

SYNTHESIS, FUNCTIONALIZATION AND CHARACTERIZATION OF GOLD  
NANOPARTICLES

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# SYNTHESIS, FUNCTIONALIZATION AND CHARACTERIZATION OF GOLD NANOPARTICLES

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## **ABSTRACT**

### **SYNTHESIS, FUNCTIONALIZATION AND CHARACTERIZATION OF GOLD NANOPARTICLES**

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Metallic nanoparticles (NPs) with various elemental composition, size, shape and physical or chemical properties has become active field of research. Among all the metal NPs noble metal ones are receiving much attention due to their special optical properties which make them useful for different applications. Noble metal NPs have bright colors resulting from strong surface plasmon resonance absorption usually in the visible region. The colors are size and shape dependent and provide the tuning of optical properties. The optical properties of NPs are also strongly depending on the nature of the NPs surface which plays a crucial role on chemical sensing. Therefore, surface modification of NPs has become increasingly important. In this study, gold NPs were prepared in aqueous phase by seed-mediated growth method. To enhance the optical properties, surface functionalization was performed by coating NPs with silver. The coating process was achieved by chemical reduction of silver ions on NPs

surface. Thickness of silver layer on the NPs were attempted to be controlled by the amount of silver salt added into NPs solution. Coating process of different types of gold NPs (rod, octahedral, star) was done by the same procedure. Moreover, this attempt yielded control over silver layer thickness on sphere, rod and octahedral shaped gold NPs, but not on branched NPs. The structure, composition and spectroscopic properties of Au-Ag core shell NPs were characterized by UV-Vis spectroscopy, Field Emission Transmission Electron Microscope (FE-TEM) and Energy-dispersive X-ray (EDX) studies, Scanning Electron Microscope (SEM), and X-Ray Photoelectron Spectroscopy (XPS). The analysis showed that all NPs studied were successfully coated with silver and promising for further explorations in sensing and imaging applications.

**Keywords:** Gold NPs, Core-shell NPs

## ÖZ

### ALTIN NANOPARÇACIKLARIN SENTEZİ, FONKSİYONLANDIRMASI VE KARAKTERİZASYONU

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Çeşitli elemental kompozisyona, boyuta, şekle ve fiziksel veya kimyasal özelliklere sahip metalik nanoparçacıklar aktif bir araştırma alan haline gelmiştir. Metal arasında soy metal nanoparçacıklar değişik optik özellikleri nedeniyle çok ilgi çekmektedir. Soy metal nanoparçacıklar genellikle görünür bölgede güçlü bir yüzey plazmon rezonans doğurma özelliğinden dolayı parlak bir renge sahiptir. Bu renkler boyut ve şekle bağlıdır ve optik özellikleri ayarlamada büyük katkıda bulunur. Bunların yanı sıra, metal nanoparçacıkların fonksiyonel özelliklerinin arttırılması bakımından, yüzey niteliğine bağlı bulunmaktadır. Bu nedenle, nanoparçacıkların yüzey modifikasyonu her geçen gün artarak önem kazanmaktadır. Bu çalışmada, nanoparçacıkların tohum-aracılı büyüme yöntemi ile sulu fazda hazırlanmıştır. Optik özellikleri geliştirmek için, yüzey gümüş nanoparçacıklarla kaplayarak

fonksiyonlandırma yapıldı. Kaplama işlemi nanoparçacıklar yüzeyinde gümüş iyonları kimyasal indirgeme ile elde edilmiştir. Nanoparçacıklar üzerindeki gümüş tabaka kalınlığı eklenen gümüş tuz miktarıyla kontrol edilmiştir. Farklı şekildeki altın nanoparçacıkların kaplama işlemi aynı prosedürle yapılmıştır. Dallı nanoparçacıklar dışında, küre, çubuk ve oktahedral şekilli altın nanoparçacıkları için gümüş tabakasıyla kaplama prosedürü ve tabaka kalınlığı kontrolü başarıyla yapılmıştır. Au@Ag çekirdek kabuk nanoparçacıkların yapısı, bileşimi ve spektroskopik özellikleri Elektron Mikroskop (SEM) UV-Vis Spektroskopi, Alan Emisyonu Transmisyon Elektron Mikroskobu (FE-TEM) ve Enerji Dağılımlı X-ışını (EDX), ve X-ışınları Fotoelektron Spektroskopisi (XPS) çalışmaları ile karakterize edildi. Altın nanoparçacıkları başarıyla gümüş tozuyla kaplandı ve algılama/görüntüleme uygulamalarında daha fazla araştırma için ümit olduğunu gösterdi.

**Anahtar kelimeler:** altın nanoparçacıklar, çekirdek kabuk nanoparçacıklar

**To my lovely parents...**

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## CHAPTER 1

### INTRODUCTION

The word “nanotechnology” covers the brilliant properties of matter and devices on the 1-100 nm scale. In a way, the nanomaterials are very old and used since ancient time. For instance, nanoparticles (NPs) have been used in art for more than 2000 years as dyes in ceramics and paintings because of their beautiful colors [2]. In mid-1800s Michael Faraday prepared brightly colored gold NPs solutions and they are still being displayed in Royal Institution’s Faraday Museum in London [3]. Then, Richard Feynman set the stage for the nanotechnology revolution in his famous lecture “there is plenty of room at the bottom”, in which he predicted the inevitable miniaturization of devices into nanometer size with enhanced performances [4].

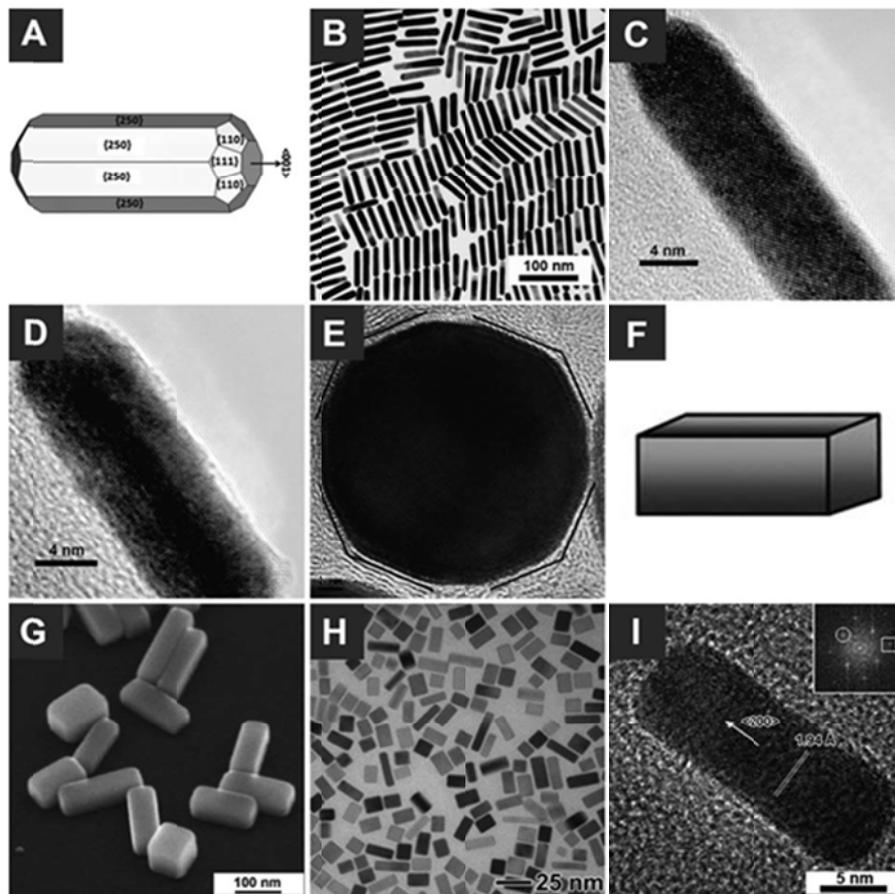
The advent of new analysis techniques lead to development of new, innovative synthesis methods and discovery of new NPs with better understanding. Now there are numerous ways (i.e. chemical, physical, physicochemical and biological) of synthesizing NPs in different media. Among these methods, chemical methods have the longest history and are the most commonly utilized ones. Synthesis of 10-20 nm gold NPs by Turkevich [5] and Frens [6] in 1951 with a simple, effective solution based method opened up the ways of synthesizing new NPs by just chemical reduction in solution [7].

Among all the metal NPs noble metal ones are especially exciting due to their special optoelectronic properties and applications associated with those properties [8-12]. Noble metal NPs have beautiful colors resulting from strong surface plasmon resonance absorption usually in the visible region [8, 10, 11, 13-17]. The colors of

the NPs vary with their size and shape. Therefore, optical properties of NPs can be tuned by modifying their sizes and shapes [10, 11, 14, 15, 18-20]. Noble metal NPs with anisotropic morphologies yield strong electromagnetic field at the tips of the NPs with sharp features [1, 21-24]. This electromagnetic field processed at the metal surface/tip where molecules absorbed. By this way, the molecules can be detected in trace amounts. The special optical properties of anisotropic shaped noble metal NPs lead them to various uses in sensing and imaging techniques such as Surface Enhanced Raman Scattering (SERS) spectroscopy [8, 11, 13, 14, 19-22, 25-35]. Surface of the metal NPs play an important role on enhancing particles' functionalities and controlling the properties (e.g. reactivity, stability, electronic structures, etc.) to fit to a particular application [9, 25, 36]. Therefore, possibilities of chemical modification of the NPs surface lead to development of new research avenues where the functionalized particles can be used in construction of super lattices, targeted drug delivery, therapeutic agents in cancer imaging and etc. [14, 37-39]. Functionalization of NPs surface can be achieved by coating with various materials such as polymers, biofunctional molecules, or with different metal to obtain core-shell NPs system [40-45]. One of the very attractive core-shell NPs system is gold core and silver shell. Gold colloids has the advantage of easier preparation with higher degree of homogeneity compared to silver colloids. However, their optical properties are not as superior as the ones of silver. Therefore, coating gold NPs with silver is a very promising practice to have a NPs system with high structural homogeneity and enhanced optical properties.

In this study, gold NPs with various structural morphologies (i.e. sphere, rod, octahedral, branched) were coated with silver. The used method has the various advantages such as being simple, reproducible, and affordable. The synthesized Au@Ag core-shell NPs are believed to be promising addition to growing class of hybrid systems.

a High Resolution Transmission Electron Microscope (HRTEM) study of cross section of gold nanorods. Liz-Marzan and co-workers reported that the side facets of gold nanorods are enclosed by high- index (250) facets. Figure 1.2 (F), (G) shows TEM and SEM images of nanobars, which all six faces enclosed by (100) facets [50, 51]. They have relatively simple structure. The TEM and HRTEM of palladium nanobars are represented in Figure 1.2 H and I, respectively [51].

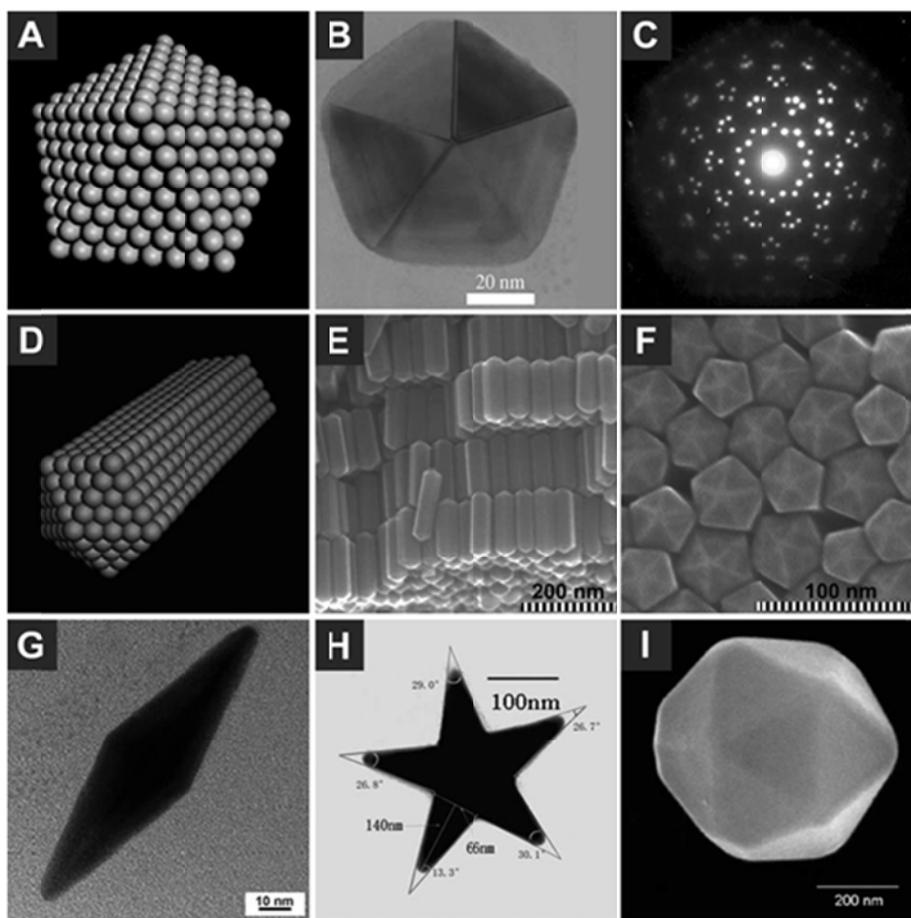


**Figure 1.2** One-dimensional single-crystalline noble metal nanocrystals: (A) geometrical model of gold nanorods [46], (B) TEM images of gold nanorods [49], (C and D) HRTEM image of a gold nanorod oriented in the (110) direction and (100) direction, respectively [48], (E) HRTEM image of a standing gold nanorod, showing the cross-section of gold nanorods [52], (F) geometrical model of nanobars [51], (G) SEM image of a silver nanobar [53], (H) TEM image of palladium

nanobars, (I) HRTEM image of a single palladium nanobar and the corresponding Fourier transform pattern (inset) [51].

Other structures, such as singly twinned, multiple planar twinned, cyclic penta-twinned and multiple twinned icosahedral structures, are also important.

Decahedral nanocrystals, nanorods, nanowires, bipyramids, and starfish-like nanocrystals are related to cyclic penta-twinned structures.



**Figure 1.3** Noble metal nanocrystals with cyclic penta-twinned structures: (A) geometrical model of a decahedral nanocrystals [54], (B and C) HRTEM image and a representative selected area electron diffraction pattern of a single decahedral silver nanocrystals [55], (D) geometrical model of a penta-twinned nanorod [54], (E and F) SEM images of silver nanorods [56], (G) TEM image of a gold bipyramid [57], (H) TEM image of a starfish-like gold nanocrystals [58], (I) SEM image of an icosahedral gold nanocrystals [46].

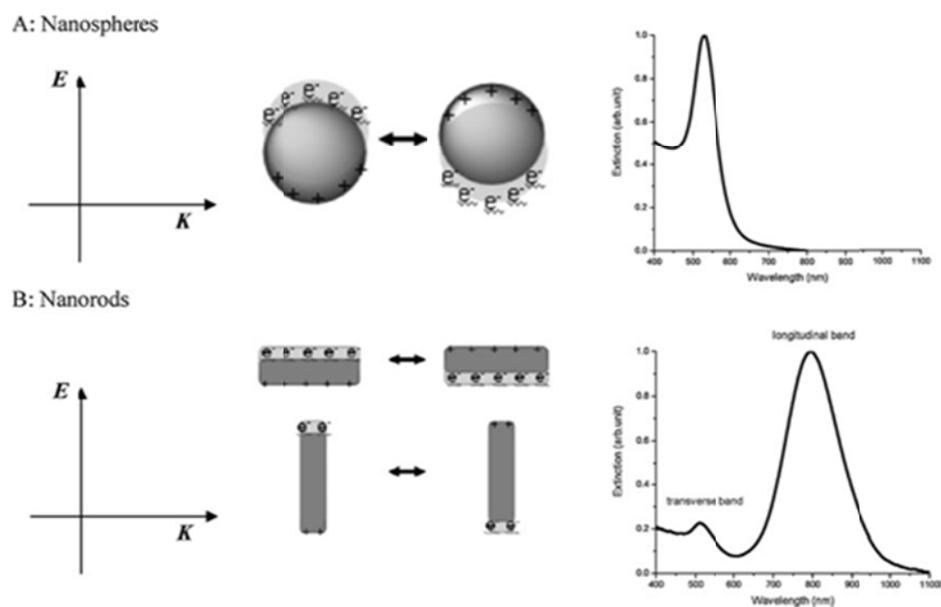
Moreover, the optical properties of anisotropic gold and silver NPs rely on their aspect ratio and they are tunable throughout the visible, near infrared and infrared regions of the spectrum. In addition to that, the plasmon resonance absorption of anisotropic shapes is even stronger causing increased detection sensitivity. Finally, strength of absorption in isotropic materials is hardly depend on its size which cause limitation in sensing application. However, in the case of anisotropic materials all properties are strongly dependent on their size and shape [59]. This is one reason of why this work was focused on anisotropic shape of noble metal NPs.

In solution phase, thermodynamic and kinetic parameters are responsible for the final shapes of noble metal nanocrystals. Thermodynamic parameters consist of temperature and reduction potential, while kinetic parameters consist of reactant concentration, diffusion, solubility, and reaction rate [46]. Anisotropic material growth in kinetic manner, since it identifies preferential and directional growth. Preferential absorption of capping molecules to specific facets can force or enhance the crystal growth in some direction. This is how various types of NPs are produced. By modifying and controlling these parameters nucleation and growth stages can be controlled. Finally, desired shape can be obtained [46].

The preparation of different types of noble metal NPs such as silver and gold has received more attention. Creating the desired size, shape and monodispersity of NPs is required continuous working on it. Therefore, developing and refining of new synthetic techniques is an important task. By better understanding of NPs behavior, lead to use of these NPs in more applications. Thus, the preparation of NPs is continuous to be an active area of research.

## **1.2 Optical properties of noble metal NPs**

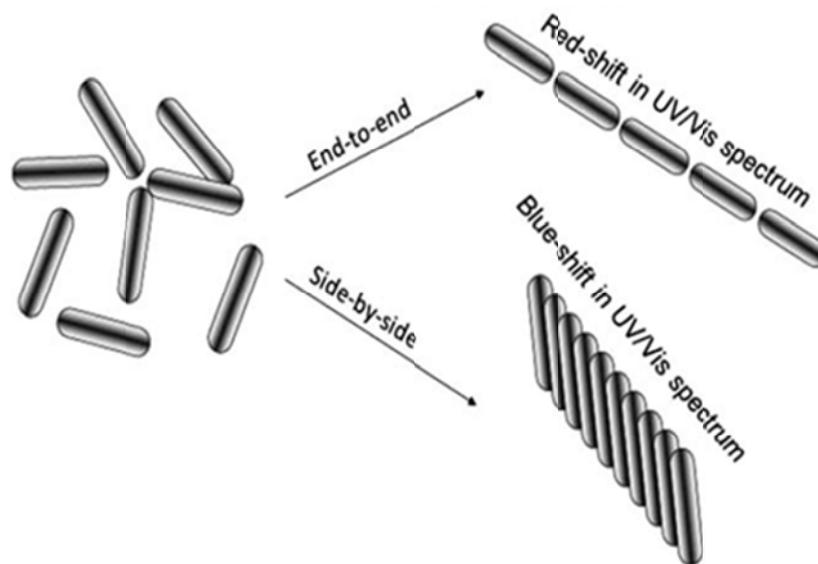
The most magnificent example showing the beautiful colors of noble metal NPs Lycurgus Cup from the 4<sup>th</sup> century AD. Analysis has revealed that the cup glass contains small amounts of silver and gold (~ 70 nm). The cup looks green in the reflected light and appears red when a light is shone from inside (Fig 1.6). This is



**Figure 1.8** The interaction of polarized light and gold nanospheres (A) an nanorods (B) [13].

The resonance condition is determined from absorption and scattering spectroscopy and referred as the surface Plasmon resonance since it is located at the surface [8]. The Surface Plasmon Resonance (SPR) causes a strong absorption of light. The SPR condition is rely on the particle size, shape, structure, and the dielectric properties of the metal and surrounding medium [62]. Spherical NPs such as gold and silver, and copper reveal a strong SPR band in the visible region [63]. However, anisotropic NPs exhibit better optical properties than spherical one. For instance, gold nanorods have a one million times stronger fluorescence yield than spherical NPs. Moreover, hollow or core-shell structures and anisotropic NPs such as triangular and branched structures show very large red shift of the SPR band wavelength compared to the spherical. In nanorods polarization of the incident light oscillation can occur in two directions: the short and long axis. Plasmon oscillation through short axis exerted an absorption band in the visible region, while long axis has much stronger absorption band. The short axis called the transverse band and long axis as the longitudinal band (Figure 1.8 B). Longitudinal band is red shifted and extended to near infrared region by increasing aspect ratio (length/width). These optical properties can be explained

by Gans theory. This theory based on a discrete dipole approximation [13]. Different interaction of nanorods also affects the UV-Vis spectrum of nanorods. For instance, side by side assembly cause blue shift and end-to-end assembly gives rise to a red shift in the UV-Vis spectrum (Figure 1.9).



**Figure 1.9** The different ways of arranging the nanorods.

Changing the dielectric constant of the surrounding material results in altering of the oscillation frequency [8]. However, altering the capping material is most important in determining the shift of the plasmon resonance. Capping material induces the electron density of the surface resulting in a shift in the surface plasmon resonance absorption maximum [8]. For example, forming a silver shell around the gold nanorods, shifts the longitudinal plasmon resonance to shorter wavelength [12]. This is the main reason for the use of noble metal NPs as sensitive sensors. Maxwell equation solutions are used to understand the interactions of an electromagnetic wave with NPs. Maxwell equations depend on analytical formulations. Therefore, there are a lot of types of calculation methods for metal NPs. For instance, Mie theory is desirable for solid sphere, concentric spherical shells, a spheroid, and an infinite cylinder. For another geometrical shapes different calculations with some approximations are required [64]. However, there is lack of analytical solutions for

many NPs shapes. This lack leads to a barrier to understanding their spectra quantitatively and to taking further information about their near field properties. In order to solve Maxwell's equations numerically a various types of methods have been developed. For example, T-matrix method, the discrete dipole approximation (DDA), and finite difference time domain method (FDTD) [65].

### **1.3 Synthesis of noble metal NPs**

Interesting properties and tiny volumes of NPs have made them desirable in many scientific and technological areas. Due to many properties of NPs differ with size, shape, crystal structure, surface chemistry and chemical composition; synthesis methodologies that can produce new NPs require continuous working. These tunable amazing properties trigger researchers to produce various types of NPs through physical and chemical methods of synthesis. With exploring new synthesis methods, new nanomaterials with unique properties have been generated. Thus, they pave the way to new scientific studies and technological application.

NPs can be produced by “top down” and “bottom up” basic approaches in solid, liquid, solution or gaseous state. In the top down approach, NPs are achieved by the lowering materials from large scale to nanometer range. In this approach, a physical and lithographic principle of micro and nanotechnology is used. NPs producing by top down approach are carried out in expensive tools, which are hardly possible to use in industrial application. Therefore, bottom up method is used to fabricate NPs in high yield and structural purity by differing size, shape structure, composition and surface chemistry. The bottom up approach includes assembly of atomic, ionic, molecular units to produce structures of nanometer range scale. Various processes in chemical synthesis method are implemented by “bottom up” approach. The “bottom up” approach principle is to design and produce any size and morphology via atom by atom deposition. This method also named as “chemical colloidal”[66]. The main advantage of these methods is versatility, affordability and easiness in technological implementation. Due to their colloidal composition, they are preferable in integrating NPs in complex system and devices. Therefore, chemical colloidal methods are

mostly used in preparation of a wide variety of NPs and composites of different materials such as metals, alloys, intermetallics, semiconductors and ceramics. Chemical colloidal synthesis method also widely used to prepare metal NPs, especially noble metal NPs. Chemical colloidal synthesis of these particles involves different methods. For instance, chemical reduction of metal salts, photochemical and electrochemical methods, thermal decomposition of metallic composition in aqueous or organic solvents in the presence of different additives such as surfactants, ligands, polymers and so on [66].

In the case of colloidal synthesis, the nucleation process determines the shapes of metal NPs. There are two types of nucleation process: homogeneous and heterogeneous. In homogeneous nucleation, nucleation and growth take place in one step. Whereas, heterogenous nucleation consists of two steps. The seed and growth solution prepared separately. As prepared seed particles is introduced to growth medium to facilitate the reduction of metal ions. Due to nucleation and growth step carried out in separate stages, it paves the way to introduce seed particles of one metal into a growth solution of a different metal. Moreover, by choosing right seed particles for overgrowth solution various shapes and sizes of NPs can be produced, which could not be achieved by homogeneous nucleation routes [67].

The growth mechanism can be affected by different additives and parameters. The particle is arrested and size can be controlled. The NPs shape can be controlled by charging of the NPs and passivation of the NPs surface by adsorption of suitable species. Charging of the NPs is a well known contribution to the stability of particles. Here, net charges and/or an electric double layer surrounding the particle cause to the stabilization. The second way stabilizing NPs is the intentional use of appropriate capping agents. The capping agents have a physical and chemical similarity with the surface layer of nanostructures. They form a protective layer that makes the NPs surface unreactive against agglomeration or precursor incorporation [68]. Since capping agents selectively adsorb to specific crystal planes, shape control can be achieved. There are different types of molecules that can facilitate shape control. They are polymers, biomolecules, and small molecules such as adsorbed gas and

atomic species such as different metal ions. The most frequently used surfactant molecules for synthesizing metal NPs are cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS), or bis(2-ethylhexyl) sulfosuccinate (AOT) are used. These surfactants possess hydrophilic head group and hydrophobic tail. Depending on the concentration of cosurfactants surfactants readily self assemble into spherical or rodlike micelles in water. However, it is difficult to explain the exact role of the surfactants. Recent works reveal that surfactants could behave as growth directing adsorbates on metal surfaces. Consequently, selective adsorption of surfactants assigns future shape of nanostructures [67]. The most frequently used methods for synthesizing metal NPs are explained below.

### **1.3.1 Polyol process**

The polyol process was first developed by Fievet et.al [46]. The main principle of this method is heating polyol solutions with a polymeric capping agent and metal precursor. In general, during this process Polyvinylpyrrolidone (PVP) is used to stabilize and control shape of nanocrystals. In order to crystallographically control the synthesis of noble metal NPs, the polyol process has turned to diversified method [69, 70]. In the polyol synthesis crystal facet control rely on different parameters such as adding surfactants, polymers, small molecules, and atomic species. To promote the formation of preferable facets of noble metal NPs, these additives especially absorb to specific crystal facets. In general, in the polyol process ethylene glycol, 1,5-pentanediol, and di(ethylene glycol) are used as the solvent and reducing agent [50, 71]. Moreover, the shape of platinum nanocrystals could be controlled by adding silver nitrate [72].

### **1.3.2 Electrochemical process**

The electrochemical method, was first used by Reetz and Helbig to produce metal NPs [73]. In this method, chemical reaction occurs in an electrolyte solution under an applied voltage. In the case of metal NPs nanoporous membrane templates are used. The pores of membrane templates are used for deposition of electrochemically reduced metal ions. NPs can be removed from the template by physicochemical way

[66]. By using this method synthesis of single crystalline gold nanorods can be achieved [49]. For the first time the dependence of optical properties of gold nanorods to aspect ratio was observed. The morphology and size of NPs can be controlled by changing the electrodeposition parameters (e.g. potential, number of coulombs passed, deposition time, temperature, surfactants, etc.) [66]. In the past decade, the electrochemical method also has been used to the crystallographic control of noble metal NPs. By altering the reaction parameters of the electrochemical methods shapes and crystal facets of nanocrystals can be controlled [74].

### 1.3.3 Photochemical process

The metal salts can be reduced to metal nanocrystals under effects of light. The final aspect ratio of metal nanorods could be detected by the amount of silver ions. Moreover, by using light metal nanocrystals shape can be transformed from one crystal facet to another. For example, Mirkin et al. has converted large amount of silver nanospheres into triangular nanoprisms by photoinduced methods [75]. In this method, preferable size (30-120 nm) of nanoprisms could be synthesized by using dual-beam illumination of silver NPs. The process is preceded by surface plasmon excitation. The shape of nanoprisms can also be induced by altering the pH of the growth solutions. The careful selection of some parameters such as stabilizing agents and structural direction agents could promote control of the silver nanocrystals structure during the light driven conversion process. The photochemical method also is very sensitive to growth kinetics [46]. Au@Ag and Ag@Au core shell NPs synthesized by Henglein et al. using  $\gamma$ -irradiation process [66]. Moreover, UV-Vis irradiation also used for shape controlled synthesis of Au, Ag, and Pt NPs.

### 1.3.4 Seed mediated method

In the past ten years, seed-mediated process has been used as most appropriate colloidal method for controlled synthesis of noble metal NPs [25]. The method is a widely used method for synthesizing different types of anisotropic NPs such as rod, stars, triangles, flowers and so on. This method derived from Zsigmondy's 'nuclear' method, which involved two step process [76]. Thus, seed-mediated process also involves two steps. In the first step, 'seed NPs' are prepared by reduction process. Here, metal salt is reduced by strong reducing agent in the presence of stabilizing agents. In general, sodium borohydrate is preferred as reducing agent. In the second step, 'seed NPs' grow into the desired shape in the presence of surfactant or shaping agent and mild reducing agent. The metal salt in the growth solution will be reduced on the surface of the seed NPs. The surfactant molecules serve as templates to yield NPs of desired morphology. The amount of the 'seed NPs' can affect the final size of the NPs synthesized. Addition of different molecules or ions can change the growth direction of the NPs and cause to differently shaped NPs [59]. For instance, the addition of small amount of iodide ion to the gold nanorod solution change shape into triangular nanoprisms [77]. In this process, iodide ion absorption cause to changing crystal growth along the Au (111) direction. Chloride ions also cause to drastic change in the morphology of the rod. The effectively absorbed halide ions alter the morphology from rod to rice shape. Another factor that influences size and shape of nanostructures is concentration of surfactant molecules. For instance, Millstone et al [78] reveal the dependence of surfactant concentration on the morphology determination. In this study, nanoprisms formed only when saturated CTAB solution was used. It indicates the concentration dependence on the morphology of the NPs. The main advantages of this method are no need for specialized equipment, and high yield of NPs can be obtained by solution based processing and assembly can be readily implemented [67].

#### 1.3.4.1 Seed mediated synthesis and mechanism for gold nanospheres formation

Spherical gold NPs are one of the more easily synthesized one. Citrate reduction of gold (III) NPs ( $\text{HAuCl}_4$ ) in water, which was introduced by Turkevich [5] is the most popular methods using for a long time (Table 1.1) [6].

**Table 1.1** Preparation of spherical gold NPs

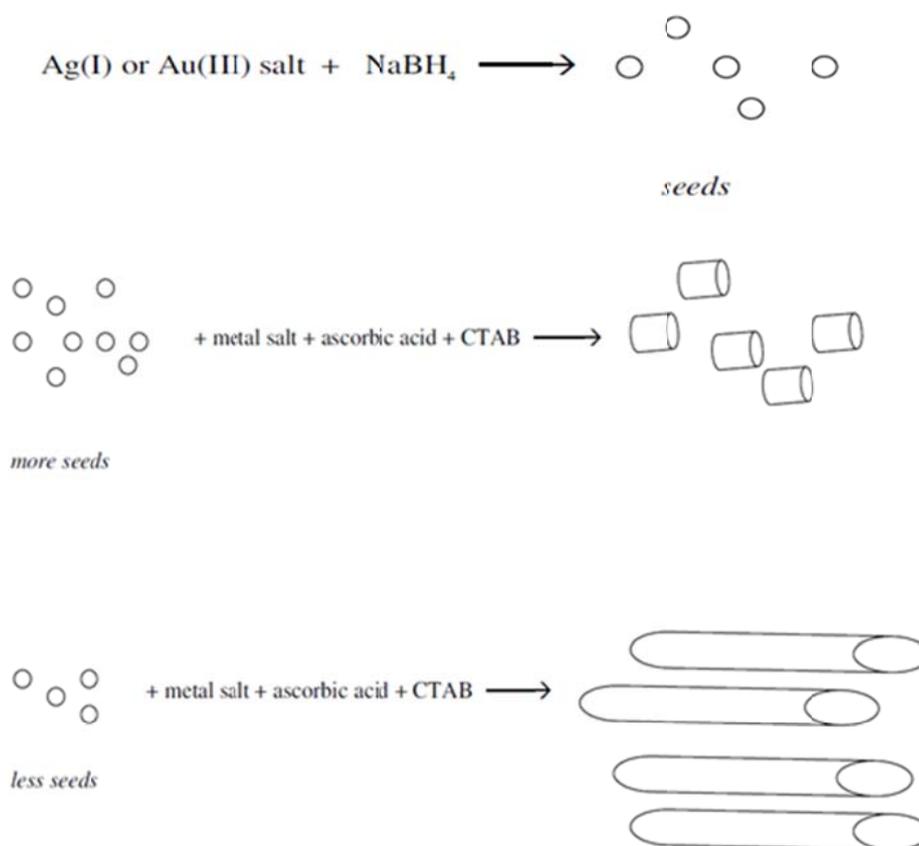
Size	Synthesis method	Stabilizing agent	Distinctive property
10 to 150 nm	Turkevich/ Frens	Citrate	Surface Plasmon band~520 to 580 nm (Au)
1.5 to 15 nm	Brust/modified Brust	Alkane- thiols	Surface Plasmon band ~520 nm

The seed-mediated method is the mostly used method for preparation of spherical NPs. This method, based on reduction of corresponding metal salts and using seeds for further growth process. For example, gold nanospheres in the size range between 3-15 nm were successfully prepared in high yields using a seed mediated growth method [79]. The chemical synthesis of metal particles by reduction of the corresponding metal salts is an easy task. The only main requirement is the mixing of reagents at well defined conditions [80]. Synthesis of monodisperse spherical gold NPs is very important, because in the most cases they are used as seeds for formation of anisotropic metal NPs. In this case, their role is very important since they dictate the final structure of the NPs.

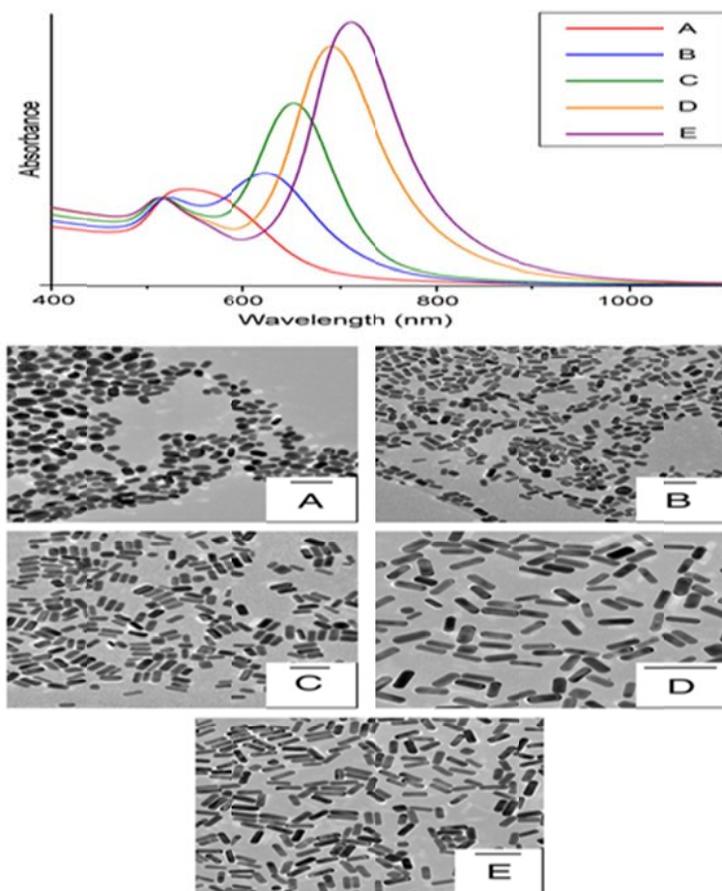
#### 1.3.4.2 Seed mediated method synthesis and mechanism for gold nanorod formation

Gold/silver nanorods are subject of numerous studies due to their special optical properties. It is important to synthesize them with controllable aspect ratio [81]. Mie group were first used seeded-mediated growth method for shape controlled growth of

silver and gold nanorods [82]. The seed-mediated growth approach to make silver and gold nanorods and nanowires with controllable aspect ratio in aqueous solution is properly explained in the study of Murphy and Jana et al. [83]. In this study, the gold nanorod synthesis starts with the reduction of a metal salt in aqueous solution. 3-5 nm 'seed NPs' was prepared in the presence surfactant to prevent the seeds from aggregating and precipitating. "Growth" solution is made from metal salt, and a surfactant, cetyltrimethylammonium bromide, CTAB, that directs the growth of NPs into nanorods and nanowires. Growth is started by introducing of a weak reducing agent, ascorbic acid. Moreover, the amount of seed NPs can identify the final length of nanorods or nanowires. Figure 1.10 demonstrates schematic representation of seed-mediated growth of gold/silver NPs. It is obvious from this figure that the length of nanorods can be controlled by the amount of seed particles.



**Figure 1.10** Schematic representation of the seed-mediated growth approach to the synthesis of metallic nanorods of controllable aspect ratio.

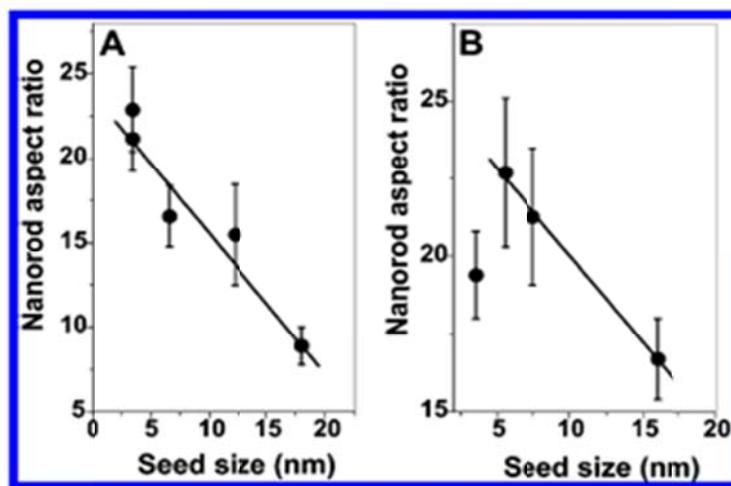


**Figure 1.11** Top: ultraviolet–visible spectra of short gold nanorods with aspect ratios (A)  $1.42 \pm 0.32$ , (B)  $1.82 \pm 0.49$ , (C)  $2.31 \pm 0.55$ , (D)  $2.65 \pm 0.43$ , and (E)  $2.80 \pm 0.37$ . The UV–Vis spectra were normalized to the same absorbance at  $\sim 515$  nm for clarity. Lower panels: transmission electron micrographs of the gold nanorods corresponding to spectra A, B, C, D, and E; all scale bars are 100 nm [84].

The exact mechanism of formation of nanorod particles in aqueous surfactant media remains unclear. According to Murphy et al. CTAB head group preferentially binds to crystallographic faces of gold particles by zipping mechanism [86].

Hydrocarbon tail length in the  $C_nTA^+$  composition is critical for controlling the length of the nanorods and the yields. As the tail length  $C_n$  increases the yield and aspect ratio of the nanorods are increased [88].

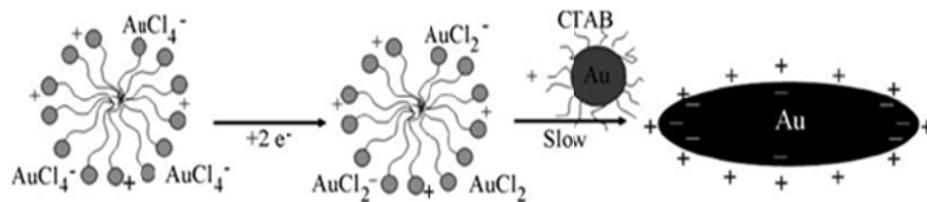
Gole and Murphy [89] report the role of the seed on the gold nanorod synthesis. They show that seed nature also contribute to shape and size of the gold nanorod synthesis. The seed surface can be functionalized with negative or positive charges. Consequently, the effects of this different seeds were studied in their work. Figure 1.14 shows the effect of seeds on the aspect ratio of the gold nanorods. Figure 1.14 A shows the effect of positively charged seeds. By decreasing the seed size linear increase in aspect ratio can be observed. Whereas in the case of positively charged seeds (Fig 1.14B), when seed size reduced, increasing in the aspect ratio can be followed up to some point. Then, decreasing in the aspect ratio is observed again. In both case, the concentration of the seed is same.



**Figure 1.14** (A) The negatively charged seeds (B) the positively charged seeds used for the synthesis of nanorods.

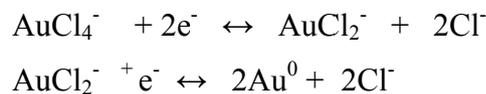
An electric-field-directed growth of gold nanorods in aqueous surfactant solutions was proposed by Perez-Juste et al. [87]. This mechanism is relying on series of observations.

- The monodispersity of the seeds increase the yield of gold nanorods
- Bromide ion act as rod inducing agent
- The aspect ratio can be controlled through seed to  $\text{HAuCl}_4$  ratios
- $\text{AuCl}_4^-$  and  $\text{AuCl}_2^-$  are absorbed to CTAB
- CTAB directs Au to the tips and also prevent the rate of metallic gold formation



**Figure 1.15** Reducing process of gold solution complexes.

Ascorbic acid reduces  $\text{AuCl}_4^-$  CTAB complex to  $\text{AuCl}_2^-$  CTAB through the following reaction.



The silver nitrates are essential for the preparation of nanorods in high yields. Important progress in seed mediated growth of nanorods with silver nitrate was done by Nikoobakht and El Sayed [90]. They were able to take 100% yields of gold nanorods and also manage to control the aspect ratio of gold nanorods from 1.5 to 15. Then, seed mediated method of synthesizing gold NRs were developed by Kou et al [91]. Sau, and Murphy [92]. Since then, this method has become a very popular approach for the synthesis of nanorods with high reproducibility and quality.

There have been various types of proposed explanation about the role of silver nitrate in synthesis of gold nanorod. To understand how the silver affect the growth of nanorods possible reaction products of silver nitrate and growth solution containing

some morphological changes step by step. They become first peanuts, then truncated octahedral and finally evolving into faceted spheres.

#### **1.3.4.4 Seed-mediated synthesis and mechanism for branched gold NPs**

Branched NPs attract great interest due to their sharp edges and the correspondingly high localization of any surface plasmon modes [15]. Now, it is possible to routinely produce branched nanostructures such as nanoflowers, nanostars, and nanodendrites, for various metals including Au, Ag, Pt, Pd, Rh, and their alloys. One of the main difficulties in preparation branched gold nanostructures is that noble metal nanocrystals usually show a highly symmetric, face-centered cubic (fcc) structure.

Again the seed-mediated method is one of the most preferred and useful synthesis types for the preparation of branched structures. Table 1.2 reveal synthesis of different types of branched NPs by seed mediated method.

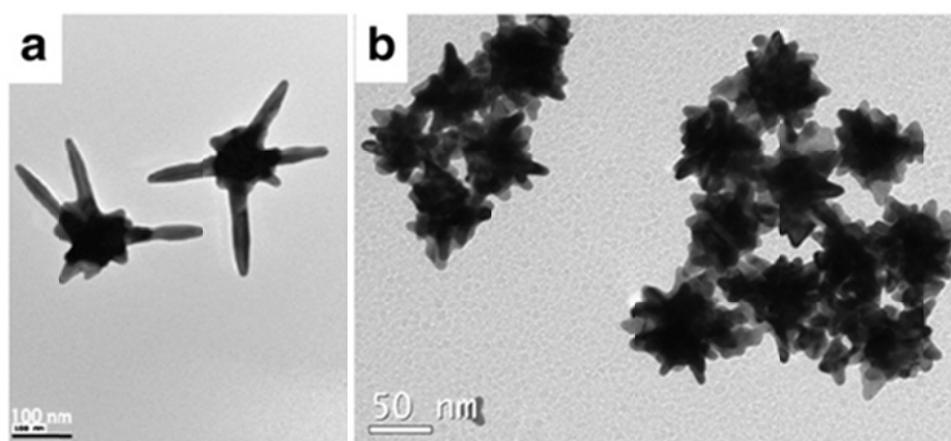
**Table 1.2** Reaction conditions for preparation branched NPs by seed-mediated growth method.

Metallic precursor	Reducing agent	Capping molecules	Additives	Size Monodispersity	Branching control
H <sub>2</sub> AuCl <sub>4</sub>	Mild reducing agents (ascorbic acid, hydroxylamine sulfate, and DMF)	CTAB, CTAC  SDS, citrate, PVP, and gelatin	AgNO <sub>3</sub> , NaOH	High (70–300 nm)  High (40–150nm)	Moderate — high (multipods 1–6 arms)  Low (multi-branched)
[Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> [PdCl <sub>4</sub> ] <sup>2-</sup>	Ascorbic acid	PVP, citrate  CTAB	No additives  Cu(OAc) <sub>2</sub>	High (80 nm)	
K <sub>2</sub> PtCl <sub>6</sub> , PtCl <sub>2</sub> , and RhCl <sub>3</sub>	Polyol	PVP, oleylamine	No additives	Moderate (200 nm)	High

One of the most popular methods for synthesizing gold branched NPs has been inspired by the well-known growth process used in the synthesis of gold nanorods [90]. Sau et al. [92] offered the synthesis of branched NPs by changing the seed to gold salt ratio. Moreover, the volume of the reducing agent also was changed to increase the rate of gold ion reduction and thus pave the way to branched particles.

Wu et al. showed that addition of AgNO<sub>3</sub> at different stages of nanocrystals growth allows a higher degree of control on the shape of gold nanostars synthesized by seeded-growth of pentatwinned NPs seeds [96]. Moreover, they also show the influence of bromide ion by replacing CTAB with its chloride equivalent (CTAC). The authors not only control the final nanostar morphology, but also increase the yield of branched NPs. Even though the detailed mechanism of reaction incorporation

during synthesis is not clear, the most results show that the nature of the seeds can strongly affect the final morphology of the particle [97]. The reducing agent can also play important role on the morphology of the NPs [34]. The use of different reducing agent such as N,N-dimethylformamide (DMF) has proven extremely successful in the high yield fabrication of branched gold NPs [98]. Here, 15 nm PVP capped gold seeds used to obtain branched nanostructures. This process can be carried out at room temperature with high yield, 100% production of NPs with sharp spikes. The key factor based on reducing effect of PVP molecules in DMF.



**Figure 1.18** TEM images of gold NPs prepared by seeded growth: (a) reduction by hydroxylamine in the presence of  $\text{Ag}^+$  [99]; and (b) reduction in a PVP/DMF mixture [1].

In conclusion, in the shape control synthesis of anisotropic NPs by seed mediated method chemical interactions are very important. Every reactant in growth solution or in seed solution affects the direction of growth NPs. Thus, by careful control of these parameters the size and shape of noble metal NPs can be controlled.

### **1.3.5 Comparison of seed-mediated growth method with other methods**

Among these four methods (polyol, electrochemical, photochemical methods and the seed mediated methods) seed mediated methods of preparing noble metal NPs is more preferred one. Firstly, in polyol methods, where polyol acts as reducing agent, relatively high temperature is used. As a result of this high temperature metals are oxidized to different aldehyde and ketone species which then cause a problem in removing them from NPs [67]. However, in seed mediated methods reaction can be completed in short amount of time temperature. Secondly, metal reduction in polyol process is much slower. For instance, in photochemical reaction metal reduction can take up to days for reaction consumption which is time consumable. In seed mediated method reaction can be completed in short of time. Thirdly, in electrochemical process two electrotype electrochemical cell is needed for preparation of NPs. However, in seed mediated method no specialized set up is necessary. Hence, in this study, seed mediated method was used since more investigated an easy one.

### **1.4 Functionalization of NMNPs**

Functionalization of NPs surfaces is need for stabilizing them in solution or for improving the properties [100]. Recently, there have been a great demand for their functionalization of noble metal NPs with different components such as acids, biocompatible polymers, enzymes, proteins and also with another metal NPs. Thus, biocompatibility, sensing and targeting specificity are increased [101, 102]. Noble metal NPs surface can be functionalized with various materials such as polymers or biomolecules (DNA, antibody, biotin and etc.). Functionalization can also be achieved by coating one metal NP with another to obtain core-shell NPs system.

core Au shell, and random alloyed particles. However, at that time detailed analyses of these bimetallic NPs were not possible. Only the difference of UV-Vis spectra between bimetallic NPs and physical mixtures were discussed. Today, due to new era of spectroscopic diagnostic tools, it is possible to obtain detailed analyses of these bimetallic NPs. There has been a great amount of studies on preparation of bimetallic NPs. For instance, the well controlled Au@Ag core shell nanorods were prepared by tuning pH and temperature of the solution [106]. In this study, structure of the core shell was characterized properly using spectroscopic tools such as HRTEM, TEM, and SEM characterization. The core and shell of the composition can be easily observed.

There is a great interest on Ag NPs with anisotropic morphologies due to their superior optical properties [107]. However, synthesizing of anisotropic silver NPs in an uniform shape has proven as challenging task. The uniformities of silver anisotropic NPs were not as good as gold NPs [71]. Therefore, in order to prepare anisotropic shaped silver NPs, new approaches have been followed. Recently, researchers try to solve this problem by deposition silver on gold NPs. Thus, structural morphologies are conserved with added enhanced optical properties.

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 CHEMICALS

Hexadecyltrimethylammoniumbromide (CTAB) (98%), sodium borohydride (99%), L-ascorbic acid, hydrogen tetrachloroaurate (III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , >99.9%), silver nitrate, silver trifluoroacetate, poly(sodium 4-styrenesulfonate) (average  $M_w \sim 70,000$ ), silver acetylacetonate (98%), sodium chloride, and hexadecylpyridinium chloride monohydrate were obtained from Sigma-Aldrich. All reactions have been done at room temperature.

#### 2.2 Noble metal NPs characterization methods

The gold and Au@Ag core-shell NPs were characterized in T 80+ UV-Vis spectrophotometer, PG Instruments Ltd. Products of seed-mediated method were analyzed by scanning electron microscopy (SEM) (QUANTA 400F Field emission SEM) operated between 10-30 kV voltages. High-resolution transmission electron microscopy (HRTEM) was acquired using a JEOL TEM 2010F which was operated at 200 kV. PHI-5000 Versaprobe, equipped with aluminum  $K\alpha$  at 1486.92 eV x-ray source was used to perform x-ray photoelectron spectroscopy (XPS) analyses.

## **2.3 Preparation of gold nanorods**

### **2.3.1 Seed Solution**

CTAB solution (3.76 mL, 0.20 M) and HAuCl<sub>4</sub> solution (1.25 mL, 0.002 M) were mixed with 2.74 mL of ultra pure water, then mixed homogeneously. The color of mixed solution quickly changed from light yellow to orange. To this solution, 0.90 mL of ice-cold 0.01 M NaBH<sub>4</sub> was added by vigorous stirring. The stirred solution was kept at 25 °C for 2 h.

### **2.3.2 Growth Solution.**

HAuCl<sub>4</sub> solution (400 μL, 0.01 M), CTAB (4.75 mL, 0.20 M) and AgNO<sub>3</sub> (60 μL, 0.01 M) solutions were added to 4.15 mL ultra pure water. After gentle mixing 640 μL of 0.01 M ascorbic acid was added. Finally, the 2 h aged 31.25 μL seed solution were added to this growth solution. Then, the mixed solution left undisturbed for 24 h at room temperature. In order to use this solution in TEM observation excess of CTAB was removed by centrifugation. The gold nanorod solution is centrifuged for 20 min at speed of 9000 rpm. This procedure was repeated for two times.

added and after gentle mixing the color of this solution changed from brown-yellow to colorless. The growth process completed 3 h after addition of 10  $\mu\text{L}$  of indiluted 10 nm gold colloid seed (Ted Pella).

#### **2.4.2 Preparation of branched gold NPs with surfactant stabilized seeds**

The growth solution was prepared by the same way as mentioned above. Here, the seed solution was prepared in laboratory condition. Briefly, to 7.5 mL of 0.1 M CTAB solution 0.250 mL of 10 mM  $\text{HAuCl}_4$  solution was added. Next, freshly prepared ice cold 0.6 mL of ice cold  $\text{NaBH}_4$  was added resulting in light brown seed solution. Then, 10  $\mu\text{L}$  of this seed solution was added to as prepared growth solution. To this mixture, 0.032 mL of 0.1 M ascorbic acid was added and color of the solution changed to colorless. Finally, 0.025 mL of 0.1 M  $\text{NaOH}$  was added by gentle mixing and stored for 2 h at room temperature.

#### **2.5 Preparation of gold octahedral single crystalline NPs**

Single crystalline octahedral NPs were prepared by seed mediated method. Gold nanocrystals, capped by cetylpyridinium chloride (CPC), with diameters of 41.3 nm were prepared and used as the seeds in the seed-mediated growth method.

##### **2.5.1 Seed solution**

###### **2.5.1.1 Preparation of CTAB capped gold seeds (~1.5 nm)**

The gold seed solution was first prepared by the addition of 125  $\mu\text{L}$  of aliquot 0.01 M  $\text{HAuCl}_4$  solution to 5 mL of 0.1 M CTAB solution at 30  $^\circ\text{C}$  by gentle mixing. Then, to this solution 0.3 mL of 0.01 M ice cold  $\text{NaBH}_4$  solution was added, which resulted in the formation of a brownish yellow solution. The solution was stirred, and then was kept at 30  $^\circ\text{C}$  for future use.

###### **2.5.1.2 Preparation of gold nanorods for octahedral growth**

As prepared ~1.5 nm CTAB capped gold seeds were used in preparation of gold nanorods. Briefly, the gold nanorod solution was made by adding 2 mL of 0.01 M

HAuCl<sub>4</sub> solution, 240  $\mu$ L of 0.01 M AgNO<sub>3</sub> solution, 320  $\mu$ L of freshly prepared 0.1 M ascorbic acid solution, and 48  $\mu$ L of the  $\sim$ 1.5 nm CTAB-capped gold seed solution to 40 mL of 0.01 M CTAB solution at 30 °C. After each addition the solution was accurately mixed and was left undisturbed for 2 h.

### **2.5.1.3 Preparation of the CPC capped gold seeds from gold nanorods by secondary overgrowth of gold nanorods**

30 mL of the as synthesized gold nanorod solution was centrifuged for 20 min at speed of 9000 rpm to precipitate the particles and redispersed in water. After second centrifugation (9000 rpm, 20 min) the solution was redispersed in 30 mL of 0.01 M CTAB solution at 40°C. Finally, in secondary growth additional HAuCl<sub>4</sub> (1.5 mL, 0.01 M), and ascorbic acid (0.3 mL, 0.1 M) solutions were added and accurately mixed. After this, combination was allowed to react at 40 °C for 1 h.

### **2.5.1.4 Preparation of CPC capped gold seeds**

In order to prepare CPC capped gold seeds as prepared the overgrown gold nanorods were transferred to near spherical NPs [108]. Briefly, the overgrown gold nanorod solution was centrifuged at 9000 rpm for 20 min and redispersed in 30 mL of 0.01 M CTAB solution. Then, 0.6 mL of 0.01 M HAuCl<sub>4</sub> solution was added at 40 °C by gentle mixing and aged for 12 h. In the last step, this solution was washed three times with 0.1 M of CPC solution by centrifugation at 9000 rpm for 20 min. Finally, the combination was redispersed in 30 mL of 0.1 M CPC solution and used as CPC capped seeds.

### **2.5.2 Seed-mediated growth of gold octahedral nanocrystals**

In order to prepare the octahedral gold nanocrystals as prepared CPC capped gold NPs was used as seeds. In typical procedure, to 5 mL of 0.01 M CPC solution at 30 °C, 100  $\mu$ L of HAuCl<sub>4</sub> solution and 13  $\mu$ L of 0.1M ascorbic acid solution were added by accurate mixing after each addition. Finally, 200  $\mu$ L of the CPC-capped seed solution was added and the solution kept at room temperature for 2 h. In order

### **2.6.2 Preparation of 8 nm gold nanospheres**

In the second step, for the preparation of 8 nm gold nanospheres the reactants were mixed in the following order:

- CTAB (45 mL, 0.08 M)
- H<sub>AuCl</sub><sub>4</sub> (1.125 mL, 0.01 M)
- Ascorbic acid solution (0.25 mL, 0.1 M)

Then, the citrate stabilized 3.5 nm seed solution (5 mL) was added and stirred vigorously for 10 min.

### **2.6.3 Preparation of 15 nm gold nanospheres**

In the third step, as prepared 8 nm gold nanospheres were used as seeds for the growth of 15 nm gold nanospheres. The growth solution was the same as in 8 nm gold nanospheres:

- CTAB (45 mL, 0.08 M)
- H<sub>AuCl</sub><sub>4</sub> (1.125 mL, 0.01 M)
- Ascorbic acid solution (0.25 mL, 0.1 M)

The 8 nm gold seed solution was introduced with vigorous stirring, for 10 min. Then, the solution was kept at room at least for 3 h before use.

## **2.7 Preparation of sphere, rod, octahedral, and star Au@Ag core-shell composition**

Coating process of different types of gold NPs (rod, octahedral, star) was done by the same procedure. As prepared gold NPs was coated with different volume of silver salts. Briefly, 1 mL of gold NPs solution (rod, octahedral, star) was centrifuged (at 9000 rpm for 20 min for two times) and washed with DI water. In order to coat Au nanorod solution with polymer, 100  $\mu$ L of 0.01 M NaCl solution and 200  $\mu$ L of sodium polystyrene sulfonate (PSS), which was diluted in 0.01 M NaCl solution, was added to this solution. Following, this solution was transferred into 50 mL glass bottles with screw cap and stirred for 30 min. After stirring the gold solution was centrifuged at 7000 rpm for 6 min and re-suspended in 1 mL of DI

## CHAPTER 3

### RESULT AND DISCUSSION

Silver coated gold NPs are very distinctly interesting since they provide the advantage of having both structural purity and enhanced optical properties in one NPs system. Gold NPs are relatively easier to synthesize with better control over morphology compared to silver ones. On the other hand, silver has superior optical properties than gold. Therefore, the combination of these properties in one NPs system makes these particles very attractive for sensing applications such as SERS.

Numerous reports on silver coated gold NPs with various morphologies can be found in literature [106, 109-112]. Different methodologies have been developed to obtain Au@Ag core-shell NPs system for each different NPs shape [106, 109-114]. Among all NPs morphologies, the ones with rod-shapes are the mostly studied for silver coating. [106, 109-111]. Okuno et al. [106] were able to obtain uniformly coated Au@Ag core-shell nanorods with control over the shell thickness. However, they have used very expensive molecule, hexadecyltrimethylammonium chloride (CTAC), as a surfactant. Moreover, the procedure involves high reaction temperature and long experimental time in order to control shell layer of Au@Ag core-shell composition.

Tsuji et al. reported silver coating on octahedral shaped gold NPs by microwave polyol method [115]. The process involves heating of the reaction mixture by microwave radiation and the procedure take place in organic solvent (Ethylene glycol). The gold nanostructures with planar morphologies (i.e. cuboctahedron and hexagonal) were also frequently studied for silver coating [113-116]. However, no report on silver coated branched NPs, yet. The major drawbacks of the reported methods of silver coating are requirement of expensive stabilizing chemicals (i.e.

biomolecules, DNA, antibody etc.), high temperature reactions, complex and long experimental procedures. Also, uniform silver layer on gold could not be achieved in most cases and one method might not be utilized for different NPs shapes.

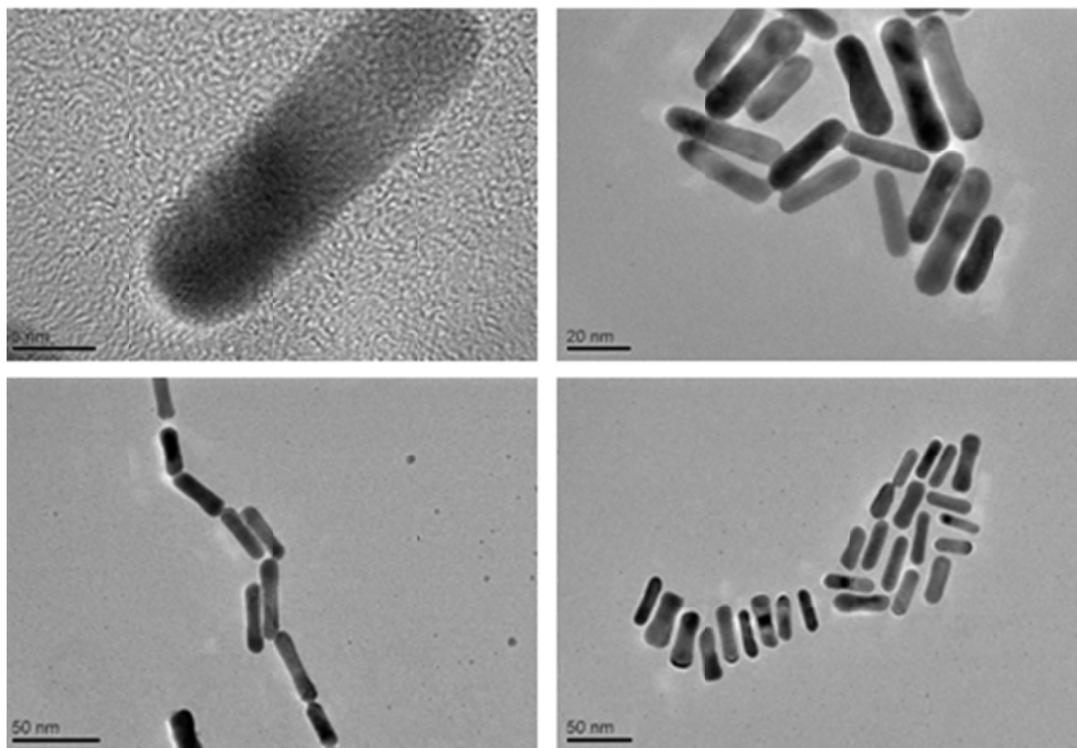
In this study, a facile way of silver coating on gold NPs was developed. The surface of Au NPs with four different morphologies; rod, branched, octahedral, sphere were successfully coated with silver. The main advantages of the method are:

- ✓ Simple (no need for complicated setup)
- ✓ Affordable
- ✓ Synthesis in aqueous medium
- ✓ Room temperature process
- ✓ Reproducible
- ✓ Implementation to different NPs morphologies

Au NPs were synthesized based on a method called “seed-mediated growth method” [23, 79, 117, 118]. Silver coated gold NPs were synthesized by first coating NPs with a polymer (polystyrene sulfonate (PSS)) then by addition of a silver salt (silver trifluoroacetate) to the polymer-coated, gold NPs solution. Finally, addition of NaOH to this solution results in the formation of a silver layer on the gold NPs. The as-prepared gold NPs are positively charged due to bilayer of surfactant molecule (i.e. CTAB, CPC). Coating them with a single layer of a negatively charged polymer promote electrostatic binding of positively charged silver ions which are further reduced to form a bound silver layer. Thickness of silver layer on the NPs were attempted to be controlled by the amount of silver salt added into NPs solution. This attempt yielded control over silver layer thickness on sphere, rod and octahedral shaped gold NPs, but not on branched NPs.

The Au@Ag core-shell NPs systems have been fully characterized by a combination of UV-Vis spectroscopy, Field Emission Transmission Electron Microscope (FE-TEM) and Energy-Dispersive X-ray (EDX) studies, Scanning Electron Microscopy (SEM), and X-Ray Photoelectron Spectroscopy (XPS). The results for each NPs system were discussed in following sections.

TEM studies were performed to analyze the morphology of gold nanorods before silver coating. Figure 3.2 demonstrate TEM images which verify rod-shaped nanostructures with an aspect ratio  $\sim 4$ .



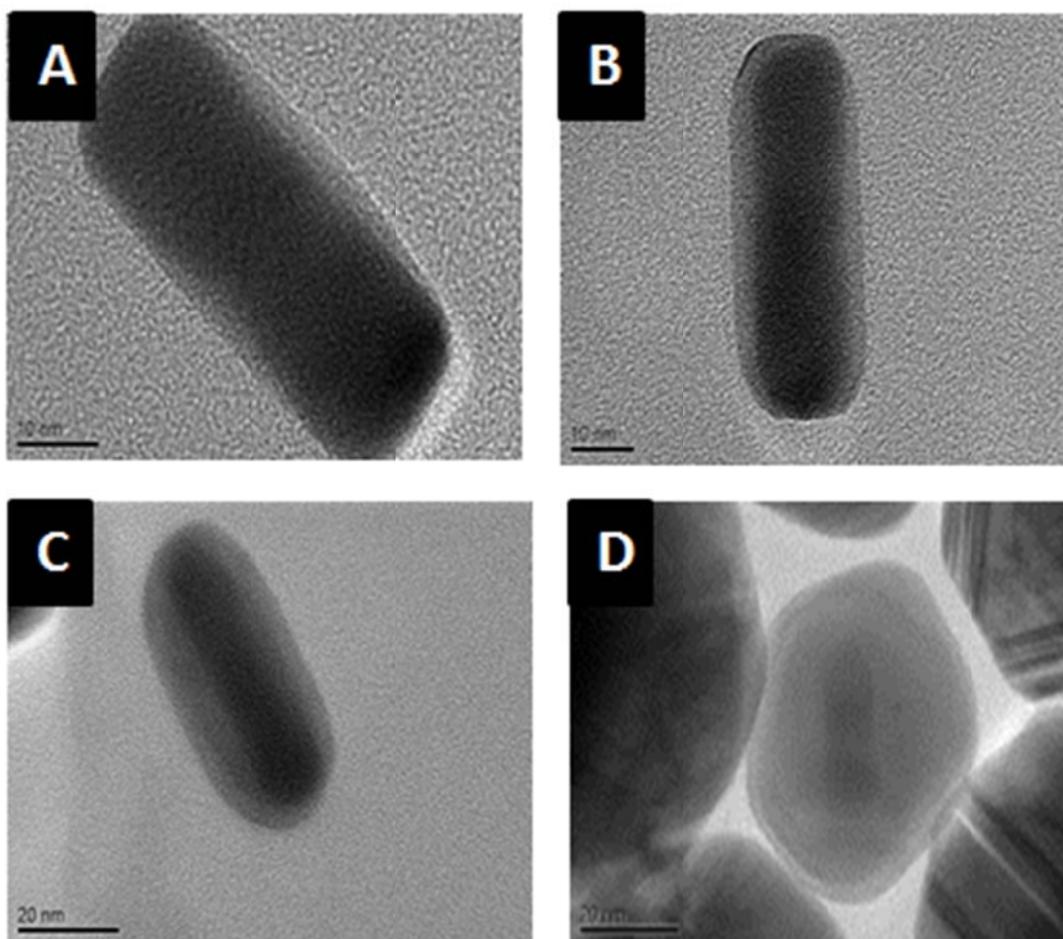
**Figure 3.2** TEM images of gold nanorods.

The silver coating on gold nanorods was monitored firstly by change in the color of the NPs solution. Addition of different amount of silver salt resulted in different solution color. (Figure 3.3 (A)) For instance, after addition of 0.1 mL of silver salt makes the color of the NPs solution turn from violet to light gray. The solution become green and orange upon addition of 0.25 mL and 0.5 mL silver salt, respectively. This is most likely due to formation of different thickness of silver layer on gold NPs results in the change of NPs size, shape and thus optical properties.

Change in the surface morphology of NPs was also monitored by UV-Vis spectroscopy. Figure 3.3 (B) shows absorption spectrum of silver coated gold

nanorods with presumably different thickness of silver layer. The spectrum demonstrates one absorption band instead of two bands after silver coating. The bands of gold nanorods almost disappear into baseline when NPs were coated with the addition of 0.1 mL silver salt. As the silver salt amount was increased only one absorption band was observed in lower wavelength (around 400 nm) [110]. This observation evident the formation of silver layer on gold NPs as the absorption bands characteristic to silver NPs appear around 400 nm [119]. The observed spectral change (blue shift) is most likely due to variation in the dielectric function, overall aspect ratio and formation of interface between gold NPs and silver layer after silver coating [120, 121].

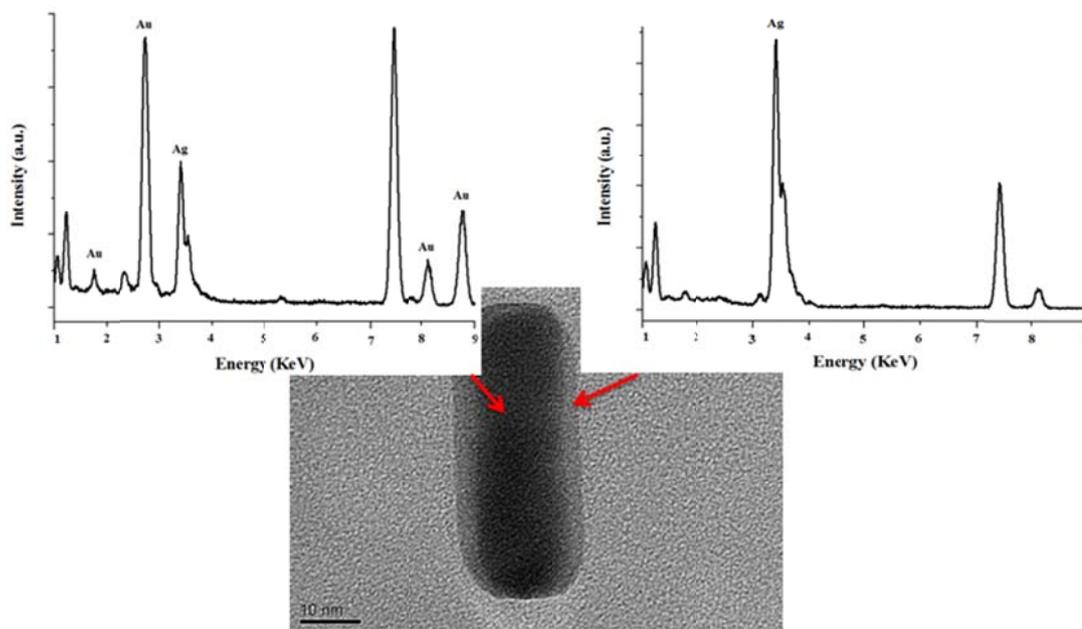
Figure 3.4 demonstrate TEM images of Ag coated Au nanorods prepared with different amount of silver salt. The TEM analysis of several NPs from various preparations demonstrated that the entire NPs surface has been covered. The light colored layer corresponds to the silver shell and the dark part to the gold core. This difference in their transparency is due to electron density difference between gold and silver parts [122]. TEM analysis also demonstrated that shell thickness can be controlled by altering the amount of silver salt added. As the amount of silver salt solution increased, silver layer thickness was increased and morphology of the NPs changes. Rod shape was still conserved when 0.1 and 0.25 mL silver salt was added. However, the NPs had ellipsoid and pentagon-like shape as 0.5 and 1.0 mL silver salt was added, respectively. This shows formation of new silver NPs by utilizing gold nanorod as seed at excess amount of silver salt addition.



**Figure 3.4** TEM images of Au@Ag core-shell nanorods prepared by different amount of silver particles. (A) Au@Ag core-shell nanorods (0.10 mL of silver salts), (B) Au@Ag core-shell nanorods (0.25 mL of silver salts), (C) Au@Ag core-shell nanorods (0.50 mL of silver salts), (D) Au@Ag core-shell nanorods (1 mL of silver salts).

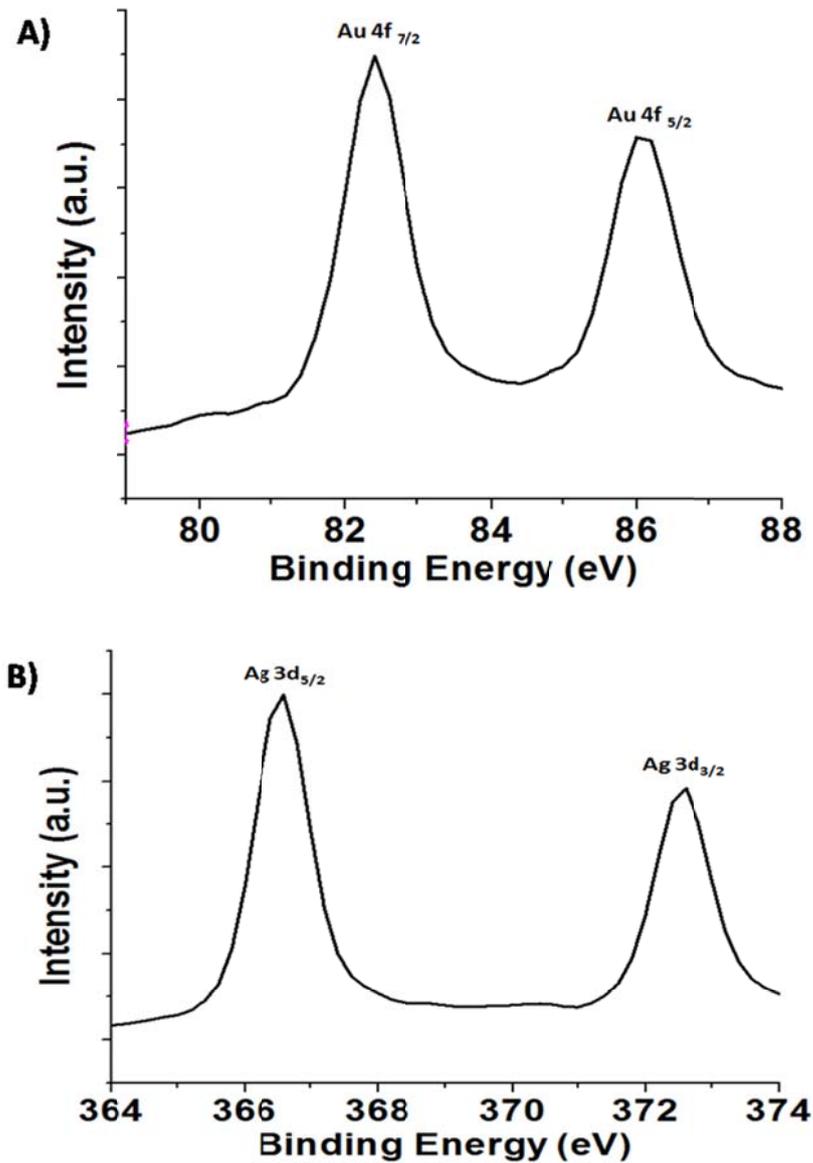
The surface coating on the gold nanorods is probed by EDS. Scans from various syntheses also verified that silver was successfully coated on gold nanorods. The EDS point spectra acquired from a different region of various NPs show a silver coating at the edge with bulk gold at the center. Figure 3.5 shows EDS spectra of Ag coated Au nanorods prepared with addition of 0.25 mL of Ag salt solution. The results for the Au@Ag NPs system prepared with addition of different amount silver salt are demonstrated in Appendix (A1, A2, A3). The results showed that increase in

the amount of silver lead to increase in the shell thickness. This suggests the control of the shell thickness with the amount of silver added.



**Figure 3.5** EDS spectrum of shell layer of Au@Ag core-shell nanorod composition: atomic percent of core Ag -52.05%, Au – 47.98%, and shell Ag -100% (0.25mL silver salts).

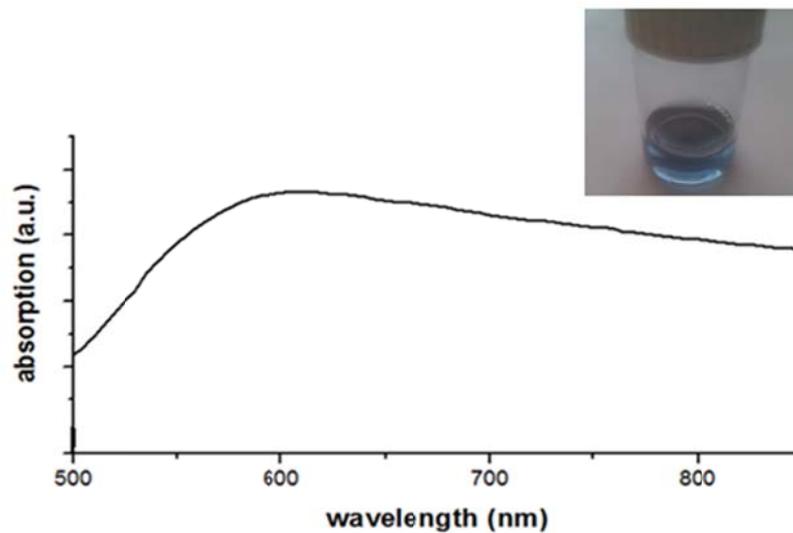
Further analysis via XPS confirmed the identity of coating on gold NPs as silver. Figure 3.6 (A) reveals characteristic spin-orbit doublets of Au ( $4f_{7/2}$ ) and Au ( $4f_{5/2}$ ) at 82.5 eV and 86.5 eV, respectively. The doublets of Ag ( $3d_{5/2}$ ) and Ag ( $3d_{3/2}$ ) are also observed at 366.5 eV and 372.5 eV, respectively. (Figure 3.6 (B))



**Figure 3.6** XPS spectra of Au (A) and Ag (B) in Au@Ag core-shell nanorods.

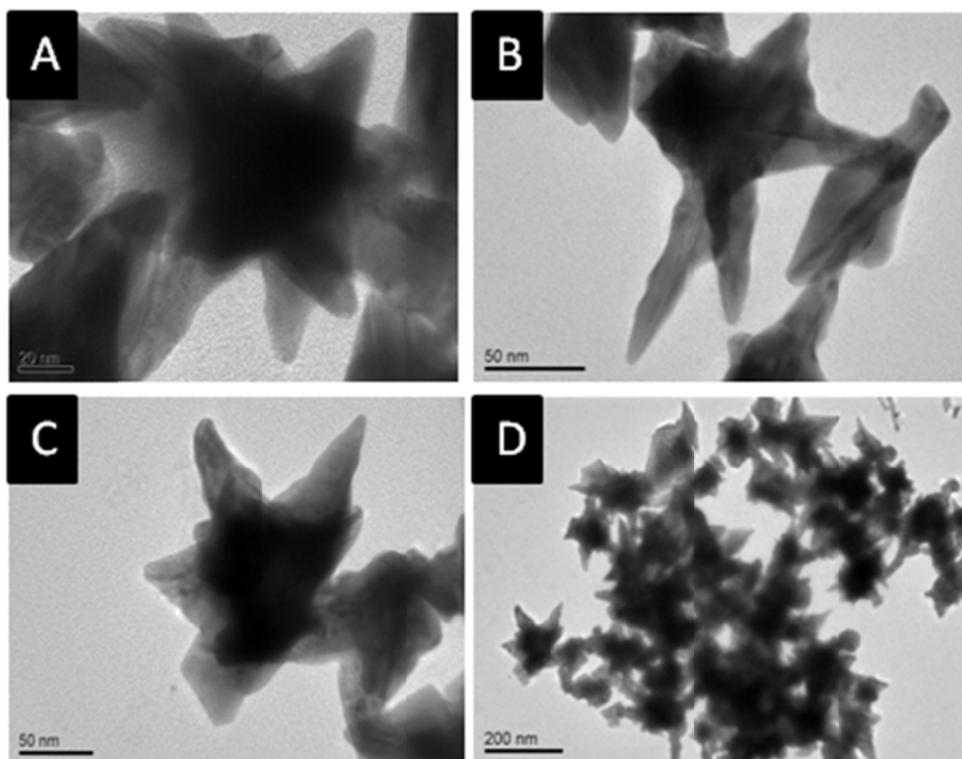
### 3.2 Au branched core @ Ag shell NPs

The UV-Vis absorption measurements of the branched gold NPs demonstrated a very broad plasmon band with maximum intensity around 600 nm. (Figure 3.7) The breadth of the band is most likely due to the structural diversity.



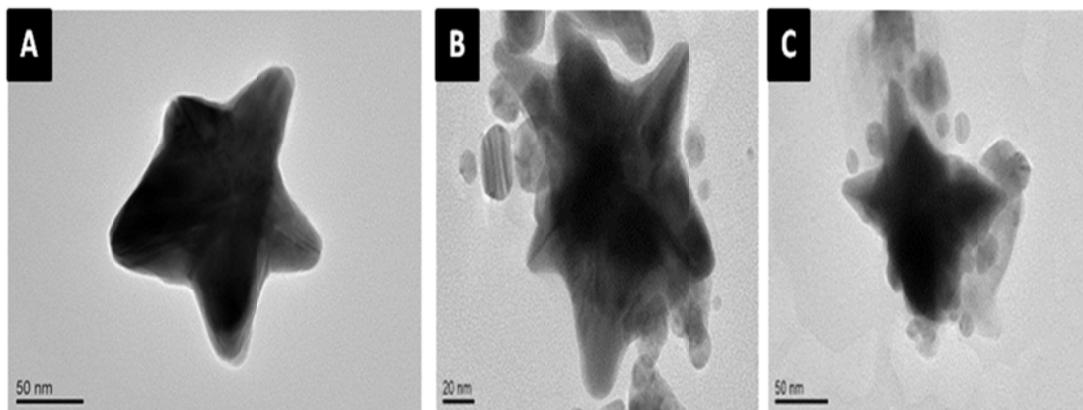
**Figure 3.7** UV-Vis absorption spectrum of the branched gold NPs. The inset shows the color of the branched gold NPs solution.

TEM analysis showed that branched nanostructures have average size of ca 144 nm (Figure 3.8 a-d). These NPs have three-dimensional structures with various numbers of tips growing out of the NPs core.



**Figure 3.8** TEM images of gold branched NPs.

The color of the NPs solution changed from dark blue to orange upon addition of silver salts. As the silver amount was increased the color of the solution becomes more intense (Figure 3. 9 (A)). The change in the optical properties of NPs with silver coating is monitored by UV-Vis spectroscopy. (Figure 3. 9 (B)) The blue shift in plasmon band of the NPs was observed after silver coating, as expected. The band is more shifted toward lower wavelengths as the amount of silver salt increased. (Figure 3. 9 (B))

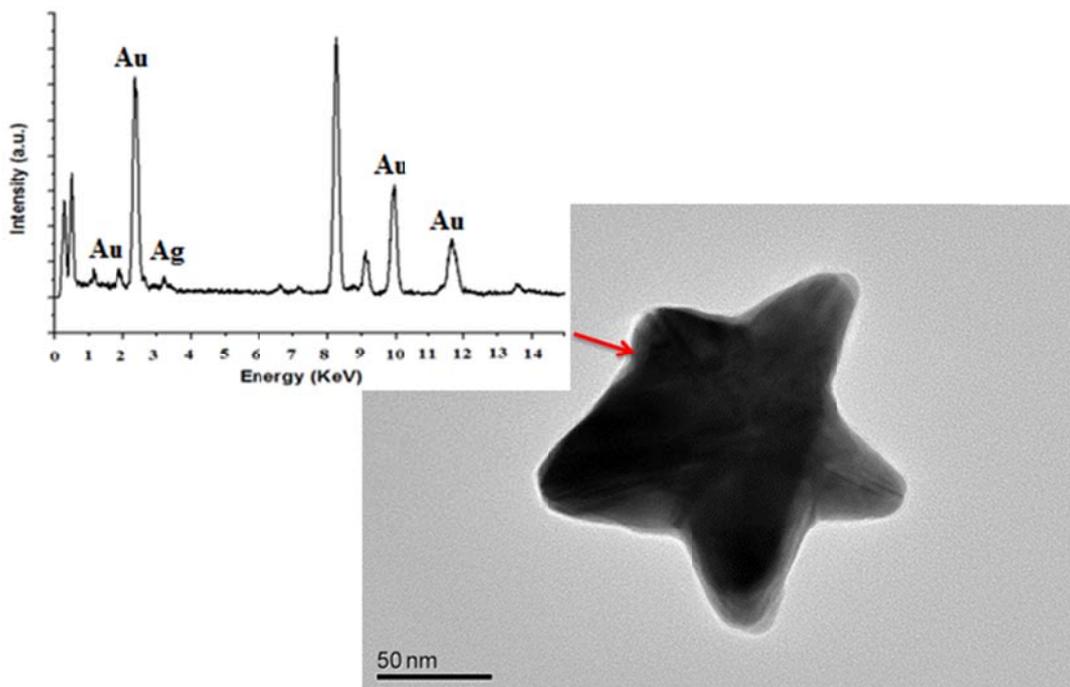


**Figure 3.10** TEM images of Au@Ag core-shell branched NPs prepared by different amount of silver particles. (A) Au@Ag core-shell nanorods (0.25 mL of silver salts), (B) Au@Ag core-shell nanorods (0.5 mL of silver salts), (C) Au@Ag core-shell nanorods (1 mL of silver salts).

TEM analysis show silver coating on branched gold NPs was not successful for all added amounts of silver salt solution. Very thin coating on the NPs was achieved with the addition of 0.25 mL silver salt. However, individual silver nanocrystals were formed as the amount of silver was increased. Some of the formed silver nanocrystals are adsorbed on gold NPs surface and attempts to remove these particles from solution were not successful. After many efforts 0.25 mL of silver salt solution was decided as an optimum amount for obtaining desired silver coating on branched gold NPs. The non-uniform structural and surface morphology of branched NPs are considered as the most likely reasons for not having control over silver shell thickness as it was achieved on gold NPs of other morphologies studied.

EDS analysis was performed on an individual NPs to analyze elemental character of the synthesized NPs system. Figure 3.11 shows EDS data acquired from different parts of the core-shell NPs system prepared with addition of 0.25 mL silver salt. Strong signals of gold and relatively weaker signals of silver suggesting the formation of a very thin layer of silver on NPs surface. EDS data for silver coated branched gold NPs prepared with different amounts of silver salt are given in Appendix (A6 and A7). EDS analysis also verified that the nanocrystals formed with

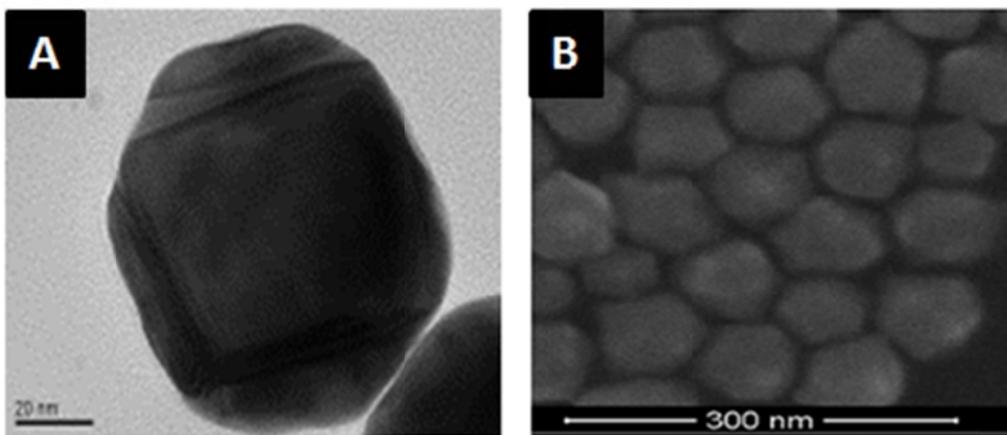
addition of excess silver (0.5 mL and 1.0 mL of silver salt solution) were solely composed of silver (Appendix A6 and A7).



**Figure 3.11** EDS spectrum of Au@Ag core shell branched composition: atomic percent Ag - 37.75%, Au – 62.25% (0.25 mL silver salts).

### 3.3 Octahedral gold NPs

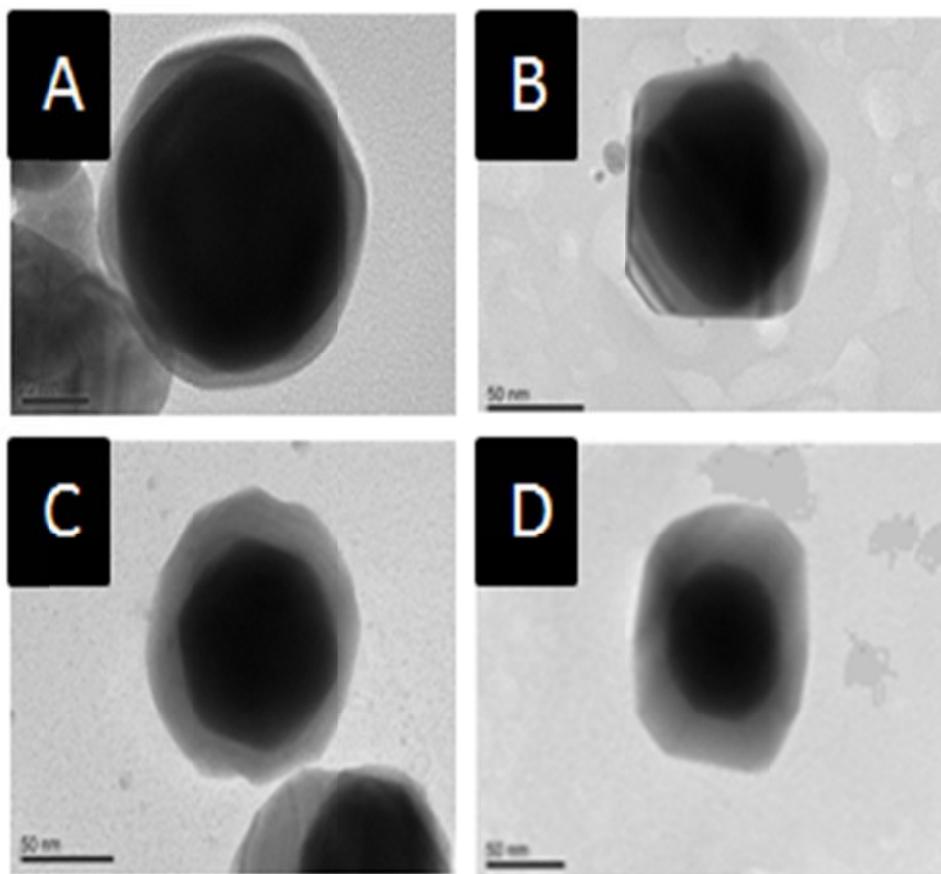
Octahedral gold NPs were prepared with a method described in the literature [118]. The procedure includes use of CPC capped gold nanorods as seeds for growth of octahedral NPs. Before capping with CPC, gold nanorods were oxidized by Au (III) – CTAB complexes. Then, this oxidation induces the formation of near spherical NPs. In the formation of single crystalline gold NPs the nucleation step, the size and crystal structure of seeds plays important roles. Therefore, preparation of octahedral NPs consists of several steps, which should be accurately followed.



**Figure 3.13** TEM (A) and SEM (B) images of gold octahedra.

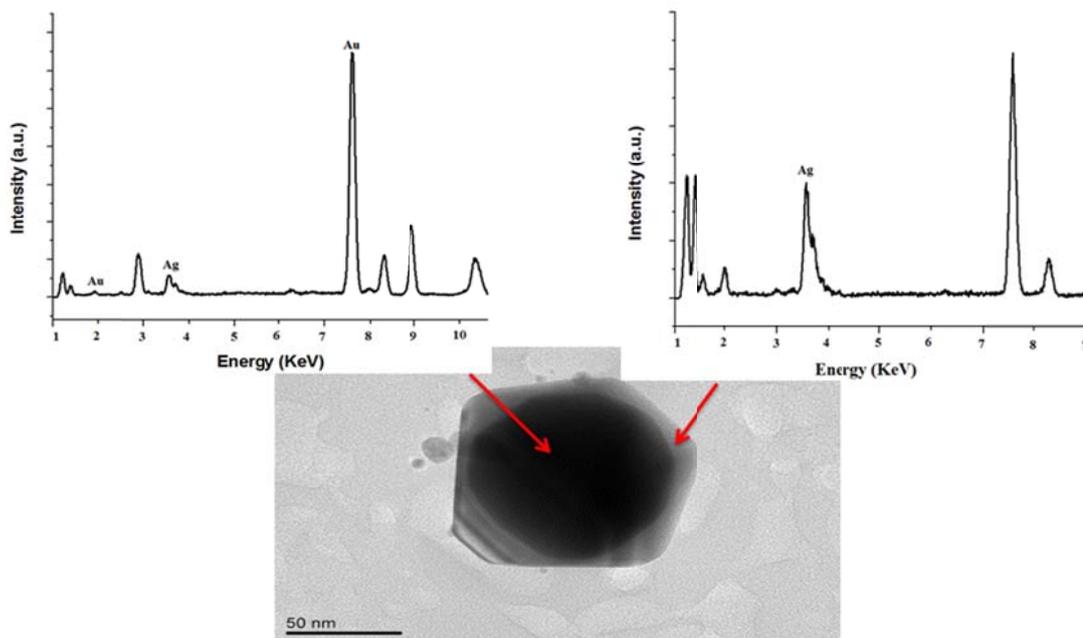
After preparation of single crystalline octahedral gold NPs, they were coated with silver. The change in the color of the NPs solution from pink to yellow indicates the change in the surface properties of NPs. The change in color and absorption wavelength with silver amount was shown in Figure 3.14. A single surface plasmon resonance peak in UV-Vis spectra of Au@Ag core-shell octahedral was noted (Figure 3.14 (A)). After coating the octahedral NPs with silver, the surface plasmon resonance peak was blue shifted and become broader. This is most likely due to change of the NPs's morphology and size.

The plasmon band of the Au@Ag component becomes strong. Moreover, by increasing the amount of silver salts considerable rise in the intensity can also be observed. Increase in the silver amount on gold NPs is most likely reason for change in the optical properties.



**Figure 3.15** TEM images of Au@Ag core-shell octahedral composition prepared by different amount of silver particles. (A) Au@Ag core-shell octahedrals (0.1 ml of silver salts), (B) Au@Ag core shell octahedrals (0.25 ml of silver salts), (C) Au@Ag core-shell octahedrals (0.5 ml of silver salts), (D) Au@Ag core-shell octahedrals (1ml of silver salts).

Figure 3.15 demonstrates TEM images of octahedral shaped NPs prepared with different amount of silver salt. As in the case of nanorods, here too, the increase in the silver layer thickness with increase in amount of added silver salt was observed. Average silver thickness is about 6 nm, 10 nm, 20 nm and 30 nm for core shell NPs system prepared with the addition of 0.1 mL, 0.25 mL, 0.5 mL and 1.0 mL silver salt solution, respectively.

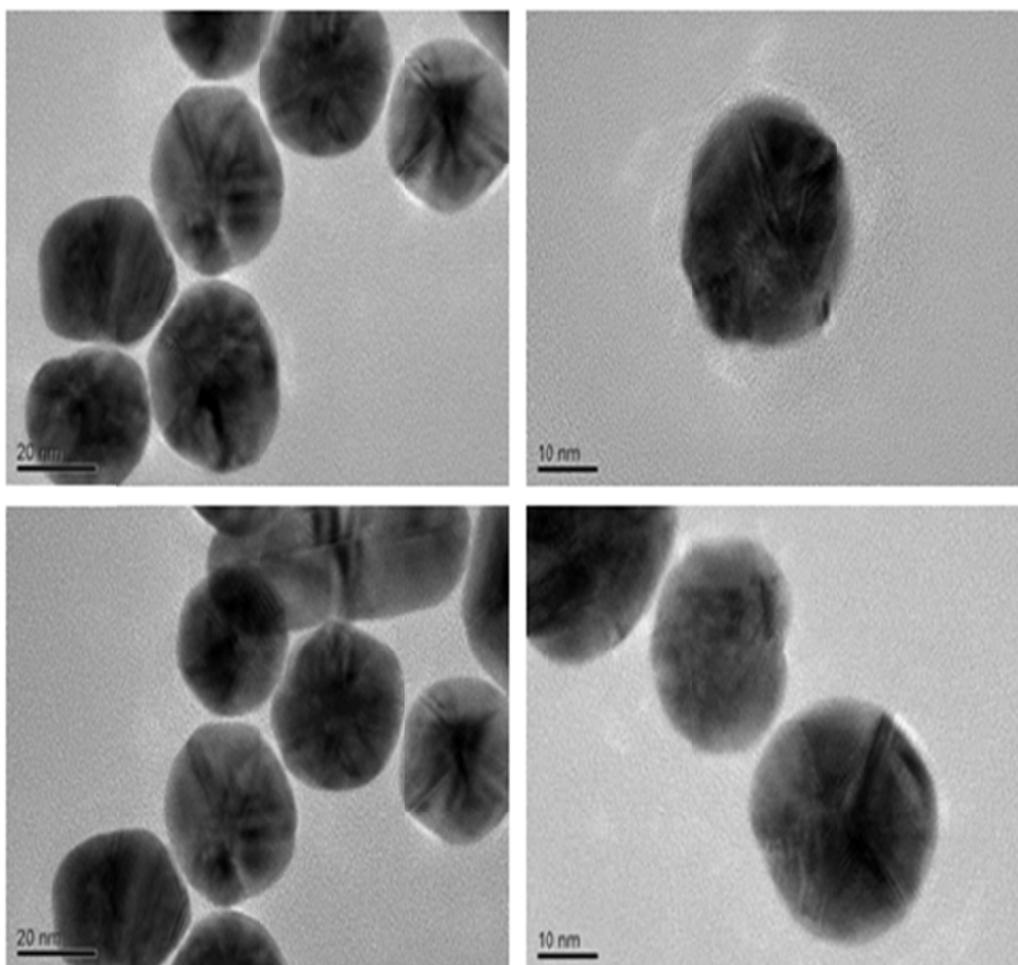


**Figure 3.16** EDS spectrum of Au@Ag core-shell octahedral composition: atomic percent of core Ag -17.73% , Au – 82.27% and shell Ag -100% (0.25mL silver salts).

Figure 3.16 demonstrate EDS results of of Au@Ag core-shell octahedral composition with addition of 0.25 ml silver salt (silver trifluoroacetate). Results for other addition of silver salts (0.1, 0.50 and 1 ml silver trifluoroacetate) were given in Appendices.

### 3.4 Au spherical core @Ag shell NPs

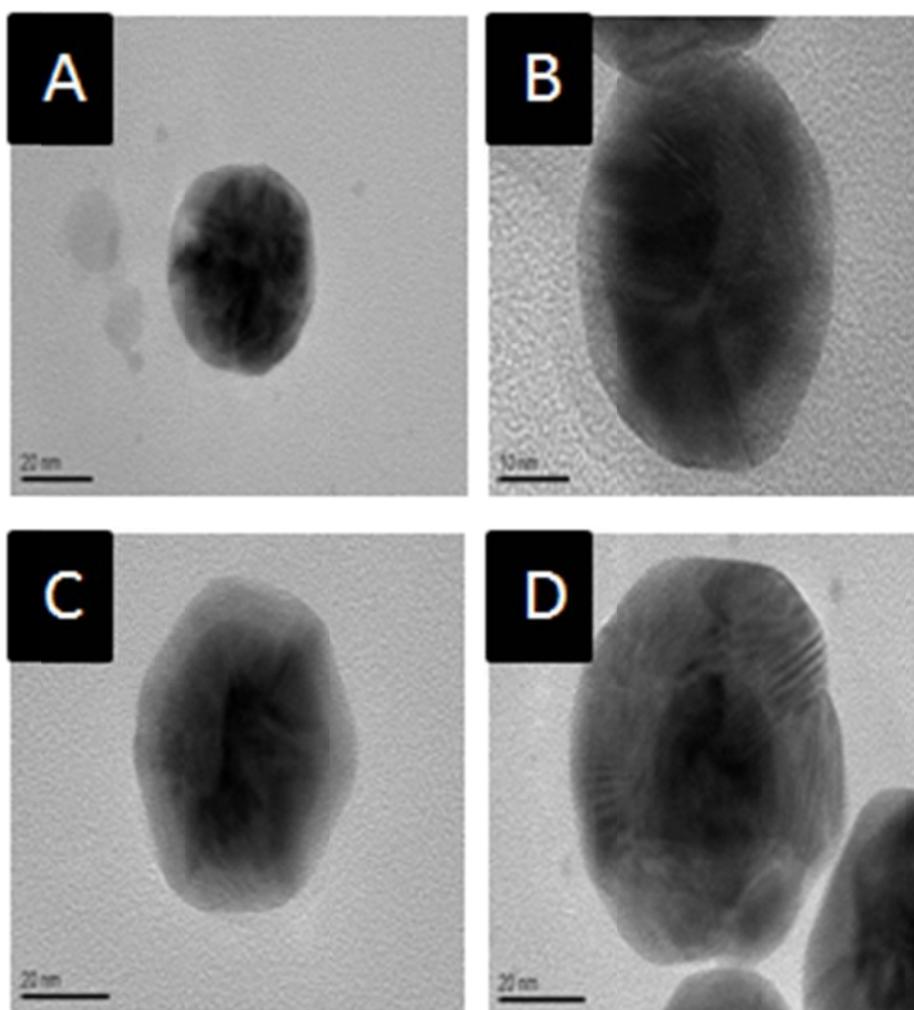
Gold nanospheres were prepared by using the seed-mediated growth method. CTAB were used to stabilize gold nanospheres. In the first step, gold seeds with size is in the range of 3-4 nm were synthesized by chemical reduction of gold salt with strong reducing agent ( $\text{NaBH}_4$ ) in the presence of citrate. Then, these seeds were introduced to a mixture of solution containing more metal salts, a weak reducing agent like ascorbic acid, and CTAB as a surfactant. UV-Vis analysis shows absorption band around 525 nm for spherical gold NPs (Figure 3. 16).



**Figure 3.18** TEM images of spherical gold NPs.

absorption bands shift to lower wavelength with increasing intensity as the silver amount was increased gradually (Figure 3.19. (B)).

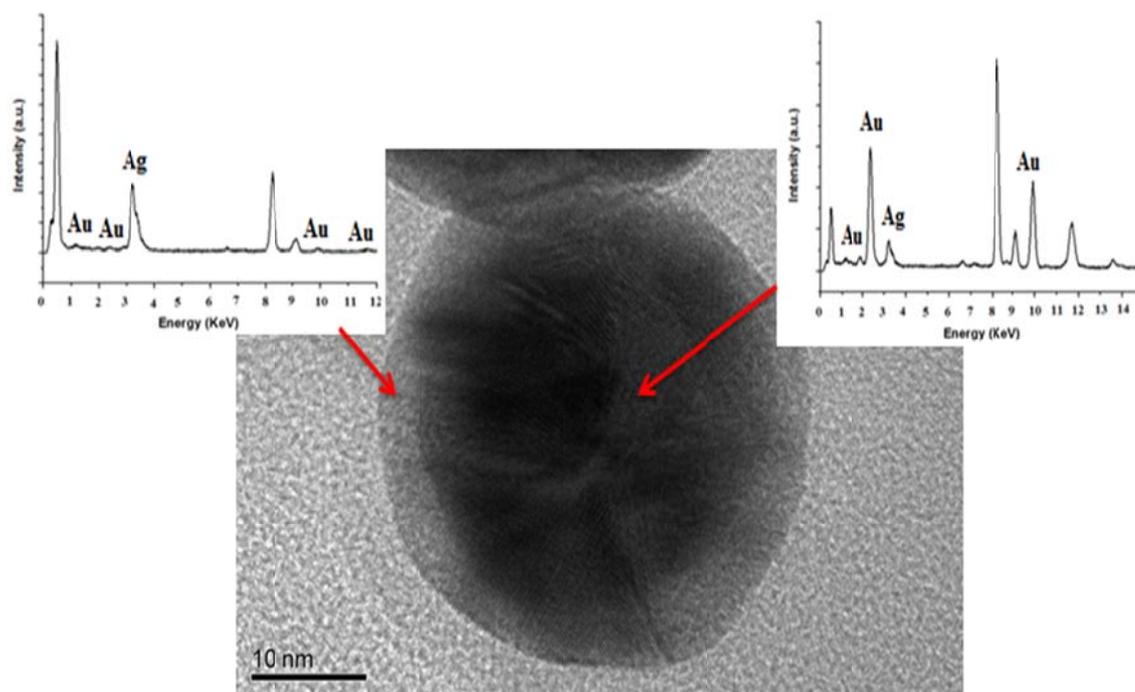
Figure 3.20 demonstrates TEM images of Au@Ag core-shell composition. Thickness of the layer increased as the amount of added Ag salt increased (Figure 3.20). The average silver thickness was measured as 4 nm, 5 nm, 9 nm and 14 nm as a result of 0.1 mL, 0.25 mL, 0.5 mL and 1.0 mL silver salt solution addition, respectively.



**Figure 3.20** TEM images of Au@Ag core-shell nanospheres prepared by different amount of silver particles. (A) Au@Ag core-shell nanospheres (0.1 mL of silver salts), (B) Au@Ag core-shell nanospheres (0.25 mL of silver salts), (C) Au@Ag

core-shell nanospheres (0.5 mL of silver salts), (D) Au@Ag core-shell nanospheres (1mL of silver salts).

The silver coating on gold nanospheres was confirmed by EDS study. The data demonstrate that maximum silver intensity was reached at the edges of the NPs as the gold amount is highest in the core part of the NPs system (Figures 3.20).



**Figure 3.21** EDS spectrum of Au@Ag core-shell spherical composition: atomic percent of core Ag -16.30% , Au – 83.70% and shell Ag -94.50% , Au – 5.50% (0.25 mL silver salts).

## CONCLUSION

Different morphologies of gold NPs (sphere, octahedral, nanorod and branched) were prepared using seed-mediated method and coated with silver to obtain core-shell composition. Gold colloids have the advantage of easier preparation with higher degree of homogeneity compared to silver colloids. On the other hand, silver has superior optical properties than gold. In order to have the advantage of both metal (gold and silver), core-shell NPs systems as Au@Ag were prepared. The combination of these properties in one NPs system makes these particles very attractive for sensing applications such as SERS.

Au NPs were synthesized based on a method called “seed-mediated growth method”. Silver coated gold NPs were synthesized by first coating NPs with a polymer (polystyrene sulfonate (PSS)) then by addition of a silver salt (silver trifluoroacetate) to the polymer-coated, gold NPs solution. Finally, addition of NaOH to this solution results in the formation of a silver layer on the gold NPs. The as-prepared gold NPs are positively charged due to bilayer of surfactant molecule (i.e. CTAB, CPC). Coating them with a single layer of a negatively charged polymer promote electrostatic binding of positively charged silver ions which are further reduced to form a bound silver layer.

The change in the optical properties for all shapes (sphere, octahedral, nanorod and branched) were observed by UV-Vis spectroscopy method. The TEM analysis demonstrated that shell thickness can be controlled by altering the amount of silver salt added. As the amount of silver salt solution increased, silver layer thickness was increased. Thus, all NPs optical properties varied and were successfully controlled for further explorations in sensing and imaging applications. Moreover, EDS scans from various syntheses also verified that silver was successfully coated on gold nanorods.

The main advantages of the procedure developed in this study are being a facile way of silver coating on gold NPs and utility of same method to coat four different morphologies; rod, branched, octahedral, sphere. There is no need for special set up for preparation of core-shell NPs system with the procedure used. Also, the experiments are done in aqueous medium and at room temperature.

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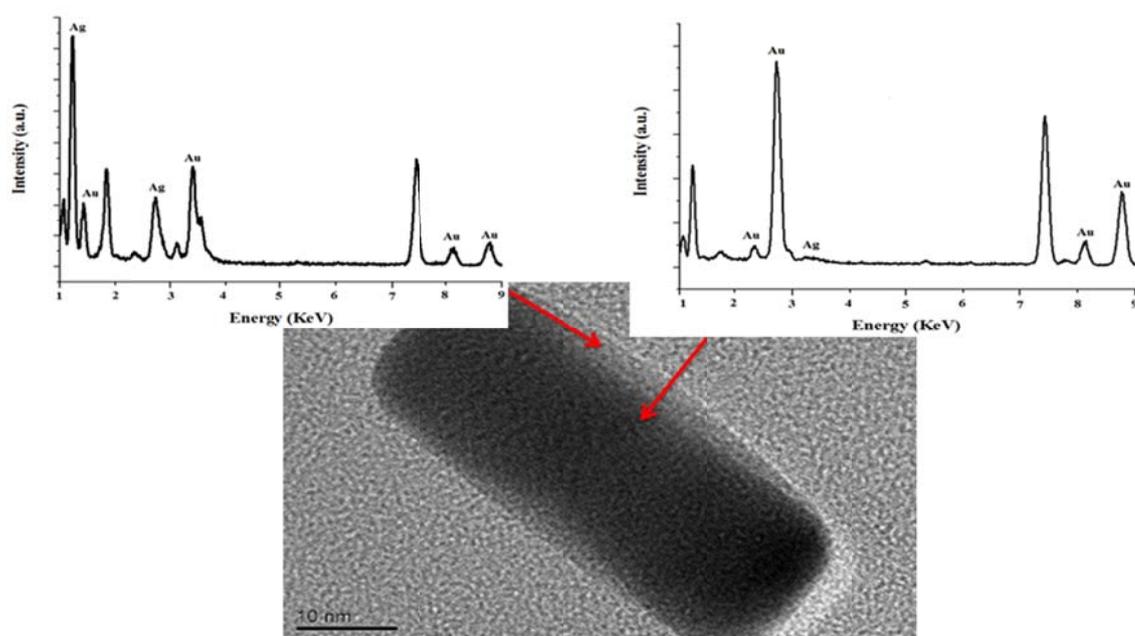
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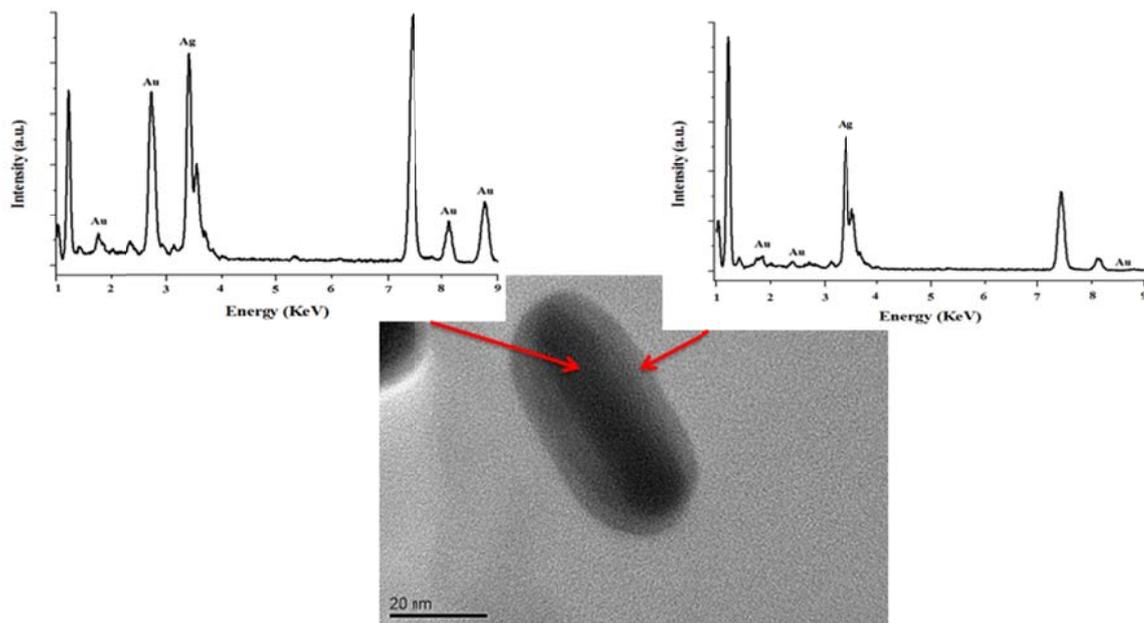
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## APPENDIX A

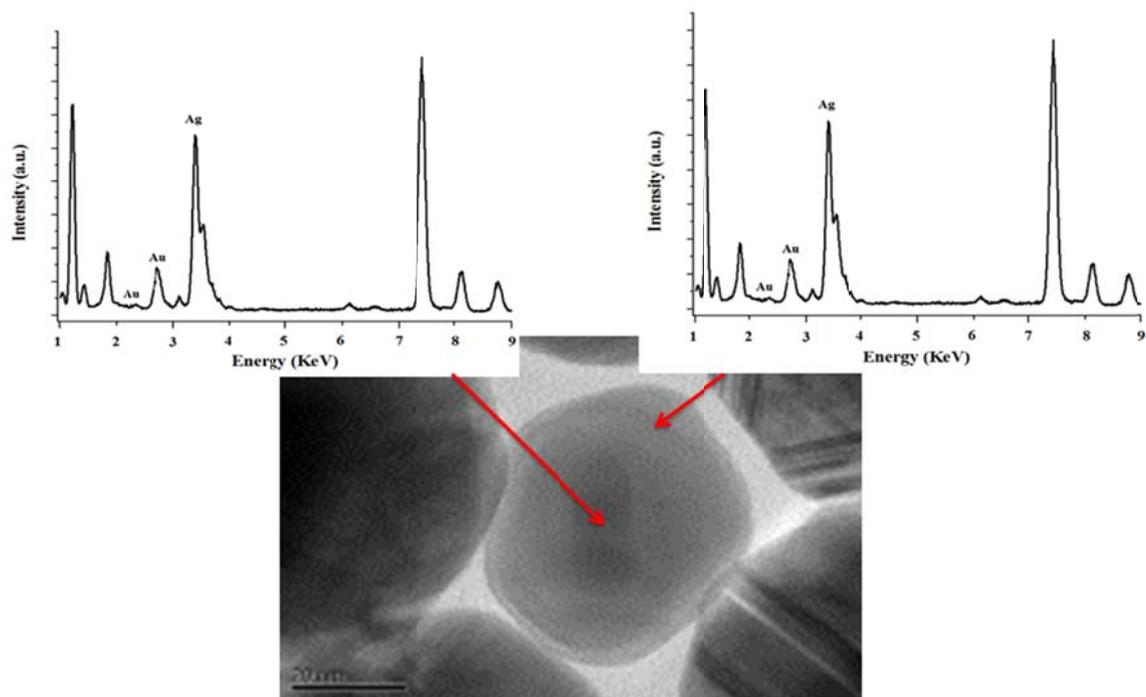
### DATA RELATIVE TO CHAPTER 3



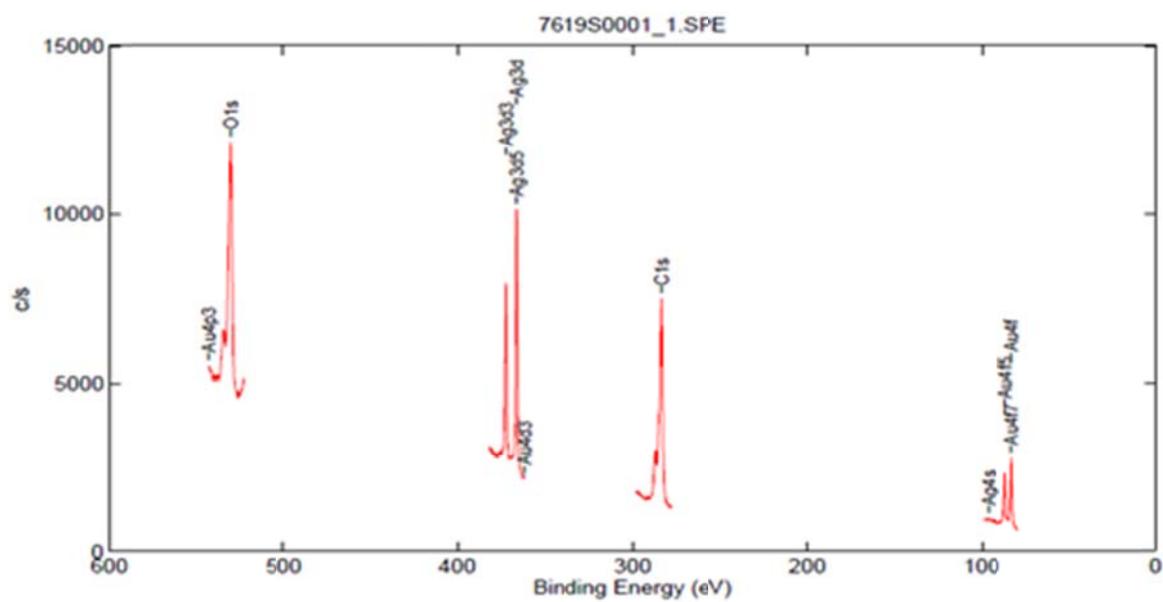
**Figure A 1.** EDS spectrum of shell layer of Au@Ag core shell nanorod composition: atomic percent of core Ag -1.50% , Au – 98.50%, and shell Ag - 77.65% , Au – 22.35% (0.1mL silver salts).



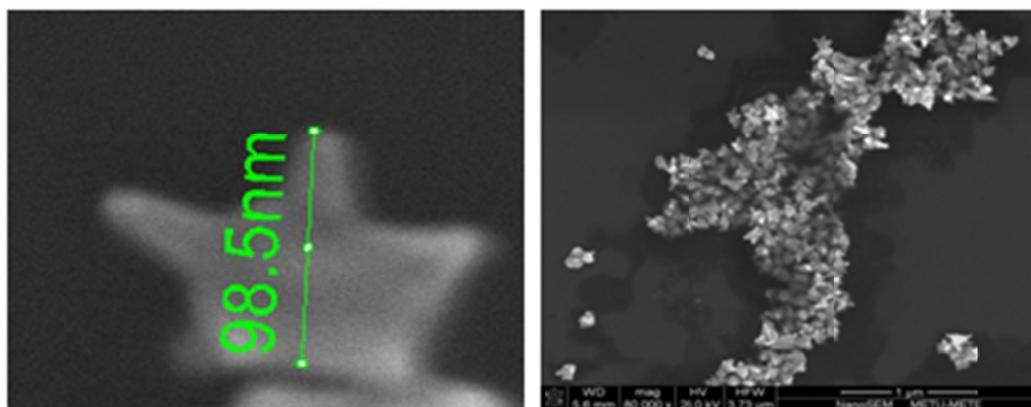
**Figure A 2.** EDS spectrum of shell layer of Au@Ag core -shell nanorod composition: atomic percent of core Ag -70.75%, Au – 29.25% , and shell Ag - 98.84% , Au – 1.16% (0.5mL silver salts).



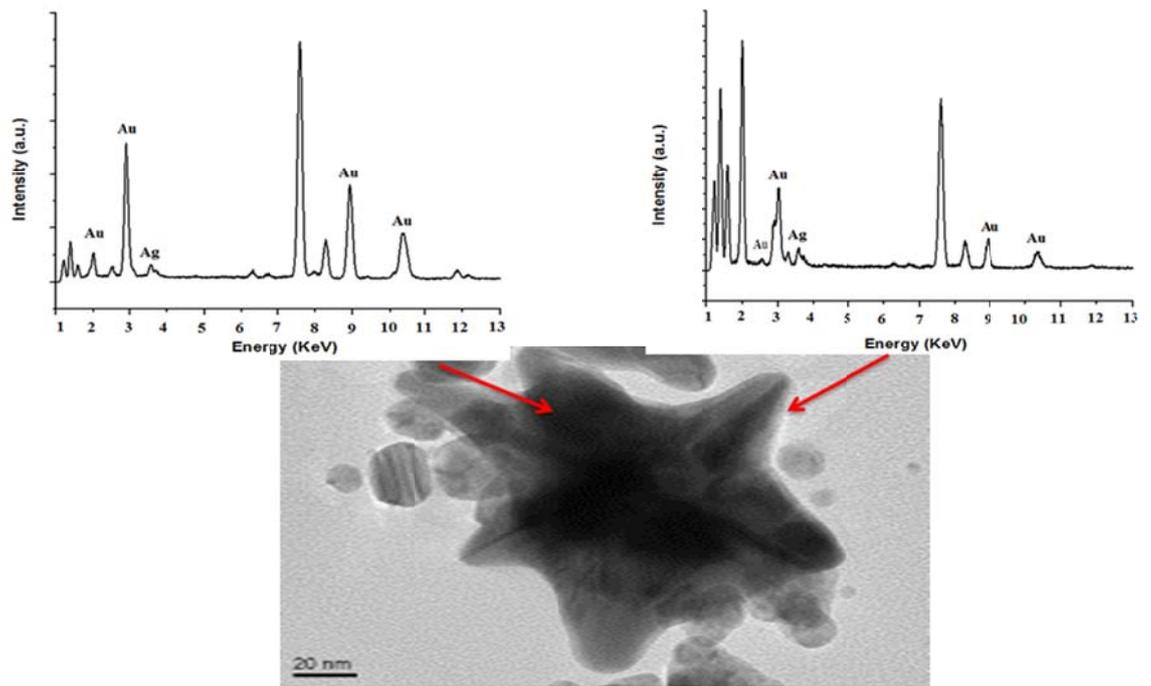
**Figure A 3.** EDS spectrum of shell layer of Au@Ag core shell nanorod composition: atomic percent of core Ag -98.57% , Au – 1.43% and shell Ag - 81.75% , Au – 18.25% (1mL silver salts).



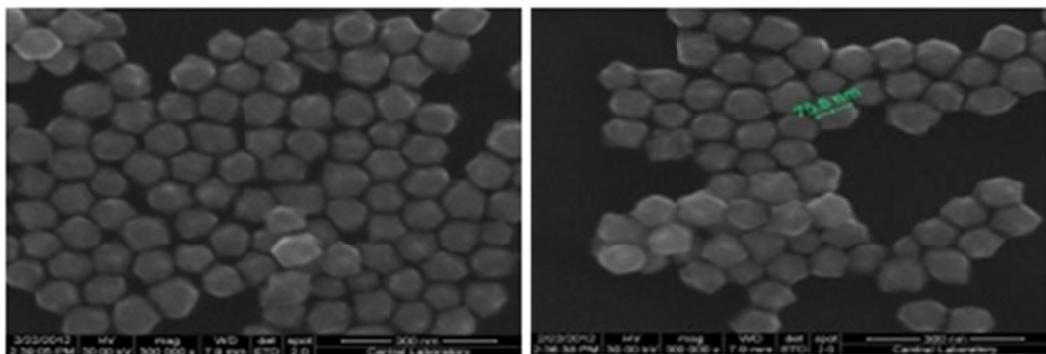
**Figure A 4.** XPS survey spectra of Au@Ag core shell nanorods.



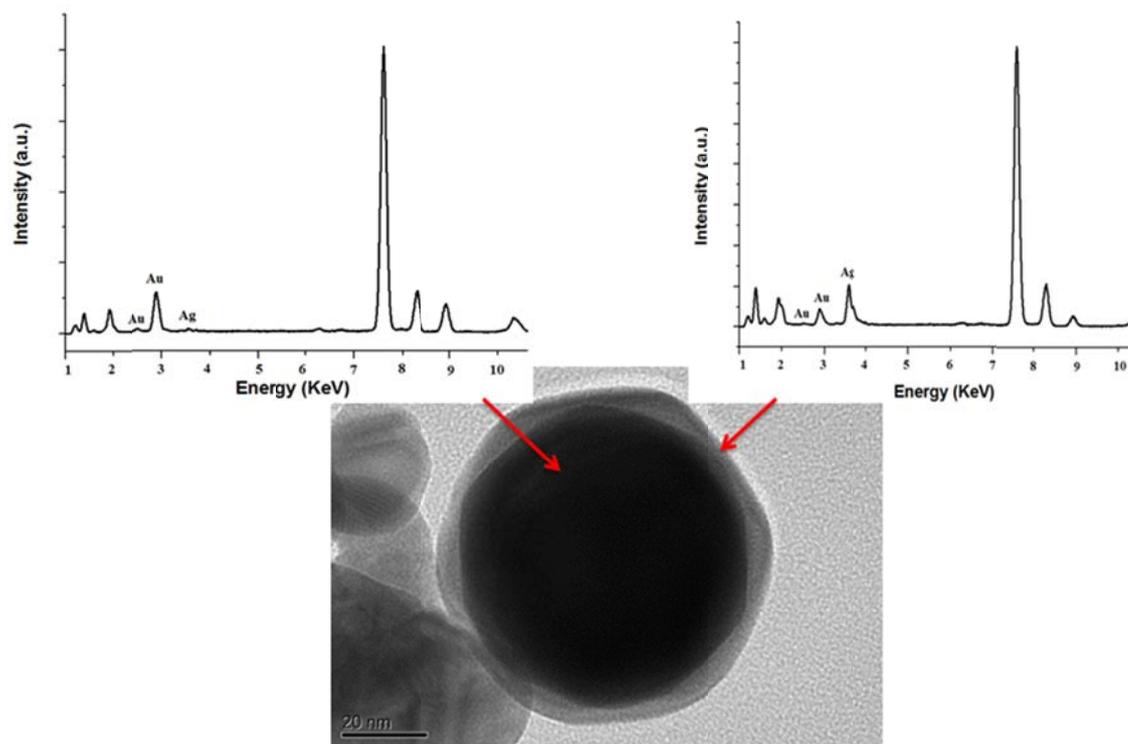
**Figure A5** SEM (a,b) images of gold branched NPs.



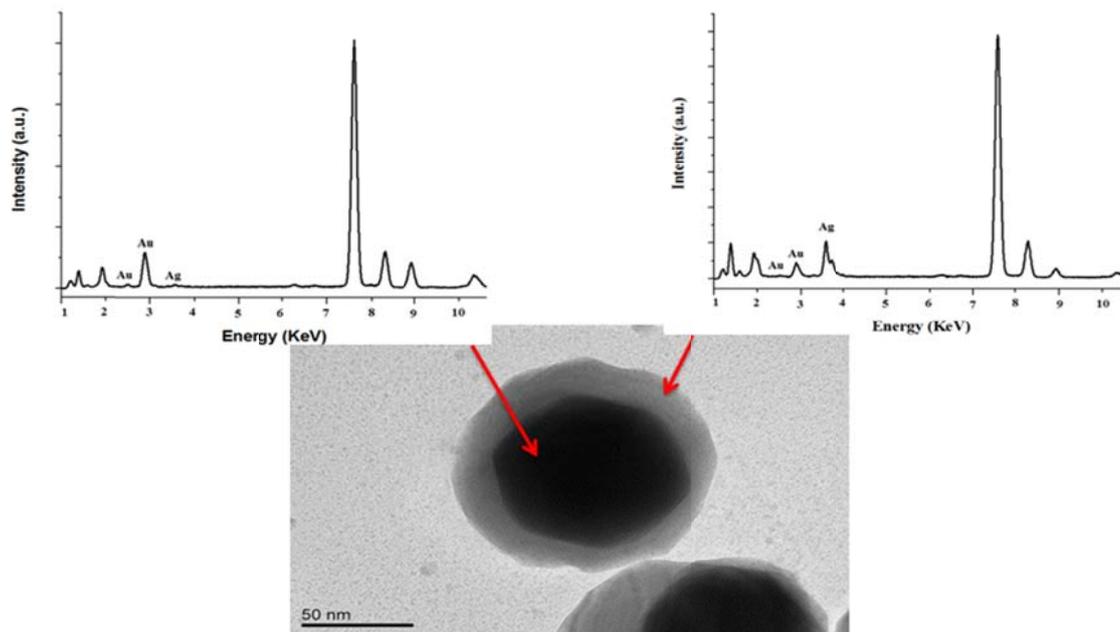
**Figure A6.** EDS spectrum of Au@Ag core shell nanostar composition: atomic percent of core Au - 100% and shell Ag -7.20% , Au - 92.80 % (0,5mL silver salts).



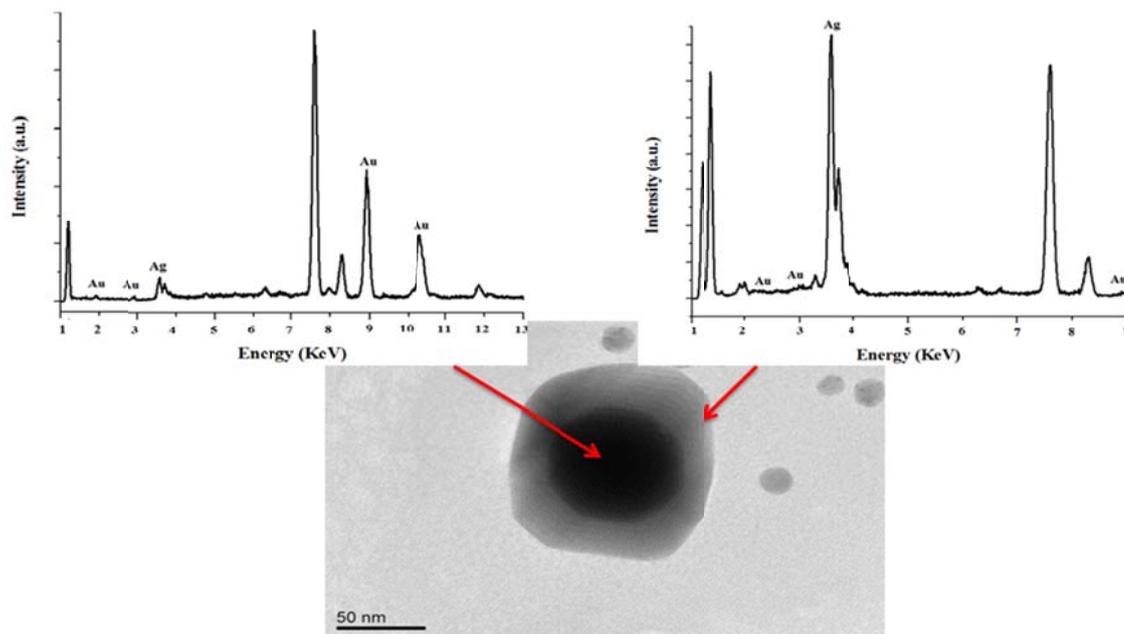
**Figure A7.** SEM images of gold octahedral solutions.



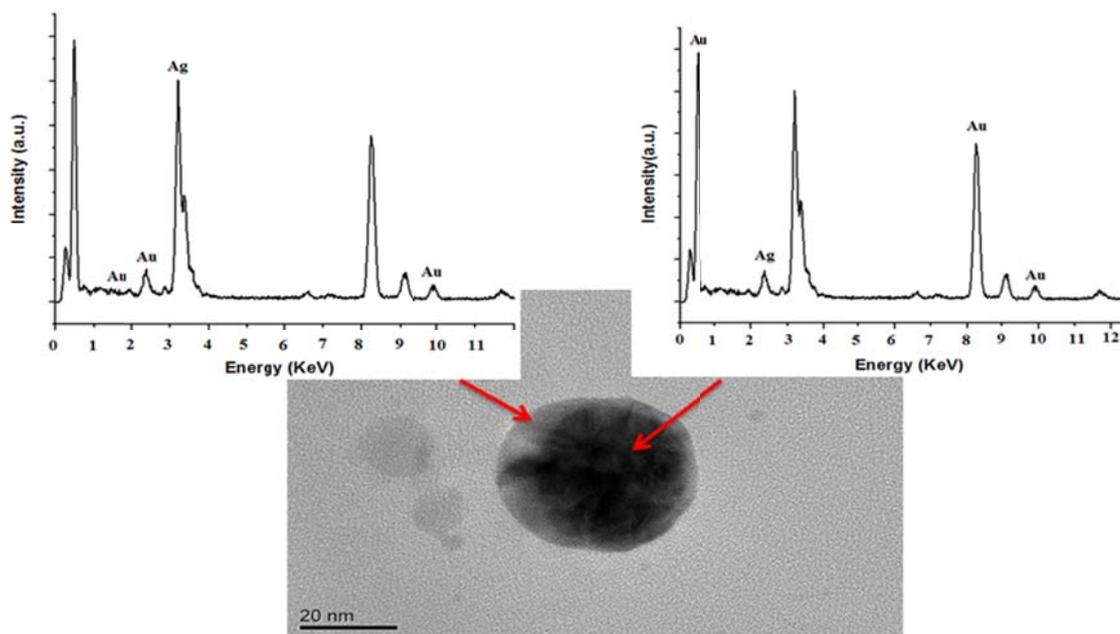
**Figure A8.** EDS spectrum of Au@Ag core-shell octahedral composition: atomic percent of core Ag -6.18% , Au – 93.82% and shell Ag -74.21% , Au – 25.79% (0.1mL silver salts).



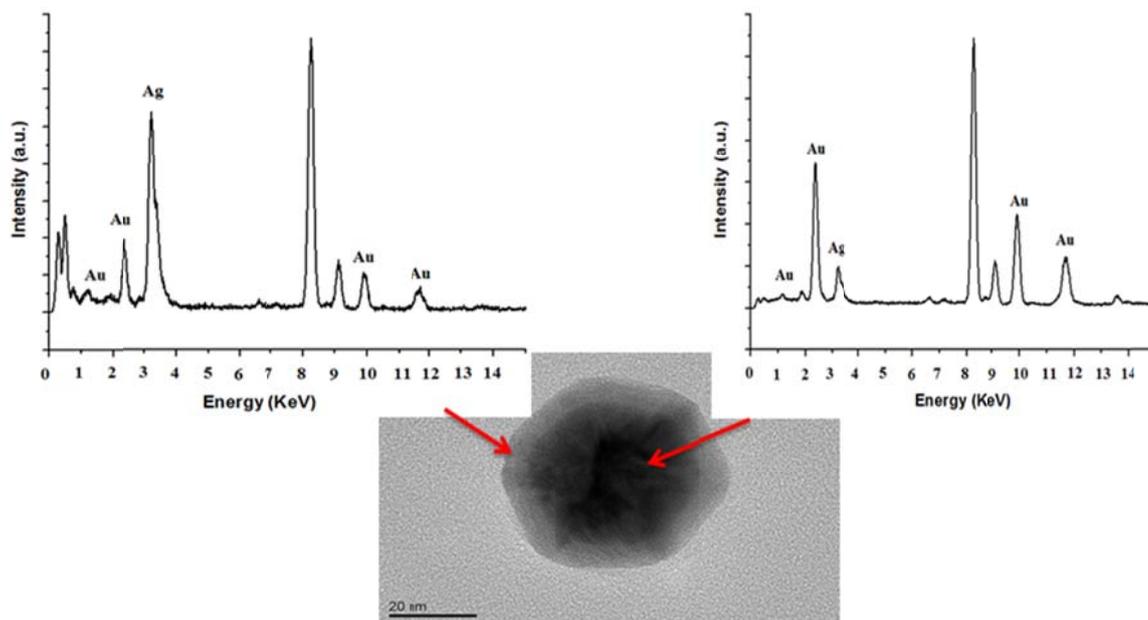
**Figure A9.** EDS spectrum of Au@Ag core-shell octahedral composition: atomic percent of core Ag -21.70% , Au – 73.30% and shell Ag -98.47% , Au – 1.53% (0.5mL silver salts).



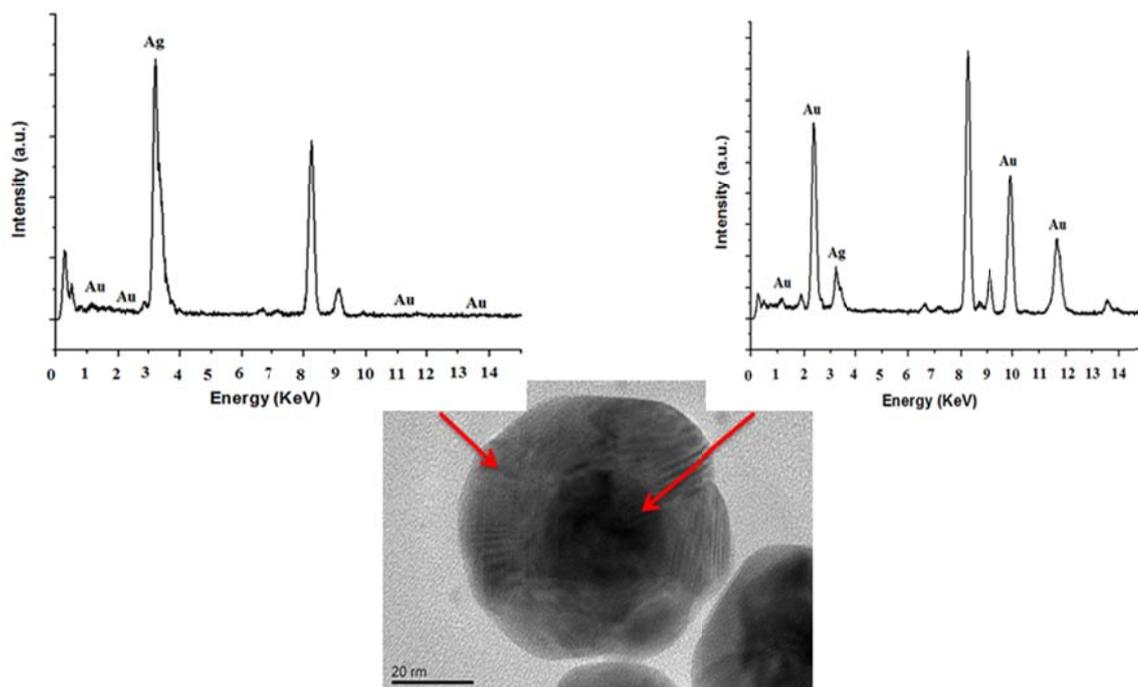
**Figure A10.** EDS spectrum of Au@Ag core-shell octahedral composition: atomic percent of core Ag -11.46% , Au – 88.54% and shell Ag - 100% (1mL silver salts).



**Figure A11.** EDS spectrum of Au@Ag core shell spherical composition: atomic percent of core Ag -11.45% , Au – 88.55% and shell Ag -91.17% , Au – 8.83% (0.1mL silver salts).



**Figure A12.** EDS spectrum of Au@Ag core shell spherical composition: atomic percent of core Ag -21.32% , Au - 78.68 % and shell Ag -78.98% , Au – 21.02% (0.5mL silver salts).



**Figure A13.** EDS spectrum of Au@Ag core shell spherical composition: atomic percent of core Ag -16.71% , Au - 83.29 % and shell Ag -98.78% , Au- 1.22% (1 mL silver salts).