# SYNTHESIS AND CHARACTERIZATION OF GOLD AND GOLD-CUPROUS OXIDE NANOSTRUCTURES

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# DEDICATION

*To my beloved parents, who without their enthusiasm and encouragement, I would never step in this way*

*and*

*to my kind, mindful understanding husband, who supported me and did way more than his share on each step of the way*

*and*

*to someone special….. Abiha, Haitham & Isbah*

*Thank you for waiting all this while.*

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# ABSTRACT

In the past few years, substantial efforts have been invested into the synthesis and characterization of plasmonic gold nanostructures owing to their unique size and shape-dependent physical and chemical properties. Gold (Au) nanostructures (NSs) are of great interest for scientific research because of their attractive applications in numerous fields, built upon their interesting surface plasmon resonance (SPR) features and biocompatibility. Corresponding to these fascinating features, multi-faceted Au NSs have been synthesized using a quaternary ammonium cationic surfactant, methyltrioctylammonium chloride (Aliquat 336), as a shaping and stabilizing agent. Transmission electron microscopy (TEM) and ultraviolet-visible (UV-Vis) spectroscopy analyses confirm the existence of Aliquat 336 stabilized NSs that are demonstrated to achieve minimal ligand density in the form of mono-molecular layer onto the Au surface. Thermogravimetric analysis (TGA) and dynamic light scattering (DLS) experiments have been performed to quantify the ligand density on the surface of Au. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements are accomplished to determine the structure and binding of ligand molecules to the Au surface. Zeta potential (+24.3 mV) of the nanoparticles (NPs) shows that the particles are positively charged and sufficiently stable in nature. The quats surfactant also manipulates the growth of extremely elongated Au nanorods (aspect ratio within 10-57) and nanowires following one-step hydrothermal syntheses. A pronounced change in the shapes of Au NSs strongly depends on the growth parameters including ligand contents, reaction temperature and reaction duration. As-synthesized Au NSs i.e. multi-faceted and cubic nanoparticles are coated with cuprous oxide to form Au-$Cu_2O$ core-shell nano-morphologies in which efficient shape evolution of the $Cu_2O$ shell is achieved through fine adjustment of the ratio $H_2O$:$NH_2OH{\cdot}HCl$. The effect of particle morphology and shell thickness on the optical properties of truncated-octahedra, cuboctahedra and nanoflowers Au-$Cu_2O$ having sizes within 90-230 nm shows that the SPR band of the Au-core shifts progressively to red with increasing shell thickness. A comparative study to correlate the photoluminescence (PL) analyses of core-shell nanostructures with their photocatalytic activities towards the decomposition of methyl orange shows that truncated-octahedra and nanoflowers, bounded by (111) facets, are photocatalytically more active. The results are in good agreement with the PL analysis in that cuboctahedra with more (100) catalytically inactive sites reveal a comparatively sharp emission peak.

## ABSTRAK

Beberapa tahun kebelakangan ini, usaha yang besar telah dilaburkan dalam sintesis dan pencirian nanostruktur plasmonik aurum kerana sifat fizik dan kimia yang bergantung kepada saiz dan bentuknya yang unik. Nanostruktur (NS) aurum (Au) mendapat perhatian yang tinggi untuk penyelidikan saintifik kerana aplikasinya yang menarik dalam pelbagai bidang yang terbina di atas ciri resonans plasmon permukaan (SPR) yang menarik dan keserasian-bio. Sepadan dengan cirinya yang menarik, pelbagai bentuk NS Au telah disintesis menggunakan surfaktan kation ammonium kuaterner, metiltrioktilammonium klorida (Aliquat 336), sebagai agen pembentukan dan penstabilan. Analisis mikroskop elektron (TEM) dan spektroskopi ultra lembayung-nampak (UV-Vis) mengesahkan kehadiran nanostruktur yang distabilkan oleh Aliquat 336 yang menunjukkan pencapaian ketumpatan ligan minimum dalam bentuk lapisan molekul mono di atas permukaan Au. Analisis termogravimetri (TGA) dan serakan cahaya dinamik (DLS) telah dijalankan untuk mengukur ketumpatan ligan di atas permukaan Au. Pengukuran analisis spektroskopi inframerah (FTIR) dan specktroskopi fotoelektron sinar-X (XPS) disempurnakan untuk menentukan struktur dan ikatan molekul ligan pada permukaan Au. Keupayaan zeta nanozarah (+24.3 mV) menunjukkan bahawa zarah tersebut bercas positif dan berkeadaan cukup stabil. Surfaktan quats ini juga memanipulasi pertumbuhan nanorod Au memanjang (nisbah aspek antara 10-57) dan nanowayar mengikut sintesis hidroterma selangkah. Perubahan ketara pada bentuk NS Au amat bergantung kepada parameter pertumbuhan termasuk kandungan ligan, suhu tindak balas dan masa tindak balas. NS Au tersedia sintesis iaitu pelbagai permukaan dan nanozarah kubus adalah diselaputi oleh kuprus oksida untuk membentuk petala teras Au-Cu2O nanomorfologi yang mana evolusi bentuk petala Cu2O yang efisyen diperolehi melalui pelarasan kecil nisbah H2O:NH2OH·HCl. Kesan morfologi zarah dan ketebalan petala terhadap sifat optik Au-Cu2O oktahedron terpenggal, kuboktahedra dan nanobunga dengan saiz sekitar 90-230 nm menunjukkan bahawa jalur SPR dari teras Au berganjak ke arah merah dengan pertambahan ketebalan petala. Satu kajian perbandingan untuk mengaitkan analisis kefotopendarcahayaan (PL) dari nanostruktur petala-teras dengan aktiviti pemangkinan berfoto mereka terhadap penguraian metil oren menunjukkan bahawa oktahedron terpenggal dan nanobunga disempadani oleh permukaan (111), adalah lebih aktif secara pemangkinan berfoto. Keputusan adalah sepadan dengan analisis PL yang mana kuboktahedra yang mempunyai banyak permukaan (100) yang tidak aktif katalitik mempamirkan puncak pemancaran lebih tajam.

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# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| A336 | - | Aliquat 336 |
| $AgNO_3$ | - | Silver Nitrate |
| $CH_3$ | - | Methyl |
| $CH_2$ | - | Methylene |
| CTAB | - | Cetyltrimethyl Ammonium Bromide |
| CTAC | - | Cetyltrimethyl Ammonium Bromide |
| CTEAB | - | Cetyltriethyl Ammonium Bromide |
| $C_{25}H_{54}ClN$ | - | Methyltrioctyl Ammonium Chloride/Aliquat 336 |
| $CuCl_2$ | - | Copper Chloride |
| $Cu_2O$ | - | Cuprous Oxide |
| DI | - | Deionized Water |
| DLS | - | Dynamic Light Scattering |
| EDX | - | Energy Dispersive X-rays |
| FRET | - | Fluorescence Resonance Energy Transfer |
| FTIR | - | Fourier Transformation Infrared |
| $HAuCl_4$ | - | Hydrochloroauric Acid |
| HR-TEM | - | High Resolution Transmission Electron Microscopy |
| $H_2S$ | - | Hydrogen Sulfide |
| JCPD | - | Joint Committee for Powder Diffraction |
| KBr | - | Potassium Bromide |
| LSPR | - | Localised Surface Plasmon Resonance |
| MO | - | Methyl Orange |
| $NaBH_4$ | - | Sodium Borohydride |
| NaBr | - | Sodium Bromide |
| NaOH | - | Sodium Hydroxide |
| NCs | - | Nanocubes |
| NPs | - | Nanoparticles |

| | | |
|---|---|---|
| NRs | - | Nanorods |
| NSs | - | Nanostructures |
| NTs | - | Nanotriangles |
| NWs | - | Nanowires |
| oop | - | Out-of-plane |
| PL | - | Photoluminescence |
| Quats | - | Quaternary Ammonium Cations |
| rpm | - | Revolution per Minute |
| RTILs | - | Room Temperature Ionic Liquids |
| SDS | - | Sodium Dodecyl Sulphate |
| SHE | - | Standard Hydrogen Electrode |
| TEM | - | Transmission Electron Microscopy |
| TGA | - | Thermogravimetric Analysis |
| TOAB | - | Tetraoctyl Ammonium Bromide |
| UV-Vis | - | Ultraviolet-Visible |
| XPS | - | X-ray Photoelectron Spectroscopy |
| XRD | - | X-ray Diffraction |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| Å | - | Angstrom |
| Al | - | Aluminium |
| Au | - | Gold |
| a.u. | - | Arbitrary unit |
| Ag | - | Silver |
| Br | - | Bromine |
| C | - | Carbon |
| ca. | - | Circa |
| Cl | - | Chlorine |
| $cm^{-1}$ | - | Frequency |
| Cu | - | Copper |
| $^{o}$ | - | Degree angle |
| $^{o}C$ | - | Degree Celsius |
| eV | - | Electron volt |
| h | - | Hours |
| H | - | Hydrogen |
| kV | - | Kilo volt |
| λ | - | Lambda |
| L | - | Length |
| µL | - | Micro litre |
| mg | - | Milli gram |
| mL | - | Milli litre |
| mV | - | Milli volt |
| min | - | Minute |
| M | - | Molarity |
| nm | - | Nanometre |
| N | - | Nitrogen |

| | | |
|---|---|---|
| $N$ | - | Number |
| $n$ | - | Number of carbon atoms |
| O | - | Oxygen |
| Pd | - | Palladium |
| % | - | Percentage |
| R | - | Radius |
| $\rho$ | - | Density |
| s | - | Second |
| $\theta$ | - | Theta |
| W | - | Watt |
| $x$ | - | Volume of $NH_2OH{\cdot}HCl$ in mL |
| Xe | - | Xenon |
| $\zeta$ | - | Zeta |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Undeniably, plasmonic gold (Au) nanostructures (NSs) are promising material for their novel applications in various emerging fields of science, technology and engineering [1, 2]. They have been a material of choice owing to a combination of unique properties including the flexibility for surface alteration, the tunable localized surface plasmon resonance (LSPR), the fascinating catalytic activities at the nanoscale, and biocompatibility. Indeed, these Au NSs exhibiting strong resonances in the visible/NIR region are model candidates for the enhancement of Raman signals [3, 4] and diverse biomedical applications [5].

The growth of plasmonic Au NSs through wet chemical processes typically requires a surfactant as capping and shape-directing agent. In fact, cationic quaternary ammonium salts (**quats**) are used as the most essential surfactants [6]. It is acknowledged that cetyltrimethylammonium bromide (CTAB) being very efficient as directing agent allows the formation of Au nanoparticles (NPs) with varying shapes including nanorods, hexagons and triangles [7, 8]. Especially, Au nanorods with high aspect ratio are prepared using a seed-mediated growth method in an aqueous micellar template by properly adjusting the CTAB concentration during the reaction [9, 10]. The CTAB analogue, cetyltrimethylammonium chloride (CTAC) is also used for the synthesis of anisotropic Au NPs with different shapes such as cubic, trisoctahedra, and rhombic dodecahedra [11]. Nevertheless, these long chain cationic ligands with higher ligand density in terms of bilayer have appeared to be more toxic and thus limit their potential biomedical applications [12].

Methyltrioctylammonium chloride (Aliquat 336) is another **quats** reagent. It is a less stable cationic ligand than the usual CTAB/CTAC ligands due to its three dimensional short hydrocarbon chains and low affinity. However, it is more stable against air and moisture attack than other cationic ligands and easier to handle [13]. Unlike a bilayer in CTAB/CTAC ligands, a mono-hydrophobic layer of Aliquat 336 molecules can stabilize Au NPs, where three hydrocarbon chains of the ligand molecule overlap on three sides with those of another ligand molecules on the NPs surface. Accordingly, the formation of a hexagonally patterned monolayer of the ligand molecules on the Au NPs surface may overcome the ligand density problem related to in vivo applications.

Another limitation with the CTAB assisted, seed-mediated gold nanorods (NRs) synthesis is that the growth conditions control using these synthetic strategies usually offers complexes like its aspect ratio reduction with the growth progression [14, 15]. In this research, Au NRs of very high aspect ratio (ranging from 10 to 57) have been prepared in an aqueous solution at 85 $^{o}$C using Aliquat 336 as a phase transfer reagent. Such anisotropic Au nanoparticles (NPs) have been used for various biological and sensing applications due to their unique size, composition and structure dependent optical properties [5]. However, the stability and surface functionalization of Au NPs still remain problematic in many situations [16] due to physicochemical limitations associated with them. An ideal solution is to encapsulate these Au NPs with a semiconductor protective shell.

The interest in cuprous oxide, $Cu_2O$, as a semiconductor began with the invention of the $Cu_2O$ rectifier by Grondahl in the 1920s [17]. Cuprous oxide is a semiconductor material with p-type conductivity due to copper vacancies. The energy band gap of $Cu_2O$ is 2.17 eV and it has a high optical absorption coefficient in the visible region [18]. The crystal structure of $Cu_2O$ is cuprite with a lattice constant of 4.27 Å [19]. Considerable work was done on $Cu_2O$ characterization from 1930 to 1940. Photosensitive devices based on $Cu_2O$ were investigated in the 1930s and B. Lange reviewed this work in 1939 [20]. The successful preparation of $Cu_2O$ nanocrystals with systematic shape evolution from cubic to hexapod and octahedral structures by a facile aqueous solution approach have shown enhanced photocatalytic activity [21].

Formation of localized surface plasmon resonant (LSPR) cuprous oxide coated gold (Au-$Cu_2O$) core-shell nanostructures, during the last few years, with precise geometrical and shape control of the components and their characterization has presented remarkable attention. The characterization of these metal-semiconductor core-shell nanostructures plays an important role either in fundamental research or in technological uses, covering from fabrication and characterization to device processing. It has been investigated that several geometrical parameters (shell thickness, size of the core, spacing between core and shell, etc.) of Au-$Cu_2O$ core-shell nanoparticles systematically fine-tune the light absorption and scattering properties of these particles across the visible and near-infrared regions [22]. Despite significant lattice mismatch of 4.3% between the different gold surfaces and the lattice planes of $Cu_2O$, excellent interfacial epitaxial growth and systematic morphological evolution of these structures can still be achieved [23] to have enhanced optical and catalytic properties.

## 1.2 Problem Statement

Quaternary ammonium cations/**quats** surfactants such as CTAC, CTAB and cetyltriethylammonium bromide (CTEAB)-stabilized Au NSs have drawn an interesting attention for applications based on their size and shape dependent optical properties [24-26]. The drawback of these bilayer-surfactants protection of nanoparticles has been their toxicity due to higher ligand density for in vivo [27] and deficient long-term stability in terms of aggregation as the long alkyl chains of CTAB/CTAC tend to trigger more van der Waals interactions among themselves [28]. This research involves the use of another cationic ligand, metyhyltrioctylammonium chloride (Aliquat 336), with rather short alkyl chains as a phase transfer reagent to produce multi-faceted Au nanoparticles stabilized by monolayer of the ligand molecules.

The preparation of Au NRs traditionally involves a seed-mediated growth mechanism in the presence of cetyltrimethylammonium bromide/CTAB as a shape directing and capping agent [3] and has been reported many times. This seed-growth approach can produce Au NRs with aspect ratios (length/diameter) as much as 27:1. However, the growth conditions control usually offers complexes [15] with another limitation related to its aspect ratio reduction with the growth progression [14]. Thus, an alternative synthesis method is required to achieve dispersed and elongated Au NRs with localized surface plasmon resonance (LSPR) effects in the IR region.

The surface ligand and aspect ratio of Au NRs are prerequisite for near-field optical response [29]. Usually, NRs aspect ratio is directing surfactant's nature dependent (in an aqueous solution) [30] and a surfactant's (CTAB) concentrated solution is necessary. CTAB binds to the surface of Au as bilayer structure and has limitations in terms of its toxicity and stability [27, 31]. Often, $AgNO_3$ is used as additive for selective binding and packing of CTAB but it reduces the repulsion between the surfactant head groups [32]. Despite this additive, preparation of NRs with aspect ratio > 7 becomes difficult [9]. Many experiments exhibited the effect of alkyltrimethylammonium (surfactant) tail length [30] and surfactant's head group [26] on Au NRs growth. The change of Au NRs morphology (aspect ratio) via different synthesis temperature programs has been reported [33], but the impact of reaction time duration on morphological change is not yet documented. Here, an alternative single-step synthesis method is adopted to achieve dispersed and elongated Au NRs and nanowires (NWs) with localized surface plasmon resonance (LSPR) effects in the near IR region to avoid a complex seed-mediated growth mechanism in the presence of CTAB as a shape directing and capping agent.

Au NRs of very high aspect ratio (ranging from 10 to 57) have been prepared in an aqueous solution at 85 $^{o}C$ using Aliquat 336 as a phase transfer reagent. The effects of the ligand concentration, reaction temperature and time on the structure, optical behavior, and the product yield are determined. Aliquat 336 has also shown a capability to produce a variety of Au NSs, like Au nanocubes (NCs) and nanotriangles (NTs), by controlling the growth parameters during the reaction.

As one distinctive combination of metal nanoparticles with localized surface plasmon resonance and metal-oxide semiconductors, Au-$Cu_2O$ metal-semiconductor core-shell nanostructures have attracted a great deal of attention because of their novel structure and potential application in solar energy conversion [34]. Despite the recent achievements in the systematic growth of these heterostructures at different levels and their catalytic activities, further investigation on various shapes-dependent optical properties of Au-$Cu_2O$ nanocrystals are lacking. For example, a lot of attention has been given to measurements of photocatalytic performance of Au-$Cu_2O$ core-shell nanostructures [35], but the effect of various shaped Au-$Cu_2O$ nanoparticles (*e.g.* cuboctahedron, octahedron) on other optical properties like photoluminescence has not been systematically investigated. Furthermore, most studies are lacking the rich structural variety of semiconductor-shell that may be produced by employing core particles of different shapes, and their characterization.

In this research, Au-$Cu_2O$ core-shell nano-morphologies are synthesized by facile wet chemical approach and exposed to light with different shapes in order to investigate for correlation between photoluminescence and photocatalytic performance. Furthermore, the cooperative morphology between plasmonic metal and semiconductor nanostructures is explored along with their special plasmon resonant optical properties that show interesting tunability during the structural evolution.

## 1.3 Research Questions

The study involves following research questions:

**i.** How the shape evolution of gold (Au) and Au-$Cu_2O$ core-shell nanostructures can be obtained by using Aliquat 336 surfactant and gold-cores of different shapes, respectively?

**ii.** Does the surface functionalization of these nanostructures require the ability to tune the nanoparticles morphology?

**iii.** How does the shape and surface orientation of gold and Au-$Cu_2O$ nanostructures affect the LSPR based optical properties and how these can be harvested towards applications, like Photoluminescence and photocatalysis?

## 1.4 Research Objectives

The research objectives of the study include:

**i.** To synthesize **quats**-functionalized gold (Au) nanostructures (NSs) for the measurement of the ligand density on the surface of Au NSs.

**ii.** To prepare Au-$Cu_2O$ core-shell nanostructures using gold-cores of different shapes, for improved LSPR based optical properties.

**iii.** To determine the influence of growth parameters on the structural/optical properties of Au and Au-$Cu_2O$ core-shell nanostructures.

**iv.** To determine the relationship between photoluminescence and photocatalytic properties of Au-$Cu_2O$ core-shell nanostructures.

## 1.5 Scope of the Research

This research involves the syntheses of functionalized gold (Au) and cuprous oxide coated gold (Au-$Cu_2O$) core-shell nanostructures with various shape evolution by varying the growth parameters. In the first, preparation of multi-faceted Au nanoparticles (NPs) with minimal ligand density using a quaternary ammonium cationic ligand as a shaping and stabilizing agent was encountered. The stability and nature of binding of the ligand to the Au NPs surface was accomplished by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), Zeta potential and thermogravimetric analysis (TGA). Then, the effect of different synthetic parameters like reaction temperature, reaction duration, gold precursor and the ligand concentration on the syntheses of other Au NSs (*e.g.* cubic, triangular, rod and wire-like) were studied. The modification of multi-faceted and cubic Au NSs with Au-$Cu_2O$ core-shell nanostructures for enhanced LSPR based optical properties was successfully accomplished. The unique surface plasmon absorption of various gold nanostructures and Au-$Cu_2O$ core-shell nanostructures was taken by UV-Vis spectroscopy. The size, morphology and chemical composition of these nanostructures were studied by transmission electron microscope (TEM), X-ray diffractometer (XRD) and energy dispersive X-ray (EDX). Influence of growth parameters on structural and optical properties of Au-$Cu_2O$ core-shell nanostructures was investigated. Gold and Au-$Cu_2O$ core-shell nanostructures were also supposed to explore the influence of the LSPR on the photoluminescence emission peaks of these nanostructures. The Au-$Cu_2O$ core-shell nanostructures were also examined comparatively as photocatalysts towards the decomposition of organic dye. The results showed that the core-shell nanostructures with more exposed (111) surfaces were catalytically more active, in good agreement with PL analysis where catalytically inactive (100) surfaces revealed a comparatively sharp emission peak.

## 1.6 Significance of the Research

In this research, the motivation for the syntheses of plasmonic Au NSs with shape-dependent optical properties comes from the choice of another cationic ligand, methyltrioctylammonium chloride/Aliquat 336, having superior properties while altering the growth parameters. Especially, Aliquat 336 surfactant is utilized to prepare high aspect ratio Au NRs and NWs without any usual seed-mediated growth mechanism. The modification of Au NSs with Au-$Cu_2O$ metal-semiconductor core-shell NSs resulted in enhanced LSPR based optical and photocatalytic properties.

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