

**SYNTHESIS AND CHARACTERIZATION OF COPPER
NANOPARTICLES: ARCHITECTURAL MORPHOLOGIES AND
APPLICATIONS IN SURFACE ENHANCED RAMAN SPECTROSCOPY**

By

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A thesis submitted in partial of the requirements for the degree of

MASTERS IN SCIENCE

IN

Chemistry

UNIVERSITY OF PUERTO RICO

MAYAGUEZ CAMPUS

2009

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ABSTRACT

The preparation of copper colloidal suspensions was conducted by three different methods. These methods used wet chemical synthesis, in which a metal salt solution was mixed with a solution containing the reducing agent. Preparation of the copper seed involved chemical reduction using trisodium citrate. Steadiness varied under conditions such as stirring rate, rate of addition of reducing agent and temperature control. Sizes of nanoparticles prepared ranged from 2 to 20 nm. Morphology and sizes were characterized using High Resolution Transmission Electron Microscopy (HR-TEM). Enhanced Raman spectra of *o*-dinitrobenzene on prepared nanoparticles suspensions of Cu were obtained with visible excitation at 488 and 514.5 nm. It was found that enhanced Raman signal intensities resulted from the interaction of the analytes with the metallic surface resonance plasmon of Cu nanoparticles excited at the laser frequency. The adsorption behavior of the analytes on the Cu nanoparticles was modeled using Density Functional Theory (DFT) of the Gaussian 03 software package. The simplified model used worked reasonably well in describing some enhancement results for the Raman experiments on the noble metal colloidal suspensions.

In another chemical procedure copper nanoparticles were synthesized via a one step process. In this procedure the reactant concentration and temperature strongly influenced the shaped of the copper particles. As a result bigger diameters (e.g. 100 nm) were produced. Different shapes and narrow sized distributions were also obtained. At low reagent concentration, the particles were cubic and at high reagent

concentration, the particles were spherical. SERS activity was studied for different nitro aromatic compounds at different temperatures and copper colloid concentration.

Beta-cyclodextrin (β -CD) in alkaline solution has been observed to produce mono and bimetallic nanoparticles of silver and gold and to provide in-house stability to both of the particles. We report on the use of copper-gold bimetallic nanoparticles to obtain the Raman activity spectra of crystal violet on the surface of these nanoparticles. UV-VIS spectrophotometry was used to characterize the bimetallic nanoparticle architecture and the evolution of the architecture. It was found that the approximate size of the nanoparticle was 20 nm and the morphology of the nanoparticles was club-shaped seeds. Based on experimental data, average FWHM of the absorption band in the visible region for bimetallic structures was around 45 nm which indicates a colloidal suspension of modest monodispersity. Based on these results, synthesized colloids tend to form sort of like double layer cluster architecture, since the composition of the nanoparticles showed a narrow spectrum of sizes and shapes. Raman activity of crystal violet ion using as excitation sources 514.5 and 532 nm lasers was measured. It was found that at an excitation source of 514.5 nm, the signal enhancement of crystal violet (5.0×10^{-6} M) was much greater than at 532 nm. Results suggest that the orientation of crystal violet ion is perpendicular to the surface of the bimetallic structure.

RESUMEN

La preparación de suspensiones coloidales de cobre se llevó a cabo mediante tres métodos distintos. Estos métodos utilizaron síntesis química en estado líquido, en la cual una solución que contiene la sal metálica es mezclada con una solución que contiene el agente reductor. Se prepararon suspensiones coloidales que produjeron semillas de cobre utilizando citrato de sodio. La estabilidad variaba bajo ciertas condiciones, tales como: la razón de agitación de la solución, la razón de la adición del agente reductor y el control de temperatura. Los tamaños de las nanopartículas variaban de 2-20 nm. Morfología y tamaño fueron caracterizadas utilizando Microscopia de Transmisión de Electrones de alta resolución (HR-TEM). Espectros Raman de señal aumentada de o-dinitrobenceno en las suspensiones coloidales de cobre se obtuvieron con excitación en la región visible a 488y 514.5 nm. Se encontró que las señales del espectro Raman de señal aumentada fue resultado de la interacción entre el analito y el plasmon de superficie de las nanopartículas de cobre metálico excitadas a las frecuencias del láser. El comportamiento de adsorción del analito en la superficie de cobre metálico fue modelado utilizando cálculos de Teoría de Densidad Funcional con el programa Gaussian 03. El modelo sencillo funcionó bastante bien en la descripción de los resultados de los espectros Raman modificados en la superficie de la nanopartículas de cobre.

En otro procedimiento químico nanopartículas de cobre se sintetizaron mediante un proceso de un paso. En este procedimiento la concentración del reactivo la temperatura en la cual fue llevada a cabo el proceso influenciaba el tamaño de las nanopartículas

de cobre. Como resultado se obtuvo nanopartículas de alrededor de 100 nm. Se produjeron también distintas formas y distribuciones angostas. A concentraciones bajas de reactivo, las partículas producidas eran de forma cúbica y a concentraciones altas de reactivos, las partículas producidas eran de forma esférica. Actividad SERS fue estudiada con varios compuestos nitroaromáticos a distintas temperaturas y concentración del coloide de cobre.

Beta-ciclodextrina (β -CD) en solución alcalina se ha observado que produce nanopartículas de oro y plata mono y bimetálicas la cual le provee una gran estabilidad a ambas partículas. Se reporta el uso de nanopartículas bimetálicas de cobre con oro para obtener el espectro de la actividad Raman de cristal violeta en la superficie de estas nanopartículas. Se encontró que el tamaño aproximado de las nanopartículas fue de 20 nm y su estado morfológico parecido a una habichuela. Basado en datos experimentales, el FWHM aproximado de las estructuras bimetálicas fue alrededor de 45 nm lo cual es indicativo de una suspensión coloidal de monodispersidad modesta. Se midió la actividad Raman del ion de cristal violeta usando unas fuentes de excitación a 532 y 514.5 nm. Se encontró que la señal producida por cristal violeta ($5.0 \times 10^{-6}\text{M}$) fue mucho más intensa que la señal obtenida a 532 nm. Los resultados sugieren que la orientación del ion de cristal violeta es perpendicular a la superficie de la estructura bimetálica.

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***This work is dedicated to my mom, dad and grandmother
For your unconditional love and support***

ACKNOWLEDGEMENTS

First of all I would like to thank my mother Doris Betancourt and my father Edgardo Rivera, for the unconditional love, support and sacrifice. You have helped me through good and bad times in my personal life and my life as a student and for that I am very grateful. Thank you for giving me the gift of life.

I would also like to thank my advisor Dr. Samuel P. Hernandez. Thank you for the opportunity of letting we work in your research lab. Overall thanks for all your support, empathy and kindness, I couldn't have picked a better place and environment to work. All my love goes to my grandmother Myrna Colon, to all my brothers for their love and support.

I am very thankful to all my friends for also giving me your love, support and all the fun times we have had together. I'm grateful to all my colleagues at Center for Chemical Sensors Development for helping me with parts of my research.

Thanks to Aaron LaPointe from Night Vision and Electronic Sensors Directorate, Department of Defense for his contributions. High Resolution TEM images were measured at the Materials Characterization Center of the Rio Piedras Campus of the University of Puerto Rico by Mr. Oscar Resto, whom we recognize for his dedication and commitment to the scientific community in Puerto Rico.

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CHAPTER I

INTRODUCTION

Raman spectroscopy (RS) is a popular nondestructive probing tool used to characterize molecular structure and usually imposes very little constraint on the substrate size [1]. The vibrational spectrum provided by Raman spectroscopy is a molecular “fingerprint” that can be used to differentiate target analytes in complex media or differentiate molecules with very similar structure and most often provides unambiguous sample identification. Owing to its scattering nature, spontaneous or normal RS is an inherently weak process. This fact has motivated physicists, chemists and engineers to constantly seek means of increasing the strengths of vibrational intensities observed in normal RS experiments. There are two general schemes of increasing vibrational RS signals: Resonance Raman scattering (RRS), which depends on the probability of closely matching the excitation laser energy to the energy gap between the ground electronic state and an excited state; and Surface Enhanced Raman Scattering (SERS) in which signal enhancement comes from an analyte adsorption to a roughened noble metal substrate. The largest signal enhancements arise from the observation of these two phenomena simultaneously in a process termed Surface Enhanced-Resonance Raman Scattering (SERRS).

There is a large variety of SERS substrates other than metallic colloidal suspensions, including electrodes, metal island films, and others. However, wet chemistry preparations provide an inexpensive and versatile approach to metal nanoparticles fabrication. Colloidal nanoparticles are commonly used for SERS/SERRS

studies either in a suspension as sols, or the analyte-colloid system is cast onto a supporting surface and allowing to dry on the solid support forming particles of a variety of shapes and aggregates. The use of colloidal suspensions for detection of a modest (10^3 - 10^5) SERS enhancement has several advantages; the presence of a solution tends to minimize the burning of the sample allowing the use of higher powers and the use of more energetic laser lines. Also, the use of sols permits the acquisition of an average spectrum due to the Brownian motion that governs the colloidal suspension [2]. Common metals used as SERS substrates include silver, gold, and copper. Various methods have been developed to prepare nanoparticles using these metals. The procedures include chemical reduction, laser ablation and photoreduction. The most widely used method is based on chemical reactions in solutions (wet chemistry) that yield metal nanoparticles. Wet chemistry methods are performed by mixing metal salts, which are reduced by a chemical agent to produce colloidal suspensions producing metal nanoparticles [3]. Sodium borohydride and trisodium citrate are widely used as reducing agents. Both of these agents have proven to produce effective colloids, but synthesis with trisodium citrate is more common because it gives rise to monodispersed colloids of desired size and characteristics [4-5].

The optical properties of these nanoparticles depend on the size, shape, and dielectric constant of the medium. Spherical metallic nanoparticles exhibits a single surface plasmon (SP) absorption band in the visible region of the electromagnetic spectrum, attributed to the coherent oscillation of the conduction electrons caused by oscillating electric field when they are irradiated by light [6-7]. The size and shape determinations correlate with the visible absorption data, and the full width at half maximum (FWHM)

can be used to estimate nanoparticle dispersion [8]. In recent years, bimetallic nanoparticles have fascinated scientists because of their superior optical, electronic, catalytic, and magnetic properties compared to monometallic counterparts. These interesting physicochemical properties result from the combination of two kinds of metals and their fine structures, evolving new surface characteristics [9]. The structure of bimetallic nanoparticles is defined by the distribution modes of the two elements and can be oriented in random alloy, alloy within and intermetallic compound, cluster-in-cluster, and core shell structures.

Surface Enhanced Raman Spectroscopy is used to significantly increase scattering signals of analytes adsorbed on the nanoparticles surfaces. Large enhancements (10^6 - 10^8) of the Raman scattering cross section can be obtained for adsorbed molecules. The theoretical explanation of the origin of this effect has been in dispute for several years, but recent advances in production of nanostructures with very precise control of their size, shape, and spacing have allowed both greater understanding of the origin of the effect and its control [10]. Two mechanisms have been widely accepted to account for the SERS effect observed on coinage metal surfaces (Ag, Au, and Cu): the electromagnetic (EM) and the charge-transfer (CT) mechanisms [11]. EM effect occurs due to the strong electromagnetic fields and field gradients in available so called “hot spots” or areas of very high enhancements of the metal colloidal nanoparticles clusters. The molecules involved are those adsorbed on the aggregates favorable for surface plasmon resonances. Small metal nanoparticles or nanostructures have localized surface plasmon resonances that appear to provide most of the Raman enhancement, maximized when the localized surface plasmon resonance (LSPR) frequency overlaps

that of the excitation laser. There also appears to be a modest “chemical” contribution ($\sim 10^2$) to the enhancement caused by changes in the bond polarizability of an adsorbed molecule [12].

Even though Surface Enhanced Raman Scattering has been used to investigate the information of certain molecules, uncertainty still remains concerning the adsorption geometry of analyte molecules on the surface of metal colloidal particles. The symmetry of adsorption of the adsorbate molecule is also an important factor to consider when explaining the SERS spectra obtained: relative intensities of the bands could be different from the neat solid or calculated spectra. Quantum chemical investigations seem to treat the problem in two ways, one being periodic Density Functional Theory (DFT) and the other using a cluster model of the surface studied [12]. The DFT based calculations have been used in many areas [13-15].

CHAPTER II

THEORETICAL BACKGROUND

The number of methods for the preparation of colloidal nanostructures with SERS activity is numerous and synthesis continues to be a very active field of research in the development of nano-based sensors. SERS can be used to try to solve a vast range of chemical and biophysical related problems. Consequently, it has been accepted as mayor analytical tool in many research areas. For quantitative analysis there has been an urgency to develop homogenous, stable and reproducible SERS substrates fit for various needs.

2.1. Preparation and Properties of Metallic Colloidal Suspensions

Metal colloids can be prepared by a variety of different procedures: chemical reduction in aqueous media (wet chemistry methods), laser ablation and photoreduction are the most frequently employed methods. However, by far the most universally employed method for the preparation of metal nanoparticles in suspension for SERS is chemical reduction. Wet chemistry is usually performed by using a starting metal, which is reduced by a chemical agent to produce colloidal suspensions containing nanoparticles of various sizes, a property that is dependent of the method used to produce such nanoparticles. Sodium borohydride and trisodium citrate are widely used as reducing agents. Both of these reducing agents have proven to produce effective, SERS producing colloids, but the synthesis with trisodium citrate is more common because it is easy to prepare colloidal suspensions of right size and characteristics for SERS effects [4-5].

SERS phenomena are associated with the generation of surface plasmon resonances. The nanoparticles prepared will possess different surface plasmon resonances, depending on size, shape and dielectric constant of the metal used. A surface plasmon resonance is a charge-density oscillation that may exist at the interface of two media with dielectric constants of opposite signs; for instance, a metal and a dielectric (see Figure.1). The charge density wave is associated with electromagnetic waves, the field vectors of which reach their maxima at the interface and decay evanescently into both media.

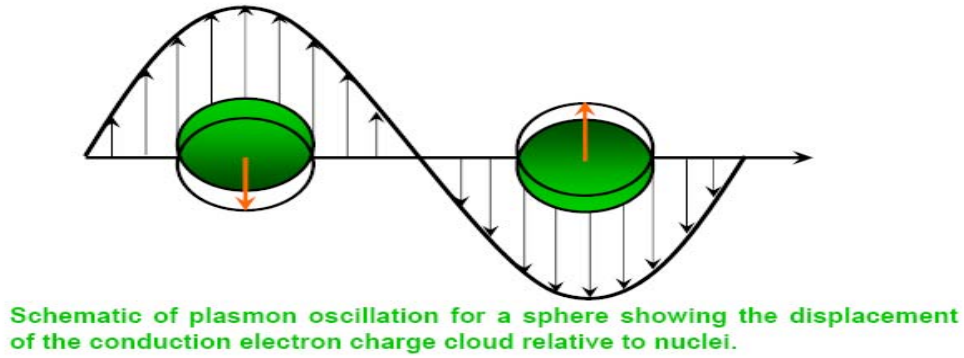


Figure 1. Schematic representation of a surface plasmon.

This surface plasma wave (SPW) is a transverse mode (TM)-polarized wave (magnetic vector is perpendicular to the direction of propagation of the SPW and parallel to the interface plane). The propagation constant of the surface plasma wave propagating at the interface between a semi-infinite dielectric and metal is given by Equation 1:

$$\beta = k \sqrt{\frac{\epsilon_m n_s^2}{\epsilon_m + n_s^2}} \quad (1)$$

where k denotes the free space wave number, ϵ_M the dielectric constant of the metal ($\epsilon_M = \epsilon_{MR} + i\epsilon_{mi}$), and n_S the refractive index of the dielectric [16-17]. The size and shape parameters can be partially controlled by appropriate choice of preparation methods. The most important factor to consider is the nature of the metal, the reducing agent, temperature, the stabilizing agents and the metal ion concentration.

Nucleation and growth are two closely interlinked processes that depend markedly on the nature of the reduction and capping agents. Strong reducing agents as borohydrides and superhydrides induce the formation of nucleation centers which then grow into small clusters whose final size is determined by the nature of the capping agent. Weak agents such as hydrazine, ascorbic acid, tartrate and trisodium citrate exhibit slower reduction process. Early methods of preparation of nanoparticles required aqueous media as well as many applications (particularly biological ones) required them to be water soluble and remain suspended in water with no loss of physical or chemical properties. Among the methods described, the citrate reduction method is most widely used in which the citrate anion acts both as a capping agent as well as reducing agent at elevated temperatures. In general, the use of a chemical reducing agent has the advantage of feasibility and rapid preparation of the colloidal suspension, together with the higher stability of the suspended nanoparticles. However, these colloids display several disadvantages such as the existence of impurities resulting from the residual oxidation of species and the counter ions of the employed salts.

2.2. Stability of Metallic Colloidal Solutions

The stability of metal colloidal solutions in aqueous media tends to diminish as time passes. Two factors that affect the stability are electrostatic and steric origin [16-17]. Colloidal metal particles in solution develop a net surface charge that affects the distribution of ions in the neighboring interfacial region, resulting in an increased concentration of counter ions close to the surface, forming an electrical double layer (EDL) in the region of the particle-liquid interface. The surface charge decay rate slows with increase in concentration. In colloidal nanoparticles this charge can be monitored by means of measurements of the potential at the interface between the moving and the stationary solvent layers at the edges [18]. Figure 2 presents the metal colloid electric double layer, illustrating the nomenclature for the distance dependence of the surface charge. The inner layer also called the compact Helmholtz or Stern layer contains solvent molecules and sometimes other species as molecules or ions (Fig. 2). The inner Helmholtz Plane or slipping plane is an imaginary surface separating the thin layer of liquid bound to the solid surface showing elastic behavior compared with the rest of the liquid [19].

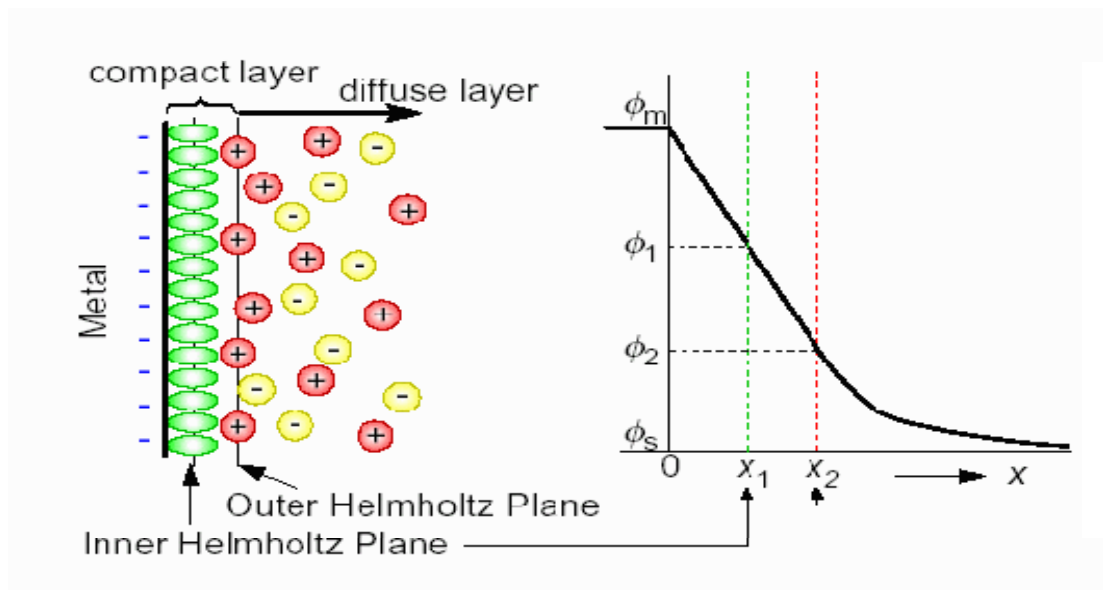


Figure 2. Representation of the metal colloid electric double layer, illustrating the nomenclature for the distance dependence of the surface charge

The structure of the double layer can affect the specific rates of adsorption of analyte. The double layer must be stabilized against the van der Waals forces which cause coagulation. This can be achieved in a number of ways; physisorbed surfactant and polymers create steric or electrosteric barriers, physisorption of ions produces purely electrostatic barriers, while depletion stabilization occurs in the presence of some polymers due to osmotic pressure [8].

2.3. Preparation and Properties of Bimetallic Colloidal Structures

Bimetallic colloids, in which two kinds of metals are contained in one particle, have unique catalytic, electronic and optical properties distinct from those of the corresponding monometallic particles [20]. There are three main groups of bimetallic colloids: alloys, random alloys and layered (core-shell) colloids. These are shown in Figure 3 [21]. Bimetallic colloids can be prepared by simultaneous co reduction of two

kinds of metal ions with or without the protective agent (usually a polymer or a surfactant) or by successive reduction of one metal over the nuclei of another.

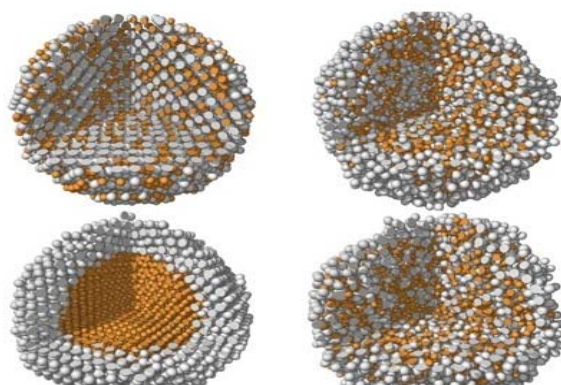


Figure 3. Representation of the various structures proposed for bimetallic clusters. (a) core- shell, (b) cluster- in-cluster and (c) random alloy. (Adapted from ref. 20).

The optical absorption spectra of Au-Ag alloy nanoparticles generally exhibit one surface plasmon band whose maximum depends on the alloy composition. Although the values of the free electron plasmon frequency (ω_p) are almost equal, the difference in their frequency location is mainly due to the differing contributions of the interband transitions to the dielectric functions of the two metals. The surface plasmon oscillation in alloy particles is a hybrid resonance resulting from excitations of conduction as well as the d-band electrons [17].

2.4. Characterization of Colloidal Nanostructures

Characterization of nanostructures is in itself a growing field of research [3]. In particular, linear optical techniques form a group of methods used for the characterization of nanomaterials and they are vital to forecasting a given nanoparticle's probability as a successful field enhancer. When focusing on a particle's SERS potential, the properties that are particularly important to the SERS phenomena are morphology, size, shape, crystal structure, tertiary structures, dipole plasmon absorption, surface potential, chemical composition and which materials are present at the surface, be it stabilizers or contaminants. Morphological properties are attained primarily from electron microscopes such as TEM, where size and shape can be inferred. Scanning Probe Microscopy (SPM), Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) can be used to determine particle sizes for carefully prepared samples. On the other hand, direct information of size and shape in solution also can be obtained by means of dynamic or static light scattering techniques. Crystal structures can be attained readily with X-ray diffraction. Material compositions of nanoparticles can be measured by XPS or EDAX. The characterization of the chemical species adsorbed on the metal surface can be done by a number of techniques employing electrons (Electron Energy Loss Spectroscopy, Auger spectroscopy), ions (Secondary Ions Mass Spectroscopy) and most commonly photons. Between the last techniques those based on X-rays (X-Ray Absorption Spectroscopy, X-Ray Absorption Fine Structure and X-Ray Photoelectron Spectroscopy) and vibrational spectroscopies (Reflection-Absorption IR Spectroscopy, SERS, Surface Enhanced IR Absorption) are the most frequently used. The optical properties of nanoparticles are dependent on a

particle's electronic states which have been shown, for materials in the nano-regime, to be strongly dependent on a particles size, morphology, its interactions with other particles, and the dielectric constant of the solvent or substrate the colloids reside in. The optical responses of nanomaterials are easily determined in the UV–Visible spectral region. These absorptions are primarily due to collective electron resonances and are commonly referred to as dipole particle plasmon resonance (DPPR). UV-Vis spectroscopy is used to determine within population of particles suspended in the colloids, the dispersity of particle sizes in the population. The absorption maximum or surface plasmon in the spectrum of the colloidal solution provides information on the average particle size. The full width at half maximum (FWHM) can be used to estimate particle dispersion.

2.5. Surface Enhanced Raman Spectroscopy (SERS)

2.5.1. Raman Spectroscopy

Raman spectroscopy is a popular nondestructive, ambient probing tool used to characterize molecular structure and usually imposes very little constraint on the substrate size. Figure 4 illustrates the main events that occur when a light quantum $h\nu_0$ impinges on a surface. The elastic scattering process (Rayleigh scattering) of quanta with energy $h\nu_0$ occurs without energy loss [1]. This process has the highest probability among other competing scattering phenomena.

However, there inelastic processes in which the vibrational energy is altered by $h\nu_s$ also prevail with much lower probability of occurrence. These inelastic processes are called Raman Scattering and quanta of energy $h\nu_0 \pm h\nu_s$ are emitted. According to

Boltzmann's law, at ambient temperature vibration of molecules in the excited state is much less probable than that of the ground state molecules. Thus, it is more efficient to excite ground-state molecules to a vibrationally excited state than to receive the radiative decay energy from the vibrating molecules.

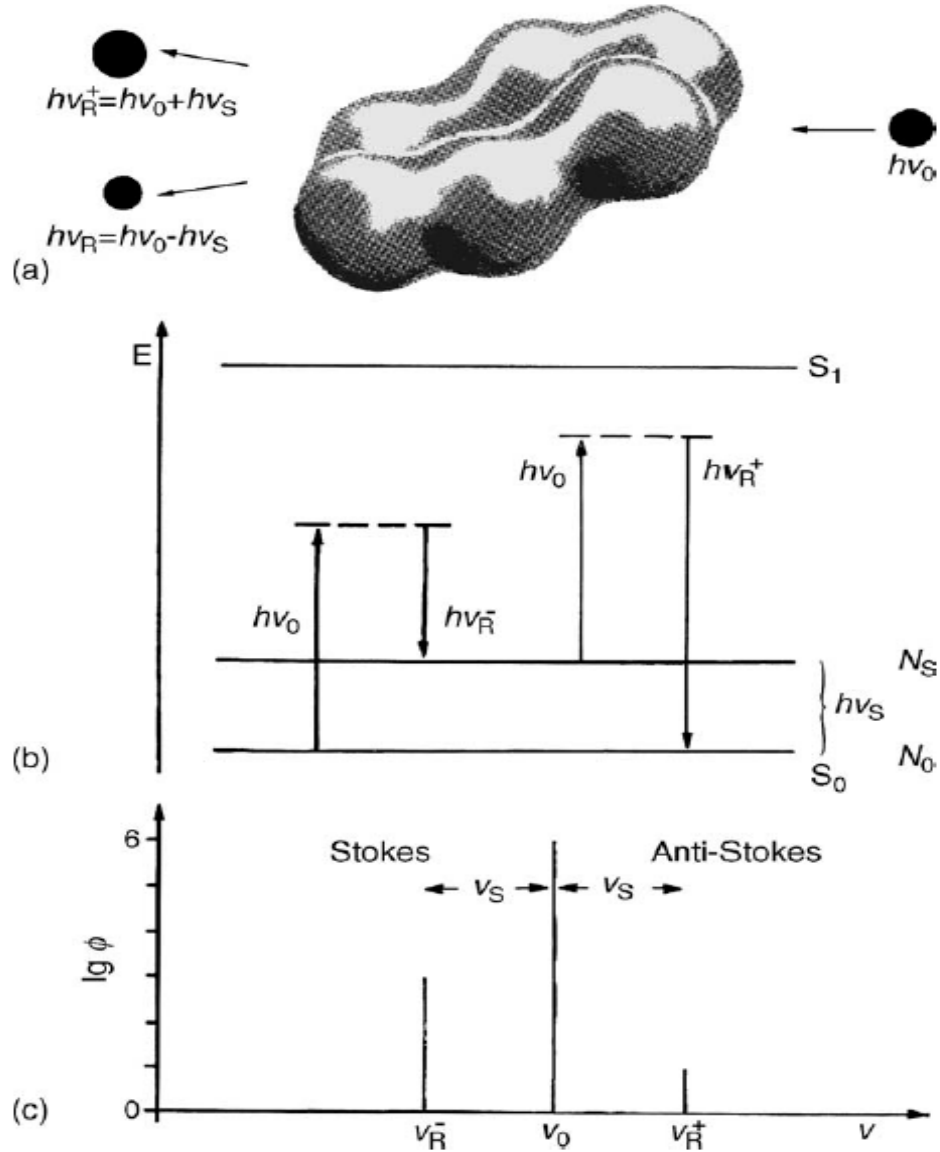


Figure 4. Schematic diagram of the principle of Raman scattering : (a) inelastic scattering of an optical quantum impinging on the material; (b) term diagram; (c) Raman spectra. Because vibration of atoms in the excited state is much less than that of the ground state atoms, the Stokes line is stronger than anti-Stokes line. (From Reference 1)

Hence, the emitted quanta having energy of $h\nu_0 - h\nu_s$ are more prevalent than the emitted quanta with energy of $h\nu_0 + h\nu_s$. The Raman lines corresponding to the quanta with energy of $(h\nu_0 - h\nu_s)$ are referred to as the Stokes lines whereas the higher energy lines $(h\nu_0 + h\nu_s)$ are called the anti-Stokes lines. As the intensities of the anti-Stokes

lines are lower, only the Stokes lines are usually recorded in a typical Raman spectrum. The light scattering processes are illustrated in Figure 4.

2.5.2. SERS Mechanism on Coinage and Transition Metals

Elucidation of the mechanisms that enable the SERS phenomena is always an important area of research in SERS. This active area of research has attracted much interest from the communities of surface science, spectroscopy, condensed phase physics and nanoscience. Two well established factors that contribute to the SERS mechanisms include the Electromagnetic Enhancement and the Chemical Enhancement.

2.5.2.1. Electromagnetic Enhancement Mechanism

In order to understand the Electromagnetic (EM) enhancement, one must consider the size, shape and material of the nanosurface. Nanoscale roughness features affect the electromagnetic field enhancement of Ag, Au, and Cu and is considered to mainly come from geometrically defined local surface plasmon resonances (LSPRs) at metal nanostructures. If the correct wavelength of light strikes a metallic roughness feature, the plasma of conduction electrons will oscillate collectively. The surface Raman enhancement arising from the LSPR of a spherical nanoparticle can be estimated using the following equation:

$$G(\omega) \propto \left| \frac{\epsilon_i - \epsilon_0}{\epsilon_i + 2\epsilon_0} \right|^2 \cdot \left| \frac{\epsilon_s - \epsilon_0}{\epsilon_i - 2\epsilon_0} \right|^2 \cdot \left(\frac{r}{r+d} \right)^{12} \quad (2)$$

where ϵ_0 is the dielectric constant of the medium, ϵ_i is the wavelength-dependent complex dielectric constant of the metal nanoparticles, r is the radius of the nanoparticles, and d is the distance of the point to be measured to the center of the nanoparticle [11]. The EM enhancement mechanism contributes more than 10^4 times enhancement over normal Raman scattering. The LSPR allows the resonant wavelength to be absorbed and scattered, creating large electromagnetic fields around the roughness features. When the incident light is resonant with the collective modes of oscillation of the metal conduction band electrons, there is an enhancement of the electromagnetic field at the surface at both the incident and Raman scattered wavelengths. This enhancement in turn induces a change in polarizability of the molecule leading to intense Raman signals. For the electromagnetic enhancement effect to be operative, it is not necessary to be in contact with a metal surface [17].

Considering that in most of SERS studies the medium is water and $\epsilon_0 = 1.77$, when the real part of ϵ_i approaches -3.54 and the imaginary part approaches 0, the enhancement reaches the maximum. Some free electron metals, such as Ag, Au, and Cu, can meet this condition and therefore produce very high enhancement. When the shape of the nanoparticles deviates from the spherical nanoparticles, such as ellipsoids or rods, the lightning-rod effect should be considered due to the existence of the high curvature points. Furthermore, more and more experimental and theoretical studies demonstrate that the coupling between nanoparticles can effectively increase the enhancement effect. These general conclusions can also be borrowed to analyze the case of transition metal systems. Most transition metals show a large imaginary part of the

dielectric constants and therefore are not effective in generating high SERS activity over the visible light region [11].

2.5.2.2. Chemical Enhancement Mechanism

Chemical enhancement, according to its definition, includes any enhancement of the Raman intensity of surface species resulting from its chemical interaction with the surface or other surface species and is clearly correlated to the charge transfer between the probed molecule and surface or other surface species. One should note the following three types of charge-transfer process that contribute to the chemical enhancement: (1) when a molecule interacts with the surface or other surface species, the electron distribution and therefore the polarizability of molecule will change. Such a change may cause different enhancements for different vibrational modes; (2) metal ion, probed molecule, and electrolyte ion may form a surface complex, leading to the change of the polarizability of the molecule. Some surface complexes may even create a new electronic level in resonance with the incident laser energy, similar to the resonance Raman Effect of a complex; (3) the third type is the most complicated one and called photon-driven charge transfer process or often simplified as charge transfer. This process occurs when the incident laser energy matches the energy difference between the surface molecules' HOMO or LUMO and Fermi level or surface state of the metal substrate. This process could also be associated with the excited state of the whole molecule/metal system and with the charge transfer between the molecule and the metal surface (or surface ad-clusters). This could result in a considerable increase in the Raman intensity of probe molecules. The photon-driven charge-transfer

mechanism has been used to explain the change of intensity–potential profile with the changing excitation line and is the most important type of chemical enhancement mechanism. The chemical enhancement mechanism, now thought to contribute an enhancement factor of 10^2 , states that a charge-transfer state is created between the metal and adsorbate molecules [11].

CHAPTER III

JUSTIFICATION

The sensitive detection of explosive nitrocompounds in real time at ambient pressure and temperature is a key issue for law enforcement, defense applications and airport security [22]. The identification of landmines and explosive compounds at trace levels has become a serious issue for the government. That is why recently many government agencies are trying to look for innovative and cost effective ways to detect any threats made to civilian's lives. Many people working in the fields of science as well as engineering are doing research to develop chemical and biological sensors to detect explosives and other threat agents that can harm peoples health or even take their lives. It is therefore necessary to find rapid and cost-effective solutions. For this reason it is essential to selectively detect explosives and chemical threat agents at ultra low concentration levels. Modern security systems require the development of sensors capable of achieving such selectivity [23].

Current explosive and threat chemical detection methods span the range from simple colorimetric screening to more sophisticated speciation with advanced spectroscopic measurements. Raman spectroscopy is a popular nondestructive, ambient probing tool used to characterize structure and usually imposes very little constraint on the substrate size. SERS is an extremely powerful analytical tool that yields information about bulk explosives and other threat agents.

The methods used to detect explosives and threat agents can be subdivided into those that detect vapors or particles emitted from the materials, those that detect dissolved or

suspended solids in solutions, and those that probe solid materials. Raman spectroscopy provides a simple method of detecting and identifying explosives in bulk samples or as crystals under a microscope. The sharp spectral features obtained usually enable the identification of individual components of mixtures without the use of sophisticated mathematical separation procedures. However, the inherent lack of sensitivity of Raman scattering makes it less effective for the identification of low concentrations of target molecules in dispersed samples in solution or the vapor phase [24]. Noble metal nanostructures or nanoparticles can cause large enhancements (up to 10^6) of the Raman scattering cross section for adsorbed molecules. The origin of this effect has been in dispute, but recent advances in production of nanostructures with very precise control of their size, shape, and spacing have allowed both greater understanding of the origin of the effect and its control. For many years there has been an interest in metal colloids due to their successful application in SERS [10] and catalytic properties [25]. Metal colloids can be prepared employing wet chemistry methods. Wet chemistry provides an inexpensive and versatile approach to metal nanoparticle fabrication. The chemical reduction synthesis method was selected due to its low cost and versatility. Among the variety of metal nanometer-sized particles, the coinage metal group, Cu, Ag, and Au, is probably studied the most [26]. Among the coinage metals Ag and Au have been studied the most because of their stability and their intense absorption band in the visible region, often called surface plasmon absorption. Cu in turn, is the least studied out of the coinage metals, due to their high instability for oxidation, and most of the time it forms complexes with water molecules in aqueous media [27-28].

This work focused on the synthesis of copper particles by controlling different properties, such as size and shape, by means of different reducing agents. The goal was to obtain stable copper and Cu/Au alloy colloids that would exhibit chemical properties and thermodynamic stability associated to their size. There has been a growing interest to synthesize copper particles due to the difficulty of dealing with the synthesis and the stability of the colloids when exposed to ambient temperatures for a long time. Recent research shows that copper particles as well as alloy colloids show potential to develop novel optical, catalytic, electronic and magnetic devices. In this study, we also show how the technique of SERS, enables the detection of the threat agents o- and p-dinitrobenzenes at low concentration levels. In SERS, an analyte which contains a chromophore is adsorbed onto a roughened metal (usually silver, gold and silver/gold alloy) and the enhanced Raman scattering measured. The dye crystal violet was also used in this study to study the Raman activity of a newly synthesized Cu/Au alloy colloid.

3.1. Investigated Compounds

3.1.1. 1,2-Dinitrobenzene (o-DNB)

o-DNB is a colorless to yellow solid. Sinks and slowly mixes with water and other polar solvents. Emits highly toxic fumes of oxides of nitrogen and may explode. Severe explosion hazard when exposed to heat or flame, or when shocked. It could react vigorously with oxidizing materials. Reaction with nitric acid (nitration) will lead to a mixture of trinitrobenzenes possessing high-explosive properties. If heat and reaction conditions of the nitration are not controlled, detonation comparable to TNT may occur.

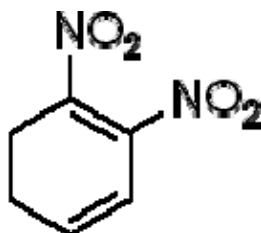


Figure 5. Structure of 1,2-dinitrobenzene.

3.1.2. 1,4-Dinitrobenzene (p-DNB)

p-DNB is a colorless to yellow crystalline solid. Dust explosion is possible if in powder or granular form, mixed with air. On combustion, forms toxic gases and fumes including nitrogen oxides. It reacts violently with strong oxidants, strong bases and metals (tin and zinc), causing fire and explosion hazard. Mixtures with nitric acid are highly explosive. It is highly soluble in water and other polar solvents.

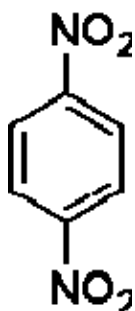


Figure 6. Structure of p-dinitrobenzene

3.1.3. Crystal Violet (CV)

Crystal violet is also known under the name of gentian violet. It is a protein dye which stains the fatty portions of sebaceous sweat to a deep purple color. Being a protein dye, crystal violet dye can also be used as an enhancer for bloody fingerprints. Crystal violet

(CV), in aqueous solution is in an ionic state (CV^+) in which it possesses two different isomeric forms. CV has no permanent dipole moment due to its C_3 symmetry. It was chosen as an analyte, due to its excellent SERS enhancement and low fluorescence interference as seen in single molecule experiments. It is a green to dark-green powder with a brown cast powder. Once it is mixed with water it ionizes, forming a clear purple to dark purple-blue solution.

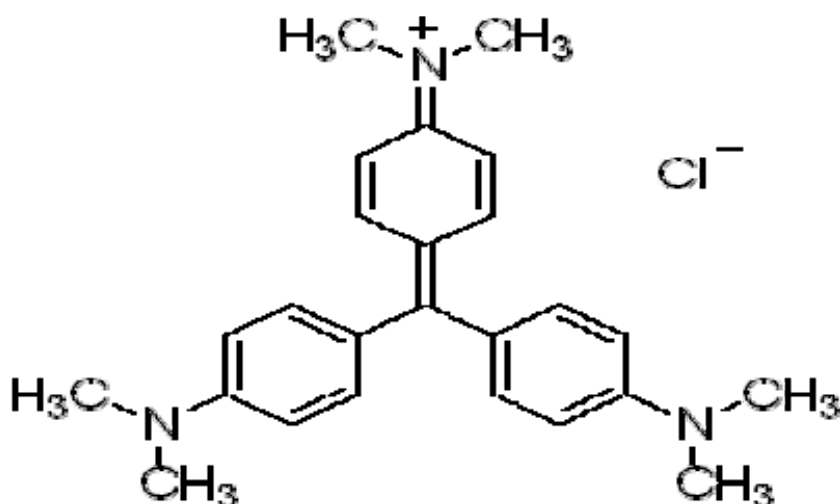


Figure 7. Structure of crystal violet.

CHAPTER IV

PREVIOUS WORK

Since the observation and discovery of Surface-Enhanced Raman Scattering phenomenon of adsorbed species on roughened Ag surfaces in the mid-1970s [29–30], SERS has received wide application in fields including surface sciences, electrochemistry, analytical chemistry, biological and biomedical sciences and forensic science. Two mechanisms have been widely accepted to account for the SERS effect observed on coinage-metal surfaces (Ag, Au, and Cu), the electromagnetic (EM) and the charge-transfer (CT) mechanisms. The EM effect is the major contribution to the observed SERS signal while the CT effect, mainly arising from a photo-driven charge-transfer process, has also been found in numerous experiments to change the SERS signatures of specific systems and is considered a short-range effect [11].

Shortly after the discovery of the SERS effect, it was found that the giant enhancement for practical application is limited to the three coinage metals Ag, Au, and Cu with free electrons, on which the surface plasmon resonances can be easily excited in the visible to the near-infrared light region [7,11, 31]. This work focuses on work done with copper nanoparticles. Copper particles have been widely studied because of their roles in electronics, catalysts, resins and thermal conducting [7]. The group comprised of Sanchez *et al.* [32] was one of the first groups to synthesize copper seed colloidal solutions from a method employed by Creighton [33] to synthesize gold and silver sols. In this work they characterized the copper seed using transmission electron microscopy (TEM) and UV-VIS spectrophotometry and studied the morphological changes occurring

in the copper colloid when 1,5-dimethylcytosine was added to them. This adsorbate gave rise to intense SERS spectra. Later Ding and Fang [34] employed the same synthesis as Sanchez, *et al.* to study the adsorption geometry of p-hydroxybenzoic acid on the surface of the copper seeds. They adopted a computational method to calculate Raman frequencies. Many authors today employ computational methods to describe adsorption geometries among many other applications. The theoretical results are compared with the experimental values, and the reliability of the models and the calculation methods are analyzed.

Recently Ren, Cheng and Tang [35] synthesized copper particles with different shapes and narrow size distributions. They used a one step method to produce novel spherical and cubic particles without using any capping agents. The reagent concentration and temperature exerted a strong influence on the shape of the copper particles in this synthetic procedure. The particles were cubic at low reagent concentrations and they obtained particles that were spherical at high reagent concentrations. The number of hollow particles greatly increased when the synthesis was performed at a low temperature. No SERS experiments have been reported on any probe molecule up until the point when the copper particles prepared in this study were tested for Raman activity.

Recently bimetallic nanoparticles have fascinated scientists because of their superior material properties for chemical, biological, physical and engineering applications. Colloidal solutions of noble metals, such those as gold and silver have been studied extensively because of their intense absorption band in the visible region. Because of these attractive plasmon absorption features, the optical properties of the bimetallic

nanoparticles of gold and silver are the subject of considerable interest in the fields of nanoscience and nanotechnology. The comparison of calculated and measured surface plasmon (SP) extinction spectra has frequently been employed as a criterion for distinguishing between alloyed layer and layered core-shell structures of bimetallic Au-Ag/Ag-Au nanoparticles [36-37].

Other articles found in the literature focus on simple synthesis of nanometer sized monolayered-protected alloy clusters that can be isolated in solvent free forms and redissolved in air-stable forms without change. The removal of the solvent generally leads to the complete loss of the ability to reform a colloidal solution. An alkanethiolate monolayer is the key to prevent metal core aggregation [38-40]. An unusual property of these thiol-derivatized metal nanoparticles is that they can be handled and characterized as a simple chemical compound [39]. Metal alloys of Au/Cu and Ag/Cu have been synthesized yielding as a final product a solid. Elemental, XPS, and TEM analyses have shown the overall metal core ratios vary with, but differ from, the metal feed ratio, and that incorporation of the more noble metal into the core is favored. There have not been any reports of Au/Cu bimetallic structures that can be formed from a colloidal solution. In this work, Au/Cu bimetallic structures were synthesized in colloidal solutions and Raman activity of these structures were measured.

CHAPTER V

METHODOLOGY

5.1 Reagents and Chemicals

Sodium borohydride (NaBH_4 , 99.9%), sodium hydroxide (NaOH , 99%), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 99.999% Cu), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.999% Cu), Hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot \text{H}_2\text{O}$, 99.999% Au) and copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99.999% Cu) were purchased from Strem Chemicals, Newburyport, MA. The nitroaromatic explosives 1,2-dinitrobenzene, 1,4-dinitrobenzene and N-methyl-p-nitroaniline were purchased from ChemService, West Chester, PA. Methanol and crystal violet were purchased from Fisher Scientific, Fair Lawn, NJ. Trisodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$, 99%) and β -Cyclodextrin, (98% minimum) were purchased from Sigma-Aldrich Chemical Co., Milwaukee, WI. Hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98 %) was purchased from Alfa Aesar, Ward Hill, MA.

5.2 Cleaning Method

Several methods were developed for the preparation of copper colloids by chemical synthesis. Before beginning each synthesis, all glassware was vigorously cleaned using *aqua regia*, strong acid mixture of $\text{HCl}:\text{HNO}_3$ (3:1) which was handled with extreme care as copious amounts of gas were liberated. The use of *aqua regia* can cause explosions if the acid is stoppered and bad burns may occur if it comes into contact with skin. Finally, all glassware was washed several times with Nanopure®, Barnstead

International, Dubuque, IA. (Thermo-Fisher Scientific) ultra high purity water (UHP, 18.2 M Ω).

5.3 Preparation of Colloidal Suspensions

The preparation of the colloidal suspensions was conducted by three different methods described next.

5.3.1 Sanchez-Cortez Method

Cu colloidal suspensions were prepared according to the method described by Sanchez-Cortes *et al.*, with some modifications [32]. Metallic copper colloids in the zero valence state were prepared by chemical reduction. The amount of the aqueous solution of trisodium citrate ($C_6H_5O_7Na_3$) was varied in the different colloidal copper suspensions.

The preparation of Copper Seed 1 was conducted by a typical experiment that consisted on adding 20mL of 5.6×10^{-3} M aqueous solution of trisodium citrate ($C_6H_5O_7Na_3$) to 1667 μ L of 1×10^{-2} M copper(II) sulfate ($CuSO_4$) in a 50 mL centrifuge tube. Then a 10 mL mixture of sodium hydroxide (NaOH) 2×10^{-2} M and 2×10^{-2} M sodium borohydride ($NaBH_4$) was added. Samples were purged with dry N_2 after mixing the three solutions. Finally the tube was sealed and placed in an ice cold bath 0°C for 24 hours.

The preparation of Copper Seed 2 was conducted by a typical experiment that consisted on adding 40mL of 5.6×10^{-3} M aqueous solution of trisodium citrate ($C_6H_5O_7Na_3$) to 1667 μ L of 1×10^{-2} M copper(II) sulfate ($CuSO_4$) in a 50 mL centrifuge

tube. Then a 10 mL mixture of sodium hydroxide (NaOH) 2×10^{-2} M and 2×10^{-2} M sodium borohydride (NaBH_4) was added. Samples were purged with dry N_2 after mixing the three solutions. Finally the tube was sealed and placed in an ice cold bath 0°C for 24 hours.

Prepared Cu colloids were found to be relatively unstable as reported by others authors [34]. At the beginning of the synthesis they turned brown color with different intensities, depending on the amount of trisodium citrate solution added. After a 24 h period the colloidal solution turned black-olive green with different intensities (see Figure 8).



Figure 8. Synthesis of Copper Seeds resulted in an olive-green color

5.3.2 Shape Controlled Synthesis Prepared at Different Temperatures

Copper particles were synthesized as follows: A 45 mL aqueous solution containing different concentrations of CuCl_2 (e.g. 0.15 mM, 0.43 mM and 0.62 mM) were prepared separately. Next, N_2H_4 solution was added dropwise into the CuCl_2 solution under constant stirring and purging with N_2 . The molar ratio of N_2H_4 and CuCl_2 was 20. The light blue solution turned yellow, indicating the formation of the copper particles. On separate experiments the temperature was varied (e.g. 5, 15, 25 and 35°C). The

aqueous suspensions were placed in carbon grids for TEM and HR-TEM analysis. The products obtained were washed thoroughly with redistilled water and dried in a vacuum oven at 60°C for 4 h [35].

5.3.3 Preparation of Gold Covered Copper Particles

Unmodified β -CD has been previously used to prepare gold and silver nanoparticles in the presence of different reducing agents such as dimethyl formamide, ethanol, methanol, ethylene glycol and sodium citrate [36]. B-CD has similar properties to glucose, due to its reducing and capping properties for the preparation of size- and shape-selective metal nanoparticles in alkaline medium. In this study β -CD was used because it reduces metallic salts to well stabilized metal nanoparticles. B-CD in aqueous solution acts as both a reducing and stabilizing agent in alkaline medium.

5.3.3.1 Preparation of Monometallic Gold and Copper Colloids

The metal nanoparticles (copper and gold) were synthesized by the method described by Pande *et al.* [36] with a few modifications. A sample of 39.6 mg β -CD was dissolved in 4.93 mL of water and shaken well. After dissolving the β -CD, 50 μ L of NaOH 1.0 M was added to the solution so that the pH of the solution became $\sim$ 10-12. After completing this procedure 40 μ L HAuCl₄ were added and the solution was then heated for 20 min until the solution turned pink color.

Different aliquots of Cu(NO₃)₂ at different concentrations were added to the β -CD solution to form the copper colloidal suspension at different concentrations. Amounts of

$\text{Cu}(\text{NO}_3)_2$ solutions at different concentrations to prepare Cu colloidal solutions are mentioned in Table 1. After heating 30 min, the suspensions turned pale yellow.

Table 1. Preparation of Cu colloidal suspensions

$[\text{Cu}(\text{NO}_3)_2]$ Solutions (mM)	Amounts of $\text{Cu}(\text{NO}_3)_2$ Solutions (μL)	Name of Cu Colloidal solution
1	110	1 mM Cu Colloid
2	100	2 mM Cu Colloid
4	80	4 mM Cu Colloid
6	60	6 mM Cu Colloid
8	40	8 mM Cu Colloid

5.3.3.2 Preparation of Gold covered Copper Particles

The gold covered copper nanoparticles were synthesized adding different aliquots of HAuCl_4 (10 mM) to the Cu colloidal suspensions previously mentioned (Table 1). Aliquots of HAuCl_4 (10 mM) were added to the different Cu colloidal suspensions are shown in Table 2.

Table 2. Preparation of Gold Covered Copper Particles

Name of Cu Colloidal solution	Aliquot of H _{AuCl} ₄ 10 Mm Added (μL)
1 mM Cu Colloid	40
2 mM Cu Colloid	50
4 mM Cu Colloid	80
6 mM Cu Colloid	140
8 mM Cu Colloid	160

The solutions were heated on a water bath for about 20 min, the pale yellow solutions turned different intensities of pink depending on the concentrations of the Cu colloidal solutions, and this is shown in Figure 9. This is an indication that gold covered the copper nanoparticles, i.e., the formation of gold covered copper nanoparticles. During the process, the pale yellow color disappeared while the pink color appeared. No extra β -CD or NaOH was added to induce chemical reduction that lead to the formation of the gold covered copper nanoparticles.



Figure 9 .Gold covered Copper particles at different concentrations of Cu Colloids

5.4. Sample Preparation for SERS Analysis

For SERS analysis, 800 μL of the copper colloidal suspension, 100 μL of the sample to be analyzed (o-dinitrobenzene, p-dinitrobenzene, and crystal violet), and 100 μL of the sodium chloride solution (NaCl, 0.1 M) were combined in a small centrifuge vial (1.5 mL). The solution was stirred in a mini vortex agitator for a period of 30 s. A small amount of this mixture was transferred to a capillary tube sealed on one end (melting point 1.8 x 90 mm) for SERS measurements [55-56].

5.5 Theoretical Calculations and Models

To determine the type of interaction between o-DNB and Cu nanoparticles, two calculations were performed: first, a simple system of a Cu atom was considered and second, a portion of a copper surface model interacting with o-DNB was performed. The results of both models were used to explain the possible interaction mechanism between Cu and o-DNB molecules.

Two assumptions were considered to construct the simple Cu atom model. One was to assume that the primary interaction between a Cu atom and o-DNB should be the most important. Second, was to assume that other interactions between distant Cu atoms on a surface are minimal and they were negligible. This is a vague assumption to predict physical property values, but it could be used to extrapolate so that we could determine the interaction energy.

To construct the Cu surface, Cu atoms were arranged in a similar way to its crystal structure of face centered cube. All copper atoms were placed at a distance of 0.3610 nm from each other. Two models were constructed for the interaction of o-DNB and the

Cu surface. One consisted in which one of the two nitro groups of o-DNB interacting more closely with the Cu surface than the other nitro group. The other model consisted of assuming that both nitro groups interact closely to the Cu surface. One of these two models was later chosen as the best one based on how close were the theoretical Raman spectrum to the experimental one.

Density Functional Theory (DFT) based models were used to determine the energies, atomic charges, molecular orbitals diagrams, and Raman spectrum for neat o-dinitrobenzene (o-DNB), and complexes formed between o-DNB and a copper atom and the corresponding complexes formed with a limited portion of a Cu surface. All calculations were carried out with Gaussian 03 software [16]. DFT employed methods employed for the optimized structures, atomic charge, molecular orbitals, and Raman frequencies were calculated by DFT-B3PW91/Lan12DZ.

Minimum energy values were calculated at different interaction distances from different single point calculations of energy. The geometry of the Cu surface structure is a crystalline structure face centered cube with a lattice constant a of 3.610 Å. A surface portion was selected of a cube of 200 Cu atoms and the portion contains five Cu atoms on the first layer and four Cu atoms in the second layer, for a total of nine Cu atoms. The miller index for the surface is (100). The molecular geometry of o-DNB was obtained by the optimization geometry option. Next, only the distance between the surface and o-DNB was modified for different interactions. The interaction energy (ΔE_i) was calculated by eq. 3

$$\Delta E_i = E_{\text{complexed}} - (E_{\text{Molecule}} + E_{\text{Surface}}) \quad (3)$$

Where $E_{\text{complexed}}$, is the absolute system energy (molecule plus surface) at a given value of interaction distance. E_{molecule} , is the energy of the molecule and E_{surface} is the surface energy. The variation distance was performed on the z axis. For the one atom model, the minimum complex energy was calculated using geometric optimization option.

5.6. Instrumentation

Plasmon band location of Cu and Cu/Au colloids was performed in a Varian Cary-5000 UV-VIS-NIR double beam spectrophotometer. The morphology, size and shape of the Cu and Cu/Au nanoparticles were investigated by Transmission Electron Microscope (TEM). A high resolution Zeiss model 922 was used at 200 kV accelerating voltage. Vibrational analysis was conducted using a RM2000 Renishaw Raman Microspectrometer equipped with a Leica microscope with a 10x objective.

SERS spectra were obtained with laser lines at 488, 514.5 and 532 nm using laser power at sample ~ 15 mW. The 488 and 514.5 nm excitation source was a Coherent Inc. INNOVA 300-8 argon ion laser (488 and 514.5 nm) with a variable output power of up to 2 W. The 532 nm excitation source was a Spectra Physics EXCELSIOR solid state diode laser with available output power of up to 100 mW. The Raman spectra were collected in the range of 100-1800 Raman Shift (cm^{-1}), with an integration time of 20 s per scan. The Raman spectra were the result of the average of 5 scans.

CHAPTER VI

RESULTS AND DISCUSSION

6.1 UV-VIS and TEM Results

6.1.1 Copper Seed Nanoparticles

The method of preparation of the colloidal suspensions was optimized to have the maximum SERS signal on o-DNB vibrational signatures. The concentration of the reducing agent, the addition rate of the mixture of sodium hydroxide and sodium borohydride and the stirring rate of the solution were evaluated.

Prior to UV-VIS analysis, the colloidal suspension was prepared by transferring different proportions of the suspension and of UHP water in a 1 cm quartz cuvette. The UV-VIS spectra of the sols were acquired from 200 to 800 nm. Results of UV-VIS spectrophotometry measurements are included in Figure 10.

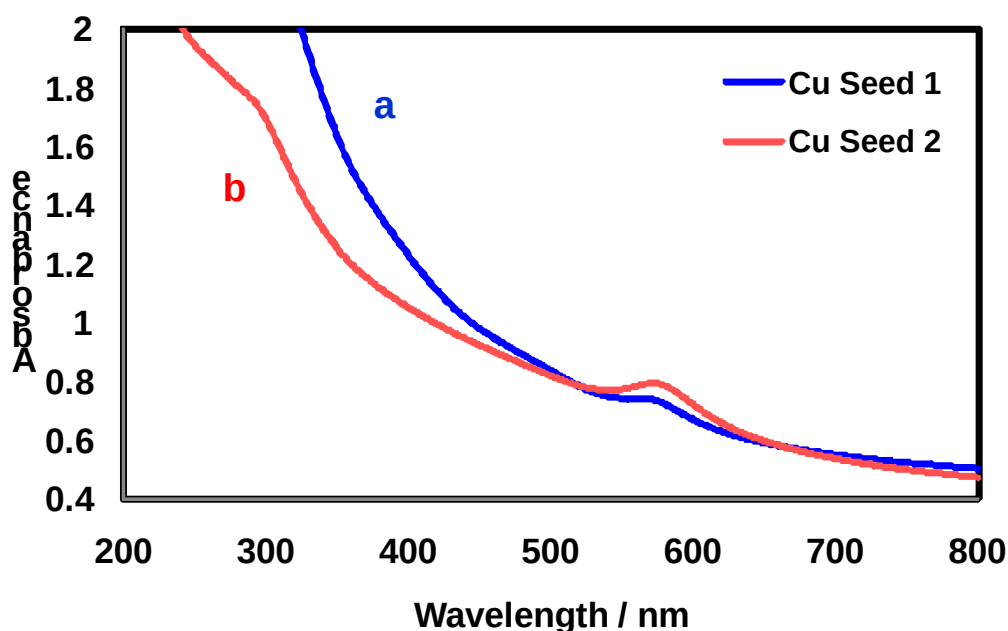


Figure 10. UV-VIS absorption spectra of the copper colloid mixture: (a) Cu seed 1; (b) Cu seed 2.

Copper colloids prepared at different volumes of reducing agent show little difference in their spectral absorption characteristics, which may be attributed to morphological similarities. The absorption maximum of the colloidal suspensions provides information on the average particle size, whereas its full-width at half-maximum (FWHM) gives an estimate of particle size distribution.

Cu colloids prepared with citrate had a surface plasmon at 571 nm for Cu Seed 2 and 568 nm for Cu Seed 1, showing small differences in average particle sizes and were comparable with previous studies [32, 34]. The formation of a second absorbance band in the UV (c.a. 293 nm) suggests the presence of an unstable complex of Cu^+ species with water molecules [27]. A FWHM of 26 nm for Cu Seed 2 and 22 nm for Cu Seed 1 is indicative of modest monodispersed colloidal suspensions (Fig. 10).

The shapes and sizes of these particles are better characterized using transmission electron microscope (TEM) images. Colloidal preparations yielded particles that were approximately spherical seeds as seen in Figure 11. A low magnification TEM image with a (20,000x) is shown in Fig 11-a. According to the TEM image with 50,000x magnification in Figure 11-b, shows that the club shaped Cu seeds with nanoparticles of sizes of 5-20 nm. Figures 12-a and 12-b present the average nanoparticle sizes. They are about 2 nm, all of the surrounding conglomerates due to the aggregation of the spherical colloidal nanoparticles. Figure 12-b shows a conglomerate with a possible network like structure. The average size and size distribution of the nanoparticles in the copper colloids depends on colloid age and temperature. The characteristics of colloidal nanoparticles vary with time, which can be ascertained from the color of the suspension

and particles. Copper nanoparticles suspensions, as demonstrated in previous results, are highly monodispersed.

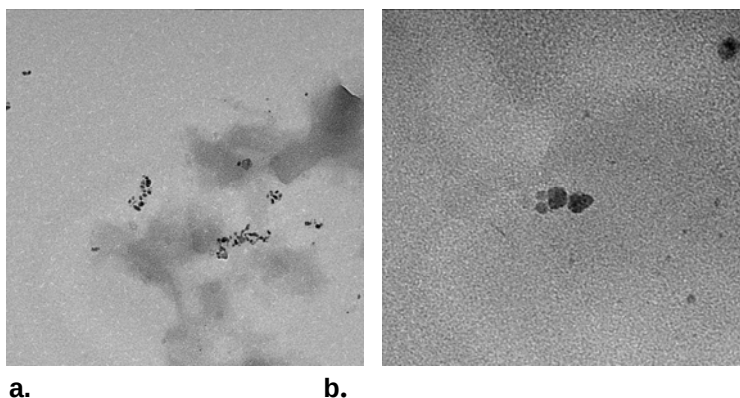


Figure 11. TEM images of Cu Seed 1 (100 nm scale): (a) Magnification: 20,000x; (b) Magnification: 50,000x.

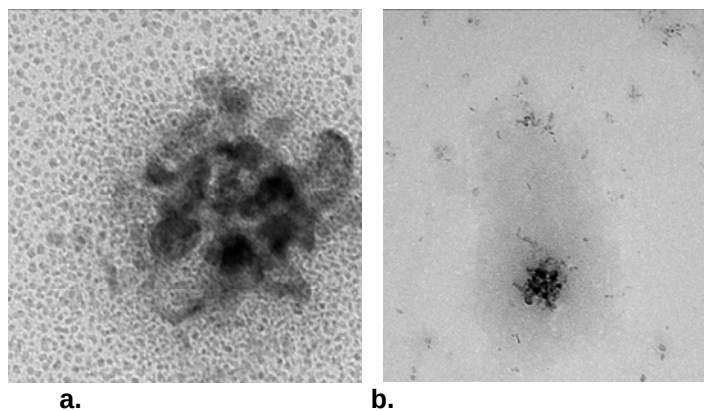


Figure 12. TEM images Cu seed 3: (a) Magnification: 50,000x ; (b) Magnification: 20,000x.

The temperature control necessary to maintain steady growth of nanoparticles, as the size distribution sharpens, it is important in order to achieve a large electromagnetic enhancement at the metallic colloidal surface. Colloids in aqueous media, prepared by chemical methods, tend to form clusters because of their complicated double layer structure. These clusters have much higher morphological heterogeneity, since they are composed by nanoparticles with a wide spectrum of sizes and shapes. This correlates

with the broader plasmon resonance extinction band, demonstrating the existence of small particles.

6.1.2 Shape Controlled Synthesis Prepared at Different Temperatures

The morphology of the product depended strongly on the reagent concentration. When the initial reagent concentration was 0.15 mM, cubic particles were the major products; when the reactant concentration was higher than 0.43 mM, spherical particles were the major products [35]. Figure 13-a presents the TEM image of the cubic ring nanoparticles at a reagent concentration of 0.15 mM. Cubic rings are formed at low temperatures (e.g. 5 and 15°C). These cubic particles exhibited nearly identical morphologies and had a mean edge of around 95 nm. Figure 13-b shows particles synthesized at higher temperatures (e.g. 25 and 35°C), the monodispersity of these copper particles decreased, but the cubic shape still remained the same.

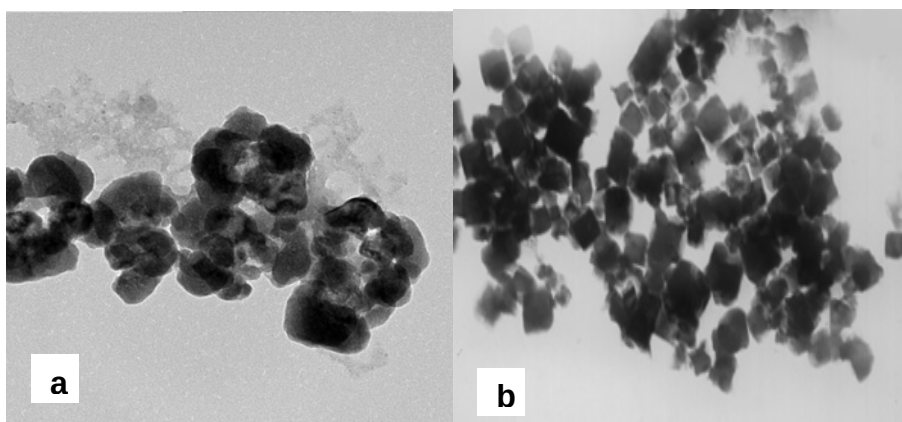


Figure 13. TEM image with magnification 50,000x of: (a) cubic ring copper particles synthesized at 15°C; (b) cubic copper particles synthesized at 35°C (from ref.35), at reagent concentration of 0.15 mM.

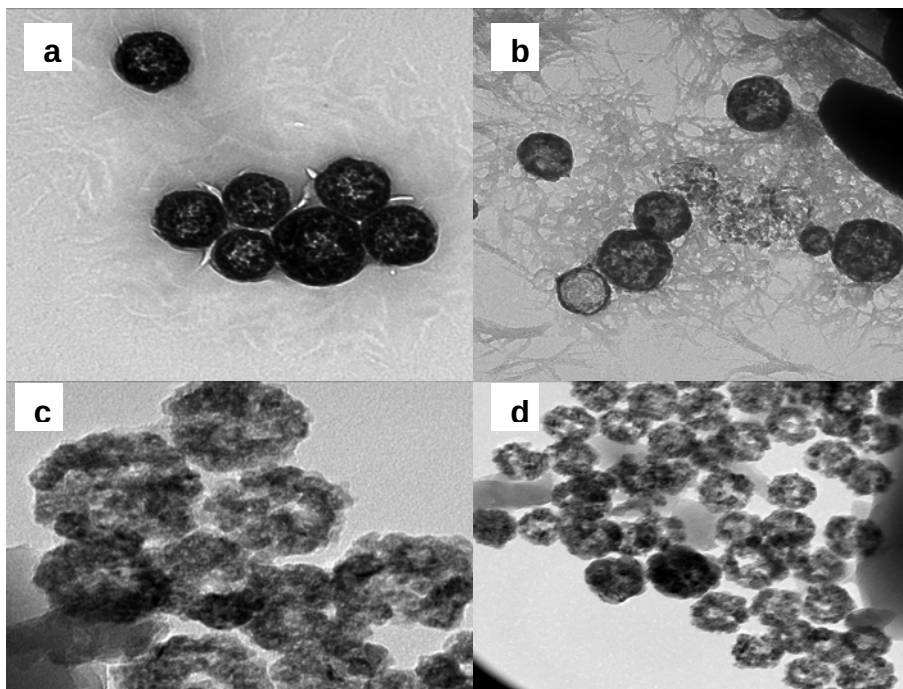


Figure 14. TEM images copper particles synthesized at high reactant concentration. (a, b) Reagent concentration of 0.43 mM at 35°C, (c, d) reagent concentration of 0.62 mM at 15°C.

Figure 14 shows TEM images of copper nanoparticles obtained with high reactant concentrations (e.g. 0.43 mM and 0.62 mM). These nanoparticles were mostly monodispersed, they were weakly agglomerated and uniformly spherical with an approximate diameter of 150 nm. It can be clearly seen that the spherical particles have a rough surface.

Another factor influencing the morphology of particles was the temperature. To explain this process samples at high reagent concentrations obtained at different temperatures (e.g. 5, 15, 25 and 35°C) were studied carefully. As a characteristic feature of these products, the central portion of each Cu particle was lighter than the surrounding edges as temperature of the synthesis decreased as seen in Figures 14-a and 14-c. This is indicative of the formation of a hollow structure with a shell thinner than the escape

depth of electrons. The synthetic procedure at higher temperatures (Figure 14-a) stimulated the increase of both thickness and density of the copper shell with temperature, probably from aggregation of smaller particles and forming this structure. A similar pattern occurs with cubic Cu particles, as temperature increase, instead of having a cubic ring, smaller particles aggregated, causing a less monodispersed cubic particle medium.

It can be concluded based on these experimental results that copper nanoparticles are composed of smaller aggregated particles (seeds). The morphology of the particles is affected by reagent concentration. The rates of aggregation at low reagent concentrations were slower than at high reagent concentrations regardless of the temperature. At higher temperatures the reaction rates were even faster.

UV-VIS absorption spectra of copper colloidal suspensions were recorded at high and low reactant concentrations, to study their optical properties. Figures 15-a and 15-b show the spectra of copper particles at concentrations of 0.15 mM and 0.63 mM respectively. Figure 15-a shows the formation of cubic particles from a cubic ring. As seen from all the curves, copper particles have a broad absorption at 400-500 nm. At higher temperatures the bands shift toward the red region. As the synthesis temperature rises we could observe that the bands in the spectrum become broader. This is due to the aggregation of smaller particles that lead to the formation of cubic nanoparticles. It could also be observed that the monodispersity of the medium diminished. This is correlated with the FWHM values at different temperatures which at 15°C is 38 nm, at 25°C is 44 nm, and at 35°C is 54 nm.

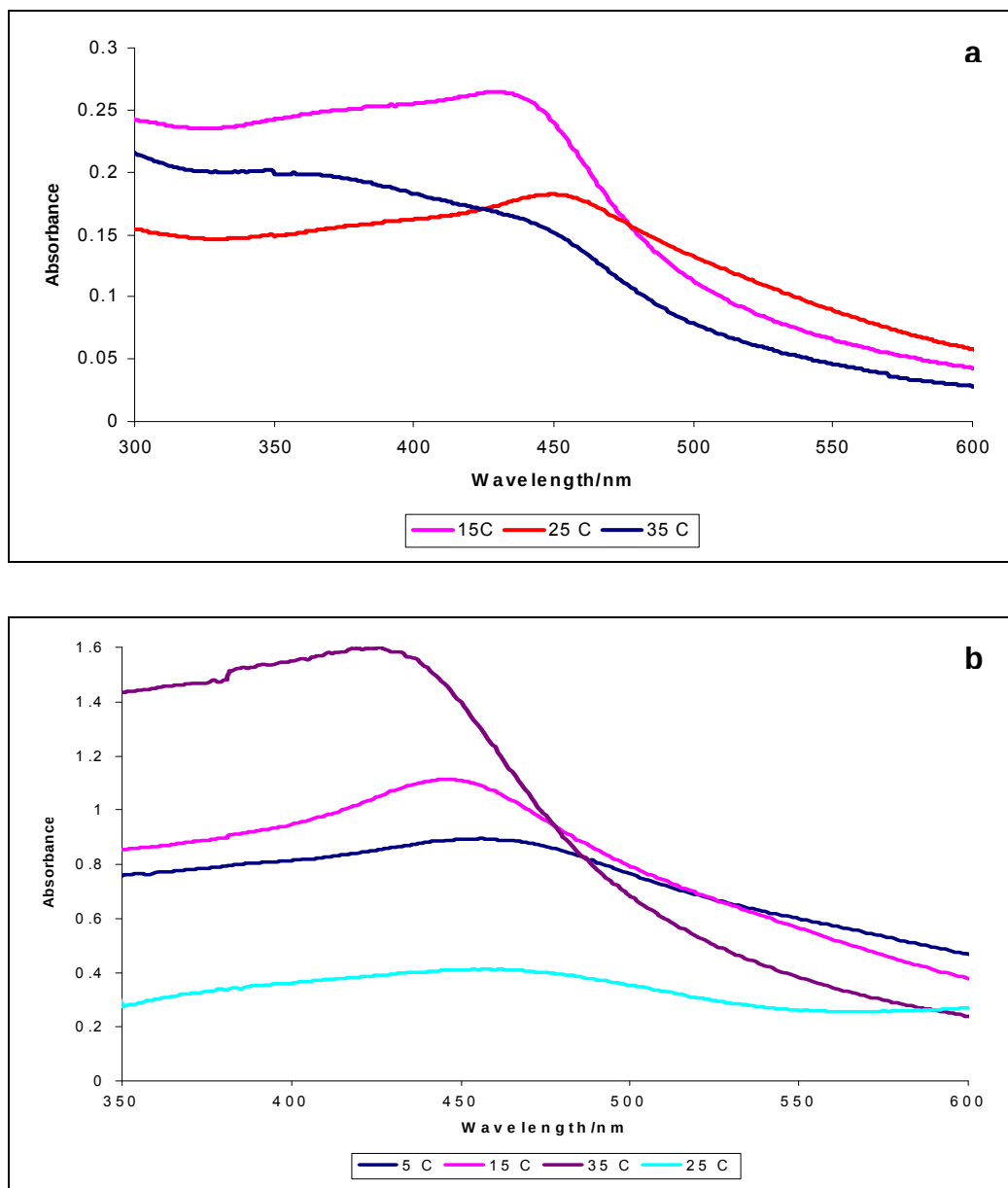


Figure 15. UV-Vis Spectra of Copper Particles Synthesized at (A) 0.15 mM ;(B) 0.62 mM at different temperatures

Figure 15-b shows the formation of spherical particles. As seen from all the curves, copper spherical particles also have a broad absorption at 400-500 nm. At 5°C and 15°C are indicative of the suspension of hollow particles, it clearly shows that this bands

tend to shift towards the red region. As synthesis temperature increases we could observe that the bands shift towards the blue region, which is indicative of the aggregation of smaller particles thus forming copper particles with thicker and denser shells. As temperature increases the monodispersity of the medium diminished. This is proved with the FWHM values at different temperatures which at 15°C is 29 nm, at 25°C is 62 nm, and at 35°C is 40 nm respectively. The UV-Vis investigation indicated that the hollow spheres showed broad adsorption in the visible region

6.1.3 Gold Covered Copper Particles

It is generally found that giant SERS enhancements for practical applications are limited to the coinage metals Ag, Au and Cu with free electrons, on which the surface plasmon resonances can be easily excited in the visible to the near infrared light region [11, 42].

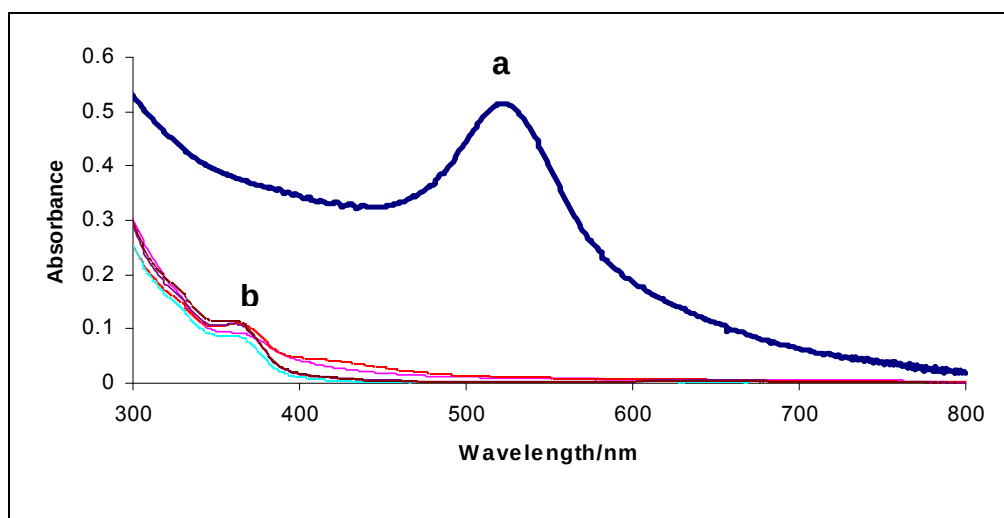


Figure 16. Absorption spectra of (a) Au (0) and (b) Cu (0).

Cu and Au exhibit two plasmonic excitation resonances, they present absorption maxima at about 362 and 525 nm respectively. Figure 16 shows the UV-VIS spectra of copper and gold reduced with β -CD at high pH.

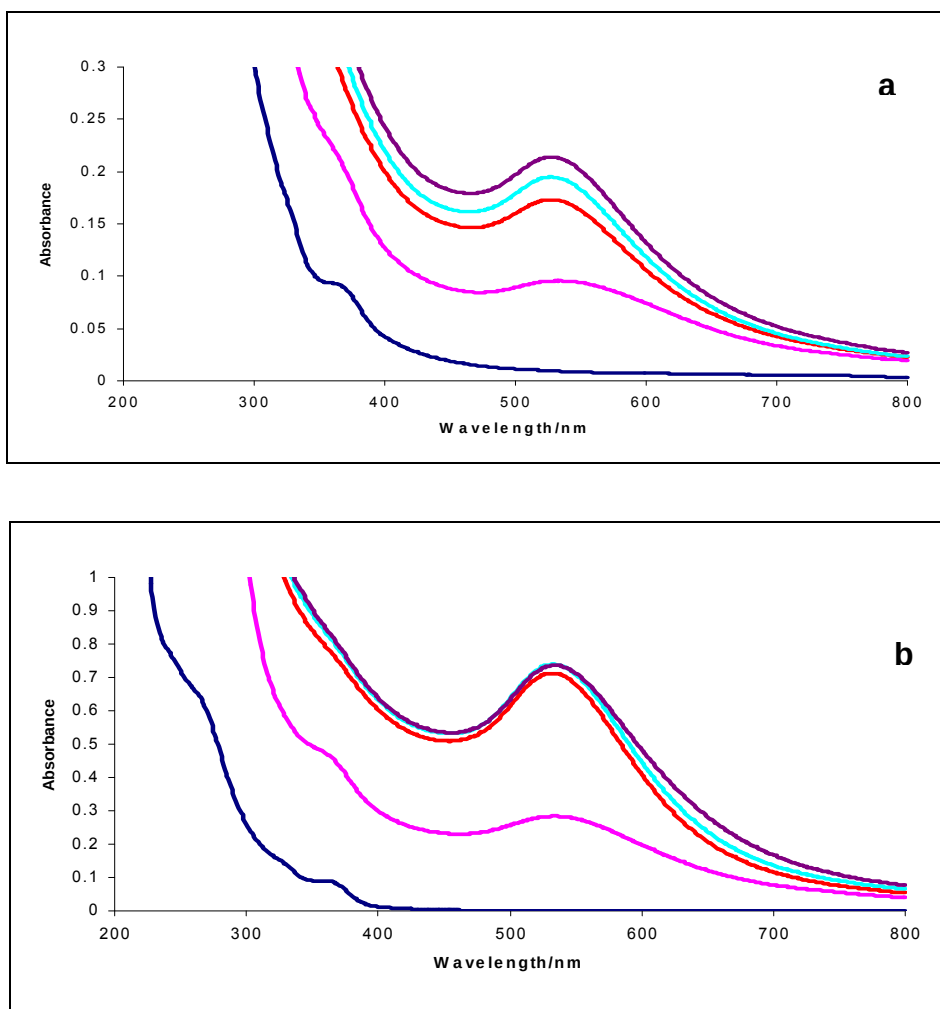


Figure 17: Time absorption spectra: (a) 1 mM Cu colloid – Au 10 mM; (b) 4 mM Cu colloid – Au 10 mM

During the formation of the bimetallic nanoparticles starting from the Cu colloids at different concentrations, UV-VIS spectra were recorded at different stages as shown in Figure 17 a-b. The modification of the plasmon band at different stages of formation of the bimetallic structure from copper seeds is illustrated in Figure 17. Initially, copper

particles were synthesized separately by the β -CD reduction method and were used as seed for the evolution of the gold covered copper bimetallic nanoparticles. The colloidal solution of the copper seed particles shows a pale yellow color with an absorption band at around 362 nm. Upon addition of gold ions to the copper seed particles, gold ions are adsorbed onto the surface of the copper seed particles and thereby reduced [43] in successive stages to form a layer over the copper particles, as seen from the absorbance measurements. In Figure 17-b, an intermediate stage of the particle evolution is shown, two plasmon bands are observed at 534 nm and 361 nm which indicates partial coverage of gold over the copper nanoparticles. After this was observed the solutions were incubated overnight at 70°C. After a day of incubation the two bands merged into one band at 530 nm. Finally, the gold covered copper nanoparticles show only one plasmon resonance at 530 nm, which can be attributed to the plasmon resonance of the gold particle alone. The color of the solution turned pink with different intensities depending on the concentration of the copper colloidal solutions. The appearance of only one absorption band corresponding to gold indicates that homogeneous mixed colloidal particles of the two metals are formed without significant formation of independent particles. The presence of only one plasmon band indicates the structure that the copper particles are indeed covered with gold that is reflected by the true gold plasmon band as if there were no monometallic copper in the medium. Therefore, it is assumed that the copper nanoparticles were then completely covered by gold.

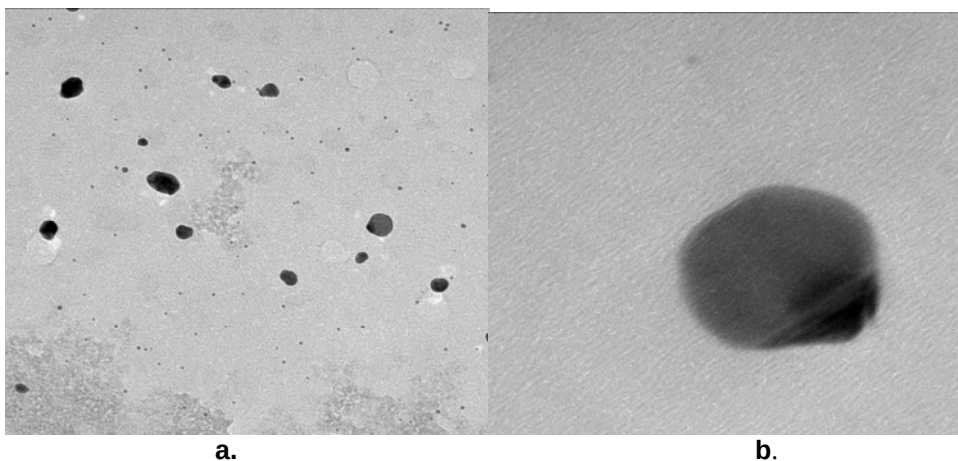


Figure 18. TEM images of 2 mM Cu Colloid -10 mM Au: (a) Image 20000x; (b) HR Image 50000x average particle size 20nm

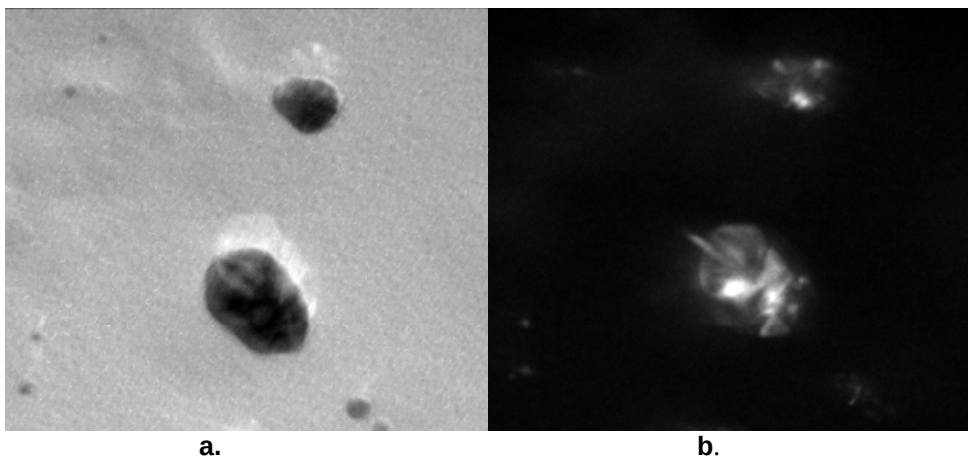


Figure 19. TEM images of 2 mM Cu Colloid -10 mM Au: (a) HR Image 50000x; (b) HR Dark Field TEM Image 50000x average particle size 20nm

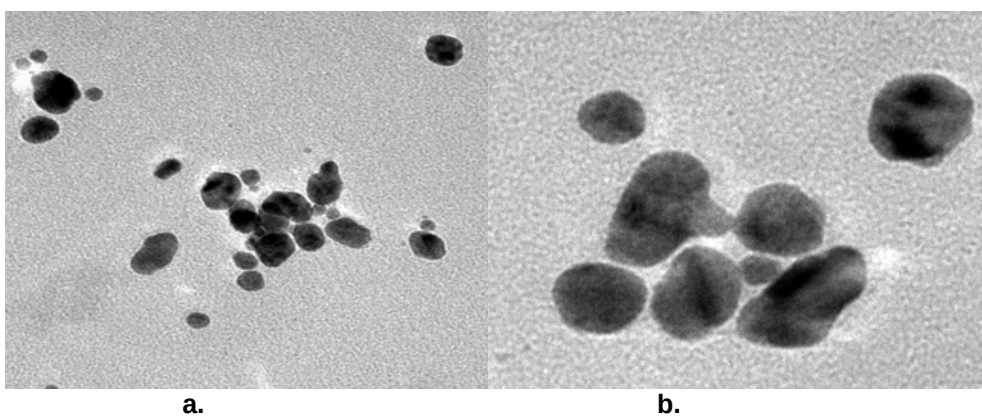


Figure 20. TEM images of Cu Colloid -10 mM Au: (a) HR Image 50000x; (b) Image 50000x average particle size 20 nm

Clear confirmation of the formation of the bimetallic structures emerged from TEM and HR-TEM. Along with UV-VIS, the absorption maximum of the colloidal suspensions provides information on the average particle size, whereas the value of full width at half maximum (FWHM) gives an estimate of particle size distribution. From the TEM images contained in Figure 18, it can be seen that the bimetallic particles are approximately 15-25 nm, and a FWHM value of 37 nm which is consistent with the results obtained by UV-VIS spectrophotometry indicative of a colloidal suspension of modest monodispersity. The HR-TEM images on Figure 19, show the same colloid as in Figure 18. It can be observed that inside the particle there is the presence of a black cluster indicative of a copper nanoparticle. From figure 19-b, the dark field image clearly shows two distinct light diffraction patterns from inside an outside of the nanoparticle, indicative of two different species present.

Figure 20 shows another bimetallic colloidal solution in which again average particle size range about 20 nm and a FWHM value of 49 nm which indicates a colloidal suspension of modest monodispersity. These synthesized colloids tend to form double layer cluster architecture with modest monodispersity, since the composition of the nanoparticles show a narrow spectrum of sizes and shapes. The data shown in Table 3 supports the facts previously mentioned, this shows absorption maxima and FWHM values of the different bimetallic solutions prepared.

Table 3. Absorption Maxima and FWHM of the different bimetallic colloidal mixtures

Au Covered Cu Colloids	λ_{MAX}	FWHM
1 mM	524 nm	41 nm
2 mM	535 nm	37 nm
4 mM	531 nm	41 nm
6 mM	533 nm	49 nm
8 mM	537 nm	56 nm

6.2. Aggregation

Aggregation is required for obtaining large surface enhancements of Raman signals of analytes adsorbed on the colloidal metallic surface. Various salts can be used for inducing aggregation. Although, the most common ion is Cl^- , the effect of the Cl^- ion on the aggregation process was also investigated.

6.3. Experimental Raman scattering spectra of o-DNB on Cu seed nanoparticles

Fresh copper nanoparticles were used for SERS analysis of o-DNB. Our vibrational experiments showed that there is a decrease of the SERS effect and the age of the nanoparticle (data not shown).

Raman scattering spectrum of solid o-DNB and SERS spectra of o-DNB adsorbed on Cu nanoparticles at different laser lines are shown in Figures 21-a-d. Solid o-DNB possesses a C_{2v} point group with 42 fundamental vibrations [44-45]. A 514.5 and 488 nm laser lines were used for SERS analyses because these two wavelengths are found near the surface plasmon.

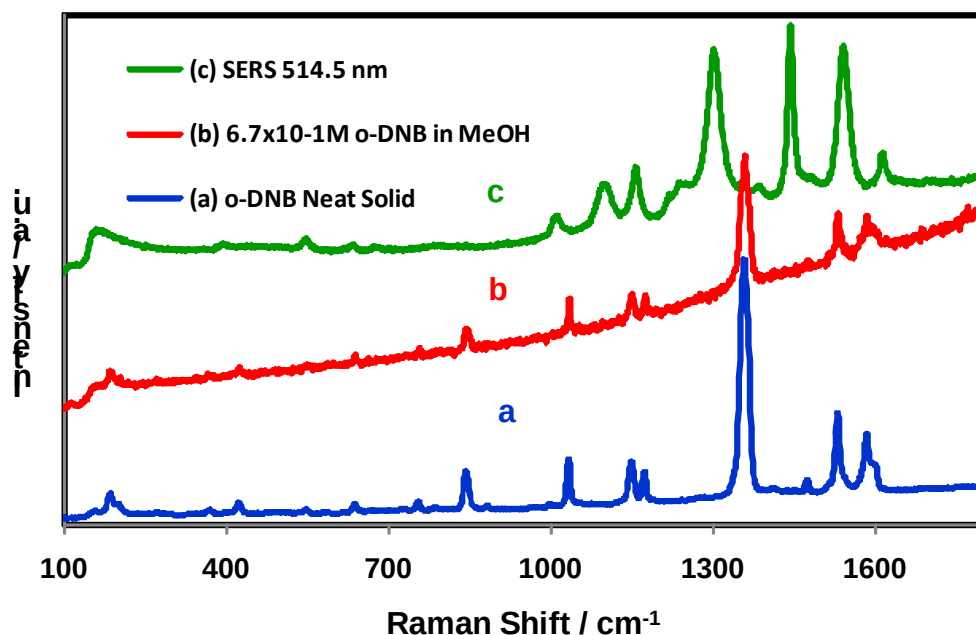


Figure 21. Raman spectra of o-DNB: (a) Solid; (b) methanol solution; (c) SERS at 514 nm laser.

The normal Raman spectrum of solid o-DNB possesses a strong band at 1360 cm^{-1} from the nitro group symmetric stretch [44]. The SERS spectra in Figure 21-b and 21-c show two bands, one at 1305 cm^{-1} and a second 1436 cm^{-1} for 514.5 and excitation. The symmetric band at 1305 cm^{-1} in the normal Raman spectra appears as a splitting in the SERS spectra in both excitation lines. These splitting can be explained from the possible chemical interaction between the copper atom and the o-DNB, causing the

rupture of the symmetric stretch degeneration. Some of the bands are shifted from their location in the spectrum for the solid, with $\Delta\nu$ values with respect to the symmetric stretch around 53 and 18 cm^{-1} respectively and for the asymmetric stretch around 15 and 39 cm^{-1} .

These SERS spectra are in good agreement with that of the solid spectrum. A weaker nitro vibrational mode that appears in the SERS spectra is due to an out of plane wagging that occurs at 556 and 557 cm^{-1} [45]. This suggests that the molecule is attached chemically to the Cu nanoparticles surface through its nitro group. The band appearing at 1160 cm^{-1} corresponds to a combination of stretching modes: the C-N stretching and to the C-H in plane bend. This effect was also observed for the band at 1109 cm^{-1} , which is a sum of the contribution of C-N and C-H stretching modes. There is also another C-H in-plane bend appearing at 1020 cm^{-1} .

Surface Enhancement Factors (SEF) were calculated according to Kneipp [46]. Methanol does not present SERS effect. This allows its use as an internal standard for estimation of SEF. SEF values are calculated using equation 4.

$$SEF = \frac{I_{BandSERS}}{I_{BandMethanol}} \times \frac{C_{Methanol}}{C_{Analyte}} \quad (4)$$

The symmetric nitro stretch band at 1307 cm^{-1} was used for the estimation. For 488 nm SEF was $\sim 2 \times 10^2$ and $\sim 9 \times 10^3$ for 514.5 nm. According to these results for both excitation lines the enhancement was attributed to a chemical SERS effect related to charge transfer (CT) between the copper nanoparticles and o-DNB.

6.4. Copper atom and o-DNB Interaction

The interaction energy was calculated taking the difference between the energy (DFT-B3PW91/Lan12DZ) of complex (Cu-o-DNB) and o-DNB plus the single copper atom. The obtained value was -192 KJ/mol. This suggests a chemical interaction for the above system [47]. The atomic charges were calculated for the oxygen and nitrogen atoms of the nitro functional group of the Cu-o-DNB and o-DNB. The results showed an increase of the charge in the nitro group. The increasing value was -0.49, equivalently to a 90% of the charge found in the copper atom. This demonstrated that a CT occurred from the Cu to o-DNB, in which 90% of the total charge was transferred to the nitro group. These results are in agreement with SEF in which indicated a chemical effect due to CT. The blue shifts found in the symmetric degenerated band can be explained for the charge increase in the nitro group which increases the O-N bond strength.

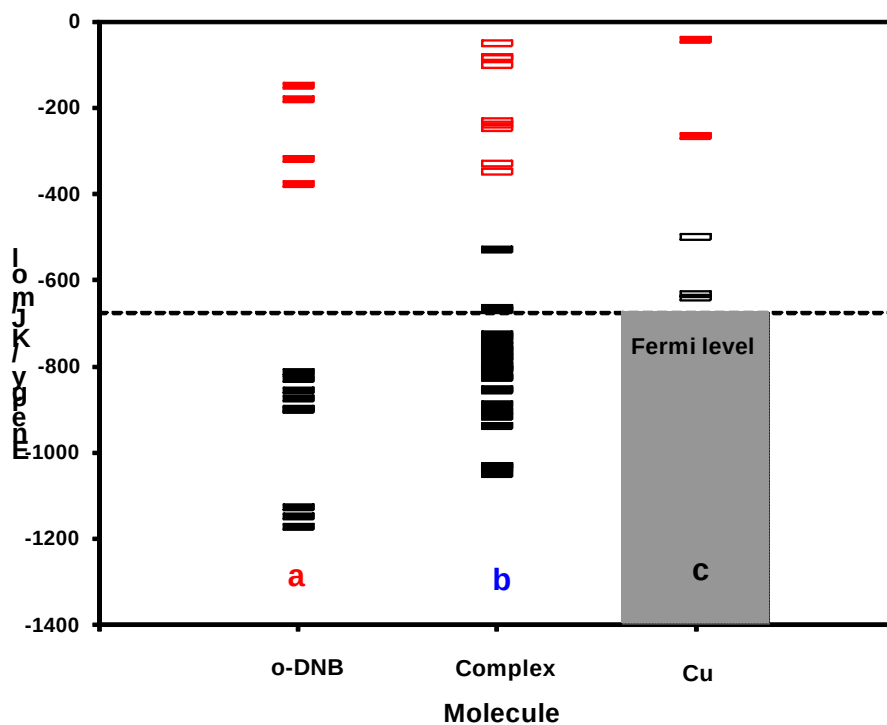


Figure 22. Molecular Orbital (MO) Diagram of: (a) o-DNB; (b) Cu-o-DNB; and (c) Cu.

A chemical enhancement process (CT) must occur between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of o-DNB for resonance Raman and for normal Raman near to LUMO. This CT can be more probable when the Fermi Level of the metal (Cu in this case) is found approximately between HOMO and LUMO of the o-DNB (see Fig. 22) [48]. In the MO for the Cu-o-DNB, it can be seen that new orbitals were formed in the region HOMO-LUMO of o-DNB, increasing the probability of CT.

DFT-B3PW91/Lan12DZ basis set was applied to calculate Raman frequencies of both computational models. The results were compared to the Raman spectra obtained experimentally at 514.5 and 488 nm to determine which model explains the best adsorption mechanism of o-DNB on the copper atom on the Cu surface nanoparticle (Figure 23).

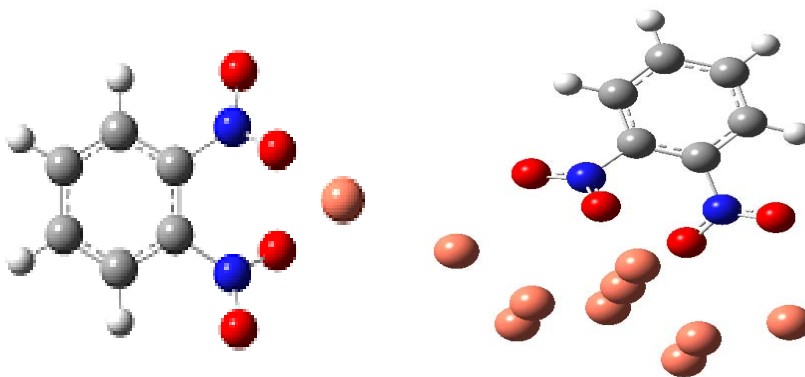


Figure 23. Proposed adsorption geometry of o-DNB on the copper atom and on the Cu surface nanoparticle. Colors: red-oxygen, Blue-nitrogen and red brownish-copper

Two different models were developed for the interaction of o-DNB with the Cu surface. One involved the interaction of one nitro group directly with the surface and the other

model involved the interaction of two nitro groups. Different calculations were developed to determine the minimum energy of interaction between the nitro groups in o-DNB at different distances to the Cu surface (see Fig. 24). Important findings are shown in Fig. 24, for the model of one nitro group of o-DNB interacting with the Cu surface the minimum energy of interaction is -128 KJ/mol at a distance of 2.1 Å. For the other model which involves two NO₂ interacting with the Cu surface, the minimum energy of interaction is -165 KJ/mol at a distance of 1.8 Å. According to the results of the DFT calculations, the interaction of both nitro groups of o-DNB on the Cu nanoparticles surface closely resembles the SERS spectra obtained, both at 514.5 and 488 nm.

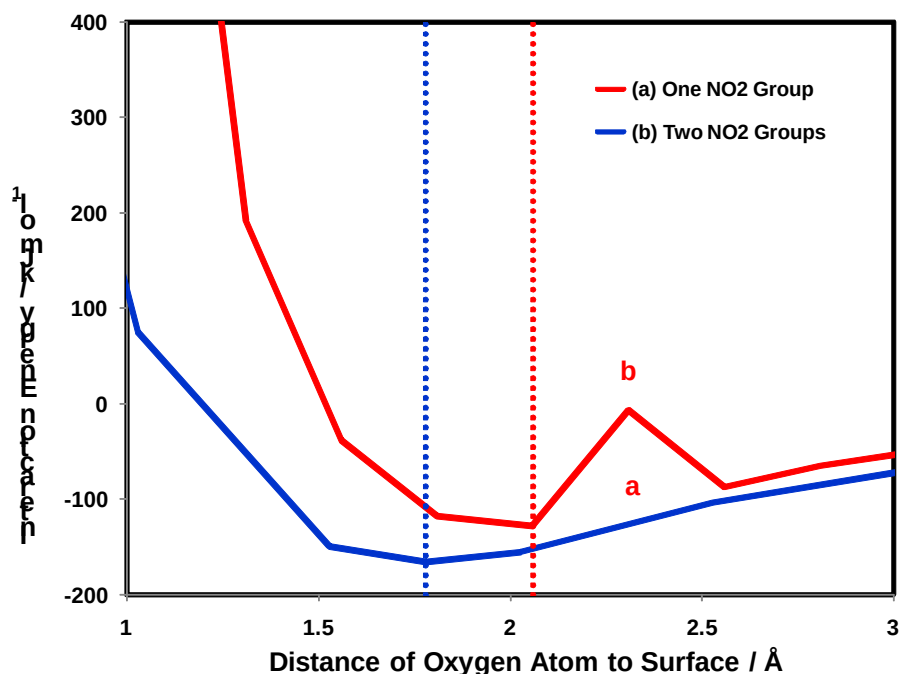


Figure 24. Potential energy of interaction of nitro groups of o-DNB and the Cu surface at different distances for (a) one NO₂ group; (b) two NO₂ groups.

6.5. Comparison between SERS of o-DNB and Calculated Raman Spectra

Normal or spontaneous Raman scattering spectrum of solid o-DNB and calculated spectra of o-DNB are shown in Figure 25. Aside from the expected shifts in frequency throughout all fingerprint region, based on the fact of the selected basis set represents a compromise between the ideal set for organic compounds and the corresponding set of functions for metallic substrates, a reasonably good agreement was found between gas phase molecule and the solid phase o-DNB. Differences in intensity patterns are not significant since polarizability components for the two molecular systems have not been tractable comparisons.

A good agreement between SERS and the calculated frequencies can be assessed by comparing SERS spectrum with the obtained model. This will lead later to the interpretation of the interaction process between o-DNB molecules and Cu colloidal nanoparticles on the surface of the later. In particular, DFT calculations on the interaction processes could be a very powerful tool to get a better insight of the correlation between the observed frequency-shifts, going from the normal or spontaneous Raman spectrum to the SERS spectrum of o-DNB and shedding light on the mechanism of the interaction between the molecule and the copper surface.

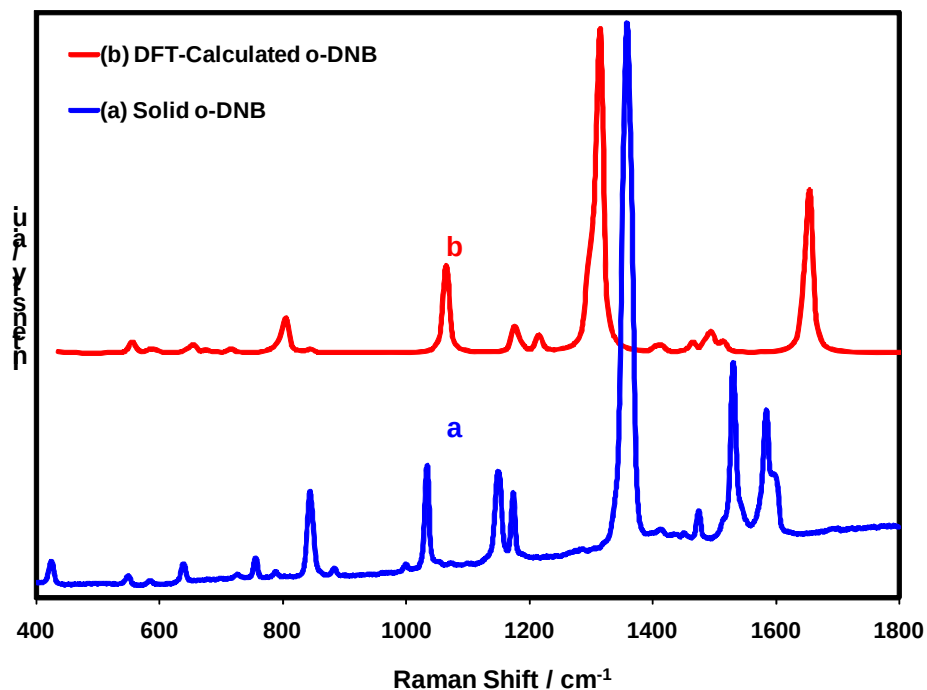


Figure 25. Raman spectra of o-DNB: a) neat solid; (b) DFT calculated.

Experimental SERS frequencies of o-DNB compared with the calculated frequencies of the single atom and surface models of the two nitro groups on the Cu surface using DFT-B3W91 with basis set LanL2DZ are shown in Table 4. Corresponding spectra are illustrated in Figures 26 and 27. As seen from Table 5, the difference (delta) in values for the Cu surface is compared to the Cu single atom model are smaller, providing better agreement with experimental frequencies.

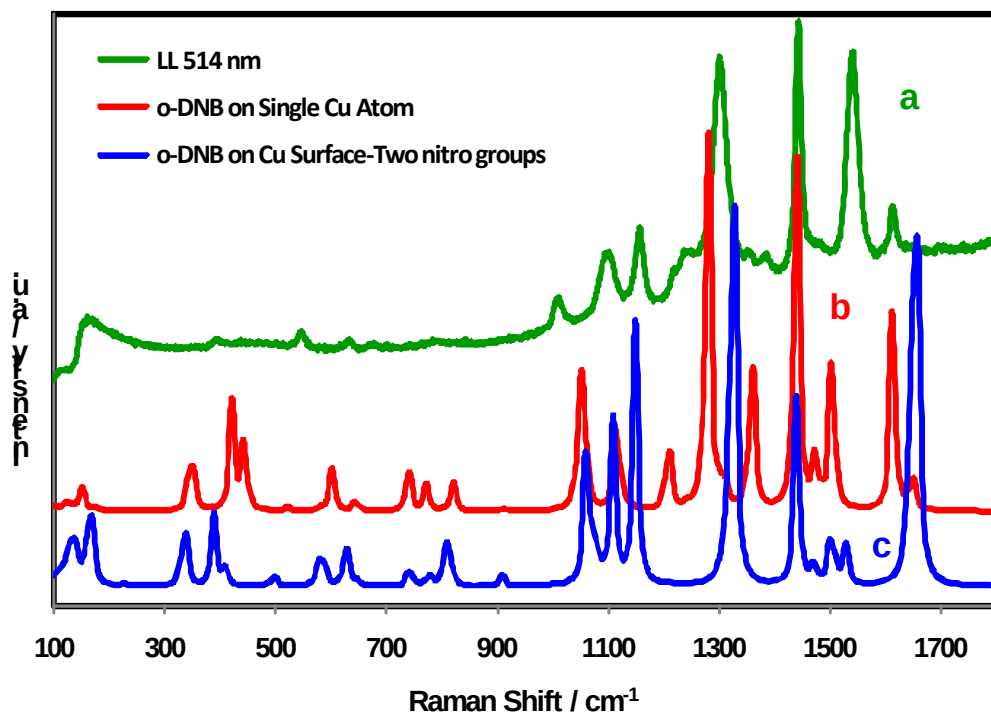


Figure 26. Comparison of SERS and theoretical spectra of interactions of o-DNB on Cu. (a) SERS spectrum excited at 514.5 nm laser line (LL); (b) o-DNB interacting with a single Cu atom; (c) interaction with a modeled Cu surface.

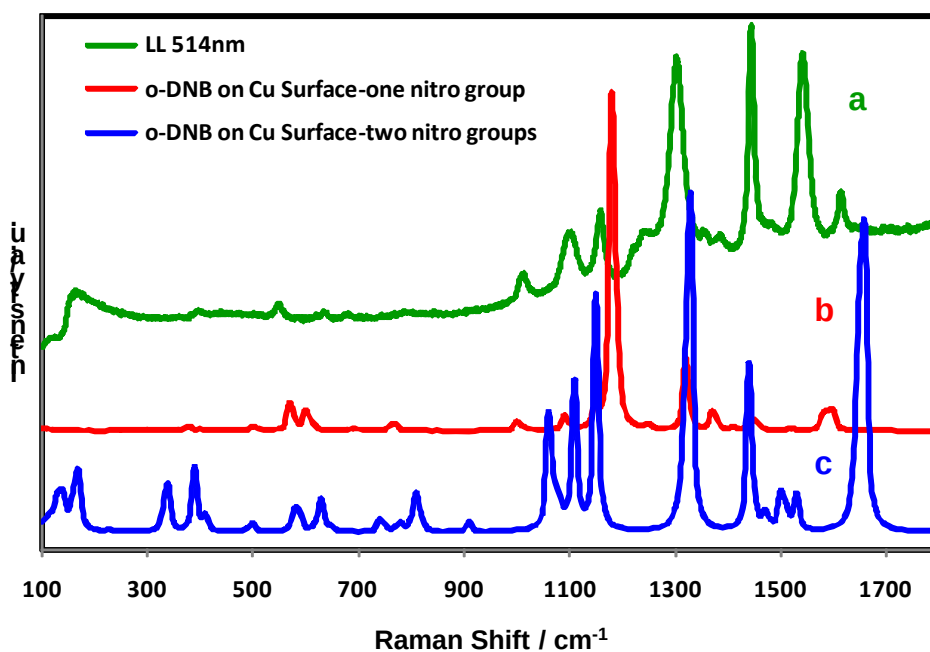


Figure 27. SERS and calculated spectra: (a) SERS spectrum excited at 514.5 nm. Calculated Raman spectra for NO₂ are attached to the Cu surface: (b) one group two NO₂ groups; (c) two NO₂ groups.

Table 4. Experimental and Calculated Raman Frequencies of o-DNB on Cu Nanoparticles

Band Assignment	Exp. 514 nm (cm ⁻¹)	Exp. 488 nm (cm ⁻¹)	o-DNB-Cu Atom	o-DNB-Cu Surface
$\nu(\text{CC})$ Stretching	1616	1618	1611	1660
$\nu(\text{CC})$ Stretching	1544	1545	1502	1520
$\nu_{\text{AS}}(\text{NO}_2)_2$	1616	1618	1611	1660
$\nu_{\text{AS}}(\text{NO}_2)_2$	1544	1545	1502	1520
$\nu(\text{CC})$ Stretching	NF	1484	1471	NF
$\nu_{\text{S}}(\text{NO}_2)_2$	1436	1446	1442	1446
$\nu(\text{CC})$ Stretching	1436	1446	1442	1446
$\nu(\text{CC})$	NF	NF	1361	NF
$\nu_{\text{S}}(\text{NO}_2)_2$	1307	1305	1274	1330
$\nu(\text{CN})$	1160	1161	1211	1150
$\beta(\text{CH})$ In plane bend	1160	1161	1211	1150
$\nu(\text{CH/CN})$	1109	1102	1112	1110
$\beta(\text{CH})$ In plane bend	1020	1020	1051	1060
$\nu(\text{CC})$ ring vibration	646	NF	650	630
$\tau(\text{CCCC})$ torsion	646	NF	650	630
$\gamma(\text{NO}_2)_2$	556	557	601	580

NF: Not found

Table 5. Comparison between Observed and Calculated Frequencies

Band Assignme nt	Obs ΔV_{514nm}	Obs ΔV_{488nm}	$\Delta V_{514nm}O-$ DNB-Cu Atom	$\Delta V_{488nm}O-$ DNB-Cu Atom	$\Delta V_{514nm}O-$ DNB Cu Surface	$\Delta V_{488nm}O-$ DNB Cu Surface
$\nu(CC)$ Stretching	14	16	-5	-7	44	42
$\nu(CC)$ Stretching	-40	-39	-42	-43	-24	-25
$\nu_{+AS}(NO_2)_2$	32	34	-5	-7	44	42
$\nu_{-AS}(NO_2)_2$	13	14	-42	-43	-24	-25
$\nu(CC)$ Stretching	-	11	-	-13	-	-
$\nu_{+S}(NO_2)_2$	-21	-11	6	-4	10	0
$\nu(CC)$ Stretching	-	-	-	-	10	0
$\nu(CC)$	15	14	-13	-12	-	-
$\nu_{-S}(NO_2)_2$	52	54	-33	-29	23	25
$\nu(CN)$	10	11	51	50	-10	-11
$\beta(CH)$ In plane bend	10	11	51	50	-10	-11
$\nu(CH/CN)$	-36	-43	3	10	1	8
$\beta(CH)$ In plane bend	-14	-14	31	31	40	40
$\nu(CC)$ ring vibration	7	-	4	-	-16	-
$\tau(CCCC)$ torsion	7	-	4	-	-16	-
$\gamma_{-}(NO_2)_2$	2	3	45	45	24	23

The deviations of the frequency shifts from the Cu single atom are larger than those found for the Cu surface model. This can be taken as an indication that the Cu Surface model provides a more adequate model to predict the adsorption behavior of o-DNB on the Cu nanoparticle surface. Information from the relative intensity of the bands can be used to judge for the explanation of the dipole mode orientation on a surface. According

to Figure 26, the nitro vibration of o-DNB on the SERS spectrum decreases in intensity compared to the solid state spectrum one. According to SERS selection rules [49] this indicates that N-O mode is not *totally perpendicular* to the surface of the Cu nanoparticles.

6.6. Raman scattering spectra of p-DNB and o-DNB on shape controlled Copper particles

Copper nanoparticles of different shapes (e.g. cubic and spherical) were synthesized by a one step method using hydrazine as reducing agent. The synthetic procedures were done at different temperatures. Our vibrational experiments showed that there is a decrease of the SERS effect. Raman scattering spectrum of solid p-DNB (p-dinitrobenzene) and SERS spectra of p-DNB adsorbed on copper nanoparticles of different shapes at different temperatures are shown in Figures 28-29. Solid p-DNB possesses a C_{2v}^* , C_{2v}^* and V_h symmetry with 42 fundamental vibrations [44-45]. A 514.5 nm laser line was used for SERS analysis because it is found near the surface plasmon of the copper nanoparticles synthesized.

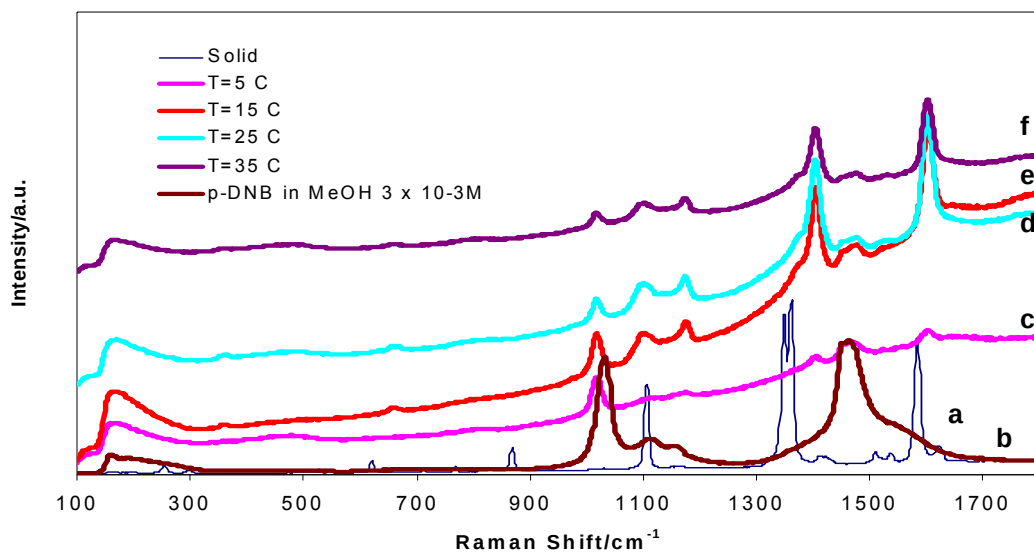


Figure 28. Raman Spectra of p-DNB on Cu nanocubes at different temperatures: (a) solid; (b) p-DNB in MeOH $3 \times 10^{-3} \text{ M}$; (c) 5°C ; (d) 15°C ; (e) 25°C ; (f) 35°C .

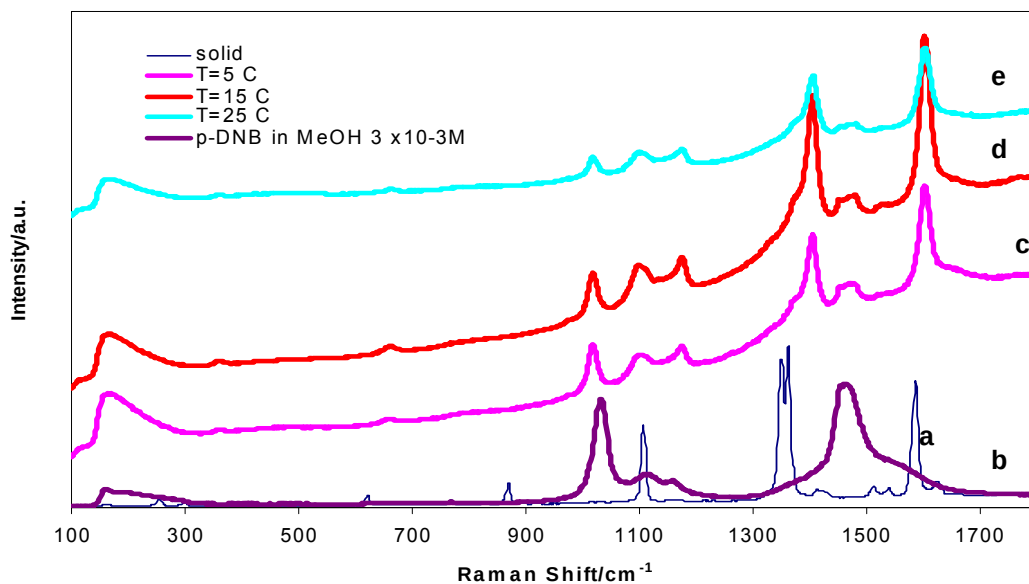


Figure 29. Raman Spectra of p-DNB on Cu nanospheres at different temperatures: (a) solid; (b) p-DNB in MeOH $3 \times 10^{-3} \text{ M}$; (c) 5°C ; (d) 15°C ; (e) 25°C

As seen in figures 28a and 29a the normal Raman spectrum of solid p-DNB possesses strong bands at 1361 and 1349 cm^{-1} respectively from the different vibrational modes of the nitro group symmetric stretch. The SERS spectra in Figures 28 c-f and 29 c-e show one band, at around 1405 cm^{-1} for both cubic and spherical surfaces, respectively. The two modes of the symmetric band merged in to just one signal in the SERS spectra of both surfaces. This merger can explain the possible chemical interaction between the copper surface and p-DNB, causing the breaking of the symmetric stretch degeneration. Figures 28 and 29 show that the two normal vibrational modes of the nitro asymmetric stretch of solid p-DNB appear as two peaks found at 1519 and 1549 cm^{-1} respectively. These two peaks disappear in the SERS spectra of p-DNB in both the cubic and spherical surface. A band located at 1626 cm^{-1} is due to another vibrational mode of the nitro asymmetric stretch. The weaker bands found below 1000 cm^{-1} disappear. This information helps us explain the symmetry of interaction of p-DNB on the copper cubic and spherical surface. In comparison to the solid p-DNB and the SERS spectra of both the cubic and spherical surface, it is noticeable that in the SERS spectra two new bands appear. The band located at 1020 cm^{-1} is due to a β (C-H) in plane bend and the band located at 1172 cm^{-1} is attributed to the contribution of two signals, a C-H and C-N in plane bend.

As concluded from section 6.1.2, the experimental results show that these copper particles are composed of small aggregate particles. The concentration of the reagent greatly influenced the morphology of the particles and the temperature of the reaction affected the rate of aggregation of smaller particles. From Figure 28 we see that as temperature increased; formation of cubic ring particles to cubic particles; there is an

increase in signal in the SERS spectra of p-DNB. Signals obtained at every temperature is probably due to the slow rate of aggregation of smaller cubic particles, the adsorption of ions is probably directional [50]. This in part has to do with the high monodispersity of the cubic particle medium. Surface charges from the synthesis done at different temperatures are probably similar. This causes p-DNB to interact with the cubic rings at lower temperatures and the cubic particles at higher temperatures. Figure 29 shows us a whole different pattern, as synthesis temperature decreases, the signals of p-DNB begin to appear. At 35°C, the highest temperature, no SERS signal is obtained, there is probably no charge transfer between p-DNB and the copper particles. A similar pattern as in figure 29 is shown in figure 30 but with o-DNB. Most of the spectral features from section 6.3 are found in figure 21. As seen at 35 °C, the highest temperature, no SERS signal is obtained, as with p-DNB, there is probably no charge transfer between o-DNB and the copper particles. Apart from p-DNB, o-DNB did not have SERS signal with neither the cubic rings nor the cubic copper particles. Another possible explanation for no SERS as proposed various authors [51] is the following. The copper spheres at a temperature of 35°C present a hollow structure with a cavity (see reference 35). It is evident that the surface of the sphere resonates at a particular frequency and the cavity of the sphere can resonate at any particular frequency within a broad spectral region. Since the formation of the spheres are aggregates of smaller particles, the cavity of the sphere might possess different localized hotspots smaller or larger than the wavelength of the incident radiation used for the SERS experiments. Probably the surface plasmon absorption of this particular spherical shape is not resonant with the incident wavelength or the absorption wavelength causing no SERS enhancement.

Surface Enhancement Factors (SEF) were calculated according to Kneipp [46]. Methanol does not present SERS effect. For p-DNB on the Cu nanospheres and the Cu nanocubes the baseline corrected nitro symmetric stretch band at 1405 cm^{-1} was used for the estimation. For the Cu nanospheres and the Cu nanocubes the SEF values were 1.3×10^5 and 1.0×10^5 . The estimated values are consistent with a SERS effect related to an electromagnetic field contribution between p-DNB and the Cu Surface. For the interaction of o-DNB with the Cu nanospheres the nitro symmetric stretch band at 1307 cm^{-1} . The SEF value obtained was 6.8×10^3 , this value is consistent with a chemical SERS effect related to charge transfer (CT).

Information from the relative intensity of the bands can be used to judge for the explanation of the dipole mode orientation on a surface. According to Figure 28 and 29, the normal asymmetric nitro vibration of p-DNB on the SERS spectrum disappears compared to the solid one, according to SERS selection rules [11] this indicates that N-O mode is not *totally perpendicular* to the surface of the Cu nanoparticles. From Figure 30 the nitro vibration of o-DNB on the SERS spectrum decrease in intensity compared to the solid one, this indicative that N-O mode is not *totally perpendicular* to the surface of the Cu nanoparticle.

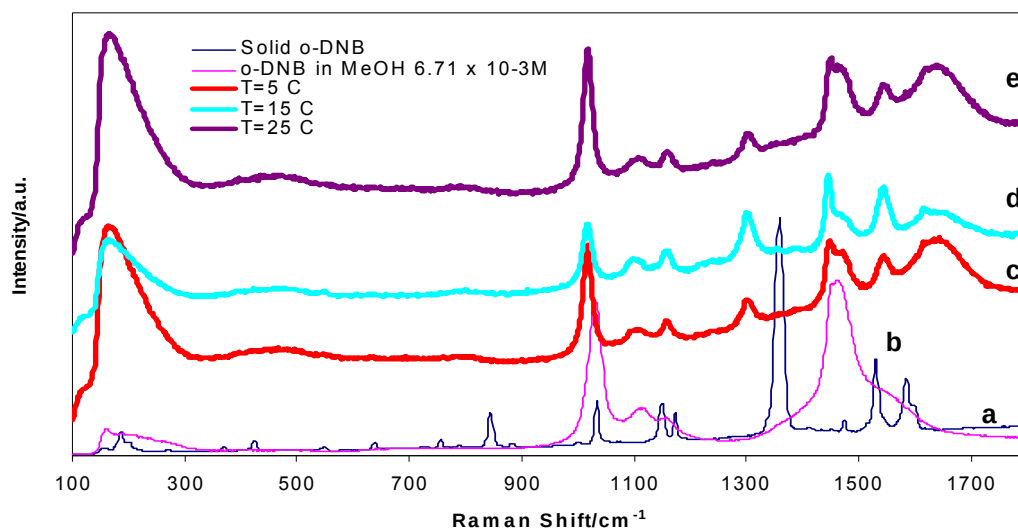


Figure 30. Raman Spectra of o-DNB on Cu nanospheres at different temperatures: (a) solid; (b) o-DNB in MeOH $6.71 \times 10^{-3} \text{ M}$; (c) 5°C ; (d) 15°C ; (e) 25°C

6.7. Raman Activity of the Gold Covered Copper Particles

The present Raman spectroscopy measurements probe on the activity of the bimetallic nanoparticles to produce signals using crystal violet as a molecular probe. There have not been any reported studies of Raman activity on the bimetallic nanoparticles as well as the copper colloid synthesized in this work, however there are numerous SERS studies of crystal violet on silver nanoparticles [51-52]. Here the probe molecule induces particle aggregation without the need of any additional electrolytes for the generation of a “hot junction”. The junction can therefore act as an electromagnetic “hot spot” analogous as to those predicted to exist in large fractal aggregates.

Crystal violet (CV), in aqueous solution is in an ionic state (CV^+) which possesses two different isomeric forms [53]. Crystal violet has no permanent dipole moment due to its

C_3 symmetry. CV was chosen as an analyte, due to its excellent SERS enhancement and low fluorescence interference as seen in single molecule experiments of Kneipp [54]. The SERS activity of the solutions was checked by recording the Raman spectrum of an aqueous solution containing 0.005 mM solution of crystal violet, 0.1M NaCl, 1 mM copper colloid, 10mM Gold colloid and the bimetallic colloidal solution. For Raman measurements crystal violet was mixed with the NaCl solution, to promote aggregation for maximum SERS enhancement, and with the individual metal colloidal solutions as well as the bimetallic colloidal solutions. Figure 31a-b shows the Raman Spectra of 0.005 mM crystal violet aqueous solution with the bimetallic solution and NaCl solution at 514.5 nm and 532 nm with laser power >15 mW.

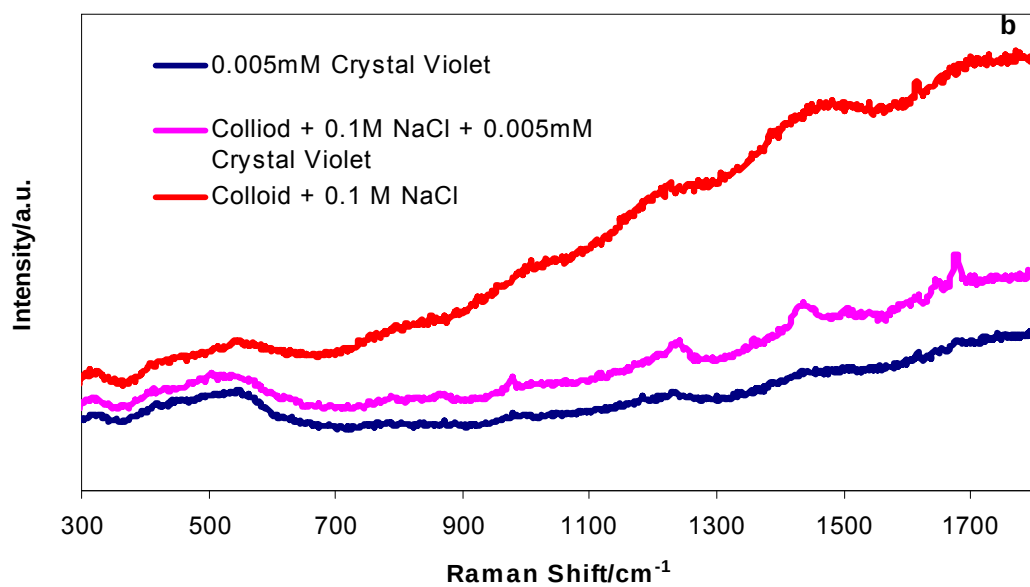
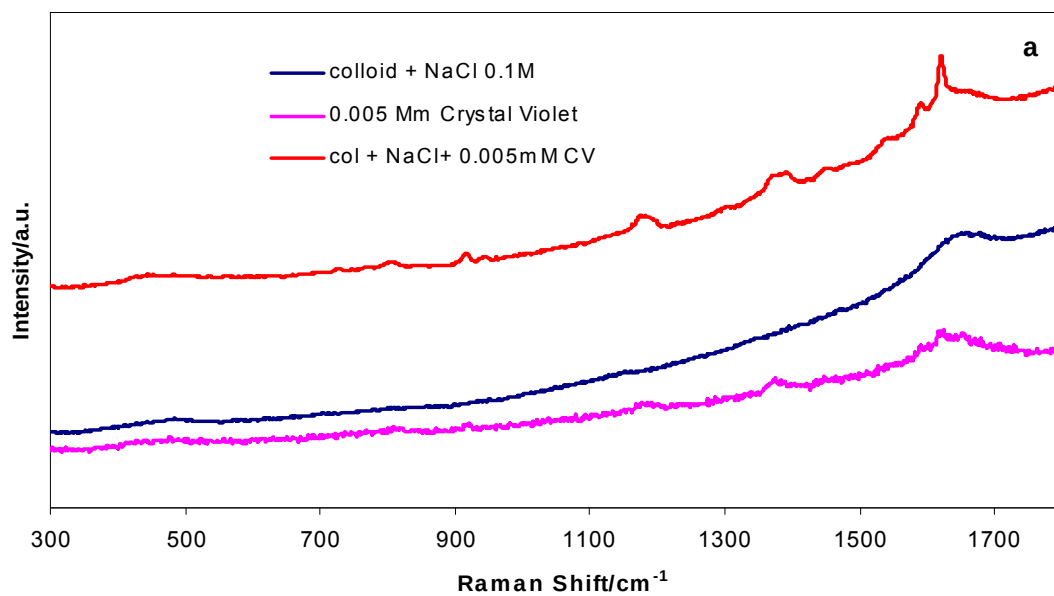


Figure 31. Raman Spectra of the bimetallic colloid with 0.005 mM crystal violet and NaCl 0.1M; (a) 514.5 nm; (b) 532 nm, Laser Power ~ 15mW

From Figure 31 it can be noticed that at both excitation laser lines, SERS signal was obtained, although the intensity of the SERS signals in Figure 31-a is much larger than those found in Figure 31-b. In both spectra prominent features at 921 and 981 cm^{-1} for 514.5 and 532 nm respectively and another at 1182 and 1247 cm^{-1} for 514.5 nm and 532 nm respectively. The Raman shifts previously mentioned are due to the ring skeletal vibrations of radial orientation and in-plane ring C-H bends, respectively [51]. Both SERS spectra of CV^+ in Figure 31 a-b show some differences. Spectra taken using the 532 nm laser line show higher wavenumber shifts than those found at 514.5 nm, in particular, the peak of the out-of-phase ring stretch (e_{41}), is split into two peaks in both experimental Raman spectra that appear at 1593 and 1620 cm^{-1} for the 514 nm measurements while for the 532 nm measurements the splitting occurs at 1651 and 1681 cm^{-1} respectively. This indicates that this e mode, which involves a synchronous stretch of two of the three benzene rings in the CV^+ ion, is no longer degenerate in the surface-absorbed ions. This may indicate that there are populations of species that adopt different orientations with respect to the surface that affect the vibrational frequency.

Surface Enhancement Factors (SEF) were calculated. The baseline corrected out of phase ring stretch of CV at 1620 cm^{-1} for the 514 nm laser light experiments and 1651 cm^{-1} for the 532 nm laser light experiments were used for the estimations. SEF values were 2.1×10^6 for 514 nm and 5.4×10^7 for 532 nm. The estimated values are consistent with a SERS effect related to an electromagnetic field contribution between CV and the bimetallic surface.

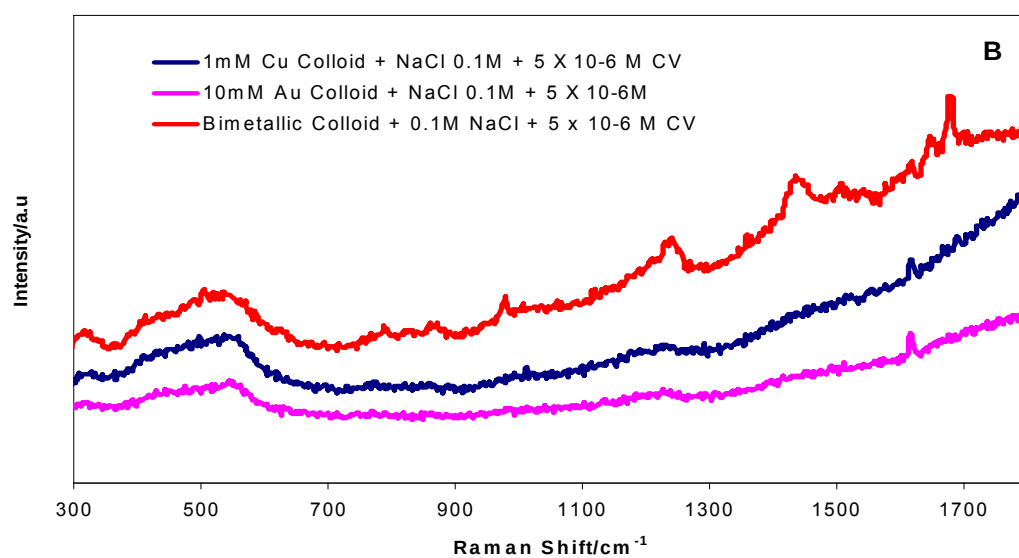
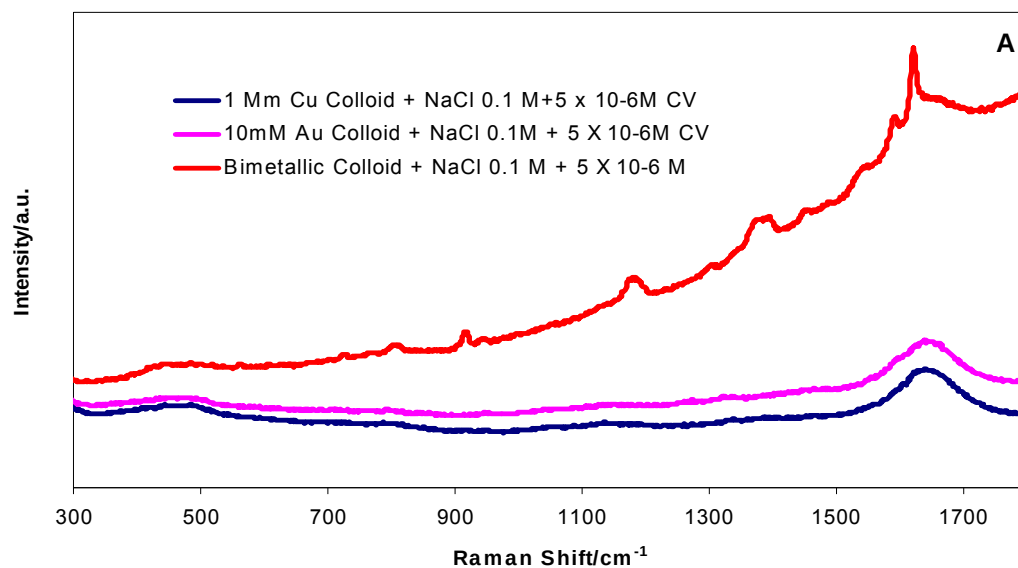


Figure 32. Raman Spectra of 0.005 mM Crystal Violet and NaCl 0.1M with the 1mM Copper Colloid, 10mM Au Colloid and the bimetallic colloid ; (A) 514.5 nm, (B) 532nm, laser power > 15mW.

From Figure 32 a-b it can be seen that CV shows distinctly different SERS features in terms of intensity at both laser lines. At both laser lines the individual metallic colloids don't show any enhancement when mixed with CV. The salient feature of physical significance is that we observe better enhancement of the SERS signal of the probe molecule when gold and copper are mixed together forming the bimetallic structure. This suggests that the copper nanoparticle is covered with a stable gold monolayer. It is known that, gold monometallic nanoparticles are better SERS substrates than copper monometallic nanoparticles, whereas these are less active. The enhancement can be explained in terms of a charge transfer interaction by electronegativity effects. Given that gold is more electronegative than copper, gold will withdraw electron density from the copper core, making the gold surface more electronegative. As a result, the copper shell will experience the electrophilic effect and gold the nucleophilic effect. Because the Fermi level is lower for copper (about -7.0 eV) than for gold (about -5.0 eV), charge transfer occurs along a direction from gold to copper.

Comparing SEF values obtained for the colloids synthesized, gives us information of which Cu structure is considered the most productive in enhancing the signals of the analytes used.

Table 6. Surface enhancement factors for o-DNB on different Cu Surfaces using different laser lights

Colloid	514 nm	488 nm
<i>Cu Seed</i>	9×10^3	2×10^2
<i>Cu Cubes</i>	-	-
<i>Cu Spheres</i>	6.8×10^3	-

Table 7. Surface enhancement factors for p-DNB on different Cu Surfaces using different laser lights

Colloid	514 nm	488 nm
<i>Cu Seed</i>	-	-
<i>Cu Cubes</i>	1.3×10^5	-
<i>Cu Spheres</i>	1.0×10^5	-

Based on the SEF values obtained for the Cu monometallic structures found on tables 6 and 7 when compared to the SEF values of the Cu/Au structure; the Cu/Au structure gives the highest SEF values. Overall the Cu/Au structure is a far superior surface for obtaining enhanced signals for the analytes used.

CHAPTER VII

CONCLUSIONS

The novelty of the chemical methods for the generation of nanoparticles lies in its complexity and ability to shape the particle without using any capping agent or template. The reagent concentration, synthesis temperature and reaction rates exert a strong influence on the shape of the copper particles in the synthetic procedures.

The synthesis of nanospheres in this work could be useful in the investigation of various optical phenomena, such as novel supported photocatalysts, or as candidates for photonic crystals. The bimetallic particles may present superior optical, electronic and magnetic properties than their monometallic counterparts. In this contribution Cu nanoparticles with optimum SERS properties were successfully synthesized. They were used as SERS substrates for the detection of o-DNB, p-DNB and crystal violet. The SEF values demonstrated that a chemical mechanism is responsible for most of the SERS effect observed in these analyte. Based on SEF values obtained the Cu/Au structure gave the strongest enhanced signal in the Raman spectra. Overall this structure provides far superior surface for analyte interaction when compared to the other colloids synthesized in this work.

Experimental and computational work was aimed at modeling the formation of a chemical complex between o-DNB and Cu atoms. Computational models together with the electromagnetic mechanism do not completely explain the SERS phenomenon, as has been widely used in the SERS literature. In the explanation of the adsorption mechanism, postulation of formation of a charge transfer complex sets a different point

of view for the obtained experimental SERS results (SEF, vibrational band shifts, strengthening/weakening of chemical bonds, etc.) and computational results (molecular orbitals analysis and charge transfer analysis). It is assumed that the other nitro groups that do not interact strongly (chemically) with the copper nanoparticles could give rise to higher SEF values: stronger SERS effects by the electromagnetic enhancement mechanism.

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