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# Controlled Crystallization of Gold Nanocrystals

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/60020>

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## 1. Introduction

Nanoscience enables the design and synthesis of nanomaterials with tailored shapes and sizes. Novel metal NCs with controllable shapes are attractive due to their size and shape-dependent properties, and reveal higher surface-to-volume ratios, which make their electrical properties extremely sensitive to surface-adsorbed species and changes in the electronic structure, which cause variations in conductivity and resistance.

Great efforts have been devoted to the chemical synthesis of noble-metal NPs with controlled shapes. Of all the synthetic methods reported, it has been found that the most productive route for the formation of NPs with well-defined and controllable shapes is the chemical reduction of a metal salt.

Syntheses of NPs based on the bottom-up approach have two main processes: nucleation and crystal growth. The mechanism for the formation of NCs and NPs was first explained by the *LaMer* model [1, 2]. The *LaMer* mechanism proposes that at the beginning of the reaction, the nucleation starts by precursor reduction into elemental atoms that form small clusters. Once the concentration of the small clusters has reached a point of supersaturation, the small clusters start to aggregate into seeds.

The continuous growth of the seeds results in the formation of metal NCs. Presence of steric or electrostatic stabilizers may be required to prevent agglomeration of the nanoclusters by providing a barrier between the particles.

Despite the simplicity of this one-pot synthetic path for NCs, a common problem is that further nuclei and seeds may be formed throughout the synthesis, leading to broad distributions in size and shape for the resultant NCs.

The one-pot route must therefore be divided into two separate steps of nucleation and growth in order to improve controllability of the synthesis and uniformity of the NCs. This idea was

fundamental to the development of *seeded-growth* synthesis (also called *seed-mediated growth*) for the preparation of Au NRs.

This book chapter provides a review on Au NRs syntheses and properties and extends the discussion on the following issues:

- The *seeded-growth synthesis* for obtaining Au NRs.
- The plausible mechanisms of *Ag(I)-assisted* and *stepwise additive syntheses*.
- Thermodynamics and kinetics control of nanostructures, particularly Au NCs.

Following this, we present the results of Au NRs that were synthesized in our study using the discussed procedures and the results for ability of those Au NRs to polarize light.

## 2. Au NRs and anisotropic structures

Anisotropic metal NPs show different physical and chemical properties along different axes, which are especially important in particles with aspect ratios (length/width) larger than 1. These anisotropic shapes have unique optical, electronic and catalytic properties, and are therefore commonly used as building blocks for a variety of applications in the areas of energy, biology and spectroscopy.

Au NRs have attracted the most attention of all anisotropic metallic NPs. Au is a highly unreactive metal and non-toxic, and Au NRs can therefore be used in drug delivery, disease therapy and biosensing applications [3-5]. In this chapter, we focus our discussion mainly on 2D NRs with anisotropic structure, particularly Au NRs. We present the Au NRs' properties, syntheses and possible structures, and our own results on the syntheses of Au NRs and their use as orientation sensors.

### 2.1. Synthetic approaches for Au NRs

Over the past few decades, anisotropic metal NRs have been prepared through a variety of synthetic approaches. The first synthesis of metal and metal oxide nanowires ("whiskers") was demonstrated in the 1960s, and used a *vapour-liquid-solid (VLS)* approach [6]. In the mid-1990s, a straightforward chemical synthesis was developed for colloidal metal NRs, using *electrochemical* methods [7]. Since then, most colloidal synthetic methods for obtaining Au NPs use the strategy of reduction of Au salt by a reducing agent [8]. Most of the reactions occur in the presence of surface-capping ligands which prevent aggregation of the particles.

The first viable method that provided a simple wet chemistry route for obtaining Au NRs was developed in 2001, and was named *seeded-growth synthesis* or *seed-mediated growth* [9]. The main limitation of this method was the low Au NR yield and the difficulty of separating the different shapes. In 2002, a second method for preparing Au NRs was developed, using the seed-mediated growth method in the presence of silver ions, which showed a substantial improvement in the NR yield [10]. These two methods are considered the basis for the synthesis of Au NRs and are described in Section 4.

In 2005, synthesis with a high yield of Au NRs in aqueous solution was described [11], as well as the modification of the different Au NR shapes [12]. In 2005, a review on Au NRs extensively described the Au NRs' optical properties, syntheses, characterization methods, mechanisms and applications [13].

A significant improvement in the synthesis of monodispersed Au NRs was reported in 2012 [14, 15]. Seed-mediated growth of a wide range of long Au NRs was reported in the same year [16], and a new technique for seedless growth of small Au NRs was also published [17].

Recent modifications have improved control over the aspect ratio of Au NRs and enabled control over the dimensions of NRs. In 2014, a further development in the one-step seed-mediated method for producing shape-controlled NRs was reported [18].

## 2.2. Seeded-growth synthesis of Au NRs

*Seeded-growth* synthesis provides a general method for synthesizing Au NRs and other anisotropic nanostructures with controlled shapes and sizes.

The synthetic path is based on two main steps:

1. *Seeding*: the first step is the formation of small seeds (1-5 nm). The seeds are generated under conditions of high supersaturation, which allow rapid growth of all crystal surfaces, but no shape control. This step typically involves reduction of  $\text{AuCl}_4^-$  aqueous solution by a strong reducing agent (sodium borohydride) where Au(III) ions are reduced to Au(0) atoms which subsequently aggregate to form nuclei. Once the nuclei have grown past a critical size, sub-nanometre clusters are formed into uniform and spherical seeds with stable crystallinity and well-defined facets. The seeds thus obtained have extremely high surface energy, hence appropriate capping agents may be used to cap the surfaces of the particles and thereby decrease their surface energy.
2. *Crystal growth*: the second step is the growth of isotropic seeds into anisotropic nanostructures. Shape control is achieved by the direction surfactants that enable symmetry-breaking in the crystallization. These surfactants are structure-guiding agents which promote the formation of non-spherical and anisotropic shapes in the growth step. In this step, a mild reducing agent (ascorbic acid) reduces Au(III) ions to Au(I). The addition of seeds into the growth solution catalyses the reduction and enables the extra reduction from Au(I) into Au(0).

The aspect ratio of the Au NRs can be adjusted by variation of the concentration of seeds added to the growth solution. For example, addition of a smaller amount of seeds produces a higher aspect ratio and can potentially provide better control over the shape and size of the NCs.

Different reaction components have a strong influence on the product and have been widely investigated [19-26]. The significant parameters that affect the yield are concluded below:

1. Different surfactants with different chain lengths, head group structures and counter-ions.
2. The presence of Ag(I) ions in the growth solution.

3. The amount of seed added to the growth solution.
4. The reaction temperature and pH.
5. The concentration of reagents.
6. The ionic strength of the growth solution.

### 3. Mechanism

#### 3.1. Reduction mechanism

The driving force of a redox reaction is defined as the difference between the redox potentials of two half cells ( $\Delta E$ ); accordingly, the value of  $\Delta E$  has a great influence on the reduction kinetics. Higher  $\Delta E$  causes a more spontaneous and rapid reaction. For instance, the use of a strong reducing agent (sodium borohydride in the seed solution) produces small seeds due to a rapid reaction and a high  $\Delta E$ , whereas a mild reducing agent (ascorbic acid in the growth solution) enables the production of larger particles due to relatively slow reaction rate and a low  $\Delta E$ .

#### 3.2. Au NR seeded-growth mechanisms

In this section, we summarize the key procedures for shape-controlled Au NRs and review the commonly known mechanisms. Different mechanisms have been proposed for the synthesis of Au NRs; nevertheless, this process is still not fully understood [27, 28].

It is commonly suggested that preferential interactions of the surfactants or additives with crystallographic facets along Au NCs provide the shape-directing mechanism for NRs.

Overall, two different methods for seeded-growth synthesis of Au NRs are mostly used: (i) Ag(I)-assisted synthesis and (ii) stepwise additive synthesis. Both methods are based on the same principle: small seeds of Au NPs (1-5 nm) are first prepared by fast reduction through a strong reducing agent and, subsequently, the seeds are used to initiate further NC growth.

At present, centrifugation is necessary to separate the Au NRs from the mixture of other Au nanostructures in the solution.

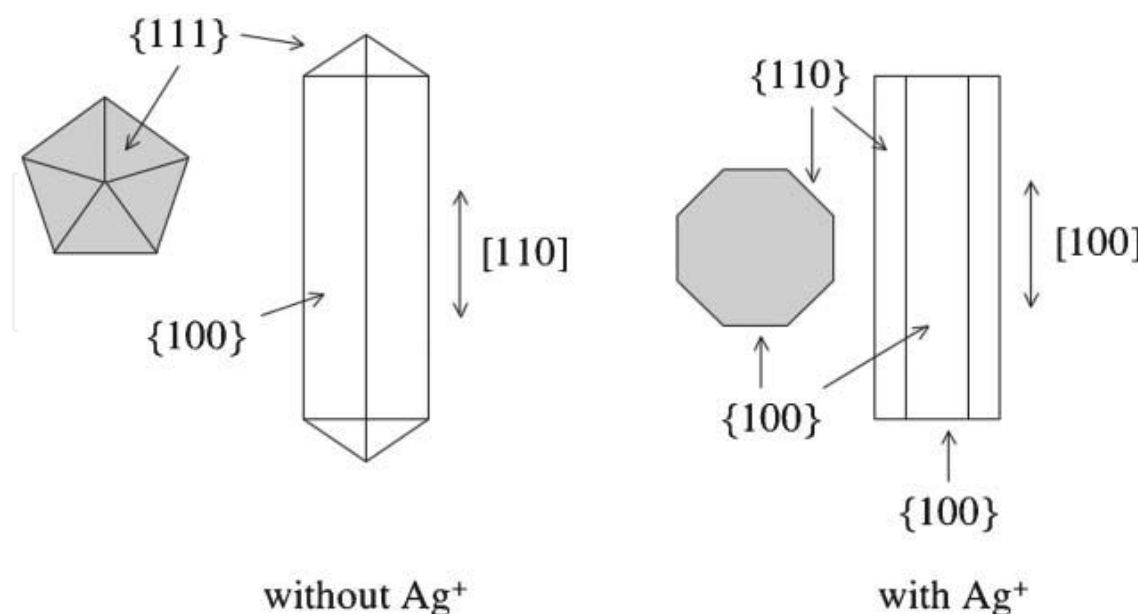
In Ag(I)-assisted synthesis, there are only two solutions: the seed and the growth, while the stepwise additive synthesis uses a total of four solutions: the seed solution and three different growth solutions. The first growth solution (A) is used as the seed solution for the next growth solution (B), and this growth solution (B) is subsequently used as the seed solution for the last growth solution (C).

The differences in the reagents and conditions between the two methods are summarized in the following table:

Seed solution	Growth solution	Au NR structure
<ul style="list-style-type: none"> <li>✓ CTAB (surfactant)*</li> <li>✓ HAuCl<sub>4</sub></li> <li>✓ NaBH<sub>4</sub> (strong reducing agent)</li> <li>✓ 1.5 nm CTAB-Au NCs with single-crystal motif</li> </ul>	<ul style="list-style-type: none"> <li>✓ CTAB (surfactant)*</li> <li>✓ HAuCl<sub>4</sub></li> <li>✓ Ascorbic acid (mild reducing agent)</li> <li>Silver nitrate</li> </ul>	<p>Ag(I)-assisted synthesis</p> <p>Product: single-crystal NR</p> <ul style="list-style-type: none"> <li>• High rod yield</li> <li>• Aspect ratio of 4.5</li> </ul>
<ul style="list-style-type: none"> <li>✓ Citrate (surfactant)*</li> <li>✓ HAuCl<sub>4</sub></li> <li>✓ NaBH<sub>4</sub> (strong reducing agent)</li> <li>3.5 nm citrate-Au NCs with twinning faults motif</li> </ul>	<ul style="list-style-type: none"> <li>✓ CTAB (surfactant)*</li> <li>✓ HAuCl<sub>4</sub></li> <li>✓ Ascorbic acid (mild reducing agent)</li> <li>✗ No silver nitrate</li> </ul>	<p>Stepwise additive synthesis</p> <p>Product: penta-twinned NR</p> <ul style="list-style-type: none"> <li>• Low yield of NRs with further morphologies</li> <li>• Aspect ratio of 6-20</li> </ul>

The two synthetic approaches produce different NR structures (Figure 1):

1. Penta-twinned-like rods obtained in the absence of silver ions.
2. Single crystal rods obtained in the presence of silver ions.



**Figure 1.** The structures for Au NR: penta-twinned with a [110] growth direction (left), and single crystal with a [100] growth direction (right) [29].



As mentioned above, the growth mechanism has not yet been fully proven for either process, but we describe here the most reasonable mechanisms for both Ag(I)-assisted and stepwise additive syntheses.

### 3.2.1. Ag(I)-assisted synthesis

The presence of small amounts of silver nitrate ( $\text{AgNO}_3$ ) during the synthesis has a dramatic effect on the final shape and crystalline structure. Silver nitrate is used as a source for Ag(I) ions which are essential for producing high yields of NRs with low aspect ratio (less than 5). The concentration of the silver ions has excessive influence on NR dimensions [10]. Higher concentration produces a larger aspect ratio in the NRs.

The commonly accepted explanations of the possible mechanism are:

1. Adsorption of silver ions at the NR surface: during growth, Ag(I) ions (in the form of  $\text{Ag}^+ \text{Br}^-$ ) adsorb on the Au-CTAB interface and stabilize it. The Ag(I) ions adsorption onto the NR surface restricts growth by binding to specific facets and therefore promotes growth on the less covered facets. For example, an Ag monolayer on the Au{110} surface acts as a strong binding agent, and therefore the total growth rate in this direction is significantly decelerated.
2. Underpotential deposition (UPD): the silver ions cause underpotential deposition, which is the deposition of the first and sometimes second monolayer of a metal at potentials more positive than the *Nernst potential* of the metal being deposited. The UPD arises during addition of metal ions (e.g., Ag ions) onto a metallic substrate (e.g., Au NRs), therefore causing the symmetry-breaking.

The growth of Au NRs is directed by silver UPD on the longitudinal faces. Slower growth of {110} side faces and faster growth of {100} end facets results in a breaking of the growth symmetry and adjustment of the final anisotropic shape [30]. The growth rate between the Au{110} and Au{100} facets of the *f.c.c* (face-centred close-packed) Au structure can be simply attuned by varying the Ag ion concentration.

### 3.2.2. Stepwise additive synthesis

The shape and size control of the Au NRs is achieved by the preferential adsorption of CTAB onto the different NR facets [26, 31]. The widely accepted explanations of the mechanism are summarized below:

1. The CTAB acts as a stabilizer and is selectively adsorbed on certain growing faces of the NC, causing anisotropic growth in the NR structures. Selective binding of bromide to the {110} or {111} surfaces stabilizes those surfaces; therefore, the Au deposition at those sites is decelerated.
2. Formation of CTA-Au-Br complexes that template NR formation and slow the rate of Au deposition.

3. The CTAB is used as a surfactant and serves as a cationic micelles template for directing the growth. The CTAB micelles bilayer is composed of a first layer of quaternary ammonium head groups (facing the Au surface) and a second layer of surfactant head groups (facing the aqueous media). There are three interfaces of the CTAB bilayer:
4. The Au nanorod-CTAB interface, where the surfactant layer is bound to the Au surface by electrostatic interactions between the cationic head group of the quaternary ammonium and the anionic sites of the Au surface.
5. The CTAB bilayer itself, where the bilayer assembly is energetically favoured owing to hydrophobic interactions between the surfactants' tails and hydrophilic interactions of the charged head group with the aqueous media.
6. The outer CTAB exposed to the water media.

## 4. Adjustment of NC morphologies

### 4.1. Kinetics and thermodynamics in NCs

Syntheses of metallic NCs with a variety of shapes, including polyhedra, plates, wires, rods, bars and tripods have been previously reported [32, 33]. The rate of crystallization, types of product, morphology, size distribution and the particular properties are dependent on a large number of parameters. Those parameters include the crystallization conditions (for instance, temperature, stirring, seed structure and volume), and the composition-dependent parameters (for instance, pH, solvent, reagents, ratio between the elements and ionic strength).

The control over the yield of NCs can be divided into thermodynamics and kinetics control:

- *Thermodynamic control* is effective when the reduction rate is relatively fast. Commonly, seed formation is favoured by thermodynamics and represents the lowest surface energy of the NC shapes. The attempt to minimize the total surface energy of the system produces thermodynamically favoured shapes.

For the face-centred cubic (FCC) Au structure, the surface energies of the crystallographic facets are in the order of  $\{111\} < \{100\} < \{110\}$ , which implies that a single-crystal seed should take an octahedral or tetrahedral shape in order to maximize the expression of  $\{111\}$  facets, and therefore minimize the total surface energy of the solvent-exposed faces.

- *Kinetic control* is dominant when the reaction rate is significantly slowed down, which enables the formation of crystals with higher surface energy. As a result of the slower reaction rate, the concentration of reduced Au atoms is very low; therefore, the atoms aggregate into small clusters and produce shapes with higher surface energy.

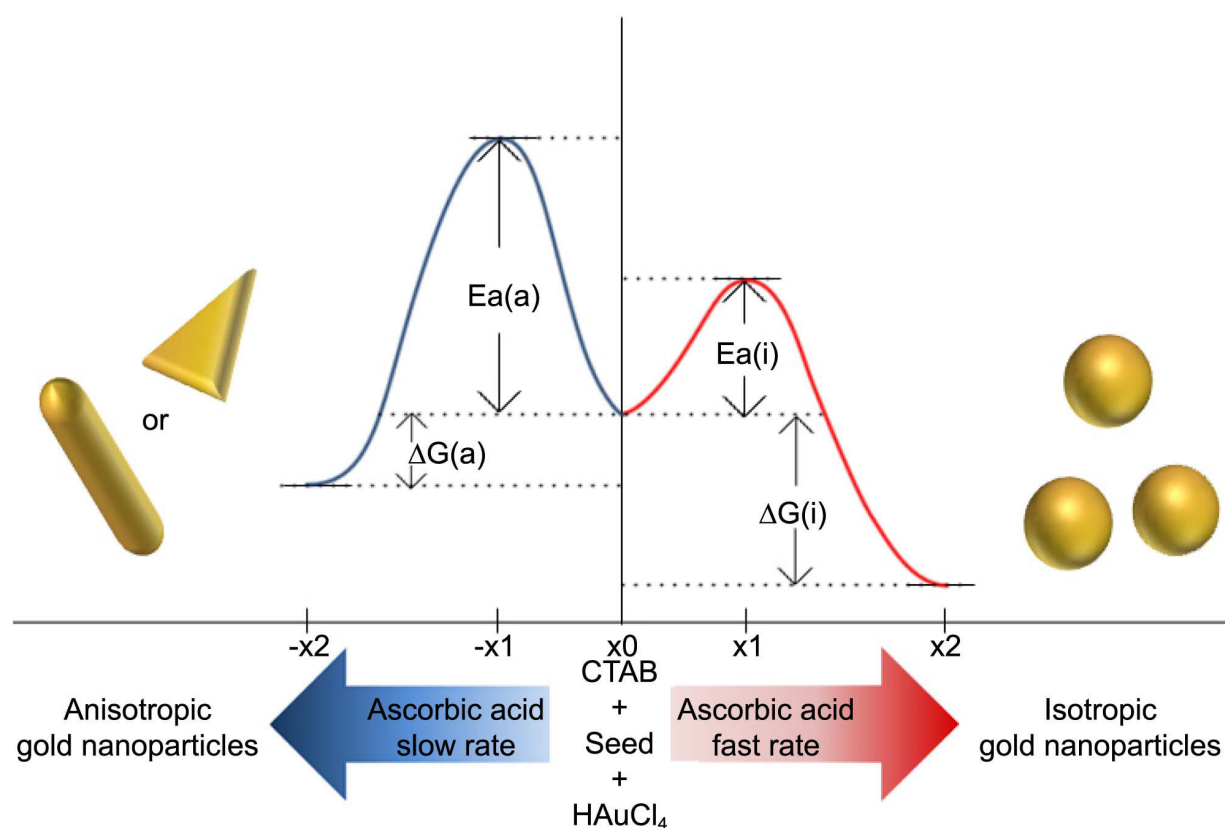
### 4.2. Control over Au NC shape

As with other metallic NCs, Au NC shapes are adjusted by varying the reaction conditions. The parameters which have the strongest influence on NC structures and the exposed facets



are the seed structure and the ions added to the growth solution. As described in previous sections, silver ions (in the case of Ag(I)-assisted synthesis) and halides (in the case of step additive synthesis) are commonly used to adjust seed growth into different morphologies. The different Au NP morphologies are regulated by silver UPD (in the presence of silver ions) or by kinetics (in the absence of silver ions). The concentration of Ag ions in the growth solution and their interactions with the NP surface adjust the product to yield Au nanostructures such as bipyramids {110} or rhombic dodecahedra {110}. Kinetic control arises in the absence of silver ions, when the rate of the reaction affects the final product to yield Au nanostructures such as truncated bitetrahedra {111}, octahedra {111} or cubes {100}.

The formation of anisotropic or isotropic Au NCs can be explained by the *Gibbs free energy* formula (where  $\Delta G^*$  is the minimum energy necessary to form a nucleus). The activation energy ( $E_a$ ) for anisotropic structures is much higher than the activation energy for isotropic structures and, as Figure 2 demonstrates, the change in the *Gibbs free energy* of anisotropic Au NPs is lower than the change in that of isotropic Au NPs. Consequently, isotropic structures are thermodynamically favoured and have a lower and more stable energy profile [25].

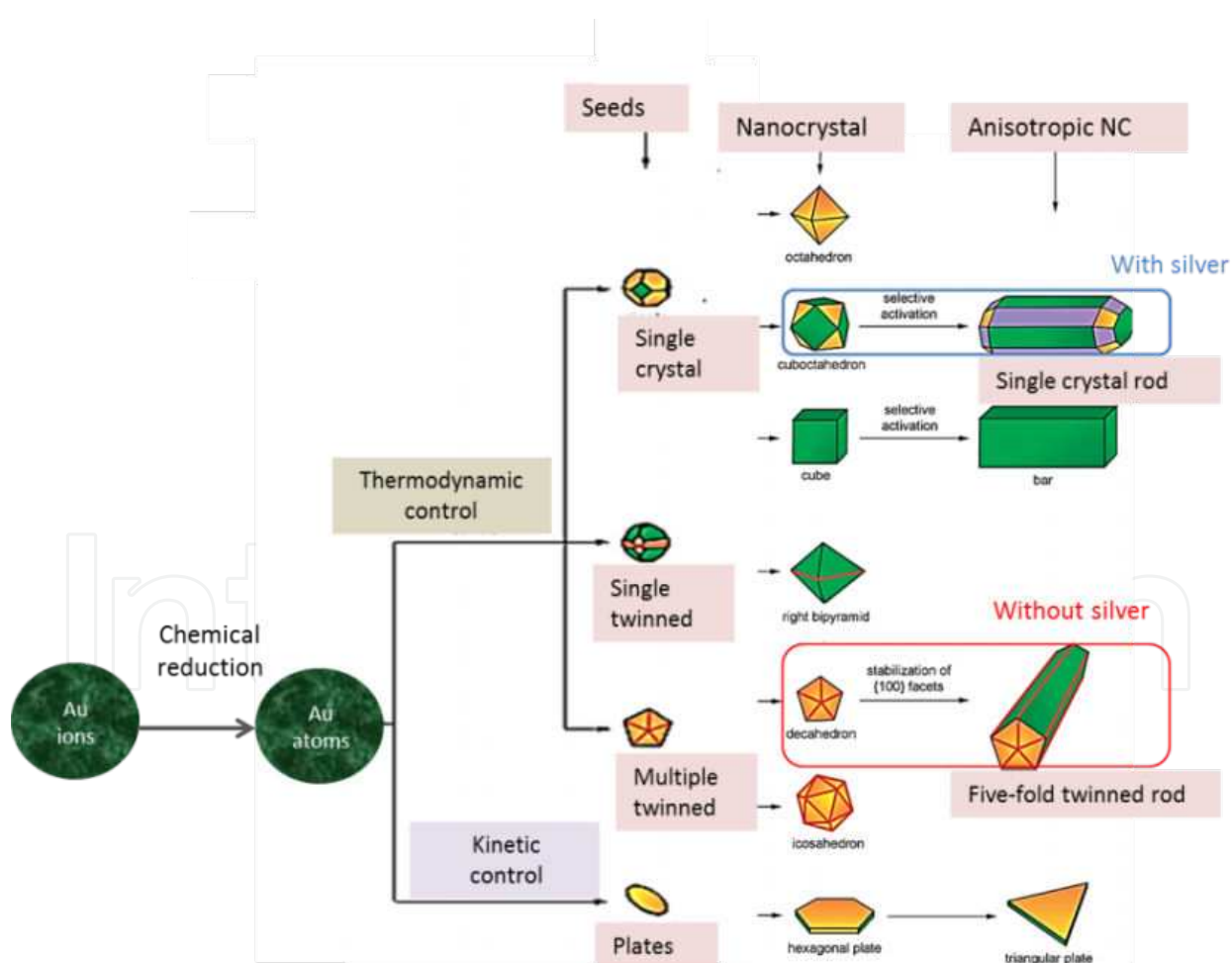


**Figure 2.** Proposed schematic diagram of the reaction pathway during thermodynamically and kinetically controlled synthesis [25].

Control of the addition rate of ascorbic acid into the growth solution changes the reaction rate and adjusts the product because, when ascorbic acid is added, the solution is supersaturated and has high Gibbs free energy. The fastest addition rate gave the highest initial concentration

of ascorbic acid, which led to small homogenous gold nanospheres obtained from the large number of small nuclei during the nucleation process. In this case, the supersaturated solution reduces the overall *Gibbs free energy* back to equilibrium by forming the thermodynamically favoured Au nanospheres. In order to increase the probability of Au anisotropic shape formation, the nucleation process has to stop while the growth process continues. In this case, the concentration of the growth species must be less than the minimum concentration of nucleation, and this is achieved by a slow addition rate of ascorbic acid.

A summary of the role played by the kinetics and thermodynamics in the case of Au NCs is presented in Figure 3. After the first chemical reduction of Au ions into atoms, the seeds' nucleation, taking the thermodynamically controlled path, produced morphologies of single-crystal, single-twinned or multiple-twinned seeds. Further growth of the seeds into NCs and anisotropic structures, in the presence of additives, obtains rod shapes (the pathways for anisotropic NRs are highlighted in blue and red). In the case of the kinetically controlled path, seeds with plate shapes are grown into hexagonal and triangular plates.



**Figure 3.** Scheme presenting the growth mechanism into different NCs and NRs. The scheme is based on reference [30] with additional explanations.

## 5. Results of Au NRs in our study

In our study, we used three well-established methods in order to synthesize Au NRs and additional shapes. The main aim was to obtain Au NRs in the absence of silver ions in order to investigate the ability of Au NRs to polarize light (see Section 7.2).

Below, we present environmental scanning electron microscope (E-SEM) images of Au NRs and other shapes that were synthesized in our work, based on the three established protocols.

### 5.1. Au NRs with aspect ratio of up to 4.7

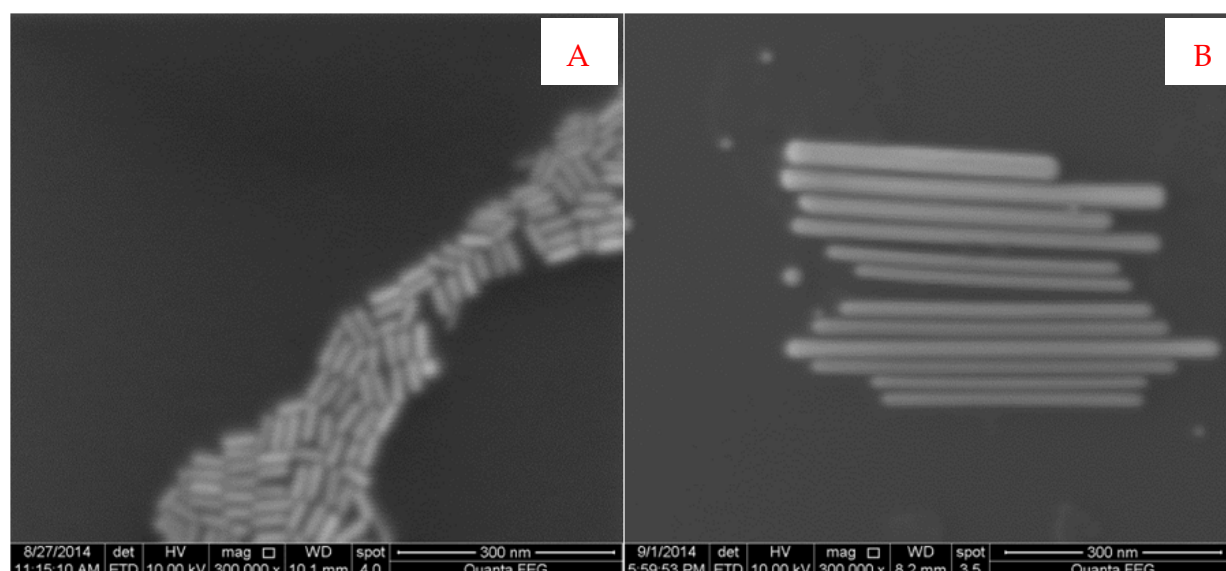
The Au NRs were synthesized using the Ag(I)-assisted procedure based on reference [10]. The E-SEM images of the Au NR solutions showed an average aspect ratio of 4.5 and a regular length of 40 nm (Figure 4A).

- *Seed preparation:* CTAB solution (5 mL, 0.20 M) was mixed with 5.0 mL of 0.5 mM HAuCl<sub>4</sub>. To the stirred solution, 0.60 mL of ice-cold 0.010 M NaBH<sub>4</sub> was added, which resulted in the formation of a brownish-yellow solution. Vigorous stirring of the seed solution was continued for 2 minutes and it was kept at 25 °C.
- *Preparation of Au NRs:* CTAB solution (5 mL, 0.20 M) was added to 0.2 mL of 4 mM Ag-NO<sub>3</sub> solution at 25 °C. To this solution, 5.0 mL of 1 mM HAuCl<sub>4</sub> was added, and after gentle mixing of the solution 70 µL of 0.0788 M ascorbic acid was added. Ascorbic acid as a mild reducing agent changes the growth solution from dark yellow to colourless. The final step was the addition of 12 µL of the seed solution to the growth solution at 27-30 °C. The colour of the solution gradually changed within 10-20 minutes.

### 5.2. Au NRs with aspect ratio of up to 20

The Au NRs were synthesized using the three-step seeding method (stepwise additive) with no presence of silver ions based on reference [26]. The produced Au NRs had a typical length of 280 nm and an average aspect ratio of 15 (Figure 4B).

- *Seed preparation:* A 20 mL aqueous solution containing  $2.5 \times 10^{-4}$  M HAuCl<sub>4</sub> and  $2.5 \times 10^{-4}$  M tri-sodium citrate was prepared in a flask. Next, 0.6 mL of ice cold 0.1 M NaBH<sub>4</sub> solution was added to the solution all at once, while stirring. The solution turned pink immediately after adding NaBH<sub>4</sub>, indicating particle formation. The particles in this solution were used as seeds within 2-5 hours after preparation.
- *Preparation of Au NRs:* Three test tubes (labelled A, B and C), each containing 9 mL growth solution, consisting of  $2.5 \times 10^{-4}$  M HAuCl<sub>4</sub> and 0.1 M CTAB, were mixed with 0.05 mL of 0.1 M ascorbic acid. Next, 1.0 mL of the 3.5 nm seed solution was mixed with solution A after 15 seconds. After 30 minutes, 1 mL of B was mixed with C.



**Figure 4.** E-SEM image of Au NRs obtained in our study using (A) Ag(I)-assisted synthesis and (B) stepwise additive synthesis. The scale bar= 300 nm.

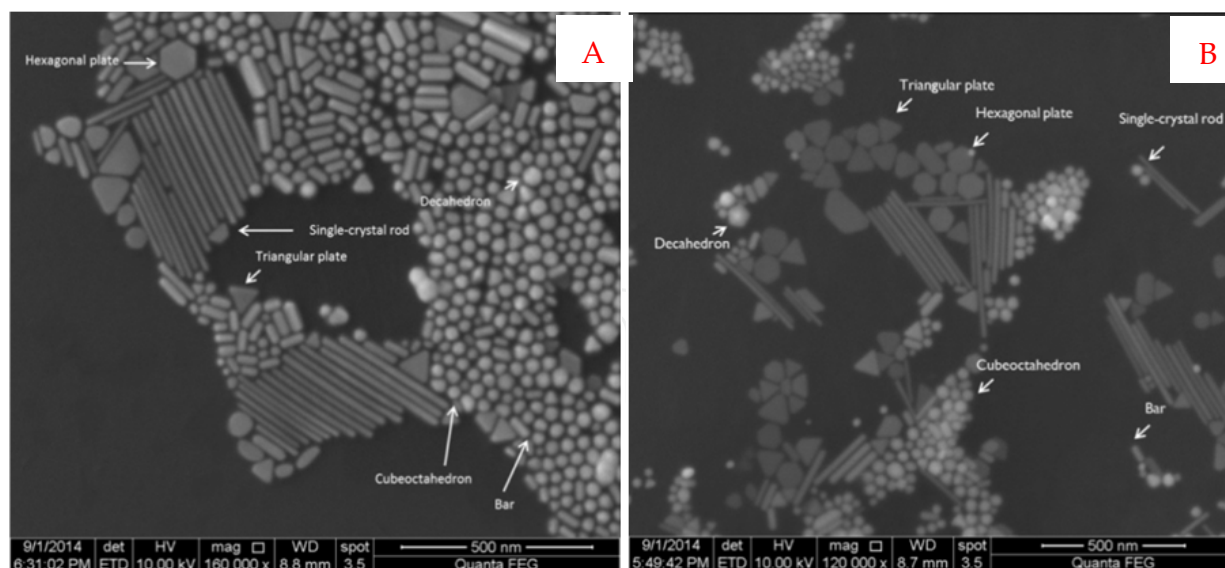
### 5.3. Au NRs and additional morphologies

The Au NRs were obtained by using one-step growth in the absence of silver ions, based on reference [26]. This sample formed different aspect ratio rods and bars, spheres, hexagonal plates, triangular plates, decahedrons and cuboctahedrons (Figures 5A and 5B). Separation of the different nanostructures using centrifugation was not successful.

- *The seed solution* was prepared using the same previously described seed preparation.
- *Preparation of Au NCs:* In a clean test tube, 10 mL of growth solution, containing  $2.5 \times 10^{-4}$  M  $\text{HAuCl}_4$  and 0.1 M CTAB, was mixed with 0.05 mL of 0.1 M freshly prepared ascorbic acid solution. Next, 0.025 mL of the seed solution was added. No further stirring or agitation was done. Within 5-10 minutes, the solution colour changed to reddish-brown.

We used the same preparation method in all of the three procedures:

- *Procedure for shape separation:* Au NRs were concentrated and separated from spheres and surfactant by centrifugation. Next, 10 mL of the particle solution was centrifuged at 2000 rpm for 6 minutes. The supernatant, containing mostly spheres, was removed and the solid part containing rods and some plates was redispersed in 0.1 mL water.
- *E-SEM images* were acquired by environmental scanning electron microscope (E-SEM) with Quanta FEG, FEI instrument at acceleration voltages of 10 kV. The samples were prepared by placing 100  $\mu\text{L}$  of the particle solution on 1 mm X 1 mm silicon wafers. The silicon wafers were previously washed with ethanol and water and dried under nitrogen stream.



**Figure 5.** Different Au NC morphologies using silver-free seed-mediated growth. A and B are two different areas of the sample.

## 6. Applications of Au NRs

Au NRs are commonly used in industrial applications, including chemical sensing and plasmon-enhanced spectroscopies, in addition to innovative biosensors, optoelectronic devices, bioimaging, drug delivery and photothermal therapy [34].

### 6.1. Plasmon resonance of Au NRs

*Plasmon resonance* is an optical phenomenon that occurs when a metallic NP of an appropriate size interacts with incident photons and induces an oscillation of the conduction band electrons at the particle surface [35]. The electromagnetic field is enhanced when there is a plasmonic interaction between the wave and the metal.

There are two kinds of plasmon resonance:

1. *Surface plasmon resonance (SPR)*: coherent oscillation of the surface conduction electrons excited by electromagnetic radiation.
2. *Localized surface plasmon resonance (LSPR)*: small spherical metallic NPs are irradiated by light. The incident light causes the electrons of the NPs to delocalize, forming an electric field opposite to that of the wave. At specific frequencies, the electron oscillation is in resonance with the light wave.

The enhancement of the frequency in the local field is determined by the dielectric function of the metal, the dielectric constant of the surrounding medium, and the size and shape of the nanostructure. The effect of plasmonic NPs' size and shape on the SPR has been widely explored [14, 36, 37]. The plasmon resonance leads to a strong extinction of light at the plasmon resonance frequency and can be used for the development of innovative applications [38, 39].



The surface plasmon oscillations in Au NRs are different from those in spherical Au NPs, as they have longitudinal direction and transverse direction. The anisotropic shape displays two separate SPRs for their width and their length. Therefore, Au NRs have complex SPR owing to their high degree of polarizability.

The broad plasmon resonance of Au NRs provides a way of manipulating electromagnetic fields at the nanoscale and enables the investigation of different shape-dependent plasmonic behaviour [40]. The adjustment of plasmon resonance peaks has been extensively reported [41, 41, 43], as well as highly sensitive SPR detection methods using functionalized anisotropic Au NPs [42, 43]. The SPR peaks can be altered by variation of the Au NR aspect ratios, for example changing the CTAB concentration [44].

## 6.2. The use of Au NRs as orientation sensors by polarized light

Local orientation sensors are extremely important tools in the study of the properties of single molecules. The usage of these sensors is widely reported in a variety of fields including: liquid crystal orientation [45], molecular motors [46, 47], the structure of glasses and polymers [48], and the study of liquids in confined spaces [49].

The combination of the lightning rod effect together with the suppression of interband damping make them ideal materials for light scattering. Light scattered off Au NRs is intensely polarized along the long axis [50], making Au NRs perfect orientation sensors in principle.

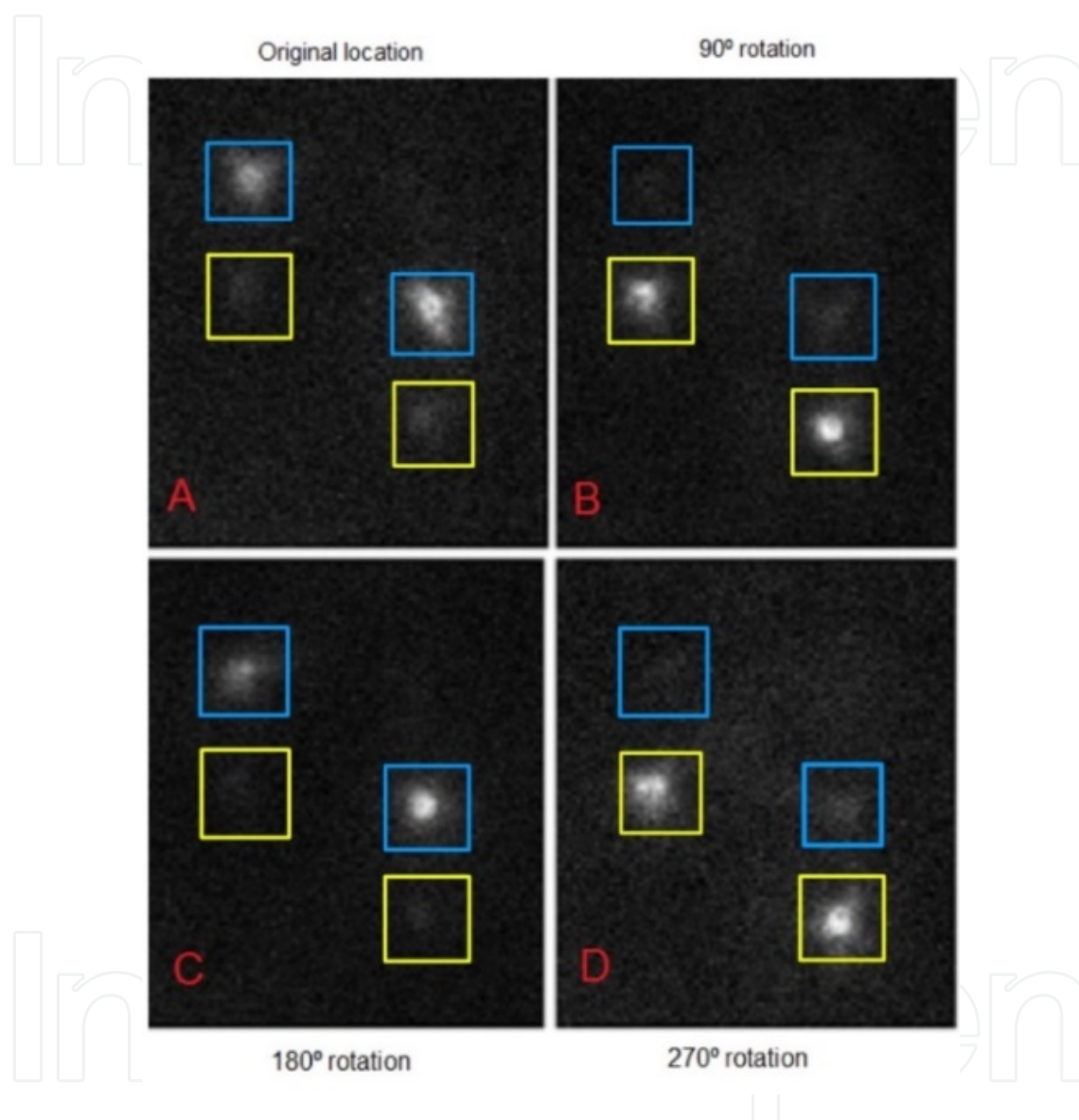
In order to examine their polarization, Au NRs prepared by the seeded-growth method described in Section 6.2 (without silver nitrate). Ideally, in order to obtain a high yield of Au NRs, silver nitrate should be used in this method as a source for Ag(I), but the presence of silver on or within the Au NRs causes unwanted effects on their optical properties. On the other hand, the production of high-yield Au NRs in the absence of silver ions is very challenging. We wanted to overcome the disadvantages of both methods by producing Au NRs with high yield but in the absence of silver ions [26]. After we obtained the desired Au NRs, we tested their suitability for use as orientation sensors using images from a dark-field microscopy setup; dark-field microscopy uses a unique illumination technique that enhances the contrast in specimens that are not imaged well under normal bright-field illumination conditions. It works by illuminating the sample with light that will not be collected by the objective lens, and thus will not form part of the image. The detector will probe only the light that is scattered by objects in the field of view, while direct reflection will not be measured. Our equipment was based on an Olympus illumination platform with a dark-field objective lens MPlan FL-N 50X, NA=0.8 and an Andor iXON+DU-855 FM-CCD camera. The polarizations are images through a SAVART plate calcite and demonstrate the separation between P and S polarization.

The obtained Au NRs were loaded on a glass slide using the following procedure:

- Firstly, we cleaned the glass slide in a solution of 10 % weight alconox using sonication for 15 minutes.
- Cleaning in a DDW solution using additional sonication for 5 minutes.



- Cleaning in an acetone solution using a sonication for 15 minutes.
- Cleaning in ethanol using a sonication for 20 minutes.
- Finally, 20  $\mu\text{l}$  from the solution was dried at the glass slide for 24 hours.



**Figure 6.** Images from a dark-field setup showing the polarization behaviour of two Au NRs through rotation of a polarizer by 90° rotations: (A) original location, (B) 90° rotation, (C) 180° rotation and (D) 270° rotation. Illumination is through a dark-field, so only scattered light is collected by an air objective, while a birefringent calcite crystal splits the light into orthogonal polarization directions. For ease of reference, the top dot of each Au NR is highlighted in blue and the bottom dot in yellow.

The sample of the dry solution of Au NRs was examined using dark-field microscopy. The Au NRs appeared as two separate dots (separated by a few pixels). This splitting is caused by the birefringent calcite crystal which displaces one polarization direction a few micrometres from the other. The scattering intensity of Au NR in one particular polarization direction is directly

related to the square of the cosine of the angle between the rod and the polarization direction (assuming a uniform illumination). Therefore, it is possible to calculate the orientation angle between the light source and the NR by measuring the intensity and using the cosine function of the arc. We concentrated on dots showing fluctuations, and therefore varying light intensity, between the two orientations. This fluctuation indicates that the light passing through the NR is polarized.

In order to verify the polarization obtained, we inserted a linear polarizer on top of the microscope. This polarizer caused a change in the intensity of the two dots directly related to the rotation of the polarizer (see Figure 6).

The rotation of the polarizer by  $90^\circ$  changed the bright dot into a dark one, and the dark dot into bright (Figures 6A and 6B, respectively). As expected, rotation of the polarizer by a further  $90^\circ$  (total  $180^\circ$ ) returned the image to its original state (Figure 6C), while rotating the polarizer by a further  $90^\circ$  (total  $270^\circ$ ) showed the same configuration as the  $90^\circ$  rotation (Figure 6D).

These results demonstrate the ability of Au NRs produced by this method to function as monitor orientation sensors at the nanoscale. Many possible applications can be developed from these new results; for example, binding Au NRs with an organic molecule would provide a method for imaging and sensing the positions of this molecule under different conditions in vitro or even in vivo.

## 7. Future inspiration

We would like to present some of the future challenges and inspirations we consider interesting for advancing innovations in the area of Au NRs.

A significant difficulty arises from the mixture of morphologies in Au NCs obtained using all synthetic methods. Separation approaches involve NR shape separation using surfactant-assisted self-assembly or centrifugation technique. However, the commonly used traditional purification methods, whereby NPs with different masses are separated using centrifugation, are not effective enough. Recently, an accurate purification method has been reported and targeted to overcome previous difficulties by separating NPs with different masses and shapes based on their surface area difference [51, 52]. A big challenge is to develop a highly effective separation technique for collecting Au NRs with different aspect ratios and to purify the rods from a mixture of additional shapes.

Furthermore, functionalization of Au NRs has been recently examined [53, 54]. Previous investigations have reported the formation of useful functional materials, devices and systems, and described their physical, chemical and biological properties. The main challenge will be to overcome the strong bond between the surfactants used in the synthesis and the Au NRs. In contrast to Au NPs, which are usually coated directly with thiols or a weakly-bound anion, Au NRs are synthesized in the presence of a strongly-bound surfactant, and the attempts to functionalize the NRs may lead to their aggregation [55, 59].

Moving forward, a challenging target ahead will be the discovery of new chemical and physical methods for functionalizing Au NRs with compounds that promote efficient binding, clearance and biocompatibility. Additionally, the development of newer characterization methods and facilities to produce further shape control of Au NRs is essential for further extensive modifications. Further advanced seed-mediated syntheses of Au NRs could produce additional control over the resulting shapes and improve reaction efficiency. We believe that the key challenge in the investigation of Au NRs is to understand and prove the seeded-growth mechanism; therefore, further investigations of the reaction kinetics and thermodynamics are still desired.

## 8. Conclusions

In this chapter, we gave an extensive report on the synthetic approaches for obtaining Au NCs, primarily NRs. We reviewed the history of Au NRs syntheses and described the improvements of the product in terms of size and shape control. We focused our discussion on the *seeded-growth synthesis* as the common method for obtaining Au NRs and additional anisotropic morphologies. We defined the two main steps of the *seeded-growth synthesis*, seeding and crystal growth, and extended the explanation of the role of different synthesis components. We specifically presented two different approaches for producing Au NRs, defined as (i) Ag(I)-assisted and (ii) stepwise additive syntheses. We broadly described the difference between the approaches in terms of the conditions, components and the resulting Au NRs' morphology and shape.

Although the mechanism for the syntheses of Au NRs is not fully understood, we presented the most plausible mechanisms. The most reasonable mechanisms for formation of anisotropic Au NCs were explained, as well as the role played by the kinetics and thermodynamics. We found it useful to continue our discussion on the overall adjustment of NCs' structures (which are divided into thermodynamics and kinetics control), and summarized the parameters which have the strongest influence on NC morphologies and shapes.

To illustrate and demonstrate the theory, we presented results of Au NRs obtained in our study based on well-established protocols. We described the experimental conditions for obtaining Au NRs with aspect ratios of up to 4.7 using the Ag(I)-assisted procedure and aspect ratios of up to 20 using the stepwise additive procedure (three-step seeding method). We presented E-SEM images of the Au NRs obtained in both of the cases, and also different Au NC morphologies using uncontrolled silver-free synthesis.

As described in the chapter, Au NRs reveal unique properties that are commonly used in nanotechnology applications. We elected to expand our discussion on two phenomenon: Au NRs' surface plasmon resonance, and the ability of silver-free Au NRs to polarize light. We offered a brief explanation of plasmon resonance and referenced some of the innovative applications. Furthermore, we examined the ability of silver-free Au NRs to polarize light. The intense of polarization along the long axis of Au NRs may lead to their extensive use as orientation sensors at the nanoscale.

## Acknowledgements

Ortal Lidor-Shalev and Zion Elani would like to acknowledge Professor Yuval Garini for fruitful discussion on the mechanism of light polarization in Au NRs. We thank Mrs Anat Vivante for her assistance in the operation of the dark-field set up and Mrs Caroline Lazar for her assistance in editing this book chapter.

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