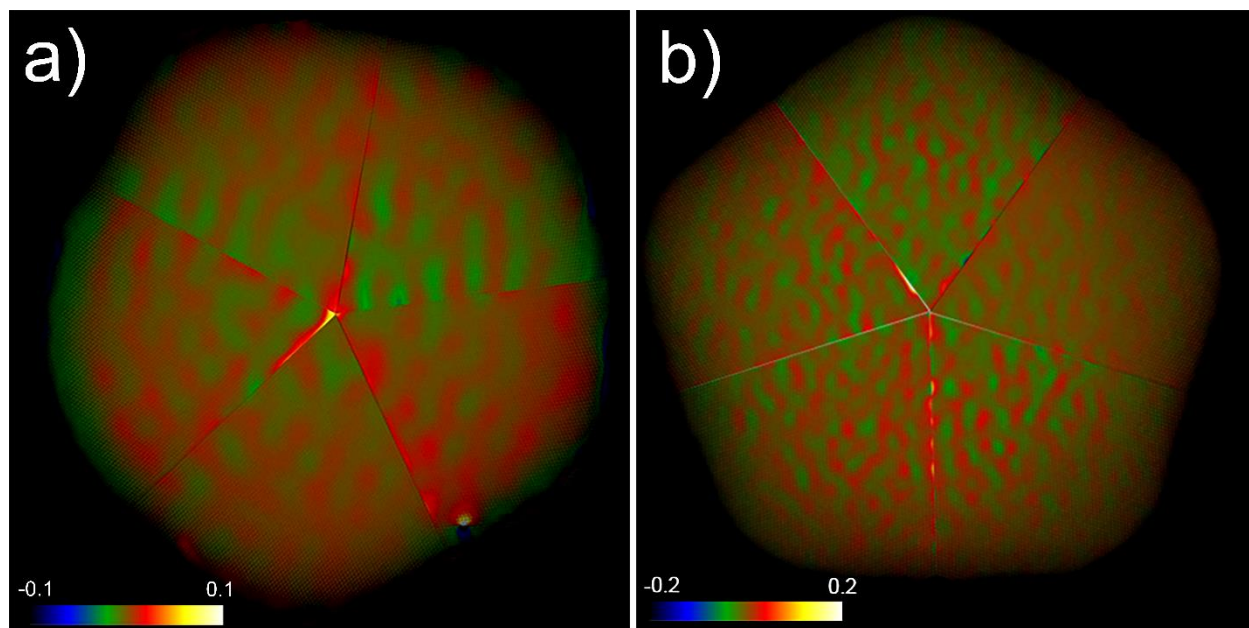


Figure 7-18: The result for the E_{xy} strain component is shown in a) and b) for two different nanoparticles. It can be seen that the strain is concentrated along the twin boundaries and along the surface regions.

decagonal structure is not. Breaking the long-range periodicity on decahedral particles creates the conditions for phason distortion. The effect observed in diffraction patterns of decahedral particles as shown in **Figure 7-21**. It will be difficult to understand this effect without phason strain. However, this is again a topic that needs further research.

7.8 Influence of the preparation method

The way nanoparticles are synthesized has a great influence on the resulting shape. In this review we did not discuss this at length. There are plenty of examples on the literature that report changes on shape with the synthesis method[46, 101, 228]. We refer the reader to those papers. At the ends it is play between kinetics and thermodynamics that control the shapes discussed in references[35, 105, 189]. A very significant example is the growth of Ag nanowires. These are by adding a surfactant that produces preferential growth in one direction. Other methods include the polyol method and the use of a soft template[229, 230]. Nanowires have a decahedral

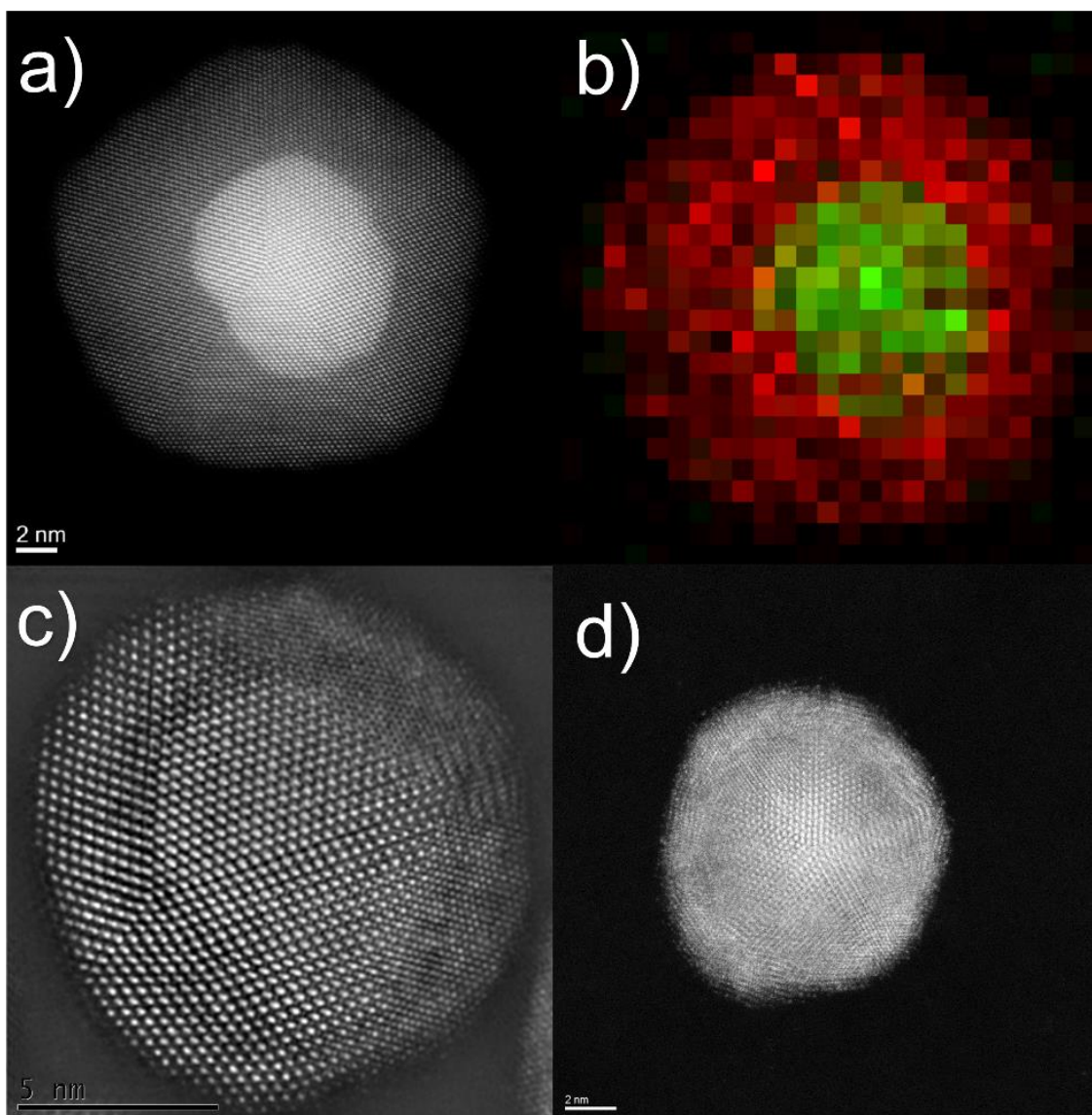


Figure 7-19: STEM-HAADF images of several bimetallic alloys. a) Au-Cu with the core and the shell have an overall decahedral shape. b) EDS map of the particle in a), red corresponds to Au and green to Cu. c) Au-Ag core shell. The Ag on the shell has a different packing than the Au core. d) Pt-Pd core shell, the overall particle is decahedral, but the Pt shell has a different packing.

structure that can be produced by a chain aggregation of single decahedra as reported by Reyes Gasga et al.[178]

7.9 Discussion and Conclusions

The decahedral and icosahedral are a fascinating subject. These structures are formed in several metals and in multimetallic nanoparticles. Decahedral nanoparticles can be produced by either growth of an initial decahedral nuclei or by coalescence of tetrahedral nanoparticles. In

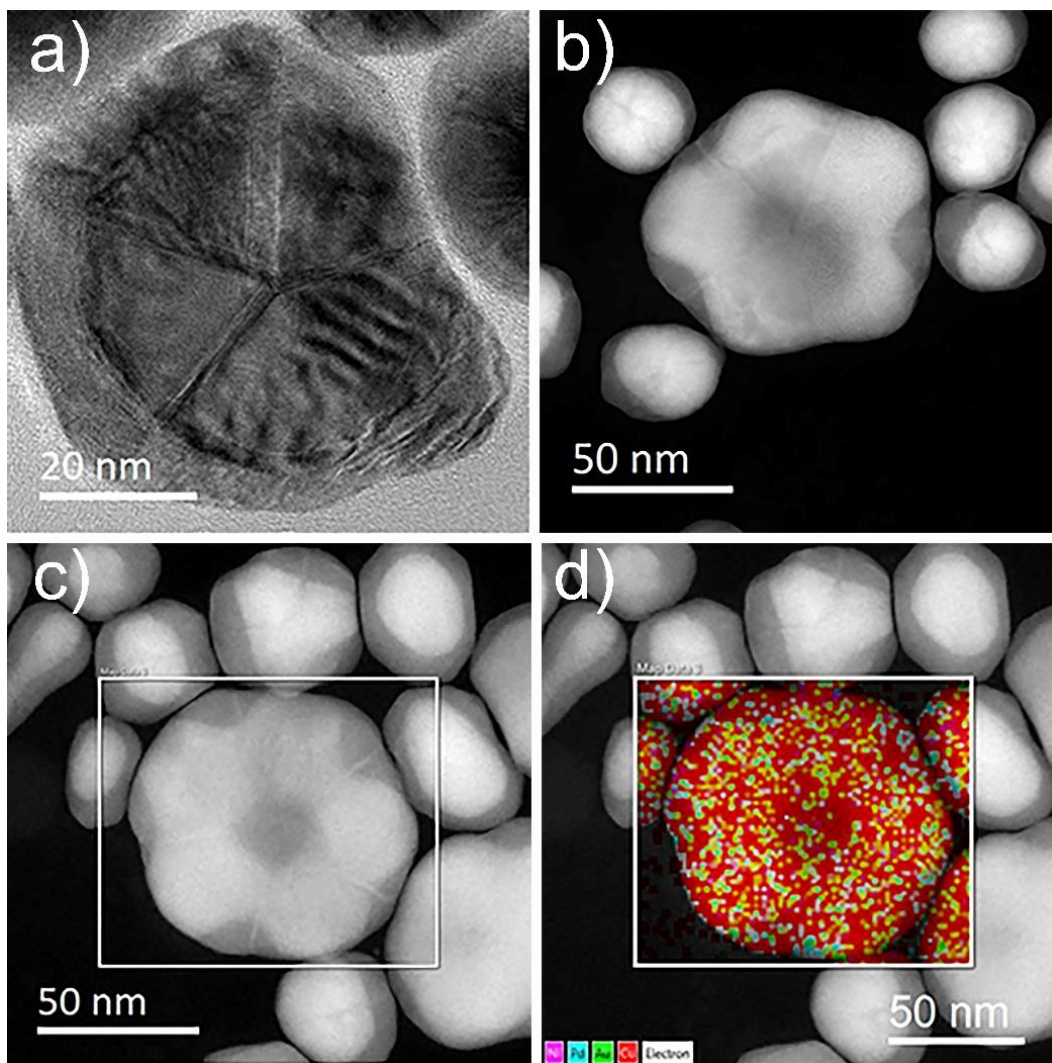


Figure 7-20: Here is an example of a five-metal a) nanoparticle Au/Cu/Pd/Ni/Co and a four-metal b) particle Au/Cu/Co/Ni. It is interesting that a core shell structure is formed with the decahedral core.

both cases these structures are kinetically stabilized, and it will be expected that if thermodynamic equilibrium is achieved, they will transform to FCC structures similar to the bulk. Nevertheless, decahedral and icosahedral nanoparticles are remarkably stable.

In SI section of reference[149] we show three videos of heating decahedral nanoparticles. In the video SI-1 we show a decahedral nanoparticle of 1.5 nm which is heated by a high dose electron beam. This corresponds to the phenomenon named quasimelting[231, 232]. The electron beam increases the nanoparticle temperature[176, 233] in a way proportional to its size. The particle is distorted but its shape remains overall decahedral. In the video SI-2 a particle of ~2.5

nm is shown, again the same trend is observed. A third example (also electron beam heating) of a larger decahedral particle ~ 3.5 nm is shown, which, despite the fluctuations remains decahedral. In SI-3 we show a sequence of heating of a large particle ~ 400 nm. In this case the heating was

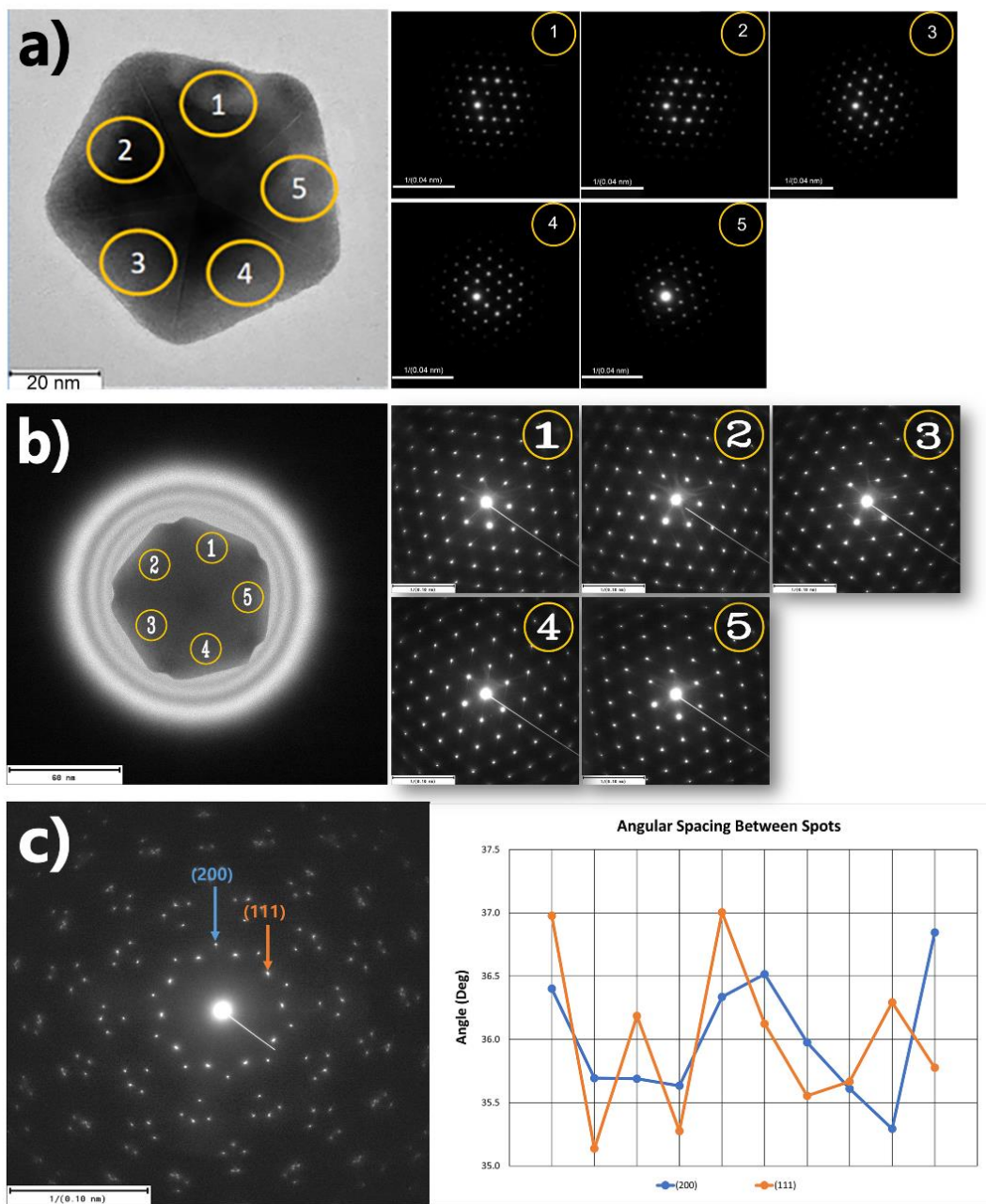


Figure 7-21: Nano diffraction of a) an individual tetrahedra nanoparticle. The pattern from the whole particle is shown along with the patterns for the individual areas that resemble (110) FCC patterns; b) a Marks decahedron with the corresponding diffraction patterns. c) shows the diffraction pattern of the tetrahedra nanoparticle showing the (111) and (200) diffraction spots. The plot shows that the angle between the spots has a zigzag pattern.

done in the TEM using a heating stage. The particle remains stable until 600°C in which it is partially evaporated. The conclusion is that the decahedral nanoparticles are exceptionally stable. The cross-twinning mechanism appears to be the most significant in the growth of decahedral (and icosahedral) nanoparticles. Once formed, twins are very stable and they contribute to the internal energy. As the particle grows, the twin boundaries contribute more to the internal energy.

The twin's movement is not very likely unless a stress is applied to the nanoparticle. Full dislocations are not likely to be formed and partial dislocations will tend to move to the twin boundaries. This situation is increased when there is more than one metal because there is strain due to differences in the lattice parameter. So even that these nanoparticles are kinetically formed, and they remain stable. The more metals the more likely that five-fold structures will be formed.

In addition, in monometallic systems the strain plays a role in the stability. There is not a single route to produce strain but rather a diversity of possibilities. As we have shown, two decahedral particles of the same size might have different stress profiles and different defects.

In this paper we have presented most of the results for the case of Au. However, several other metals (and semiconductors and oxides) show decahedral and icosahedral structures. More research is needed to explore all the metals in the periodic table. As the size grows, new shapes are formed which are, in most cases, related to five-fold symmetry such as the truncated triakis Icosahedron and the rhombicosidodecahedron. In addition, as the nanoparticle grows faceting and surface reconstruction appears which further helps to stabilize the decahedral shape. The preparation method is also important in producing five-fold structures. That includes the synthesis temperature and the cooling method.

However, macroscopic single metal crystal with decahedral shape have not been observed. We have reported decahedral structures in Au with a size up to $1\mu\text{m}$. Only in the case of quasicrystals have people been able to grow single crystals with five-fold symmetry; they always are formed by several metals. We have to assume that at one point of the growth there should be a transition from decahedral to the bulk structure of FCC. The mechanism of this transition is not known. No doubt that this is a topic which deserves attention from researchers and is part of the fascination of five-fold structures.

Chapter 8 Other areas of research

This chapter is based on the published article ref[234]

At the beginning of 2022 the world was shaken by the global pandemic. The SARS-CoV-2 virus, more commonly known as Covid-19, hit the world and infected millions of people. One of the challenges to this virus was its detection. There was critical need for rapid, and cheap, testing of high numbers of people to help contain the spread of this virus. At the time, there were two methods, the PCR test and the rapid antigen test. The rapid antigen test became very popular due to the quick turnaround time but was not very accurate. The PCR test, a type of nucleic acid amplification test (NAATs), is the most reliable test but must be sent to a laboratory and can take a few days to get the results back.

One way to bridge the gap between these two types of tests is to bring the laboratory to the field. Raman detection of the S and N proteins of the virus in saliva is a promising method to achieve this. Raman instruments can be made into or bought as small mobile instruments. To

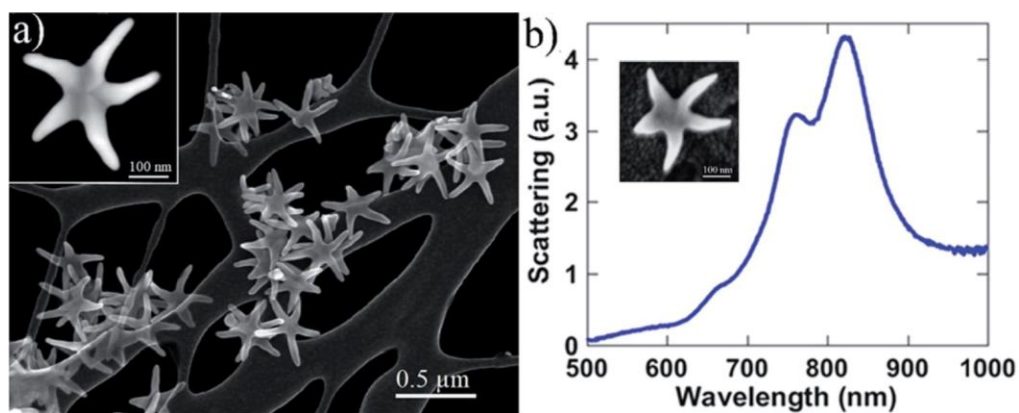


Figure 8-1: (a) SEM image of the Au–Cu nanostars used as SERS substrate. The image shows very sharp peaks which act as plasmonic antennas. (b) Optical absorption spectra of the nanostars revealed a strong peak on the near IR.

increase the signal of the proteins, Surface Enhance Raman Spectroscopy (SERS) can be used and achieve up to $\times 10^{11}$ signal enhancement.

8.1 Introduction

The number of cases of COVID-19 and its associated mortality have raised serious concerns worldwide. Early diagnosis of viral infection allows rapid intervention, disease management, and substantial control of the rapid spread of the disease[235]. The most common test used to detect the virus is the real time reverse transcriptase-polymerase chain reaction RT-qPCR utilizing nasal or pharyngeal swabs or saliva[236]. This technique detects viral RNA regions, and it is highly sensitive and very specific. However, it has a relatively long turnaround time, requires expensive equipment, and involves highly trained scientists. Additionally, this technique requires the use of DNA-binding dyes, which sometimes are difficult to obtain.

Recent improvements have cut down the response time significantly and there has been a very rapid advance in new testing methods. Developments include immunological methods, such as Enzyme Linked Immunosorbent Assays (ELISAs), chemiluminescence immunoassays (CLIAs), lateral flow immunoassays (LFIAs), and multiple others[237-241]. Recently, the development of clustered regularly interspaced short palindromic repeats (CRISPR)-based diagnostics has been used to detect the SARS-CoV-2 virus[242, 243]. This method is very promising but is still in an early stage. Several other methods based on nanotechnology and 2-D materials have also been reported[124, 244-247]. A comprehensive review of the detection methods can be found in ref.[248-250]. A general conclusion is that the methods, other than RT-PCR detection assays, have some limitations including low detection sensitivity and, thus, have not replaced RT-PCR as the gold standard.

Table 8-1: Raman shifts for the SARS-CoV-2 virion particle.

Raman shift (cm^{-1})	Assignment
501.5	S-S bond (β -sheet)
531.65	S-S bond (α -helix)
577.0	Trp, Cys
656.2	Tyr (α -helix)
716.7	Phospholipids
782.5	Histidine
846.5	Tyr doublet
902.3	C-O-C skeletal modes
951.5	Trp
983.7	Trp-Val
1060.3	Phe
1121	Trp, Phe
1150	C-N, glycogen
1207	Phe, Tyr
1263	Amide III
1297.4	Amide III
1340.4	Trp, C α -H deformation
1378	L-Alanine, N-acetyl-glucosamine
1445.1	C-H deformation
1492.1	L-Histidine
1554.0	Indole ring Trp
1600.7	Tyr, Phe, Trp

In this paper we explore the development of a new test, which, if successful, can be broadly implemented with higher sensitivity and reliability. Whereas most of the currently available testing is based on biochemical methods, we present the possibility of expanding our capabilities using the advances in techniques based on physics and, more specifically, the properties of condensed matter and its interactions with light.

Raman spectroscopy is a well-established technique for the study of inorganic and organic materials[251-254]. Raman spectroscopy has been used for the detection of bacteria in food[255] in the detection of bacterial infections[256-258] and HIV-1 virus detection[259-262]. Recently it has been applied to the study of SARS-CoVid-2 using gold nanoparticles[263] and conventional Raman spectroscopy[264]. The Raman technique uses the inelastic fraction of light interacting with a molecule, that due to this interaction, the wavelength

Table 8-2: Raman Shift for the spike (S) protein.

Raman shift (cm ⁻¹)	Assignment
410.5	Tryptophan or histidine
432	L-Tyr
442.6	Glucose
478.0	N-Acetyl-glucosamine
498.85	S-S bond (α/β)
510.96 ^a	Phosphorylated protein and lipids
528.7	S-S bond (α -helix)
545.5	S-S bond (β -sheet)
601.0	Phe
633.8	Trp
651.7	Tyr (α -helix)
678.44	Trp
716.5 ^a	Phospholipids
786.04	Histidine
801.1	Trp
849.0	Tyr doublet
875.8	Tryptophan
891.9 ^a	Mono and disaccharides C-O-C skeletal modes
920.3 ^a	Glucose/glycogen
1033.1	Phe
1050.2 ^a	C-N and C-C protein stretching
1081.0	Histidine
1100.2	Trp, galactosamine
1115.6	ν -C-C aliphatic
1128.0 ^a	Trp, Phe
1150.2 ^a	Glycogen
1220.1	Phe
1250.7 ^a	Amide III
1270.7	α -Helix amide III
1305.9	Phe
1320.0 ^a	Amide III (α -helix structures)
1356.7	Trp, C α -H deformation
1383.9	C-H rocking in lipids
1449.8 ^a	Fatty acids, C-H stretching of glycoproteins
1463.7	C-H deformation

^a Indicates the peaks are also present on the Covid spectrum.

of the light is shifted, called Raman shift, which is directly related to the vibrational modes of the molecules analyzed and therefore represents a fingerprint of the molecule. Raman spectroscopy is intrinsically highly specific to chemicals compared to other spectroscopies, such as fluorescence or visible/near-infrared (NIR) absorption, and hence offers many advantages.

The Raman signal intensity is very low, about 10^{-6} times the initial laser light intensity and, thus, a signal amplification is required. This can be achieved using the plasmonic effects of metallic nanoparticles. Depending on the shape (aspect ratio) or chemical composition, the plasmonic field enhances the signal up to $\sim 10^8$ – 10^9 times[265, 266]. In addition, other materials such as transition metal dichalcogenides and other 2-D materials[267, 268] can produce an additional signal enhancement of $\sim 10^2$ due to electronic transfer. This method is known as

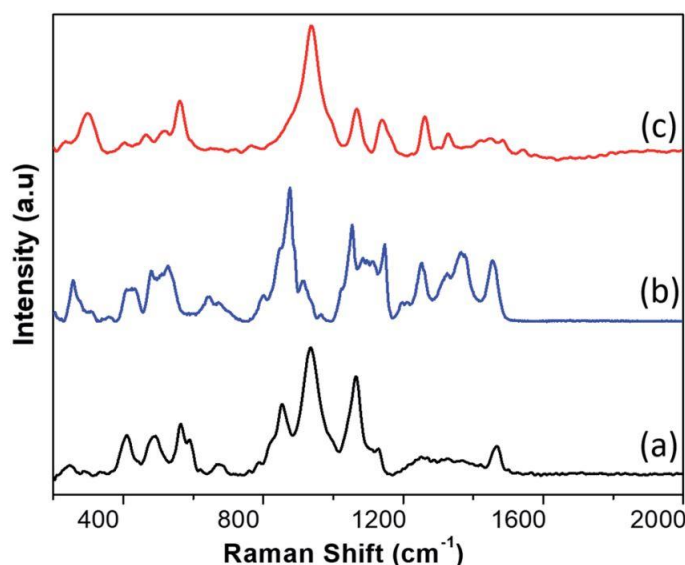


Figure 8-2: SERS spectra of (a) the N protein, (b) the S protein, and (c) the inactivated SARS-CoV-2 virion particles.

Surface Enhanced Raman Spectroscopy (SERS) can be a powerful method to detect viruses and other pathogens[259]. Raman based detection is expected to have high sensitivity and specificity as demonstrated by the detection of breast cancer using SERS[269, 270].

In this paper we report preliminary studies of SARS-CoV-2 virion particles and its spike (S) and nucleocapsid proteins (N). We developed a highly sensitive SERS substrate based on plasmonic and excitonic phenomena which allows a very complete characterization of the virion SARS-CoV-2 and its S and N proteins. We show that SERS can provide a solid platform for viral testing.

8.2 Experimental

SARS-CoV-2 proteins and virions

Purified SARS-CoV-2 spike (S) protein expressed in baculovirus insect cells was purchased from Sino Biological (40589-V08B1). This *in vitro* expressed protein, containing the S1 and S2 subunits, was purified by nickel chromatography using affinity his-6 tag and which is capable of binding to the ACE2 receptor. Similarly, we cloned the SARS-CoV-2 nucleocapsid

Table 8-3: Raman shifts for the nucleocapsid (N) protein.

Raman shift (cm ⁻¹)	Assignment
373.8	δ C-C aliphatic chains
419.6	Tryptophan or histidine
495.2	S-S bond (β -sheet)
602.1	Phe
654.5	Tyr (α -helix)
678.4	Trp
729.77	ν -C-C aliphatic chains
783.46	Histidine
823.8	Tyr
852.4	Tyr doublet
862	β -Sheet Tyr
922.3	Val-N-C α -C
975.8	Trp, Val
1050 ^a	C-N and C-C stretching
1076.7	ν -C-C aliphatic chains
1107.8	Histidine, Trp
1219.3	Phe, ν -C-C aliphatic chains
1248.6 ^a	Secondary amide bands
1266.9	Amide III
1320.65 ^a	Amide III (α -helix structures)
1390.0 ^a	C-H rocking in lipids
1458.1 ^a	General fatty acids, C-H stretching of glycoproteins
1517.4	Galactosamine, aromatic rings
1554.9	Indole ring Trp
1608.0	Trp, Tyr, Phe
1671.7	Amide I

^a Indicates the peaks are also present on the SARS-CoV-2 Raman-SERS spectrum.

(N) protein into an *E. coli* expression vector and then purified it using its his-6 tag and Ni chromatography. SARS-CoV-2 WA1 and HCoV-NL63 (BEI Resources) virions were grown on VeroE6 (SARS-CoV-2) or LLC-MK2 (HCoV-NL63) cells. Overlying media, containing virus, was harvested, and tittered to determine the number of infective particles prior to Raman analysis. Ethanol inactivation (70%) of the virus was performed prior to the Raman analysis. To examine the samples, we used Au/Cu nanostars prepared using the methods reported previously by José-Yacamán and colleagues[271]. Those authors report the controlled selective growth and high-yield production of Au_{rich}Cu concave pentagonal nanoparticles (CPNPs) and their evolution into branched nanostructures, concave “nanostars” (CNSs), *via* a seed-mediated growth method by using oleylamine (OLA) as a capping and self-assembly promoter agent. The adding of Cu is necessary to produce 5-arm structures (see Experimental section in ESI Figure S1(a–c)[†](#)) with concave facets and sharp tip surface charge distributions showed significant induced polarization

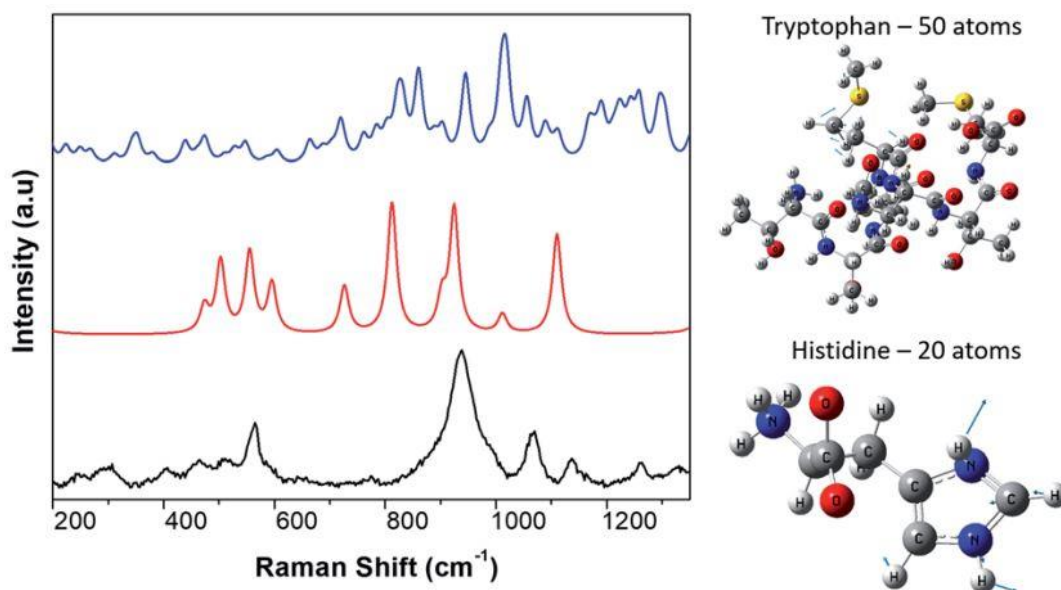


Figure 8-3: Theoretical simulation of portions of the Raman spectra of components of the protein N. We use a portion of 50 atoms from the tryptophan molecule (blue), a portion of 10 atoms of the histidine molecule (red), and a portion of the experimental spectra of the SARS CoV-2 virion particle (black). The overlap of peaks close to the 1000 cm^{-1} Raman shift can be observed.

along the arms of the CNSs, resulting in a highly localized plasmon field at the tips (785 nm), as well as a surface polarization due to the formation of image charges. Additionally, the Au–Cu nanostars have concave facets which also enhance the signal by non-plasmonic mechanisms as discussed by Lee and co-workers[259]. Therefore, by controlling the shape, we can obtain enhanced plasmon fields and make them ideal for SERS of proteins. An image of the Au–Cu nanostars is shown in Figure8-1. It has been demonstrated that every arm of the nanostars acts as an antenna for the enhancement of the Raman signal. The length and width of the nanostars arms were modified until a light absorption peak around 800 nm was obtained on the UV-Vis spectra, indicating that the nanoparticles were responding in the 785 nm wavelength of the laser excitation source.

The SERS amplification requires that the plasmonic nanoparticles be in contact with the analyte. The electric field polarization along the nanostar arms promotes that they attach to proteins or virions. However, it is necessary to promote the attachment by agitation of the

nanoparticles–protein solution. The Au–Cu nanostars were mixed with the buffer used on the virion particles or the S and N proteins. The particle concentration on the solution was 1.0% weight. The mixed solution was centrifugated/shaken for several minutes to increase the attachment of the nanoparticles to the proteins. We also used a MoS₂ of few monolayers thickness on a microscope slide, the solution of nanoparticles with proteins was dropped on the substrate. The Raman spectra were obtained using a Horiba XploRA Plus 100 spectrometer 785 nm laser – 200 mW power (100% filter) – 20 µm laser beam diameter, with 5 s acquisition time and 5 spectral accumulations.

8.3 Results and Discussion

Spectra of SARS-CoV-2 virion particles and the S and N proteins

In Figure 8-2 we show the typical Raman-SERS spectra of inactivated SARS-CoV-2 virion particles and the purified S and N proteins. Those spectra are the result of averaging 30–50 different spectra. The number of averaging spectra varies according to the surface of the sample area, and it is difficult to keep a constant number of spectra through all the analysis for all the samples, however we have kept a higher number of spectrums for reproducibility analysis purposes. The fluorescence contribution and noise were eliminated using LabSpec software from Horiba. In the case of the virion spectra, several peaks that were not present in all spectra were eliminated. Most of those peaks appear in only one spectrum so we consider them not being representative. We attribute those peaks to the inactivation procedure. In general, the spectra of the SARS-CoV-2 virus and the S and N proteins demonstrated broad peaks, which are the result of many overlapping smaller peaks related to several molecular vibrations. To obtain an accurate analysis of the virus and proteins it is necessary to deconvolute the peaks into individual components. This can be demonstrated by simulation of the Raman-SERS spectra. Vibrational

frequencies simulations were calculated using the Gaussian code based on the Hartree–Fock approximation[272] for an unrestricted isolated molecule, which is part of the N protein to obtain the Raman spectra. The N and S protein contain a very large number of diverse molecules and, thus, its full structure will be very difficult to simulate. For instance, a protein containing 25 000 atoms will be prohibitively expensive in computer time (3D structures of the N, S proteins, and the virion, as well as the region of the calculations can be found in ESI Fig. S2–S4†).

Therefore, we only calculated the spectra of some components of the N protein. We limit our calculation to two partial molecules histidine and tryptophan. Calculations were made using the Gaussian program, and Raman frequencies were resolved by using the default solvent model using water as the solvent medium. In the present work we only considered two amino acids. The results are shown in Figure 8-3, which shows the spectra of 10 atoms of the molecule histidine

Table 8-4: Raman shifts of the HCoV-NL63 virion particle.

Raman shift (cm ⁻¹)	Assignment
557.92	S-S bond (β-sheet)
626.86	Tyr
644.00	Tyr (α-helix)
656.50	Tyr (β-sheet)
684.82	ν-C-C aliphatic chains
740.93	Tyr (β-sheet)
759.64	Trp (β-sheet)
784.18	Histidine
825.18	Tyr (α-helix)
854.34	Tyr (β-sheet)
920.42	Glucose/glycogen
962.20	Trp, Val (α-helix)
1005.04	Phe ring modes
1026.20	Phe
1071.08	ν-C-C aliphatic chains
1101.00	Trp, Val
1129.43	Phe, Trp
1156.12	C-N, glycogen
1198.06	ν-C-C aliphatic chains, Tyr
1231.14	Amide III (β-sheet)
1268.94	Amide III (α-helix)
1313.23	Trp, Cα-H deformation
1323.71	Amide III (α-helix structures)
1340.92	α/β Trp, Cα-H deformation
1368.81	N-Acetyl-glucosamine
1395.94	C-H rocking in lipids
1446.42	General fatty acids, C-H stretching of glycoproteins
1454.92	General fatty acids, C-H stretching of glycoproteins
1520.56	Galactosamine, aromatic rings
1549.18	Indole ring Trp

and 50 atoms of the molecule tryptophan. The resulting peaks (around 1000 cm^{-1}) are compared to the SARS-CoV-2 virus. As can be seen, there are many peaks that overlap and fall on the observed positions for the SARS-CoV-2 spectra. All peaks for the different molecules represented in the spectra overlap, resulting in a large broad peak which is the important result of the calculation. The virion particle is even more complex because contains the S and N proteins and many other minority components. Thus, to analyze the Raman spectra of the virion particles more accurately, we need to deconvolute the peaks. The deconvolution process was performed using the Fityk program version 1.3[273], which offers an alternative of bell-shaped functions to fit the Raman bands. The choice of fitting function does not alter the wavenumber position of a given band but results in slightly different full widths at half maximum (FWHM), or line broadenings. Before the fitting was performed, careful consideration must be paid to determine as best as possible the base line of the Raman spectra. To do this, the fluorescence background was determined by fitting a fifth-degree polynomial curve to the measured spectrum from the points where no Raman signal is expected to be present, and this is subtracted from the original data. Judging from the results, only reliable identifications may be assigned to the spectral details above 400 cm^{-1} . The fit was covered to include all spectral details below 1800 cm^{-1} as all spectral details, originating of the side-chains of the amino-acids, as well as from the peptide bonds (amide fingerprints) constitutive of the virion proteins are expected to be found in this spectral region. The red line illustrates the result of the fits using Lorentzian functions to deconvolute the presence of the contributing Raman bands to the spectra. The result of the fitting is presented in Tables 8-1 through 8-3 for the SARS-CoV-2 virion, and the S and N proteins, respectively. Figure 8-4 shows an example of the peak deconvolution for the N protein and

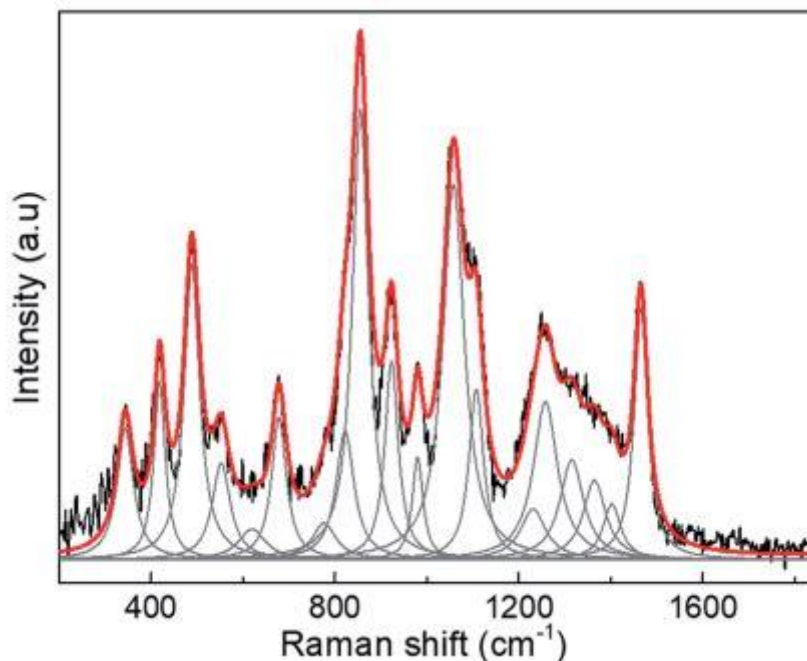


Figure 8-4: Example of the deconvolution (red line) of the SERS peaks for the N protein.

illustrates its necessity (additional deconvolution data is shown in Figure S-5(a–c) for the N, S protein and virion Raman spectra (NL-63), respectively).

To obtain the peaks reported in Tables 8-1 through 8-3, we deconvolute 50 spectra of each type and calculated the average. Our results produce a significant number of peaks that can be used as a very complete fingerprint for identification. We found that 15 of the observed peaks on the virion particle correspond to the S and N proteins. This the result of the virion particle structure. As summarized on the ESI the SARS-CoV-2 virion particles contain several other proteins such as the membrane and envelop proteins plus RNA. The membrane protein has a concentration three times more than the N protein. In addition, the virion particles S protein might have combined with some compounds. So, we do not expect the full virion particle have only peaks of S and N proteins.

Raman spectra of inactivated HCoV-NL63 virion particles

To demonstrate the capability of the Raman method for virus testing, we studied the human coronavirus HCoV-NL63. This virus causes mostly upper and at times lower respiratory tract infections, community acquired pneumonia, and croup in children[274]. This virus can be considered as a surrogate of the SARS-CoV-2 virus. Figure 8-5 shows a typical Raman-SERS spectrum of the HCoV-NL63 virus. We followed the same fitting procedure described above and the peaks are identified in Table 8-4.

8.4 Discussion

A protein Raman spectrum is typically composed of contributions from three major types of vibrational modes originating from the polypeptide backbone (amide bands) and aromatic and non-aromatic amino acid side chain residues. The Raman-SERS spectra of virion particles is complex and produces broad peaks that are the result of the many closely spaced peaks resulting from multiple chemical species[275]. A similar example is the spectra of HIV-1 virus reported by Lee *et al*[259]. A very interesting fact is that the virion spectra and the S protein are lacking peaks corresponding to the amide I bands ($1640\text{--}1678\text{ cm}^{-1}$). This has been a common observation[259]. This has been explained by Kuroski *et al.*[276] with SERS studies of different homo-peptides consisting of Gly-, Ala-, Tyr- and Trp-rich chains under a variety of experimental conditions. There, it was demonstrated that the absence of amide I bands in the spectra depended on the size of the amino acid side chain. The side chain increases the distance between the peptide bond and the metal nanoparticle preventing their immediate contact. However, it is also possible the lack of the amide peak on the virion might also be related to the virus a deactivation procedure which might break amino acids. Recently Carlomagno *et al.*[264] reported Raman studies (not using SERS) of SARS-CoV-2 in saliva samples they also do not report the amide I peaks. In other recent paper Zhang *et al*[238]. used silver-nanorods SERS array functionalized

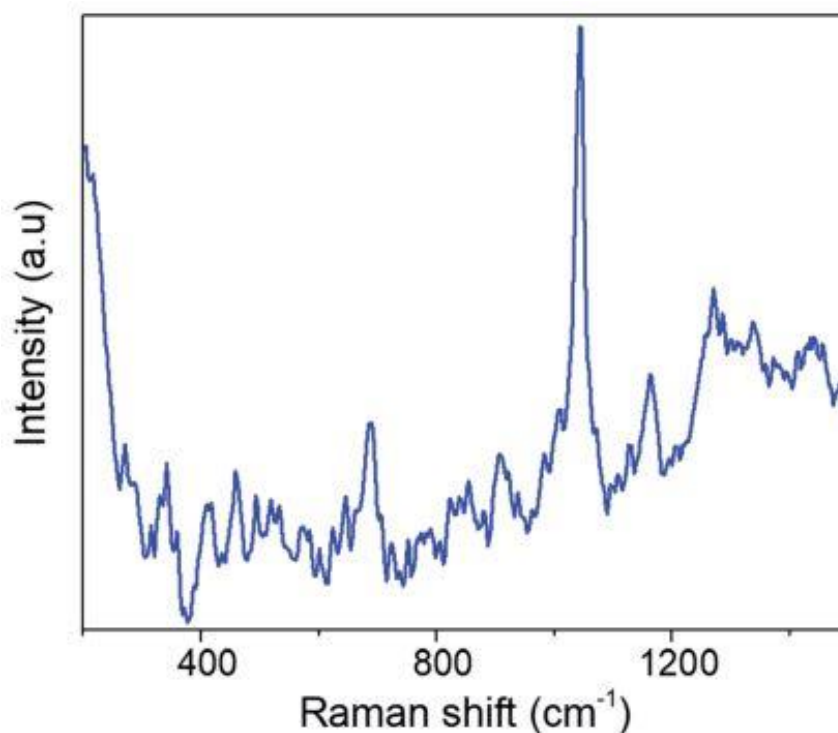


Figure 8-5: SERS spectra of inactivated CoV-NL63 virions.

with binding protein and the viral receptor of the cellular receptor angiotensin-converting enzyme 2 (ACE2). There, they reported a very weak amide I peak, which is very close to the noise. These authors used a Raman peak of 1189 cm^{-1} in the ACE-2 with a shift to 1182 cm^{-1} when the spike protein was attached, and then used the ratio of those two peaks to predict the virus presence; their SARS-CoV-2 spectra showed very few weak peaks. Another study, Desai *et al.*, [277] reported Raman study of an RNA virus in saliva, using a lentivirus vector system (based on HIV-1) and their reported Raman spectra also showed only a few peaks and no amide I peak. However, the N protein shows the amide I peak. Our N protein was complete and purified whereas the S protein was commercially available and broken in two subunits S1 and S2. This further suggest the invisibility of the amide I peak is related to the size of the amino acid chains.

On the other hand, it is well known that SERS amplification effect requires that the molecule to be in contact with the metal nanoparticle. Our approach using a SERS with a substrate that combines plasmonic and excitonic amplification and the mathematical analysis allow us to obtain a large number of peaks. In the case of the virion particles we have obtained very consistent spectrum. At least 15 of those peaks can be associated with the presence of N and S proteins. Some of the variations on the peaks that are observed can be attributed to the virion particles being deactivated. It is likely that during the process of deactivation some parts of the virus were destroyed. To reinforce the valuable information that could be extracted from the SERS spectra it was calculated the limit of detection for a calibration curve for the S protein. The SERS spectra of the InBios-Spike-Protein was collected for concentrations ranging from 744 μM to 7 nM. Then, using PLSR (Partial Least Squares Regression) with two principal components to the calibration curve the variance for the two components was calculated to be 99.9%. Thus, a detection limit was found to be 8.89×10^{-9} M with a Root Mean Square Error (RMSE) $\approx 2.27 \times 10^{-9}$, which is a good approximation for concentrations as low as nM range (see ESI Fig. S6(a-c)).

8.5 Conclusions

We have shown that using SERS produced by gold nanostars nanoparticles and MoS_2 thin layers we can obtain a very consistent signature for SARS-CoV-2 virion particles. In addition, the main proteins, S and N, produce well-defined spectra. This suggests that Raman-SERS spectroscopy can be used not only for virus detection but also to study the structure of the proteins and follow *in situ* changes produced by different conditions.

Our study is preliminary, clinical testing and a direct comparison to other tests will be necessary to assess the sensitivity and specificity of Raman. Nevertheless, our research shows

great promise for developing the technique. If developed, a Raman-SERS test on saliva will produce instant results and will only require the use of nanoparticles, which can be massively fabricated at low cost.

Chapter 9 Concluding Remarks

We are in the age of nanomaterials. Understanding nanoparticles is a key to the progress of advancing human knowledge. There have been many advances in the fields of nanotechnology, both theoretically and experimentally. There has been much work done in the field of mono metallic and bi metallic nanoparticles, but there has been far less work performed around tri and tetra metallic nanoparticles. The work presented in this dissertation builds on knowledge about multimetallic nanoparticles and looks at understanding the structure of nanoalloys using advanced electron microscopy techniques. The structure of nanoparticles is affected by the size of the particles. As seen by clusters, less than 2 nm, there are not a well-defined crystal structure. When moving to larger particles, around 20 nm, then clear crystal structure is seen. However, smaller nanoparticles, from 2 to 10 nm, clear crystal structure is seen but the atoms can take different positions, as seen by the Cu-Pt nanoparticles.

Smaller nanoparticles also show strong tendencies to form twin boundaries. This leads to decahedra and icosahedra shaped nanoparticles. As more metals are used to make the nano alloys, the tendency for these shapes seems to increase. One possibility is that these shapes are most suitable to relieving strain in the particles. The strain can be seen using GPA and is seen as periodic within the particle structure. This strain in the particles is created due to the particle finding a kinetically stable form. If sufficient energy is introduced to the nanoparticles, then the structure will change, the periodic strain will disappear, and the nanoparticle will resemble more closely its bulk counterpart. Entropy is also a key to understanding the particles. These particles could also be considered entropy stabilized particles. As looking at the Gibbs free energy, with the increased number of metals, the entropy can become the dominating factor to minimizing the energy of the system.

The addition of a third metal to a system adds complexity to the structure. As seen in the Au-Cu-Pt nanoparticles, small nanoparticles do not follow bulk alloy structure but rather can form complex core-shell structures with twin boundaries and five-fold symmetry. These twin boundaries play an important role in the stability of the nanoparticles. The twins offer a relief strain observed. These twins are observed in a wide variety of nanoparticles, some looked at here are Au-Pd, Ag-Pt-Pd, Au-Cu-Pd-Ni among others.

A route to understanding the stability of these nanoparticles is to look at how they are stabilized whether kinetically or by equilibrium. This dissertation shows research suggesting that these particles are kinetically stable due to the change in structure and grain boundaries when energy is added, as was seen in Au nanoparticles. Kinetically stable regions could be driven by the entropy of the system. As more metals are added, the entropy is increased thus adding more complex ways the particles can be stabilized. These complex shapes are formed by twin boundaries and five-fold symmetry very common in multimetallic nanoparticles Au-Pt-Cu, Au-Ag, Au-Pd, Au-Pd-Cu, Au-Cu-Pd-Ni, Au-Cu-Pd-Ni-Co, and Pt-Ni studied in this dissertation. Some of the common shapes are decahedral and icosahedral structures. These are perfect examples of five-fold symmetry and the role of twins, it is believed that twins contribute to the Gibbs free energy and thus allowing a path to kinetically stable particles.

Future work that could be continued to connect theory with experiment would be to continue to build on the Cu-Pt system. The Cu-Pt system has many interesting applications especially when a third metal is added. Different routes could be taken, since the Cu-Pt alloy has been calculated theoretical, a push to look at a Cu-Ni and a Pt-Ni system would be an interesting step. Then combine the results to look at the Cu-Pt-Ni system in depth. This could be a great avenue of research and collaboration.

Another set of systems that would be very interesting to study would be comparing Pt-Pd-Ni and Pt-Pd-Cu. This would be interesting in comparing the magnetic components effect of the Ni verse the Cu. This could be a great extension of the Cu-Pt-Ni system and building upon the theoretical calculations.

Working with four metals yields some interesting results and challenges. While four metals change the structure and complexity of the nanoalloys, getting four metals to alloy and having size control can be a tricky synthesis process. As seen in this dissertation, four metal nanoparticles have some interesting structures, look at Au-Cu-Pd-Ni or the (five metal) Au-Cu-Pd-Ni-Co. These core-shell nanoparticles, where the core has a unique shape and twin boundaries can lead to some interesting research. However, chemical reduction synthesis can be challenging in having all the metal precursors reduce at proper times to alloy is a challenge, and other synthesis methods may need to be explored. One key to this research would be size control and being able to synthesis particles less than 20 nm as this could bring interesting structural changes.

A final area of great research that could have profound implications is the work done on sp^1 carbon. There has been much research in trying to synthesis 1D carbon chains, and one method that should be explored more is using small metallic nanoparticles or clusters (Au has much promise) to stabilize the carbon chains between the particles. This would allow for large quantities of carbon chains which would move the field forward in possible applications.

These nanoalloys are complicated systems and this dissertation has worked to answer some of the structural and stability questions in the nanoparticle systems looked at. These systems are rich in knowledge and future work is needed, both theoretical and experimental, to understand these systems fully. To fully realize the importance of nanoalloys, it is important to

look at their bulk alloy counterparts. Connecting the two will add great knowledge in the crystalline structure of bulk alloys and allow for the tailoring of new materials with the desired properties.

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Supplementary Information

For chapter 8: Detection of SARS-CoV-2 and its S and N proteins using Surface Enhanced Raman Spectroscopy

Experimental section:

Chemicals and Materials

Hydrogen tetrachloroaurate(III) hydrate (HAuCl_4), copper(II) chloride (CuCl_2), oleylamine (OLA), and ethanol were purchased from Sigma-Aldrich, all reagents were analytical grade and were used for the synthesis without any further purification, the synthesis comprises three steps:

Synthesis of Au Seeds

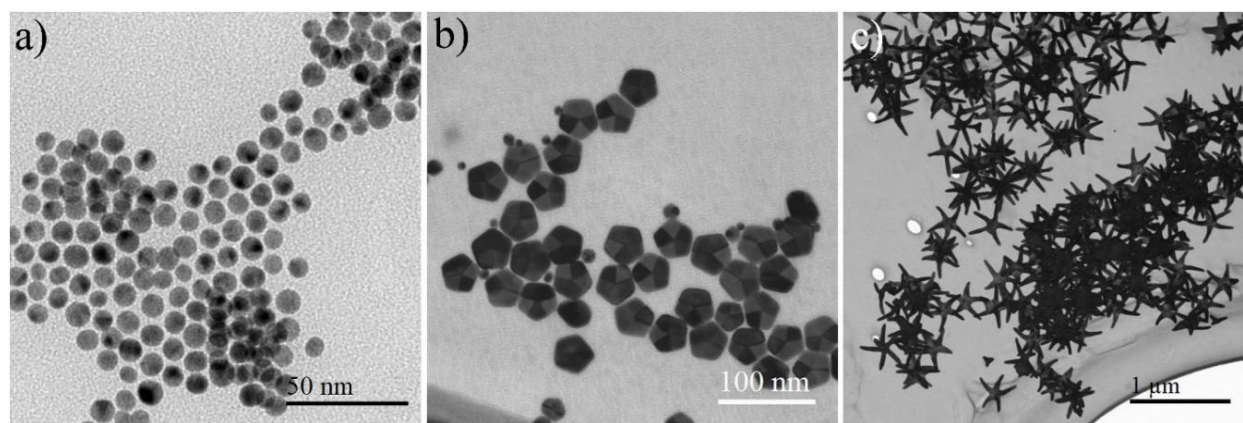


Figure SI-0-1: SEM image of the Au, Au-Cu nanostar used as SERS substrate: (a) Au seeds, (b) Au-Cu seeds, (c) Au-Cu nanostars.

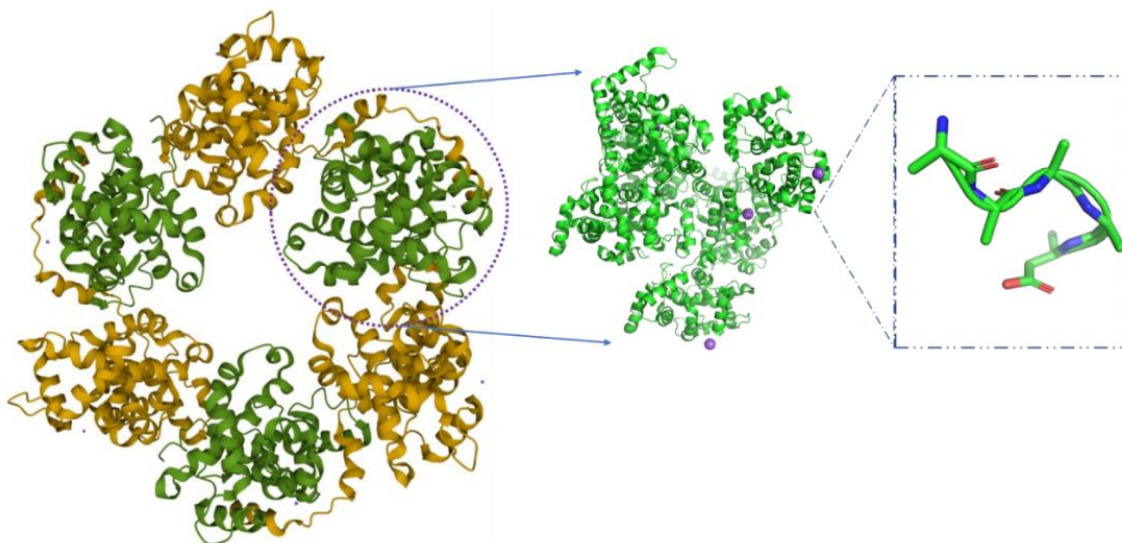


Figure SI-0-2: 3D structure of the protein - N (5fva [1]) asymmetric unit 9625 atoms and the region simulated for Raman frequencies[5].

In a 20 mL glass vial, 7 mL of OLA was combined with 50 μ L of H_{Au}Cl₄ (0.1 M) dissolved in ethanol with stirring by vortex and placed on a hot plate. Then, the temperature was increased to 120 °C. The color of the solution changed gradually from pale yellow to light pink and then to wine red, the final color. The wine-red color indicates the formation of the small Au seeds. The solution was then allowed to cool to room temperature.

Synthesis of Concave Pentagonal Nanoparticles

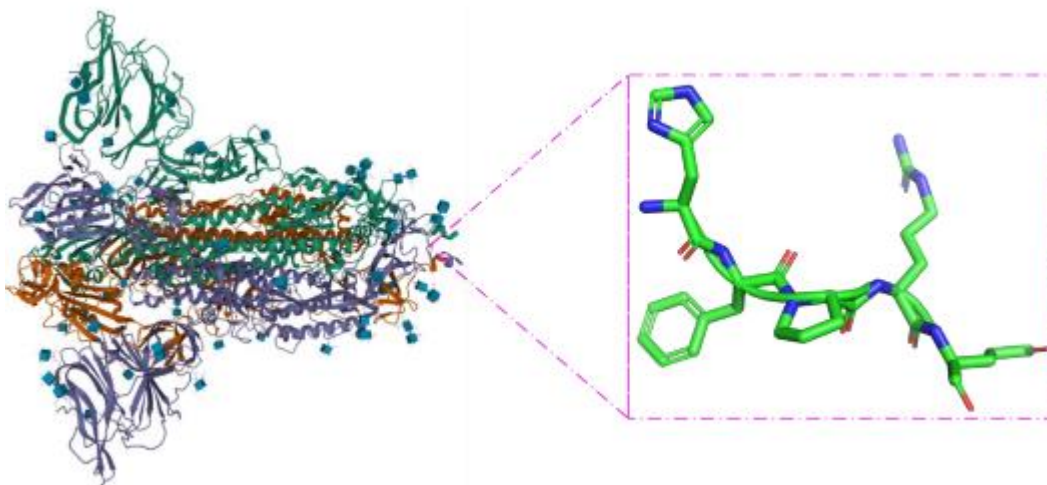


Figure SI-0-3: 3D structure of the Closed conformation of D614G SARS-CoV-2 spike protein (7bnm [2]) asymmetric unit 3207 atoms and the region simulated for Raman frequencies[5].

In a 20 mL glass vial, 5 mL of OLA and 2mL of Au seeds were mixed at room temperature. Then, 75 μL of HAuCl_4 (0.1 M in ethanol) and 50 μL of CuCl_2 (0.1 M in ethanol) were sequentially injected into the mixture and heated to 120 $^\circ\text{C}$ for 10 min.

Synthesis of Concave Nanostars

In a 20 mL glass vial at room temperature, a growth solution was prepared by adding 600 μL of CuCl_2 (0.1 M in ethanol) and 200 μL of HAuCl_4 (0.1 M in ethanol) to 7 mL of OLA (3:1). Subsequently, 400 μL of freshly prepared CPNPs were added to the mixture. The solution was heated at 120 $^\circ\text{C}$ for 30 min and then cooled at room temperature. The color of the solution at this last step was brown-green.

Characterization

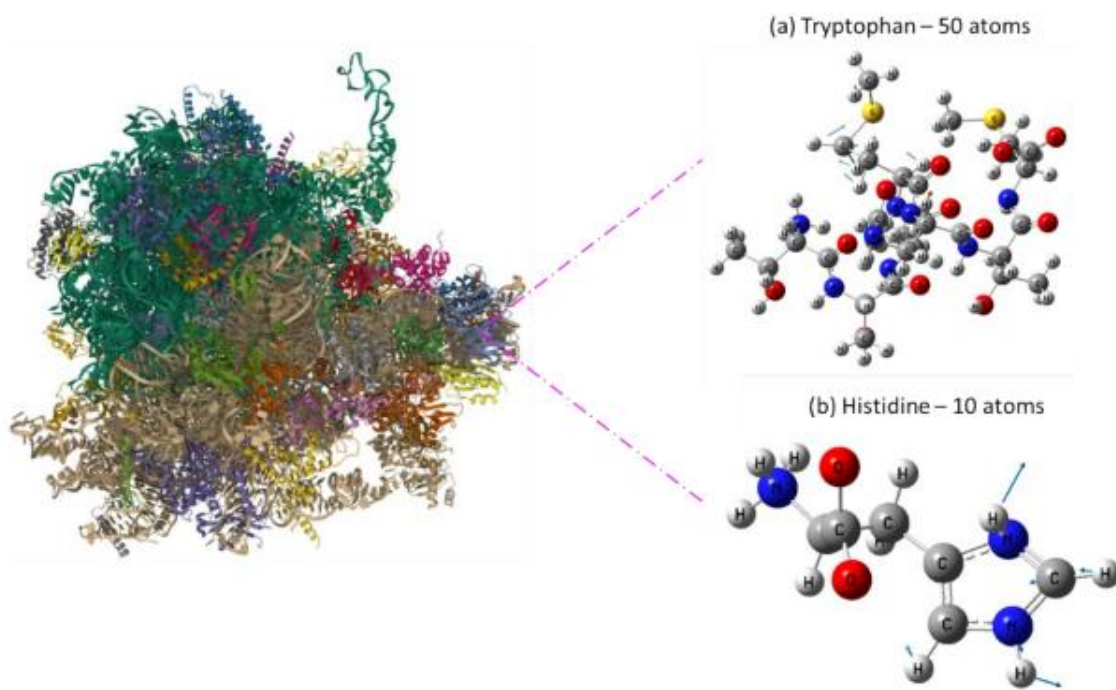


Figure SI-0-4: 3D structure of the SARS-CoV-2 Nsp1 bound to the human CCDC124-80S-eERF1 ribosome complex (6zme [3]) asymmetric unit 233375 atoms and the region simulated for Raman frequencies [5].

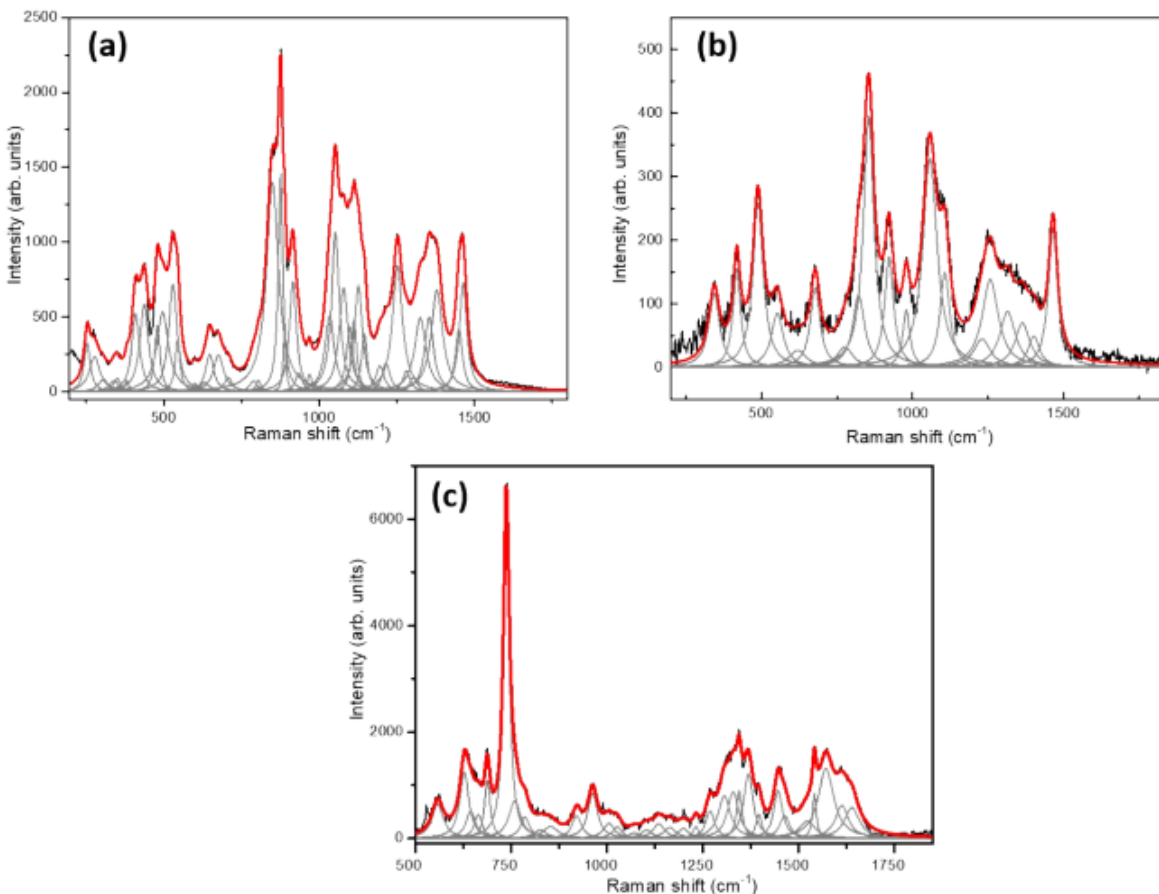


Figure S-10-5: (a-c) examples of the deconvolution (red line) of the Raman peaks for S, N protein and NL-63, respectively, all spectral details, originating of the side-chains of the amino-acids, as well as from the peptide bonds (amide fingerprints) constitutive of the virion proteins are expected to be found in this spectral region [4]. The deconvolution data was processed by averaging 30-50 different spectra and after suppressing the background of the Raman signal by fitting the spectra curve using the cyclic approximation method, i.e., a polynomial (degree varying from 2 - 11) fitting is used in order to get a low-order S/N signal and a smoothness spectrum without little to nothing data treatment.

Structural features of the produced NPs were characterized by electron microscopy. SEM was performed on a Hitachi 5500 high-resolution microscope operating at 30 kV, equipped with

b.

Results and discussion:

3D protein structures and region of interest, simulated through using Gaussian [5] to obtain the vibrational frequencies based on the Hartree-Fock approximation are shown in Figure S2 –S4.right-field and annular dark-field detectors, and a Bruker Quantax 200 EDS system.

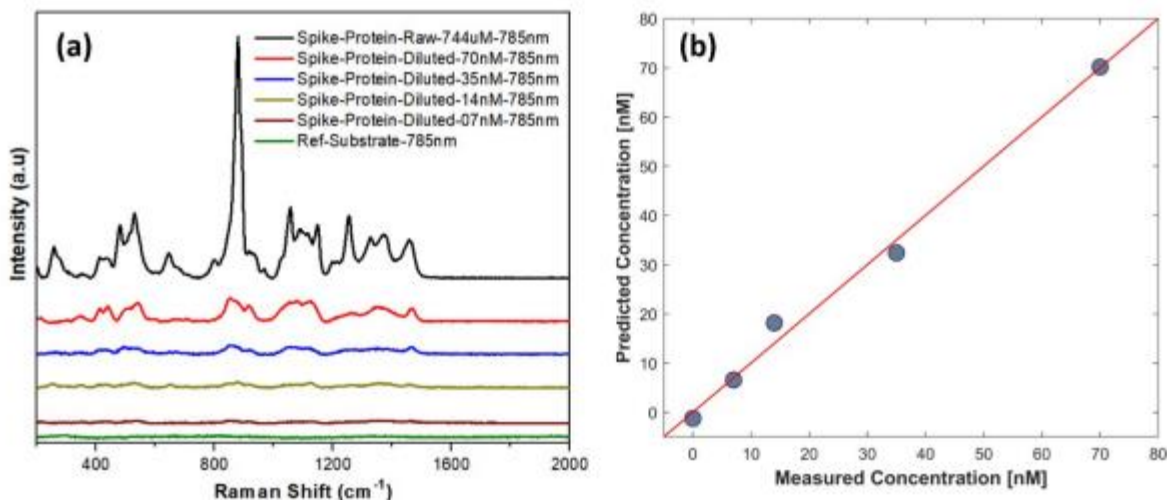


Figure SI-0-6: calibration curve and limit of detection for the S protein. (a) raw SERS spectra of the InBios-Spike-Protein for concentrations ranging from 744 μ M – 7nM. (b) calibration curve obtained by using PLSR (Partial Least Squares Regression) with two principal components. The variance for the two components was calculated to be 99.9%. Similarly, the detection limit was found to be 8.89×10^{-9} M with Root Mean Square Error (RMSE) = 2.27×10^{-9} .

Table SI-0-1: Dimensions of S, N and NL-63 proteins.

Dimensions related. SARS-CoV-2 virion	Length (nm)	Copies (Number)
SARS-CoV-2 virion	100	—
SARS-CoV-2 - Spike protein	9 - 12	—
Membrane Protein	—	2000
Nucleoprotein	—	1000
Envelope Protein	—	20

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