# The Synthesis and Characterization of Gold Nanoparticles in Water-Soluble Polymers

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## LIST OF ABBREVIATIONS

AD	After death
AuNPs	Gold nanoparticles
СТАВ	Cetylmethylammonium bromide
CTAC	Cetyltrimethylammonium chloride
DDA	Discrete dipole approximation
DNA	Deoxyribonucleic acid
FTIR	Fourier transform infrared
FWHM	Full width half maximum
HDA	Hexadecylamine
HPA	Hexylphosphonic acid
HRTEM	High resolution transmission electron microscopy
HTAB	Hexadecyltrimethylammonium bromide
HTAC	Hexadecyltrimethylammonium chloride
LED	Light emitting diode
LRP	Living radical polymerization
MCD	Magnetic circular dichroism
MLCT	Metal-ligand charge transfer
MPCs	Monolayer-protected clusters
MMPCs	Mixed monolayer protected clusters
MRI	Magnetic Resonance Imaging
MTP	Multiple twinned nanoparticle
<sup>I</sup> H-NMR	Nuclear Magnetic Resonance
NIR	Near-infrared
ODA	Octadecylamine
OEG	Oligo(ethylene glycol)
PAA	Polyacrylic acid
PANI	Polyaniline
PEG	Poly (ethylene glycol)
PVP	Poly (vinyl pyrrolidone)

PS-PVP	Polystyrene-block-poly (4-vinylpyridine)
PVA	Polyvinyl alcohol
QCE	Quantum confinement effect
QDs	Quantum dots
RT	Room temperature
SAED	Selected area electron diffraction
SERS	Surface enhanced Raman scattering
SMAD	Solvated metal atom dispersion
SPB	Surface plasmon band
SPR	Surface plasmon resonance
TEAB	Tetraethylammonium bromide
TEM	Transmission electron microscopy
TGA	Thermal Gravimetric Analysis
TMAC	Tetramethylammonium chloride
TOAB	Tetraoctylammonium bromide
ТОР	Tri-octylphosphine
ТОРО	Tri- <i>n</i> -octylphosphine oxide
UV – Vis	Ultraviolet visible
WGS	Water gas shift
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

#### ABSTRACT

Nanomaterials with critical dimensions at the nanoscale currently attract considerable attention as they show distinct chemical and physical properties that are dependent on their size and shape. A number of techniques have been used to synthesize metal nanoparticles. This thesis presents modified methods for the synthesis of gold nanoparticles, CdSe and Au-CdSe hybrid nanoparticles, capped with water soluble polymers.

Chapter one reviews some basic concepts of nanostructured materials. The electronic structure and properties of gold nanoparticles are discussed. The general synthetic routes of gold nanoparticles are also reviewed with special emphasis on their preparation in water soluble polymers. A few applications of nano-gold including electronics, catalysis and biomedical applications are presented. Finally the characterization techniques used in this study are discussed.

Chapter two describes the synthesis of gold nanoparticles from various chemical reduction techniques. These techniques have yielded a combination of both spherical and anisotropic shaped nanoparticles. Different reducing agents, such as sodium borohydride, presence of sodium hydroxide, ascorbic acid, sodium citrate, tri-sodium citrate and hydrogen peroxide have been used in the reduction of  $Au^{3+}$  ions to  $Au^{0}$ . Water soluble polymers such as poly vinylpyrrolidone (PVP), poly vinyl alcohol (PVA) and organic ligands tri-*n*-octylphosphine oxide (TOPO) and octadecylamine (ODA) were used as capping agents for the gold nanoparticles. Seed-mediated and two-phase techniques were also employed to yield anisotropic nanorods of gold. Different structure-directing agents and phase-transfer agents were used in the formation of anisotropic nanoparticles. The optical properties of the gold nanoparticles were studied by UV/Vis spectroscopy. The structure and morphology of the as prepared particles was determined using powder X-ray diffraction (XRD) and electron microscopy, respectively.

In Chapter three the anisotropic gold nanoparticles synthesized by a UV-irradiation technique through the interaction of HAuCl<sub>4</sub> and a stabilizing agent, poly (vinyl pyrrolidone) (PVP) are presented. The effect of irradiation time on the size and shape of gold nanoparticles was investigated by UV-Visible spectroscopy and Transmission Electron Microscopy (TEM). The other effects that were varied include; capping agent, polymer concentration, precursor concentration, lamp wavelength, solvent, and lastly the presence of citric acid in other reactions. The absorption spectra of all samples show a broad band with the characteristic surface plasmon resonance (SPR) peak visible at around 530 nm. The presence of an additional low intensity absorption peak at a longer wavelength suggests the presence of non-spherical nanoparticles. The TEM measurements show evidence of particle shapes such as spheres, hexagons, decahedrons and truncated triangles as the reaction time was varied.

Chapter four describes the synthesis of CdSe semiconductor nanoparticles at room temperature in the presence of PVP as the capping agent. Different cadmium sources were used and the mole ratios of the starting materials were varied in order to obtain monodispersed CdSe nanoparticles. L-cysteine and PVP-capped Au-CdSe hybrid nanostructures were synthesized at room temperature. The UV-Vis of these hybrid materials showed gold absorption features for the PVP-capped Au-CdSe while for cysteine capped hybrid particles very little features were observed on the spectrum. The denser spherical gold particles are distinctly visible in the TEM images. The high resolution TEM clearly showed the lattice fringes that confirm the crystallinity of the PVP capped Au-CdSe hybrid nanoparticles.

## DECLARATION

I hereby declare that no part of this thesis has been submitted in support of an application for any degree or qualification of the University of Zululand or any other University or Institute of learning.

M.M. Chili

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## Dedication

This work is dedicated to my brother Chris, my father (both late) and my mother, who all made sure that I get what, was the best.

CHAPTER ONE

## INTRODUCTION

#### **1.0 GENERAL INTRODUCTION**

A nanoparticle is, by definition, a particle with all three dimensions in the nanosize range. Nanoparticles are useful in a wide variety of applications in the fields of electronics, chemistry, biotechnology and medicine. For example, gold nanoparticles are being used to enhance electroluminescence and quantum efficiency in organic light emitting diodes [1], palladium and platinum nanoparticles are used as efficient catalysts [2], glucose sensors are developed based on silver nanoparticles [3], and iron oxide nanoparticles are used as contrast agents in diagnosing cancer in Magnetic Resonance Imaging (MRI) [4].

Nanoparticles contain a small enough number of constituent atoms or molecules that they differ from the properties inherent in their bulk counterparts. However, they contain sufficiently large number of constituent atoms or molecules that they cannot be treated as isolated groups of atoms or molecules (Figure 1.1). Therefore, nanoparticles exhibit electronic, optical, magnetic and chemical properties that are very different from both the bulk and the constituent atoms or molecules. For example, the striking colours of metallic nanoparticle solutions (such as gold and silver) are due to the red shift of the plasmon band to visible frequencies, unlike that for bulk metals where the plasmon absorption is in the UV region (a plasmon is a quantum of collective oscillation of free electrons in the metals). This red shift of the plasmon occurs due to the quantum confinement of electrons in the particle, since the mean free path of electrons is greater than the size of the nanoparticle [5,6]. In addition, the optical properties of nanoparticles depend significantly on their size and shape as well as on the dielectric constant of the surrounding medium [7]. For example, in spherical gold nanoparticles, the plasmon absorption is red shifted with an increase in the diameter of the nanoparticle [8]. Likewise, quantum dots (semiconductor nanoparticles such as CdSe and CdTe) exhibit a red shift in their band gap (emission) as their size increases [9,10]. Silver nanoparticles of spherical, pentagonal and triangular shapes appear blue, green and red respectively under a dark field microscope, suggesting a strong correlation between optical property and the shape of the nanoparticles [11]. Gold nanorods exhibit different optical properties when compared to

#### Chapter One

their spherical counterparts. Gold nanorods show two plasmon resonances, one a transverse plasmon at 520 nm and the other a longitudinal plasmon at longer wavelengths. Unlike the transverse plasmon mode, the wavelength of the longitudinal plasmon mode increases with increasing aspect ratio (length divided by width) of the nanorods [12]. In addition, gold nanoparticles dispersed in different solvents exhibit plasmon absorption at different wavelengths suggesting the effect of the surrounding media [7].



**Figure 1.1:** *Nanoparticles in comparison with other biological entities* [5].

One of the current major challenges in materials research is to develop experimental recipes for the systematic control of the size and shape of inorganic materials. Ever since Faraday [13] published a comprehensive report on the synthesis of colloidal gold, reasonable insight into the properties (such as nucleation, growth and kinetics of coagulation) of gold sols have been developed. Control over the size and shape of metallic nanoparticles enables tuning of their optical [14], electronic [15], magnetic [16], and catalytic [17] properties. A number of shapes ranging from rods [18] to cubes [19], disks [20], belts [21], wires [22], and mono-/bi-/tri-/tetrapod metallic nanostructures [23] can be routinely obtained by solution based methods.

However, most of these methods require improvement in yield, purity and monodispersity of the as formed anisotropic structures. With respect to gold, many reports deal with the synthesis of spherical nanoparticles by chemical methods but relatively few reports have appeared on the synthesis of metallic nanostructures with triangular morphology [24]. Such high aspect ratio nanoparticles exhibit interesting optical properties when compared to their spherical counterparts. For example, flat disks and nano-triangles of silver and gold exhibit two (or more) prominent absorption bands, a low wavelength transverse surface plasmon (SP) absorption band (out of plane SP vibration) and an often more intense longitudinal absorption band at longer wavelength (in-plane SP vibration component) similar to that observed for the nanorods [14]. Gold nano-triangles with strong near-infrared (NIR) absorption are expected to have applications in cancer hyperthermia [25] and in architectural applications such as infrared absorbing optical coatings [26].

#### **1.1 PHYSICAL PROPERTIES**

The optical properties of colloidal gold have been known for a long time. Perhaps the most commonly cited and dramatic example is the Lycurgus Cup from the 4<sup>th</sup> century AD, whose glass turns red in transmitted light and green in reflected light, as shown in Figure 1.2. The use of gold colloids for colourants and in drinkable form continues as a cure to this day. It was Faraday, in the mid-19<sup>th</sup> century, who began formal investigations into the interaction between gold colloids and light [13]. In the 20<sup>th</sup> century, physical descriptions, such as Mie theory [27] (and later Gans theory [28]) were able to describe and predict the optical properties of gold nanoparticles. This theory has been extensively utilized since its discovery because it allows the calculation of the particle extinction spectra, as long as the material's dielectric function is known and the size is smaller than the wavelength of the light. The physical origin of the light absorption by metallic nanoparticles is the coherent oscillation of the conduction band electrons induced by the interacting electromagnetic field.



Figure 1.2: Lycurgus Cup in transmitted light (red) and in reflected light (green) [13].

## 1.2 ELECTRONIC STRUCTURE AND PROPERTIES OF GOLD NANOPARTICLES

Gold nanoparticles comprise of tens to thousands of gold atoms and as such have an electronic structure that contains aspects of both the discrete energy levels found in atoms and molecules and the band structure seen in extended metallic materials. Figure 1.3 is a qualitative picture of the changes in electronic structure as gold is shrunk from its bulk state, through the nanoscale, and on to the molecular species. In bulk gold, the electronic properties are characterized by the valence and conduction bands, comprised of an infinite number of bonding and anti-bonding orbitals respectively. The Fermi level lies within the conduction band, allowing the metal to conduct using only thermal energy. As the dimensions of the metal are diminished to just a few tens of nanometers, some discrete energy levels begin to show up at the band edges. Although the properties of the gold nanoparticle remain largely metallic, some molecular transitions can be observed under certain conditions, such as low temperature. As the size is further decreased to below 2 nm, further intercalation of discrete energy levels within the band structure can be observed. As a result, the nanoparticle loses the majority of its metallic character and there is an increased likelihood of observing molecular transitions under ambient conditions.



Figure 1.3: Schematic diagram of the density of states for gold moving from the bulk state to the atomic state [29].

Further decreases in size to small clusters and molecular species see the electronic properties become dominated by molecular transitions. These changes in the electronic structure with size emphasize the need for access to well-defined gold nanoparticles with respect to the core diameter [29]. Because very small gold nanoparticles (< 2 nm) do not possess the continuous band structure of large gold nanoparticles and bulk gold, they have intriguing electronic properties that make them of utility in the emerging field of nanoelectronics.

#### **1.3 SURFACE PLASMON RESONANCE IN NOBLE METAL NANOPARTICLES**

The free electrons in the metal (d electrons in silver and gold) are free to travel through the material. The mean free path in gold and silver is  $\sim 50$  nm; therefore, in particles smaller than this no scattering is expected. Thus, all interactions are expected to be within the surface. When the wavelength of light is much larger than the nanoparticle size it can set up standing resonance conditions, as shown in Figure 1.4.

Light in resonance with the surface plasmon oscillation causes the free electrons in the metal to oscillate. The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constant of both the metal and the surrounding material. This is referred to as the surface plasmon resonance (SPR), since it is located on the surface. As the shape or size of the nanoparticle changes, the surface geometry changes causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency for the electrons, generating different cross-sections for the optical properties, including absorption and scattering.



**Figure 1.4:** Origin of surface plasmon resonance due to coherent interaction of the electrons in the conduction band with light [30].

Changing the dielectric constant of the surrounding material will have an effect on the oscillation frequency due to the varying ability of the surface to accommodate electron charge density from the nanoparticles. Chemically bonded molecules can be detected by the observed change, they induce in the electron density on the surface, which results in a shift in the surface plasmon absorption maximum. This is the basis for the use of noble metal nanoparticles as sensitive sensors. Modern methods using the discrete dipole approximation (DDA) [31] allow one to calculate the surface plasmon resonance for gold nanorods generate an increase in the intensity and wavelength maximum as the aspect ratio increases. Thus, the plasmon resonance can be tuned across the visible region by changing the aspect ratio. The increase in the intensity of the surface plasmon resonance absorption leads to an enhancement of the electric field, as exploited in many applications.

#### Chapter One

#### **1.4 GENERAL SYNTHETIC ROUTES**

The goal in preparing spherical gold nanoparticles is to produce a population of narrowly dispersed gold cores passivated and stabilized by an organic ligand shell. Most commonly, a Au(III) salt is reduced to Au(0) to form an activated species, either in a single step or via a Au(I) intermediate followed by reduction to Au(0). These activated Au(0) species are thermodynamically unstable and rapidly aggregate to form nuclei and eventually the desired gold nanoparticle, as presented in Figure 1.5. The most commonly referenced mechanism for this process comes from LaMer theory [32].



Figure 1.5: Schematic diagram of gold nanoparticle growth.

LaMer theory was originally developed to describe the formation of small sulfur clusters; however, it is broadly applicable to clusters and nanoparticles of other materials. LaMer theory is broken into three stages (Figure 1.5), (I) precursor addition / formation of the activated species, (II) nucleation and (III) core growth. In Stage I, the precursor [Au(III)] is chemically reduced to form the activated Au(0) species. As the concentration of this activated species increases, the system passes into the supersaturated regime (Stage II) at which the Au(0) species begin to aggregate and form nuclei. Nucleation continues until the concentration of Au(0) in solution drops below the supersaturated regime (Stage III), at which the formed nuclei continue to grow through diffusion. This process typically occurs in the presence of organic ligands which associate with the surface and eventually passivate it. Although some syntheses have been developed for

bare gold particles, these species are typically thermodynamically unstable and decompose to bulk metal.

#### **1.4.1 Physical Methods**

Many of the physical methods involve the evaporation of a solid material to form a supersaturated vapour from which homogenous nucleation of nanoparticles occurs. In these methods, the size of the nanoparticle is controlled by temporarily inactivating the source of evaporation, or by slowing the rate by introducing gas molecules to collide with the particles. The growth generally occurs rapidly, from milliseconds to seconds, requiring precise control over experimental parameters.

#### 1.4.1.1 Photochemistry (UV, Near-IR), Sonochemistry and Radiolysis

Photochemical synthesis of nanoparticles is carried out by the light-induced decomposition of a metal complex (photolysis) or the reduction of a metal salt by photogenerated reducing agents such as solvated electrons (radiolysis). UV-irradiation is another method that can improve the quality of the AuNPs [33,34,35], especially when it is used in synergy with micelles or seeds [33]. Near-IR laser irradiation facilitates an enormous size growth of thiol-stabilized AuNPs [36]. Esumi *et al.* [37] reported the use of hexadecyltrimethylammonium chloride (HTAC) (25 – 30 wt %) as a template for an ultraviolet irradiation technique to synthesize colloidal Au nanoparticles with morphologies ranging from spheres to needles. This was done by adjusting the concentration of HAuCl<sub>4</sub> and varying the irradiation time. Chen *et al.* [38] synthesized the shape-controlled gold nanoparticles using a novel irradiation technique at room temperature. This group found that it is not only the concentration of gold cations and the irradiation time but also the concentration and the species of the polymer capping materials that play an important role in the final morphology of the gold nanoparticles.

Sonochemistry can also be used for the synthesis of AuNPs within the pores of silica [39,40,41] and for the synthesis of Au/Pd bimetallic particles [42]. Radiolysis has been used to control the AuNP size [43] or to synthesize them in the presence of specific

radicals [44], and the mechanism of AuNP formation upon  $\gamma$ -irradiation has been carefully examined [45]. AuNPs have been fabricated via decomposition of [AuCl(PPh<sub>3</sub>)] upon reduction in a monolayer at the gas/liquid interface [46]. Laser photolysis has been used to produce AuNPs in block co-polymer micelles [47]. Laser ablation is another technique for AuNP synthesis that has been used under various conditions whereby size control can be induced by a laser [48,49,50].

#### **1.4.2 Chemical Methods**

Chemical methods have emerged to be indispensable for synthesizing nanocrystals of various types of materials. These methods are generally carried out under mild conditions and are relatively straightforward. Nanodimensional materials in the form of embedded solids, liquids, and foams have also been prepared by chemical means and such materials have been in use for some time [6,51,52]. Any chemical reaction resulting in a solvent consists of three steps - seeding, particle growth, and growth termination by capping. An important process that occurs during the growth of a colloid is Ostwald ripening. Ostwald ripening is a growth mechanism whereby smaller particles dissolve releasing monomers or ions for consumption by larger particles, the driving force being the lower solubility of larger particles.

The seeding, nucleation, and termination steps are often not separable and one, therefore, starts with a mixture of the nanocrystal constituents, capping agents, and the solvent. The relative rates of the steps can be altered by changing parameters such as concentration and temperature. One of the important factors that determine the quality of a synthetic procedure is the monodispersity of the nanocrystals obtained. It is desirable to have nanoparticles of nearly the same size, in order to be able to relate the size and the property under study. Hence, the narrower the size distribution, the more attractive is the synthetic procedure. The other important issues are the choice of the capping agent and control over the shape. Sols produced by chemical means can either be in aqueous media (hydrosols) or in organic solvents (organosols). Organosols are sterically stabilized, while hydrosols can either be sterically or electrostatically stabilized. Steric stabilization of

hydrosols can be brought about by the use of polymers as stabilizing agents. Natural polymers such as starch and cellulose, synthetic polymers, such as polyvinyl pyrrolidone, polyvinyl alcohol, and polymethyl vinylether are used as stabilizing agents.

#### 1.4.2.1 Synthesis of Metal Nanocrystals by Reduction

A variety of reducing agents are used to reduce soluble metal salts to obtain the corresponding metals. By terminating the growth with appropriate surfactants or ions, metal nanoparticles are produced. The two reduction methods are outlined as follows;

**Borohydride Reduction -** The reduction by borohydride has been in existence for a number of years [53,54]. The basic reaction involves the hydrolysis of the borohydride accompanied by the evolution of hydrogen, as shown in equation 1.1.

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$$
 1.1

Various metal nanocrystals have been synthesized via the borohydride reduction method [55]. Pt nanocrystals with a mean diameter 2.8 nm were prepared by the reduction of chloroplatinic acid with sodium borohydride [56]. Homiyama and co-workers [57,58] made Cu sols by the borohydride reduction of Cu (II) salts. Green and O'Brien [59] prepared Cr and Ni nanoparticles by carrying out the reduction with Li or Na borohydride at high temperatures in coordinating solvents. Superhydride [60] and hexadecylaniline [61] have been used as alternative reagents to NaBH<sub>4</sub> for the reduction of Au(III) in the synthesis of thiol-stabilized AuNPs. Problems associated with borohydride reduction include its irreproducibility, especially in the aqueous medium and the incorporation of boron in the product [62].

**Citrate Reduction -** The most common method of synthesizing gold nanoparticles is through the use of citrate. Turkevich *et al.* reported that adding sodium citrate to a boiling solution of chlorauric acid led to the formation of gold nanoparticles [55]. Later work showed that variations in temperature and the ratio of reactants allowed for control over

the core size from 10 - 100 nm [63]. More recent work has shown that Au/citrate solutions reduced with NaBH<sub>4</sub> allow the synthesis of nanoparticles < 10 nm in average core size. Despite being the most common method of producing gold nanoparticles, citrate-stabilized nanoparticles are disadvantageous for several reasons. First, they cannot be isolated from solution, making it difficult to store or study them in the solid state. Second, their stability with changes in pH or ionic strength is minimal. Finally, and most importantly, their functionalization, either through ligand exchange derivitization of carboxylic acids in the ligand shell, is extremely limited. To partially overcome these shortcomings, Dahl *et al.* has recently developed diafiltration methods that may allow for ligand exchange with thio1s, thus extending the utility of nanoparticles prepared via the citrate route [64].

## **1.4.3** The Brust-Schiffrin Method: Two-Phase Synthesis and Stabilization by Thiols

Mulvaney and Giersig pioneered the stabilization of AuNPs with alkanethiols in 1993. They showed that it is possible to use thiols of different chain lengths to stabilize gold nanoparticles [65]. The Brust-Schiffrin method allowed the facile synthesis of thermal and air-stable AuNPs. The particles are of reduced dispersity and controlled size, ranging between 1.5 and 5.2 nm. These AuNPs could be repeatedly isolated and redissolved in common organic solvents without irreversible aggregation or decomposition, and they could be easily handled and functionalized just as stable organic and molecular compounds. The technique of synthesis was inspired by Faraday's two-phase system [13] and uses the thiol ligands that strongly bind gold due to the soft character of both Au and S [66]. Table 1.1 summarizes the core size range for AuNPs from different synthetic methods and capping groups. AuCl<sub>4</sub><sup>-</sup> is transferred to toluene using tetraoctylammonium bromide as the phase-transfer reagent and reduced by NaBH<sub>4</sub> in the presence of dodecanethiol [66].

Aqueous borohydride is added to this mixture to bring about the reduction that is modulated by the interface of toluene and water. The thiol molecules also serve as capping agents. The capping action of the thiols is related to the formation of a crystalline monolayer on the metal particle surface. The organic phase changes colour from orange to deep brown within a few seconds upon the addition of NaBH<sub>4</sub>:

$$AuCl_4^{-}(aq) + N(C_8H_{17})_4^{+}(C_6H_5Me) \rightarrow N(C_8H_{17})_4^{+}AuCl_4^{-}(C_6H_5Me)$$
 1.2

$$m\text{AuCl}_4^-(\text{C}_6\text{H}_5\text{Me}) + n\text{C}_{12}\text{H}_{25}\text{SH}(\text{C}_6\text{H}_5\text{Me}) + 3m\text{e}^- \rightarrow 4m\text{Cl}^-(\text{aq}) +$$
  
[Au<sub>m</sub>(C<sub>12</sub>H<sub>25</sub>SH)<sub>n</sub>](C<sub>6</sub>H<sub>5</sub>Me) 1.3

 Table 1.1: Synthetic methods and capping agents for AuNPs of varying core size.

Core Size	Synthetic methods	Capping agents	References
1 – 2 nm	Reduction of AuCl(PPh <sub>3</sub> ) with	Phosphine	[67]
	diborane of NaBH <sub>4</sub>		
1.5 – 5 nm	Biphasic reduction of HAuCl <sub>4</sub> by		
	NaBH <sub>4</sub> in the presence of thiol	Alkanethiol	[66,68]
	capping agents		
10 - 150 nm	Reduction of HAuCl <sub>4</sub> with sodium	Citrate	[55,63,69]
	citrate in water		

Several research groups have fabricated delivery systems based on AuNPs bearing functional moieties, which are anchored with thiol-linkers, in their monolayers. A wide variety of monolayer protected clusters (MPCs) can be formed rapidly and in a scalable fashion using the one-pot protocol developed by Schiffrin *et al.* in 1994 (Scheme 1.1) [66]. In this preparation method,  $AuCl_4^-$  salts are reduced with NaBH<sub>4</sub> in the presence of the desired thiol capping ligand or ligands. The core size of the particles can be varied from 1.5 nm to ~ 6 nm by varying the thiol-gold stoichiometry.



Scheme 1.1: Formation of MPCs using the Schiffrin reaction and MMPCs using the Murray's place-exchange reaction [66].

The functional diversity of MPCs can be extended through the formation of mixed monolayer protected clusters (MMPCs) that can be synthesized directly or through post functionalization of MPCs. A versatile method for the creation of MMPCs is the place-exchange reaction developed by Murray (Scheme 1.1) [68]. In this protocol, foreign thiols displace the native ligands of MPCs in an equilibrium process. Taken together, the control of monolayer structure provided by nanoparticle synthesis, place displacement, and other post-synthetic modification methods [70] can be used to display a wide range of functionality at the particle surface, including biocompatible oligo(ethylene glycol) (OEG) and poly(ethylene glycol) (PEG) moieties [71].

Electron microscopy showed that the diameters were in the range 1 - 3 nm, with a maximum in the particle size distribution 2.0 - 2.5 nm, with a prevalence of cuboctahedral and icosahedral structures. Larger thiol/gold mole ratios give smaller average core sizes, and fast reductant addition and cooled solutions produced smaller and more monodispersed particles. A higher abundance of small core sizes ( $\leq 2$  nm) is obtained by quenching the reaction immediately followed by reduction or by using sterically bulky ligands [72]. Brust *et al.* extended this synthesis to p-mercaptophenol-stabilized AuNPs in a single phase system [73], which opened an avenue to the syntheses of AuNPs stabilized by a variety of functional thiol ligands [74]. Subsequently many publications appeared describing the use of the Brust-Schiffrin procedure for the synthesis of other stable AuNPs or monolayer-protected clusters (MPCs) of this kind that

contained functional thiols [75]. The ratio of thiol and AuCl<sub>4</sub><sup>-</sup> used in the synthesis controls the size of the AuNPs. Murray *et al.* reported and studied the "place exchange" of a controlled proportion of thiol ligands by various functional thiols and the subsequent reactions of these functional AuNPs [76]. Schiffrin reported the purification of dodecanethiol-stabilized AuNPs from tetraoctylammonium impurities by Soxhlet extraction [77]. The influence of nonionic surfactant polyoxoethylene (20) sorbitan monolaurate (Tween 20) on surface modification of AuNPs was studied with mercaptoalkanoic acids [78].

Digestive ripening, i.e., heating a colloidal suspension near the boiling point in the presence of alkanethiols, significantly reduced the average particle size and polydispersity in a convenient and efficient way. This technique also led to the formation of 2D and 3D superlattices [79], a subject of intense investigation [80]. For instance, AuNPs obtained using acid-facilitated transfers are free of tetraalkylammonium impurity, are remarkably monodisperse and form crystalline superstructures [81]. The truncated icosahedron structure is formed in growth conditions in which the equilibrium shape is achieved [82]. Molecular dynamics simulations showed that AuNPs with 1157 Au atoms attained an icosahedral structure upon freezing. A single-toluene phase method was also reported whereby the ammonium salt-stabilized AuNPs were synthesized, followed by an exchange reaction with dodecanethiol. Shape separation of suspended AuNPs by size-exclusion chromatography was monitored by examining the 3D chromatograms obtained by employing a diode-array detection system [83].

## 1.4.4 Microemulsion, Reversed Micelles, Surfactants, Membranes, and Polyelectrolytes

The use of microemulsions [84], reverse micelles, co-polymer micelles [85], surfactants, membranes, and other amphiphiles is a significant research field for the synthesis of stabilized AuNPs [86] in the presence or absence of thiol ligands [87]. The synthesis involves a two-phase system with a surfactant that causes the formation of the microemulsion or the micelle maintaining a favourable micro-environment, together with

the extraction of metal ions from the aqueous phase to the organic phase. This is an advantage over the conventional two-phase system. The dual role of the surfactant and the interaction between the thiol and the AuNP surface controls the growth and stabilization of the AuNP. The narrow size distribution allows the ordering of the particles into a 2D hexagonal close-packed array.

#### 1.4.5 Seeding Growth Method

The seeding-growth procedure is another popular technique that has been used for a number of years. Recent studies have successfully led to control of the size distribution in the range 5 - 40 nm, whereas the sizes can be manipulated by varying the ratio of seed to metal salt [88]. The step-by-step particle enlargement is more effective than a one step seeding method to avoid secondary nucleation. Gold nanorods have been conveniently fabricated using the seeding-growth method [89].

In a typical seeded growth reaction, a previously synthesized "seed" nanoparticle is introduced to a growth solution containing a Au(III) salt, a weak reducing agent, and a directing agent (most commonly a surfactant). Initially, the seed particles grow through the slow-diffusion of gold atoms onto their surface. After an initial period, the seeds have grown into isometric crystals with well-defined Au (111) and Au (100) crystal faces. These enlarged seeds aggregate along these well-defined faces to form pentatwinned species that serve as the starting material for rod growth. Simultaneously with the twinning events the surfactant begins to associate and assemble on the Au (100) faces acting as a directing agent and preventing further growth on the (100) face. As a result, further growth occurs on the Au (111) faces and along the (110) axis, leading to an elongation of the crystal to form nanorods [90].

#### **1.4.6 Biosynthetic Methods**

As far as the synthesis of nanoparticles is concerned there is a great and growing need to develop clean, non-toxic, and environmentally friendly synthetic procedures. Biological methods have recently been considered as possible environmentally friendly nanofactories. Shao *et al.* [91] have shown that biologically related small molecules, L-amino acids, can control the size and morphology of the resultant gold nanostructures.

Both living and dead microorganisms are gaining importance by virtue of their facile assembly of nanoparticles. Prokaryotic bacteria have primarily attracted the most attention in the area of biosynthesis of metal nanoparticles [92]. A significant demonstration of biosynthesis by prokaryotic bacteria was reported by Klaus *et al.* who described the phenomenon of biosynthesis of silver-based single crystals at the cell poles of propagating *Pseudomonas stutzeri* AG259 [93]. Fu *et al.* reported biosorption and bioreduction of silver ions by dried *Lactobacillus sp* A09 [94]. Elsewhere, Nair *et al.* showed the formation of submicron crystallites of Ag, Au and Ag-Au alloy assisted by live *Lactobacillus* strains [95]. Different research groups continued to accomplish some excellent work based on Fungi, especially extracellular synthesis of Ag or Au nanoparticles [96]. They demonstrated that the shift from bacteria to fungi as a means of developing natural 'nano-factories' has the added advantage that processing and handling of the biomass would be much simpler.

The biosynthetic method employing plant extracts has received attention as a simple and viable alternative to chemical procedures and physical methods used to synthesize the metal nanoparticles in recent years. Jose-Yacamann *et al.* firstly reported the formation of gold and silver nanoparticles by living plants [97]. Sastry attained the biosynthesis of metal nanoparticles by leaf extracts and their potential applications [98]. They studied bioreduction of chloroaurate ions or silver ions by a broth of geranium leaf [99] or Neem leaf [100]. Further, they had explored the formation mechanism of gold nanotriangles by lemongrass extracts. The nanotriangles seemed to grow by a process involving rapid reduction, assembly and room-temperature sintering of 'liquid-like' spherical gold nanoparticles [101]. They had also synthesized gold nanotriangles using Tamarind leaf extract and studied their potential application in vapour sensing [102]. In the past couple of years they have demonstrated the synthesis of gold nanotriangles and silver nanoparticles using *Aloe vera* plant extracts [103]. Most of the above research on the synthesis of silver or gold nanoparticles utilizing plant extracts employed broths resulting from boiling fresh plant leaves [104].

#### 1.4.7 Synthesis of Polymer Stabilized Gold Nanoparticles

Water-soluble polymers are widely used to prepare nanoparticles for drug/gene delivery. These polymers are of either natural or synthetic origin and include highly engineered co-polymers. The water solubility of polymers offer the potential to produce nanoparticles in water without the need of organic solvents, which are toxic and can denature labile macro-biomolecules such as proteins. Many hydrophilic polymers are charged in water. They can interact with ionic drugs, allowing controlled association and release of the drugs. Many of these polymers also carry reactive groups by permitting the modification and grafting of functional molecules. On the contrary, because of their water solubility, the polymer chains need to be associated with one another to maintain distinct nanoparticles in water. Based on whether preformed polymers or monomers are used as precursors and the fabrication methods, nanoparticles prepared from water-soluble polymers are divided into three groups: cross-linked preformed polymers, self-assembled block co-polymers and polymerized monomers.

Since the report in Helcher's treatise in 1718 [105], indicating that starch stabilizes water-soluble gold particles, it has been known that such materials, recognized two centuries later as polymers, favour the isolation of AuNPs [106,107]. With the considerably improved recent understanding of the parameters leading to the stabilization of AuNPs and of the quantum-size related interest, there has been a revival of activity in the field of polymer-stabilized AuNPs [108,109,110]. The most commonly used polymers for the stabilization of AuNPs are poly (vinyl pyrrolidone) (PVP), polyvinyl alcohol (PVA) and poly (ethylene glycol) (PEG). Reduction of metal ions in the presence of the polymer is most often chosen because the complexation of the metal cations by the

donor atoms of the polymer is crucial before reduction. In particular, it dramatically limits the particle size [111].

In general, for the synthesis of nano-scale metal clusters, molecules with long hydrocarbon chains adsorbed on the surface of metal particles can decrease particle size and increase the stability of the particles in solution [112]. The use of hydrophilic polymers with long chains as steric stabilizers is usually effective due to the intensive short-range steric repulsions that the polymers are able to produce [113]. Among the polymers, PVP is frequently used in many gel synthesis reactions as a good stabilizer. For the role of PVP, the surface regulating polymer is believed to play a key role in the control of particle size and morphology. PVP that contains nitrogen (N) and oxygen (O) easily attaches to the surface of gold and slows the growth speed of the crystal facets by reducing the surface free energy of gold. As a kinetic controller, PVP adsorbed on specific crystalline surfaces could significantly decrease their growth rate and lead to nanosized particles.

Water-soluble polymer-stabilized AuNPs were prepared from citrate-capped AuNPs by simple contact with dilute aqueous solutions of hydrophilic nonionic polymers based on the monomers *N*-[tris (hydroxymethy) methyl] acrylamide and *N*-(isopropyl) acrylamide that were functionalized with disulfide anchoring groups. The resulting-coated AuNPs could be stored in the dry state and re-dispersed in water to yield sterically stabilized AuNP suspensions. The disulfide-bearing polymers exhibited only a slightly larger affinity for the gold surface than those that do not have the disulfide groups. The polymer layers allowed the free diffusion of small solutes but efficiently minimized the non-specific absorption of large molecules such as proteins, a promising property [114]. AuNPs have been synthesized in graft copolymer micelles [115], and the diffusion of AuNPs in a polymer matrix has been analyzed [116]. Core-shell AuNPs have been prepared by the layer-by-layer technique, utilizing polyelectrolyte multilayer assembled onto polystyrene cores as thin films in which to infiltrate AuNPs, and hollow spheres were obtained by removal of the templated polystyrene cores [117]. It has been suggested that protective polymers can coordinate to metal ions before reduction by forming a

polymer-metal ion complex, and then such a complex can be reduced under mild conditions, resulting in a smaller size and a narrower size distribution than those without protective polymers [118]. Using chitosan with amino groups as protective colloid, fine metal nanoparticles have also been prepared [119].

#### **1.5 GENERAL APPLICATIONS OF GOLD NANOPARTICLES**

Gold nanoparticles have found use in different applications, and some potential applications are still being reviewed. Some of these applications are directly related to their optical properties, where the sensitivity of the plasmon resonance frequency toward the refractive index of the surrounding makes them suitable candidates for biological sensing applications [120]. On the other hand the polarization-dependent response can be extremely useful in applications such as displays or encoding security systems [121]. A further refinement of these types of applications is related to the thermal sensitivity of the nanorods. Recent results show that laser writing can be readily applicable to PVA films containing gold nanorods of various aspect ratios, and thus expanding the possibilities for practical applications of such films [122]. Industrial demand for gold has remained relatively static for a number of years. Gold has unique properties and has been prized highly throughout history.

Current applications are largely based on gold in metallic form and its bulk properties, particularly:

- Its very high corrosion resistance it is top of the electrochemical series.
- Its outstanding malleability can be beaten to leaf 0.1 mm in thickness.
- Its high thermal and electrical conductivity, which is the basis for its use in electronics.

The main use is in electronics, catalysis and biomedical applications which will be discussed in this thesis.

#### **1.5.1 Electronics**

Gold is the material of choice in many electronic applications, especially in telecommunications, information technology and other high performance and safety critical applications. In the early 2000s it was estimated that around 200 tonnes of gold found its way into electronics and electrical components. Where the voltages are small, the circuitry complex or the required reliability is high, gold is usually the preferred choice. Gold-plated connectors are an integral part of plugs and sockets for cable terminations, integrated circuit sockets and printed circuit boards. In general, the more sophisticated the equipment and the greater the need for reliability, the greater the requirement to exploit the advantages of gold as the material of choice. This means that in telecommunications, computers, automotive electronics and defence systems where safety is critical, gold is indispensable [123].

Gold's other main electronic use is in fine wire to connect parts of semi-conductors such as transistors and integrated circuits to ensure reliable connections between components. This bonding wire is specially refined to high purity (99.99 % gold) and would typically be thinner than a human hair (10 - 200 microns).

Gold's use in electronics is based upon its high electrical conductivity along with excellent tarnish resistance. Its main applications are as conductive pastes, bonding wires, connectors and low duty contacts. Where high quality, durable, safety and reliability critical applications operating in arduous environments are concerned, gold is the material of choice. Despite the substantial growth in electronics, growth in gold demand has not kept pace due to miniaturization of devices and thrifting of the gold, coupled with the use of cheaper, competing materials in the low-end, high-volume consumable electronics. The use of palladium as a cheaper alternative to gold in connectors is a typical example of this trend. The growth in automotive electronics continues; here, the electronics operate in arduous under-bonnet conditions, necessitating the use of gold. With environmental restrictions on traditional lead-tin coatings increasing, the use of electro less nickel/immersion gold protective coatings for printed circuit boards is reported to be growing [124].

#### **1.5.2** Catalysis

Catalysts drive many reactions, with the ability to lower the activation energy of the reaction, and thus increase the rate of reaction and the yield of the desired products. The use of nanoparticles as catalysts has increased exponentially as nanoparticle properties and reactions are better understood. The possibility of using less material and having different properties for different shapes of nanoparticles is very attractive. Nanoparticle catalysis has been investigated for both homogeneous and heterogeneous systems. In homogeneous catalysis, Narayanan and El-Sayed [2] have shown that shapes with more corners and edge atoms have a higher reactivity than similar nanoparticles with fewer corner and edge atoms. Thus shape and crystal structure differences can lead to different catalytic rates. Research continues to observe the connection between structure and function for nanoscale catalysts. Small clusters are also found to be very catalytically active, even for materials that display very limited reactivity on the bulk scale [125].

Bulk gold is considered a noble metal, and is very unreactive in the bulk state. However, small clusters of gold are found to be catalytically active. The explanations to this include the electronic and chemical properties of nanoparticles or the shape, size and oxidation state of the nanoparticles. The surface support is also suggested to be responsible for the catalytic activity. The crystal structure of gold has also been proposed to be important in the catalytic properties. This demonstrates new properties for nanoparticles, which are unexpected based on bulk behavior since bulk gold has no catalytic activity, and clusters are efficient catalysts, generating further interest in nanomaterials as new functionality is present on the nanoscale [126].

Catalysts are important to the chemical industry, with over 90 % of all the chemicals manufactured using catalysts. Among other chemists, gold has been traditionally viewed as the exception to the other precious metals in not being very catalytically active. All that changed in the mid-to-late 80's when Hutchings and Yamada *et al.* demonstrated that, when prepared properly, gold can be a very active catalyst [126]. The key to this is preparation of gold as nanosized particles of around 5 nm in diameter on an oxide support material. A major attribute is that gold catalysts are active at low temperatures. For the

oxidation of carbon monoxide, important in automotive pollution control, for example, gold can catalyze the reaction at temperatures as low as -77 °C. Gold can catalyze a range of important reactions – oxidation, hydrogenation, the water gas shift (WGS), reduction of NO<sub>x</sub> and many others. Importantly, its uniqueness allows it to open up new application opportunities, not available to other catalyst systems. The commercial future of gold catalysts is very promising if we consider the growth in patent activity. The bulk of these are concerned with the chemical processing, but pollution control is also strong, where catalyst manufacture and fuel cell application are also significant [127].

In the chemical processing field, the production of acetate monomer based on goldpalladium catalysts is already a commercial application of some importance. This monomer is used in the manufacture of paints and glues. Propylene oxide manufacture is another application nearing commercialization with gold catalyst. This product is used extensively in polyurethane for the automotive and construction markets. The *in-situ* manufacture of hydrogen peroxide at point of use is another application of interest, particularly to the gold mining industry in the destruction of cyanide. The ability to manufacture peroxide on-site will save considerable transport difficulties and costs [128].

As it has been remarked in the above context, pollution control is an exciting area for gold. The use of gold catalysts in diesel-engine vehicles is a possibility since diesel engines run at lower temperatures than petrol engines, at which gold catalysts should be stable. In petrol-engined vehicles, the use of gold as a cheaper replacement for platinum-based catalysts is not considered viable due to the higher temperature of operation and the instability of gold at these temperatures. However, a major area of concern is cold-start conditions when platinum catalysts are not active until the engine warms up. A dual-box system incorporating a low light-off gold catalyst for the short period when the engine is cold, switching to the platinum catalyst as the engine reaches higher temperature, is an option as emission legislation tightens [127].

Fuel cells offer potential applications for gold in both the hydrogen processing systems and as electrocatalyst constituents in the fuel cell itself. The water gas shift reaction is an important stage in producing hydrogen from hydrocarbon fuels and gold catalysts are attractive here for both technical and economic reasons. Carbon monoxide impurities in the hydrogen stream tend to poison current platinum electrocatalysts in the fuel cell and the use of gold catalysts to oxidize CO selectively under wet, hydrogen-rich conditions is another attractive application. In the fuel cell itself, there is already development in portable alkaline fuel cells for both civil and military applications where gold on carbon electrocatalysts are being used in preference to platinum-based ones [129].

The growth in demand for platinum group metals in car catalysts over 2-3 decades illustrates the potential for gold catalysts in the industrial sector and such an off-take potential has been discussed. More excitingly, other applications for gold catalysts in pollution control are emerging. Mercury emissions from electrical power plants and other big plants have led to the possibility of gold catalysts as a solution, where gold catalytically oxidizes the mercury, making its collection possible. Ozone is also another contaminant of the air at ground level raising some concern; gold catalysts could be a solution to the problem. Toxins such as dioxins are also of concern and again gold catalysts are the preferred option in catalytic combustion technology over thermal incineration. One important area attracting considerable attention is safety related – use in gas masks for mines, fire-fighters, police, military, etc. In domestic situations, the next generation of room air fresheners is likely to incorporate gold catalysts as well as fragrances. Finally, another unusual potential application is in the storage of fruit and other produce. Ripening is accelerated by ethylene, which is slowly generated and emitted by the fruit. Catalytic removal of ethylene using gold catalyst should enable longer storage, with economic benefit [130].

#### **1.5.3 Biomedical Applications**

From its early historical use in ancient cultures, gold is becoming increasingly important in many modern medical treatments, ranging from drugs to precision implants. The claims for the medical benefits of gold date back to many thousands of years. Many ancient cultures, such as those in Asia used gold-based medicinal preparations in the treatment of ailments such as smallpox, skin ulcers and measles. Apart from the obvious use of gold alloys in dental restorations, there are also a number of direct applications of gold in medical devices. As with dental applications, these are related to the excellent biocompatibility of gold as a material. Applications include wires for pacemakers and gold plated stents used in the treatment of heart disease. Gold-plated stents are used to help support weak blood vessels. Many surgeons prefer gold-plated stents because these have the best visibility under X-ray. Its X-ray opacity makes it of interest for stents and its ability to be electroformed into complex shapes is being exploited for implants such as myringtomy tubes [128].

Other recent interesting developments include the use of microscopic spheres of gold for the delivery of vaccines, pharmaceuticals, or DNA portions into the human body. Gold has the required adsorptive characteristics and biocompatibility for such applications. It has also been used in the detection of deadly poisons such as anthrax, the development of gold coated lasers to aid in skin rejuvenation and the testing of vaccines. Nano-scale gold particles are also used in biomedical diagnoses.

Gold is the perfect raw material for rapid testing. A rapid test is an inexpensive, disposable, membrane-based technique that provides visual evidence of the presence of an analyte in a liquid sample. Applications for rapid tests include clinical uses (fertility tests, tumor markers, toxicology, and allergies etc.), agricultural uses (food safety, plant and crop diseases) and environmental uses (biological and environmental contamination). Overall, the superior stability, sensitivity and reproducibility of manufacture, make gold a first class raw material component for a wide range of rapid test applications [129].

Gold's ability to be coated with specific organic ligands, including bio-ligands such as DNA, makes it possible to engineer nanostructures in 2-D or 3-D and to tailor properties for applications such as biosensors. The ability to control particle size and ligands enables tuning for specific sensing application. Pregnancy testing kits are already on the market, based on nanogold particles. The use of gold nanoparticles, located at tumors and then heated by X-rays to kill the tumour, looks a promising technique for cancer treatment, whilst the use of gold on silica nanoshells tuned specifically for application in blood diagnostics and even use of gold nanoparticles to kill unpleasant odours in socks are examples of potential medical applications of significance.

Considering its long history, it is a little surprising that the chemistry of gold is not well developed compared to other precious metals, and hence its applications has been hindered. However, its chemistry is now being researched and interesting properties are emerging. Paramount amongst these are two phenomena – luminescence and anti-tumour activity. The properties of the former are of interest in optoelectronics, non-linear optical materials, sensors and devices. Whilst gold compounds have been long used for treatment of arthritis, recent research has shown that some compounds exhibit anti-tumour activity, making them potentially suitable for the treatment of cancer. Gold is biocompatible and has anti-microbial properties, making its use in medical and related applications of increasing interest. More interesting is its proposed use for targeted drug delivery – the 'pharmacy on a chip' concept, where an electronic chip containing microdoses of drugs encapsulated in gold are implanted under the skin. Activating the chip allows drug release in the right location at the right time [130].

#### **1.6 CHARACTERIZATION**

One of the significant challenges in gold nanoparticle synthesis is sufficient characterization in order to establish average core diameter and shape, ligand shell composition and impurity profile of the synthesized material. Developing an accurate picture of the gold nanoparticles allows for a greater understanding of the optical and electronic properties and assists in the development of structure-function relationships. In order to determine the size and shape of the gold nanoparticle core, transmission electron microscopy (TEM) and UV-Visible spectroscopy (UV-Vis) are often used. Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) can be used to determine the identity of ligands bound to the surface versus those in solution or weakly bound. Thermal Gravimetric Analysis (TGA) offers the ability to determine the percentage of organic material in a nanoparticle sample. Comparison of this value versus an expected percentage allows for a determination of how much organic impurities are present in the material. X-ray Photoelectron Spectroscopy (XPS) allows chemical composition and electronic states assessments; giving an idea of how much inorganic impurity (e.g. excess salts) are present in the sample. Using this string of characterization techniques, it is possible to develop a fairly accurate picture of the gold nanoparticle sample, though the development of new characterization methods is an active area of research.

#### **1.6.1 UV-Visible Spectroscopy (UV-Vis)**

Apart from NMR, another rapid and routine characterization technique used for assessing gold nanoparticle samples is UV-Vis spectroscopy. UV-Vis was used to analyze the optical properties of gold nanoparticles, primarily through the plasmon resonance exhibited at ~520 nm; however the location may be shifted due to the dielectric constant of the solvent, ligand shell properties, aggregation or core size. In the case of nonspherical nanoparticles, there is typically more than one plasmon resonance peak due to asymmetry, allowing for assessment of shape as well. Because of the convenience of the technique, UV-Vis allows for rapid, qualitative assessment of the core size and shape.

#### **1.6.2 Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) allows for far more quantitative determination of characteristics including direct visualization of the metallic core. Additionally, electron diffraction experiments can also be carried out, allowing for an assessment of atomic packing and orientation, which is useful for shaped gold nanoparticles. In order to ensure that there is no bias in the size analysis, several images representing diverse regions of the TEM grid and several hundreds to thousands of nanoparticles are taken. This helps to avoid artificial size separation or skewing as a result of drying effects or aggregation.

#### 1.6.3 Powder X-Ray Diffraction (XRD)

X-ray diffraction is a very important technique that has long been used to determine the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, defects, etc. It is the commonly used technique to primarily analyse the characteristic and structural details of nanomaterials. For this reason this technique is normally employed at the early stages of analysis of a synthesized material to give the data on the crystal structure as well as the size of grains and nanoparticles. XRD is a powerful tool; it is non-destructive and highly qualitative. This technique involves monitoring of the diffraction of X-rays after they interact with the sample. This is a crystallographic technique used for identifying various crystalline phases present in solid materials and powder.

The X-ray diffraction patterns are obtained by measurement of the angles at which an X-ray beam is diffracted by the crystalline phases in the specimen. Bragg's equation relates the distance between two *hkl* planes (*d*) and the angle of diffraction (2 $\theta$ ) as

$$n\lambda = 2d\sin\theta$$
 1.4

where,  $\lambda$  = wavelength of primary X-rays, n = an integer known as the order of reflection (h, k and l represent Miller indices of the respective planes). From the diffraction patterns, the uniqueness of nanocrystal structure, phase purity, degree of crystallinity and unit cell parameters of the nanocrystalline materials can be determined. The average size of the nanoparticles can be estimated using the Debye–Scherrer equation:  $D = k\lambda / \beta \cos\theta$ , where D = thickness of the nanocrystal, k is a constant,  $\lambda$  = wavelength of X-rays,  $\beta$  = width at half maxima at Bragg's angle 2 $\theta$ .

#### **1.6.4 Fourier Transform Infrared Spectroscopy (FT-IR)**

Infrared (IR) spectroscopy is a powerful tool, popularly used as a characterization technique in which a sample is placed in the path of an IR radiation source and its absorption of different IR frequencies is measured. IR photon energies, in a range of 1 to 15 kJ/mol, are insufficient to excite electrons to higher electronic energy states, but cause transitions in vibrational energy states. These states are associated with a molecule bonds,

and consequently each molecule has its own unique signatures. Therefore, IR spectroscopy may be employed to identify the type of bond between two or more atoms and identify functional groups. IR spectroscopy is also widely used to characterize the attachment of organic ligands to organic/inorganic nanoparticles and surfaces. More complex molecules contain dozens or even hundreds of different possible bond stretches and bending motions, which implies the spectrum may contain dozens or hundreds of absorption lines. This means that the IR absorption spectrum can be a unique fingerprint for identification of a molecule.

#### **1.7 OBJECTIVES OF THE STUDY**

In previous sections, the concepts of well-defined nanomaterials in general and welldefined gold nanoparticles specifically were developed. Despite much progress in the last few decades, significant challenges remain in obtaining well-defined gold nanoparticles. Methods for preparing gold nanoparticles with smaller sizes, shape dispersity and increased purity are required to ensure that the promise of gold nanoparticles in future technologies is met. In this thesis, several techniques, such as chemical reduction, the seed-mediated method, the two-phase method and uv-irradiation techniques are proposed while others are modified methods for achieving the goals of well-defined gold nanoparticle samples.

The main objective of this study was to synthesize novel functionalized gold nanoparticles protected by different polymers by modification of various literature methods. The polymer-protected gold nanoparticles were expected to have different solubilities in water and in organic solvents. Accordingly, water-soluble particles were obtained, depending on the polymers used in the synthesis. Two kinds of polymers with various molar masses, polyvinylpyrrolidone (PVP), and polyvinyl alcohol (PVA), were chosen for this study and synthesis of gold nanoparticles.

Further from this, hybrid-gold nanocrystals were synthesized in the presence of either PVP or L-cysteine as capping materials. The synthesis of metal semiconductors is also

reported in this thesis. All the synthesized gold nanoparticles, hybrid nanocrystals and metal semiconductors were characterized for their optical properties using the UV-Visible spectroscopy, TEM and HRTEM for the morphology, XRD and FT-IR for their crystallinity and Selected Area of Electron Diffraction (SAED) for structural elucidation.

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