# OPTICAL CHARACTERISATION OF GROWTH DYNAMICS FOR COLLOIDAL GOLD NANOPARTICLES IN CITRATE ENVIRONMENT

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To all of us who wander in our stride, and fellows who endured my absence.

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#### ABSTRACT

This study emphasises on detection and characterisation of gold nanoparticles based on its optical response. Water dispersed gold nanoparticles are synthesised from citrate reduction with dilute gold chloride under external energy sources. Three methods (i.e. heat-reflux, UV photoreaction, and UV photoinitiation) were used as reaction energy source to produce the nanoparticles. Firstly, exact solution of Mie equations was vigorously tested by varying particle diameter for monodisperse and polydisperse size distributions to investigate its limitations and effects on extinction cross-sections respectively. Changes in peak extinction cross-sections due to effect of temperature are negligible even at 100 °C. Simulated fragmentation mechanism in the particle size distribution produced calculated extinction cross-section that are comparable to time-resolved experiments with  $\lambda_{pk}$  blue-shifted from approximately 610 nm to 520 nm. Secondly, verification of size distribution derived from photon correlation spectroscopy and small angle X-ray scattering was carried out with extinction profile used as comparison; the results shows general agreement between these instruments with mode particle size ranged from 20 nm to 80 nm. However, size distribution derived from small angle X-ray scattering produced expected extinction lower than measured values for  $\lambda > 600$  nm. Thus, the following characteristics of the colloid are as follows: in general, heat-refluxed nanoparticles are smaller compared to UV synthesised particles. Weaker incident photon energy produced consistently larger particles with broader size distribution and emerged later when compared reactants exposed to high energy UV. The isoelectric point for our colloidal system was measured at  $pI = 2.31 \pm 0.56$ . Lastly, time-resolved scattering measurements were carried out in three separate experiments involving photon correlation spectroscopy and home-built configurations. They collectively indicate the likelihood of fragmentation mechanism in particle size distribution during the time as the colloidal colour turn from transparent to blue.

#### ABSTRAK

Kajian ini menekankan pada pengesanan dan pencirian zarah nano emas berdasarkan kaedah optik. Sebaran zarah nano dalam air disediakan daripada penurunan klorida emas dengan sitrat di bawah sumber tenaga luaran yang disediakan. Antara tiga cara yang digunakan sebagai sumber tindakbalas tenaga adalah refluks-haba, fotoreaksi ultraungu, dan fotopemulaan ultraungu. Mulanya, penyelesaian tepat persamaan Mie telah diuji dengan mengubah diameter zarah monosebar dan taburan saiz polisebar untuk menentukan batasan dan kesannya kepada keratan-rentas kelenyapan cahaya. Perubahan pada puncak kelenyapan keratan-rentas disebabkan oleh kesan suhu boleh diabaikan walaupun pada 100 C°. Simulasi mekanisme pemecahan dalam taburan saiz zarah menghasilkan keratanrentas lenyapan yang setara dengan eksperimen penyelesaian masa dimana  $\lambda_{pk}$ teranjak daripada 610 nm ke 520 nm. Kemudian, taburan saiz diperolehi daripada spektroskopi korelasi foton dan serakan sinar X bersudut kecil telah disahkan dengan profil kelenyapan; keputusannya menunjukkan persetujuan antara peralatan yang diuji dalam julat saiz zarah diantara 20 nm hingga 80 nm. Namun, taburan saiz diperolehi daripada serakan sinar X menghasilkan jangka kelenyapan lebih kecil daripada nilai cerapan mulai  $\lambda > 600$  nm. Oleh demikian, kecirian koloid adalah seperti berikut: secara amnya, zarahnano refluks-haba didapati lebih kecil daripada zarah hasilan ultraungu. Pengarahan tenaga foton yang lemah tekal menghasilkan zarah yang besar dan bertaburan luas, serta muncul lebih lewat berbanding dengan bahan tindak balas yang terdedah kepada sinaran UV bertenaga tinggi. Takat isoelektrik dalam sistem koloid yang dikaji adalah ditentukan pada p $I = 2.31 \pm 0.56$ . Akhirnya, pengukuran serakan bertempoh telah dijalankan dalam tiga eksperimen yang berasingan dan secara kolektif mereka menunjukkan bahawa kemungkinan tinggi taburan saiz zarah mengalami mekanisme pemecahan semasa warna koloid bertukar daripada jernih ke biru.

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## LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
AuNP	-	Gold nanoparticle
CCD	-	Charged-coupled device
CCP	-	Cubic closed packing
Cit:Au	-	Ionic ratio of citrate to gold
CNT	-	Classical nucleation theory
DDA	-	Discrete dipole approximation
DLVO	-	Derjaguin-Landau-Verwey-Overbeek (theory)
EDL	-	Electrostatic double layer
EDX	-	Energy dispersive X-ray
HR-TEM	-	High-resolution transmission electron microscopy
LED	-	Light emitting diode
LSPR	-	Localised surface plasmon resonance
NIR	-	Near infra-red
NUV	-	Near ultraviolet
PCS	-	Photon correlation spectroscopy
PDI	-	Polydispersity index
PSD	-	Particle size distribution
RI	-	Refractive Index
SADC	-	Sodium acetate decarboxylate
SAXS	-	Small angle X-ray scattering
SERS	-	Surface enhanced Raman scattering
SNR	-	Signal to noise ratio
UV-A	-	Ultraviolet A-band
UV-C	-	Ultraviolet C-band
XRF	-	X-ray fluorescence

## LIST OF SYMBOLS

$N_T$	-	Number of atoms in Schmid's full-shell nanocrystal
n <sub>i</sub>	-	<i>i</i> -th Schmid's nuclei shell
А	-	Nanoparticle precursor species
В	-	Surface-growing nanoparticles
<i>k</i> <sub>1,2</sub>	-	Rate constants for autocatalytic reaction 1 and 2
$\gamma_S$	-	Surface energy
$U\left( D ight)$	-	Intermolecular potential energy
$d_m$	-	Distance between two interacting molecules
r	-	Intermolecular distance
$C_w$	-	Van der Waals coefficient
$B_r$	-	Born repulsion
$U_a(D)$	-	Inter-particle attractive potential energy
$ ho_e$	-	Electron density of nanoparticle
$l_p$	-	Centre-to-centre distance of nanoparticles
D	-	Surface-to-surface distance of nanoparticles
R	-	Radius of nanoparticle
Н	-	Hamaker constant
V(x)	-	Electric potential of double layer surrounding nanoparticle
$\kappa^{-1}$	-	Debye length
$\rho_q(x)$	-	Surface charge density as a function of distance x
$\mathcal{E}_0$	-	Vacuum permittivity
$\mathcal{E}_m$	-	Dielectric constant of the medium
$n_{i\infty}$	-	Number of counter ions at $x \to \infty$
Zi	-	Valence state of counter ions
e	-	Elementary charge
Т	-	Temperature
k <sub>B</sub>	-	Boltzmann constant
$\mathbf{V}_s$	-	Surface potential of nanoparticle
$\mathbf{V}_{\delta}$	-	Helmholtz potential of nanoparticle
$\mathbf{V}_{\zeta}$	-	Zeta potential of nanoparticle

$F_{np}(D)$	-	Inter-particle force
$U_R(D)$	-	Inter-particle repulsive potential energy
$U_{total}\left(D ight)$	-	Total potential energy of a nanoparticle in DLVO theory
$\mu_e$	-	Electrophoretic mobility
d	-	Diameter of single nanoparticle, $d = 2R$
$f(\kappa d)$	-	Henry correlation function
$K_a$	-	Rate constant for ionization of carboxyl ends in SADC ions
$N_s$	-	Number of surface atoms of a nanoparticle
$N_{v}$	-	Number of volume atoms of a nanoparticle
λ	-	Wavelength of electromagnetic radiation
$\varepsilon\left(\omega,R ight)$	-	Frequency and size dependent dielectric function
$I_{ext}\left(\lambda ight)$	-	Extinction intensity
l	-	Optical path length
$I_0$	-	Incident intensity
$n_v$	-	Number density of nanoparticles
$C_{ext}$	-	Extinction cross-section of nanoparticle(s)
$C_{sca}$	-	Scattering cross-section of nanoparticle(s)
$C_{abs}$	-	Absorption cross-section of nanoparticle(s)
$a_L$	-	Bessel coefficient for partial electric field modes
$b_L$	-	Bessel coefficient for partial magnetic field modes
L	-	Excitation mode order
n	-	Imaginary refractive index of gold (frequency dependent)
$n_m$	-	Real refractive index of medium (frequency dependent)
ĩ	-	Diffraction parameter
k	-	Wave-vector
$\psi_L$	-	Ricatti-Bessel spherical function
$\eta_L$	-	Ricatti-Bessel spherical function
С	-	Speed of light in vacuum
$V_0$	-	Nanoparticle volume
$f_{LN}(d)$	-	Log-normal particle size distribution function
< <i>d</i> >	-	Mode of particle size distribution
β	-	Computational bin-width of size distribution
$C_{ext}\left(\beta ight)$	-	Extinction cross-section by particle size distribution
$\lambda_{pk}$	-	Peak extinction wavelength

$\lambda_0$	-	Selected extinction wavelength for Haiss calibration fit
$L_{1,2}$	-	Haiss logarithmic fitting parameter
$E_{450}$	-	Extinction intensity at $\lambda = 450$ nm
$E_{IIIsca}$	-	Scattering electric field parallel to scattering plane
$E \perp_{sca}$	-	Scattering electric field perpendicular to scattering plane
$d_{sca}$	-	Distance from scattering event to detector
$E_{IIIi}$	-	Incident electric field parallel to scattering plane
$E \perp_i$	-	Incident electric field perpendicular to scattering plane
$S_{1,2,3,4}$	-	Scattering matrix elements
i	-	Complex number
E	-	Electric field strength
$E^*$	-	Conjugate electric field strength
Α	-	Amplitude
$\delta$	-	Phase of electric field
$I_{IIIsca}$	-	Scattering intensity parallel to scattering plane
$I \perp_{sca}$	-	Scattering intensity perpendicular to scattering plane
$S_{1,2}\left(  heta ight)$	-	Angle dependent Mie scattering matrix elements
$P_L^{l}$	-	Associated Legendre polynomials of the first kind
$S_{11}\left(  heta ight)$	-	First element of Mueller matrix
$I_{sca}\left(  heta ight)$	-	Unpolarised scattering intensity as a function of angle
$I_i$	-	Incident intensity
$D_T$	-	Translational particle diffusion coefficient
$d_H$	-	Hydrodynamic diameter of nanoparticle
$\eta (T)$	-	Temperature-dependent dynamic medium viscosity
$I\left(t ight)$	-	Time-dependent speckle intensity for PCS
$d_p$	-	Diameter of scattering centre
$d_d$	-	Diameter of scattering intensity detector
$A_{coh}$	-	Coherence area
$A_{det}$	-	Detector area
$G^{(2)}(\delta t)$	-	General correlation function
$g^{(2)}(\delta t)$	-	Normalised correlation function
Г	-	Line-width of scattering intensity
В	-	Asymptotic baseline of correlation function
f	-	Instrument constant of photon correlation spectroscopy system

q	-	Scattering wave vector
$G\left(d_{H}\right)$	-	Hydrodynamic particle size distribution, $G(d_H) = f_{LN}(d)$
σ	-	Standard deviation for particle size distribution
<i>V</i> <sub>c</sub>	-	Volume concentration of nanoparticles
V <sub>NP</sub>	-	Volume occupied by nanoparticles
$I\left(q ight)$	-	Scattering intensity vector function
$R_g$	-	Radius of gyration
μ	-	Median of particle size distribution
đ	-	Mean of particle size distribution
Isca (405 nm)	-	Scattering intensity at $\lambda = 405 \text{ nm}$
<i>Isca</i> (808 nm)	-	Scattering intensity at $\lambda = 808$ nm
$I_{sca}\left(t ight)$	-	Scattering intensity against time (time-series)
$\Delta t$	-	Correlation time
$t_c$	-	Time of last acquisition for scattering intensity time-series

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#### **CHAPTER 1**

#### INTRODUCTION

### 1.1 Background of Study

Since the discovery of optical applications involving surface plasmons, liquid dispersed metallic nanoparticles has seen an explosion of research interest since the beginning of the 1980s. A systematic procedure to synthesize citrate-stabilised gold nanoparticles was discovered in 1951 by Turkevich [1]. This procedure, favoured for its simplicity and reliability has attracted many application studies. The Turkevich method was cited 4374 times as of 2016; yet despite widespread applications, the mechanistic behaviour of the colloid during and after synthesis has elucidated us.

To this date there are no generally accepted complete mechanism to describe the physicochemical processes that occurs during nucleation and growth of the nanoparticles. LaMer *et al.* [2], proposed a nucleation mechanism for his work with sulphur sols, and was adopted by Turkevich based on applications of the Classical Nucleation Theory (CNT) but was later found insufficient to describe the changes of optical character exhibited by the colloid during synthesis. Recent investigations with ex-situ microscopy and in-situ scattering experiments [3 - 5] have reached radically different opinions on its nucleation mechanism with respect to the classical theory. On top of this confusion, it was found that nucleation can also be triggered by nonthermal methods. These new initiation methods brought contrast to the classical heatassisted synthesis, which was thought the only way to initiate the chemical reaction.

Understanding the nucleation and growth processes ultimately give us better control over the synthesis and thus the yield. Eventual industrial production of metallic colloids also drives research interest on the development of a rapid and affordable quality monitoring system by in-situ optical measurement of colloidal characteristics. It is therefore becoming a need to fulfil these gaps of knowledge.

### **1.2 Problem Statements**

Dipole approximation for the calculation of optical absorption coefficient for gold nanoparticles has been used extensively for rapid size characterisation. However, this approximation only holds true for the case when size distribution is sufficiently narrow (monodisperse) and with mode size no more than 1/10 of incoming radiation wavelength. How does polydispersity in sizes and the effects of dispersant temperature affects the spectral properties in UV-visible region such as the absorption, scattering and extinction cross-sections for spherical gold nanoparticles?

It was found that electromagnetic radiation ranging from microwave to gamma rays are able to assist the chemical reduction process of citrate-stabilised gold nanoparticles. There is yet a systematic study regarding the photochemistry and mechanistic behaviour for colloidal systems triggered by these emissions. How does the exposure to sub-bands of ultraviolet radiation (UV-A, UV-C) affect the yield and dynamics of particle size distribution for citrate-stabilised gold nanoparticles?

In the early 2010s, it was found via electron microscopy that the classical nucleation theory fails to support the observation of an intermediate nucleation stage where networks of gold nanowires or mesoscale aggregates appear as soon as nucleation occurs. Concurrently, small angle X-ray scattering utilising intense beam from synchrotron sources found such intermediate stage do not exist. Does the colloidal nuclei emerge from larger intermediate structures for citrate stabilised gold nanoparticles?

Given both heat and ultraviolet radiation are capable of assisting the reduction process of gold complexes, how does different citrate to gold (Cit:Au) ionic ratio and pH affect the electrochemistry, particle size distribution (PSD) and zeta potential in considerably long timescales? What does it implies to the stability of the colloidal system?

### **1.3** Research Objectives

The first portion of this thesis dedicates to the theoretical construct of extinction cross-sections using Mie theory. Simulations based on different particle size distributions are then used to fit experimental values. Colloidal dynamics of gold nanoparticles will be investigated by optical extinction, scattering and photon correlation spectroscopy. The aims of this thesis are:

- i. To simulate the absorption, scattering and extinction cross-sections contributed by multipole plasmon-polariton oscillations and size dependent scattering intensity of single and polydisperse gold nanoparticles.
- To verify the consistency of size characterisation methods between photon correlation spectroscopy (PCS) and small angle X-ray scattering (SAXS) with optical extinction using heat-refluxed gold nanoparticles.
- iii. To measure the time-resolved and final optical extinction, particle size distribution (PSD), colloidal pH, and volume concentration for heatrefluxed and UV-assisted reduction of gold ions in citrate environment so that the changes in particle sizes of gold nanoparticles can be characterised.
- iv. To measure scattering and baseline intensity changes in-situ correlated to formation of gold nanoparticles triggered by exposure to coherent 405 nm Near-UV laser beam at different Cit:Au ratio.

### 1.4 Scope of Study

Throughout this thesis, the focus of experiments is limited to *optical response* from water-dispersed gold nanoparticles reduced and stabilised from its ionic precursors in citrate environment. Hence, significant portions of analysis regarding particle sizes are derived from optical extinction and scattering measurements. With reference to the objectives of this thesis, the scopes are;

All simulated optical parameters are computed by exact solution of Mie theory – chosen due to immediate relevance – for calculation of extinction and scattering cross-sections. Only lognormal size distribution was considered for simulation of monodisperse gold nanoparticles; this act as a reference to find the condition where dipole approximation fails to describe experimental optical extinction of large particle sizes. Bimodal and trimodal size distribution were used to simulate realistic optical extinction that matches experimental measurements. The total range of mode particle size was computed between 20 nm to 3000 nm to describe optical extinction from the nanoscopic to the mesoscopic scale.

To verify the size distribution obtained from small angle X-ray scattering experiments, standard heat-refluxed gold nanoparticles with reliably known particle size characterised by optical extinction was used. Only two samples of the same Cit:Au ratio to be used for simplicity as the objective of the experiment was to verify characterisation methods.

The method to initiate chemical reactions are limited to reflux-heating the reagents to boiling point (100 °C) and UV exposure either through photoreaction or photoinitiation by selected sample wavelengths, representing different bands of UV at 405 nm (NUV), 366 nm (UV-A), and 253.7 nm (UV-C). The dynamics of log-normal particle size distribution (PSD) and volume concentration are derived from speckle intensity flux in a PCS instrument. Autocorrelation of scattering speckle intensity flux are analysed and fitted with built-in least square inverse Laplace CONTIN algorithm designed to describe mono- and bimodal polydisperse particle populations. Emphasis in discussions is given on the characteristics of gold

nanoparticles rather than in-depth verification of optical characterisation methods as the objective is to study time-resolved size characteristics. Also, time-resolved measurements (PCS and extinction) are limited to the speed of physical sampling, perceived changes based on extinction, and highest possible temporal resolution of our instruments, which are never shorter than 40 seconds for PCS and 10 ms for scattering time-series.

Discussions involving in-situ multiparticle scattering experiments were carried out assuming isotropic particle distribution during synthesis. The results from scattering experiments are qualitative by nature, and are meant to compliment PCS results on photoreaction and photoinitiation experiments as it is the last objective of this thesis. Subsequently, UV assisted reactions was found to be wavelength specific and thus discussions regarding particle size dynamics are strictly limited to their respective reaction energy sources.

#### **1.5** Significance of Study

The problem inherent in mechanistic studies lies at the lack of precision for in-situ characterisation. Most mechanistic studies involving size characterization are usually obtained with Transmission Electron Microscopy (TEM) or Scanning Electron Microscopy (SEM). These techniques although having the advantage of visualizations in high resolution but require the sample to be extracted and isolated from the medium. Ex-situ extraction, purification and drying involved during sample preparations ultimately leads to agglomeration or at least environmental changes for the particles. Furthermore, intensely focussed electron beams or X-rays has been shown to interact destructively with sub-micrometer sized particles. For these reasons, electron microscopy cannot reflect the actual nucleation and growth condition of the colloid.

Investigating colloidal system through optical methods has the critical advantage of being in-situ and less invasive on the particles at the cost of resolution. To the best of our knowledge, systematic studies on nucleation and growth processes for ultraviolet-assisted citrate reduced gold nanoparticles have not been investigated simultaneously by PCS and optical extinction measurements. Following careful data interpretation and verification, PCS is a powerful experimental method for extracting particle size distribution within a very short amount of time. Results from the experiments provide insight on undisturbed nucleation and growth mechanism which has seen much confusion and conflict found in the literature over the past decade.

Ongoing interest in fundamental colloid chemistry may need verification of size distribution in the viewpoint of physics such as computation of optical extinction in addition to other size characterization methodologies. This thesis served as a proof-of-concept in an interesting cross-disciplinary research where it demonstrates rapid size characterization for metallic colloids can be obtained via extinction measurements without *a priori* assumption of small monodisperse sample.

#### **1.6** Thesis Outline

This thesis begins with an introduction on the ongoing problems regarding colloidal dynamics of citrate reduced and stabilised gold nanoparticles. It is followed by stating the purpose, limitations and a summary on research significance.

The second chapter thoroughly reviews concepts on optical properties of colloidal gold and experiments involving nucleation. It provides an overview on colloidal terminologies followed by detailed description of the Turkevich-Frens synthesis pathways. Derivations and various aspects regarding optical absorbance and scattering cross-sections, PCS correlation functions and physics of small angle X-ray scattering were examined. Investigations in the past regarding nucleation dynamics are also reviewed to illustrate key points necessary for result discussions.

The third chapter states the methodologies employed in this study. This chapter is broadly separated into three sections where the first describes the equations and computational methods for simulation of optical responses from gold colloids. Second and third sections are separated into sub-sections based on synthesis parameters and experiment details on heat-assisted reduction, UV-assisted reduction, and near-UV scattering experiments.

The fourth chapter presents the outcome of computation and experimental works. Based on simulations, calculated optical extinction spectra are compared with experiments to obtain information regarding size and polydispersity. The trends in PSD from photon correlation spectroscopy and small angle X-ray scattering are compared to earlier results to find consistency. Zeta potential and pH measurements provide insights on colloidal stability for extended shelf life. Lastly, the scattering and baseline intensity changes by 405 nm laser irradiation of reagents are correlated to formation of gold nanoparticles.

The last chapter concludes the findings and discussion of this thesis. The summary includes reiteration of shortcoming and limitations of this study followed by suggestions for future investigations.

#### LIST OF REFERENCES

- J. Turkevich, P. C. Stevenson, A. Hiller, "A Study of The Nucleation and Growth Processes in the Synthesis of Colloidal Gold", *Disc. Faraday Soc.*, 1951, Vol. 11, 55-75.
- [2] LaMer and J. Kenyon, "Kinetics of the formation of monodispersed sulfur sols from thiosulfate and acid", *J. Colloid Sci.*, 1947, Vol. 2, 257.
- [3] Yuri Mikhlin, Anton Karacharov, Maxim Likhatski, Tatyana Podlipskaya, Yan Zubavichus, Alexey Veligzhanin, Vladimir Zaikovski, "Submicrometer intermediates in the citrate synthesis of gold nanoparticles: New insights into the nucleation and crystal growth mechanisms", *Journal of Colloid and Interface Science*, 2011, Vol. 362, 330–336.
- [4] A. Alshammari, Angela Köckritz, Venkata Narayana Kalevaru, Abdulaziz Bagabas, Andreas Martin, "Influence of Single Use and Combination of Reductants on the Size, Morphology and Growth Steps of Gold Nanoparticles in Colloidal Mixture", *Open Journal of Physical Chemistry*, 2012, Vol. 2, 4.
- [5] Xuelian Chen, Jan Schröder, Stephan Hauschild, Sabine Rosenfeldt, Martin Dulle, and Stephan Förster, "Simultaneous SAXS/WAXS/UV–Vis Study of the Nucleation and Growth of Nanoparticles: A Test of Classical Nucleation Theory", *Langmuir*, 2015, Vol. 31, 11678–11691.
- [6] T. Castro, R. Reifenberger, E. Choi, R. P. Andres, "Size-dependent melting temperature of individual nanometer-sized metallic clusters", *Phys. Rev. B*, 1990, Vol. 13, 8548.

- [7] A. M. Alkilany, C. J. Murphy, "Toxicity and cellular uptake of gold nanoparticles: what we have learned so far?", *J Nanopart Res.*, 2010, Vol. 12 (7), 2313–2333.
- [8] M. Haruta, "When Gold Is Not Noble: Catalysis by Nanoparticles", *Chem. Rec.*, 2003, Vol. 3 (2), 75-87.
- [9] S. Eustis, M. A. El-Sayed, "Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes", *Chem. Soc. Rev.*, 2006, Vol. 35, 209–217
- [10] J. L. Li, Min Gu, "Gold-Nanoparticle-Enhanced Cancer Photothermal Therapy", *IEEE Journal on Selected Topics in Quantum Electronics*, 2010, Vol. 16 (4), 989-996.
- [11] Huang X., Jain P.K., El-Sayed I.H., El-Sayed M.A., "Plasmonic photothermal therapy (PPTT) using gold nanoparticles", *Lasers Med. Sci.*, 2011, Vol. 23 (3), 217-228.
- [12] G. Maltzahn, A. Centrone, J. H. Park, R. Ramanathan, M. J. Sailor, T. A. Hatton, S. N. Bhatia, SERS-Coded Gold Nanorods as a Multifunctional Platform for Densely Multiplexed Near-Infrared Imaging and Photothermal Heating, Adv. Mater., 2009, 21, 3175-3180.
- [13] H. J. Parab, H. M. Chen, T. C. Lai, J. H. Huang, P. H. Chen, R. S. Liu, M. Hsiao, C. H. Chen, D. P. Tsai, Y. K. Hwu., Biosensing, cytotoxicity, and cellular uptake studies of surface-modified gold nanorods, J. Phys. Chem. C., 2009, 113(18), 1574-1578.
- [14] C. J. Murphy, A. M. Gole, J. W. Stone, P. N. Sisco, A. M. Alkilany, E. C. Goldsmith, S. C. Baxter., "Gold nanoparticles in biology: beyond toxicity to cellular imaging", *Acc. Chem. Res.*, 2008, Vol. 41 (12), 1721-1730.

- [15] P. Pimpang, W. Sutham, N. Mangkorntong, P.i Mangkorntong, S. Choopun, "Effect of Stabilizer on Preparation of Silver and Gold Nanoparticle Using Grinding Method", *Chiang Mai J. Sci.*, 2008, Vol. 35 (2), 250-257.
- [16] L. H. Bac, J. S. Kim, and J. C. Kim, Size, "Optical and Stability Properties of Gold Nanoparticles Synthesized By Electrical Explosion of Wire in Different Aqueous Media", *Rev. Adv. Mater. Sci.*, 2011, 28, 117-121.
- [17] L. H. Bac, G. S. Yun, J. S. Kim, H. S. Choi, J. C. Kim, "Preparation and Stability of Gold Colloid by Electrical Explosion of Wire in Various Media", *J. Nanosci. Nanotech.*, 2011, Vol. 11 (2), 1730-1733.
- [18] F. Correard, K. Maximova, M.A. Estève, C. Villard, M. Roy, A. Al-Kattan, M. Sentis, M. Gingras, A. V. Kabashin and D. Braguer, "Gold nanoparticles prepared by laser ablation in aqueous biocompatible solutions: assessment of safety and biological identity for nanomedicine applications", Int. J. Nanomedicine., 2014, Vol. 9, 5415–5430.
- [19] V. Amendola, S. Polizzi, and M. Meneghetti, "Laser Ablation Synthesis of Gold Nanoparticles in Organic Solvents", *J. Phys. Chem. B*, 2006, Vol. 110 (14), 7232–7237.
- [20] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, "Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid–liquid system", J. *Chem. Soc., Chem. Commun.*, 1994, Vol. 7, 801-802.
- [21] D. Gaspar, A. C. Pimentel, T. Mateus, J. P. Leitão, J. Soares, B. P. Falcão, A. Araújo, A. Vicente, S. A. Filonovich, H. Águas, R. Martins & I. Ferreira, "Influence of the layer thickness in plasmonic gold nanoparticles produced by thermal evaporation", *Scientific Reports*, 2013, Vol. 3, 1469.
- [22] M. B. E. Griffiths, S. E. Koponen, D. J. Mandia, J. F. McLeod, J. P. Coyle, J. J. Sims, J. B. Giorgi, E. R. Sirianni, G. P. A. Yap, and S. T. Barry, "Surfactant Directed Growth of Gold Metal Nanoplates by Chemical Vapor Deposition", *Chem. Mater.*, 2015, Vol. 27 (17), 6116–6124

- [23] R. G. Palgrave and I. P. Parkin, "Aerosol Assisted Chemical Vapor Deposition of Gold and Nanocomposite Thin Films from Hydrogen Tetrachloroaurate (III)", *Chem. Mater.*, 2007, Vol. 19 (19), 4639–4647.
- [24] R. G. Parkhomenko, N. B. Morozova, G. I. Zharkova, Y. V. Shubin, S. V. Trubin, V. V. Kriventsov, B. M. Kuchumov, T. P. Koretskaya, I. K. Igumenov, "Deposition of Au Thin Films and Nanoparticles by MOCVD", *Chemical Vapor Deposition*, 2012, Vol. 18 (10-12), 336–342.
- [25] J. H. Lee, S. U. S. Choi, S. P. Jang, and S. Y. Lee, "Production of aqueous spherical gold nanoparticles using conventional ultrasonic bath", *Nanoscale Res. Lett.*, 2012, Vol. 7 (1), 420.
- [26] K. Okitsu, M. Ashokkumar, F. Grieser. "Sonochemical Synthesis of Gold Nanoparticles: Effects of Ultrasound Frequency", J. Phys. Chem. B., 2005, Vol. 109, 20673-20675.
- [27] S. A. Dong, S. P. Zhou, "Photochemical Synthesis of Colloidal Gold Nanoparticle", *Material Science and Engineering B*, 2007, Vol. 140, 153-159.
- [28] M. Kaushik, P. Tarasankar, Z. L. Wang, "Seed Mediated Successive Growth of Gold Particles Accomplished by UV irradiation - A Photochemical Approach For Size Controlled Synthesis", *Journal of Photochemistry and Photobiology A: Chemistry*, 2001, Vol. 140, 75-80.
- [29] T. K. Sau, P. Tarasankar, A. Pal, N. R. Jana, Z. L. Wang, "Size Controlled Synthesis of Gold Nanoparticles Using Photochemically Prepared Seed Particles", *Journal of Nanoparticle Research*, 2001, Vol. 3, 257-261
- [30] K. D. N. Vo, C. Kowandy, L. Dupont, X. Coqueret, N. Q. Hien, "Radiation Synthesis of Chitosan Stabilized Gold Nanoparticles Comparison Between ebeam and Gamma radiation", *Radiation Physics and Chemistry*, 2014, Vol. 94, 84-87.

- [31] Y. C. Yang, C. H. Wang, Y. K. Hwub, J. H. Je, "Synchrotron X-ray Synthesis of Colloidal Gold Particles for Drug Delivery", *Materials Chemistry and Physics*, 2006, Vol. 100, 72-76.
- [32] N. Hanžić, T. Jurkin, A. Maksimović, M. Gotić, "The Synthesis of Gold Nanoparticles by a Citrate-Radiolytical Method", *Radiation Physics and Chemistry*, 2015, Vol. 106, 77-82.
- [33] S. Y. Xiong, W. H. Qi, Y. J. Cheng, B. Y. Huang, M. P. Wang, and Y. J. Lia, "Modeling size effects on the surface free energy of metallic nanoparticles and nanocavities", *Phys. Chem. Chem. Phys.*, 2011, Vol. 13, 10648-10651.
- [34] K. K. Nanda, A. Maisels, F. E. Kruis, H. Fissan, and S. Stappert, "Higher Surface Energy of Free Nanoparticles", *Phys. Rev. Lett.*, 2003, Vol. 91, 106102.
- [35] J. F. Zhou, J. Ralston, R. Sedev, D. A. Beattie, "Functionalized gold nanoparticles Synthesis, structure and colloid stability", *Journal of Colloid and Interface Science*, 2009, Vol. 331, 251-262.
- [36] Erik C Dreaden, Lauren A Austin, Megan A Mackey, and Mostafa A El-Sayed, "Size matters: gold nanoparticles in targeted cancer drug delivery", *Ther. Deliv.*, 2012, Vol. 3 (4), 457–478.
- [37] S. Bucher, J. Hormes, H. Modrow, R. Brinkmann, N. Waldöfner, H. Bönnemann, L. Beuermann, S. Krischok, W. Maus-Friedichs, V. Kempter, "Interaction between core and protection shell of N(butyl)4Cl<sup>-</sup> and N(octyl)4Cl-stabilized Pd colloids" *Surf. Sci.*, 2002, Vol. 497, 321.
- [38] Fren, G., "Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions", *Nature*, 1973, Vol. 241, 20.
- [39] Z. Lee, K. J. Jeon, A. Dato, R. Erni, T. J. Richardson, M. Frenklach, and V. Radmilovic, "Direct Imaging of Soft-Hard Interfaces Enabled by Graphene", *Nano Letters*, 2009, Vol. 9, 3365–3369.

- [40] Aduro <sup>™</sup> Application Note, downloaded from www.protochips.com on 18 May, 2016
- [41] R. Zsigmondy, P.A Thiessen, "Das Kolloide Gold", Akad. Verlag. Leipzig, 1925.
- [42] S. Kumar, K. S. Gandhi, R. Kumar, "Modeling of Formation of Gold Nanoparticles by Citrate Method", *Ind. Eng. Chem. Res.*, 2007, Vol. 46, 3128-3136.
- [43] B. Rodrígez-Gonzalez, P. Mulvaney, L. M. Liz-Marzán, "An Electrochemical Model for Gold Colloid Formation via Citrate Reduction", *Zeitschrift für Physikalische Chemie*, 2007, Vol. 221 (3), 415.
- [44] I. Ojea-Jiménez, F. M. Romero, N. G. Bastu's, V. Puntes, "Small Gold Nanoparticles Synthesized with Sodium Citrate and Heavy Water: Insights into the Reaction Mechanism", J. Phys. Chem. C, 2010, Vol. 114, 1800–1804.
- [45] H. Bönnemann, K. Nagabhushana, "Chapter 2: Metal Nanoclusters: Synthesis and Strategies for Their Size Control", in "Metal Nanoclusters in Catalysis and Material Science: The Issue of Size Control", 2008, Elsevier B.V.
- [46] C. E. Briant, B. R. C. Theobald, J. W. White, C. K. Bell, D. M. P. Mingos, "Synthesis and X-ray structural characterization of the centred icosahedral gold cluster compound [Au<sub>13</sub>(PMe<sub>2</sub>Ph)<sub>10</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>; the realization of a theoretical prediction", *Chem. Soc. Chem. Commun.*, Vol. 20, 201.
- [47] J. W. A. van der Velden, F. A. Bollenbroek, J. J. Bour, P. I. Beukskens, J. M. M. Smits, W. P. Bosman, "Gold clusters containing bidentate phosphine ligands. Preparation and X-ray structure investigation of [Au<sub>5</sub>(dppmH)<sub>3</sub>(dppm)](NO<sub>3</sub>)<sub>2</sub> and [Au<sub>13</sub>(dppmH)<sub>6</sub>](NO<sub>3</sub>)<sub>n</sub><sup>†</sup>," *Rec. J. R. Neth. Chem. Soc.*, 1981, Vol. 100, 148.
- [48] Y. Liu, W. Meyer-Zaika, S. Franzka, G. Schmid, M. Tsoli, H. Kuhn, "Goldcluster degradation by the transition of B-DNA into A-DNA and the formation of nanowires", *Angew. Chem. Int. Ed.*, 2003, Vol. 42, 2853.

- [49] Rafael A. Masitas and Francis P. Zamborini, "Oxidation of Highly Unstable
   <4 nm Diameter Gold Nanoparticles 850 mV Negative of the Bulk Oxidation</li>
   Potential", *J. Am. Chem. Soc.*, 2012, Vol. 134 (11), 5014–5017.
- [50] Steve Y. Rhieu, Vytas Reipa, "Tuning the Size of Gold Nanoparticles with Repetitive Oxidation-reduction Cycles", *American Journal of Nanomaterials*, 2015, Vol. 3 (1), 15-21.
- [51] Minh Tran, R. DePenning, M. Turner, and S. Padalkar, "Effect of citrate ratio and temperature on gold nanoparticle size and morphology", *Materials Research Express*, 2016, Vol. 3 (10), 314
- [52] J. K. Young, N. A. Lewinski, R. J. Langsner, L. C. Kennedy, A. Satyanarayan, V. Nammalvar, A. Y. Lin, and R. A Drezek, "Size-controlled synthesis of monodispersed gold nanoparticles via carbon monoxide gas reduction", *Nanoscale Res Lett.*, 2011, Vol. 6(1), 428.
- [53] J. H. El Nakat, I. G. Dance, K. J. Fisher, G. D. Willet, "Gas phase copper chalcogenide cluster ions, formed by laser-ablation", *Inorg. Chem.*, 1991, Vol. 30, 2957.
- [54] B. K. Pong, H. I. Elim, J. Chong, W. Ji., B. L. Trout, J. Lee, "New Insights on the Nanoparticle Growth Mechanism in the Citrate Reduction of Au(III) Salt
  Formation of the Au Nanowire Intermediate and its Non-linear Optical Properties", *J. Phys. Chem. C*, 2007, Vol. 111, 6281-6287.
- [55] L. H. Pei, K. Mori, M. Adachi, "Formation process of two-dimensional networked gold nanowires by citrate reduction of AuCl4<sup>-</sup> and the shape stabilization", *Langmuir*, 2004, Vol. 20, 7837.
- [56] S. Biggs, P. Mulvaney, C. F. Zukoski, F. Grieser, "Study of Anion Adsorption at the Gold-Aqueous Solution Interface by Atomic Force Microscopy", J. Am. Chem. Soc., 1994, Vol. 116 (20), 9150.

- [57] J. F. Wall, F. Greiser, C. F. Zukoski, "Monitoring chemical reactions at the gold/solution interface using atomic force microscopy", J. Chem. Soc., Faraday Trans., 1997, Vol. 93, 4017.
- [58] M. K. Chow, C. F. Zukoski, "Gold Sol Formation Mechanisms: Role of Colloidal Stability", J. Colloid Interface Sci., 1994, Vol. 165, 97.
- [59] T. Yao, Z. Sun, Y. Li, Z. Pan, H. Wei, Y. Xie, M. Nomura, Y. Niwa, W. Yan, Z. Wu, Y. Jiang, Q. Liu, S. Wei, "Insights into Initial Kinetic Nucleation of Gold Nanocrystals", J. Am. Chem. Soc., 2010, Vol. 132 (22), 7696.
- [60] Jörg Polte, R. Kraehnert, M. Radtke, U. Reinholz, H. Riesemeier, A. F. Thünemann, F. Emmerling, "New insights of the nucleation and growth process of gold nanoparticles via in situ coupling of SAXS and XANES", IOP Publishing, *Journal of Physics: Conference Series*, 2010, Vol. 247, 012051.
- [61] J. Polte, T. Torsten Ahner, Friedmar Delissen, Sergey Sokolov, Franziska Emmerling, Andreas F. Thünemann, and Ralph Kraehnert, "Mechanism of Gold Nanoparticle Formation in the Classical Citrate Synthesis Method Derived from Coupled In Situ XANES and SAXS Evaluation", J. Am. Chem. Soc., 2010, Vol. 132, 1296–1301.
- [62] Y. Yang, C. Wang, Y. Hwu, J. Je, "Synchrotron X-ray Synthesis of Colloidal Gold Particles for Drug Delivery", *Materials and Chemistry and Physics*, 2006, Vol. 100, 72-76.
- [63] R. A. Rosenberg, Q. Ma, B. Lai, D. C. Mancini, "Surface photochemistry induced by X-ray irradiation", J. Vac. Sci. Technol. B, 1998, Vol. 16, 3535– 3538.
- [64] Q. Ma, N. Moldovan, D. C. Mancini, R. A. Rosenberg, "Synchrotron radiation-induced, selective-area deposition of gold on polyimide from solution", *Appl. Phys. Lett.*, 2000, Vol. 76, 2014–2016.

- [65] F. Karadas, G. Ertas, E. Ozkaraoglu, S. Suzer, "X-ray-induced production of gold nanoparticles on a SiO2/Si system and in a poly(methyl methacrylate)", *Langmuir*, 2005, Vol. 21, 437–442.
- [66] H. Reiss, "The growth of uniform colloidal dispersions", J. Chem. Phys., 1951, Vol. 19, 482.
- [67] J. Y. Rempel, M. G. Bawendi, K. F. Jensen, "Insights into the kinetics of semiconductor nanocrystal nucleation and growth", J. Am. Chem. Soc., 2009, Vol. 131, 4479-4489.
- [68] V. Privman, "Mechanisms of Diffusional Nucleation of Nanocrystals and Their Self-Assembly into Uniform Colloids", Ann. N. Y. Acad. Sci., 2009, Vol. 1161, 508-525.
- [69] M. Watzky, R. Finke, "Transition metal nanocluster formation kinetic and mechanistic studies. a new mechanism when hydrogen is the reductant: slow, continuous nucleation and fast autocatalytic surface growth", J. Am. Chem. Soc., 1997, Vol. 119, 10382–10400.
- [70] R.G. Finke, in: D.L. Feldheim, C.A. Foss Jr. (Eds.), "Metal Nanoparticles: Synthesis, Characterization, and Applications", Marcel Dekker, New York, 2001 (Chapter 2)
- [71] E. Finney, R. G. Finke, "Nanocluster nucleation and growth kinetic and mechanistic studies: a review emphasizing transition-metal nanoclusters", J. *Colloid Interface Sci.*, 2008, Vol. 317, 351–374.
- [72] P. Georgiev, A. Bojinova, B. Kostova, D. Momekova, T. Bjornholm, K. Balashev, "Implementing atomic force microscopy (AFM) for studying kinetics of gold nanoparticle's growth", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2013, Vol. 434, 154–163.
- [73] A. Kytsya, L. Bazylyak, Y. Hrynda, A. Horechyy, Y. Medvedevdkikh, "The kinetic rate law for the autocatalytic growth of citrate-stabilized silver

nanoparticles", International Journal of Chemical Kinetics, 2015, Vol. 47, 351-360.

- [74] C. Besson, E. Finney, R. Finke, "Nanocluster nucleation, growth, and then agglomeration kinetic and mechanistic studies: a more general, four-step mechanism involving double autocatalysis", *Chem. Mater.*, 2005, Vol. 17 (20), 4925–4938.
- [75] D. T. Nguyen, D. Kim, M. G. So, K. Kim, "Experimental measurements of Gold Nanoparticle Nucleation and Growth by Citrate Reduction of HAuCl4", *Adv. Powder Tech.*, 2010, Vol. 21, 111-118.
- [76] P. Freund, M. Spiro, "Colloidal Catalysis: The Effect of Sol Size and Concentration", J. Phys. Chem., 1985, Vol. 89, 1074.
- [77] J. P. Abid, "Laser Induced Synthesis and Nonlinear Optical Properties of Metal Nanoparticles", Ph.D. Thesis, Ecole Polytechnique Federale de Lausanne, Switzerland, 2003.
- [78] X. Ji, X. Song, J. Li, Y. Bai, W. Yang, X. J. Peng, "Size Control of Gold Nanocrystals in Citrate Reduction: The Third Role of Citrate", Am. Chem. Soc., 2007, Vol. 129, 13939-13948.
- [79] K. Zabetakis, W. E. Ghann, S. Kumar, M. Daniel, "Effect of high gold salt concentrations on the size and polydispersity of gold nanoparticles prepared by an extended Turkevich-Frens Method", *Gold Bull.*, 2012, Vol. 45, 203-211.
- [80] D. Philip, "Synthesis and spectroscopic characterization of gold nanoparticles", *Spectrochim. Acta, Part A*, 2008, Vol. 71, 80.
- [81] S. K. Sivaraman, S. Kumar, V. Santhanam, "Monodisperse sub-10 nm fold nanoparticles by reversing the order of addition in Turkevich method – The role of chloroauric acid", *Journal of Colloid and Interface Science*, 2011, Vol. 361, 543-547.

- [82] W. Patungwasa, J. H. Hodak, "pH tunable morphology of the gold nanoparticles produced by citrate reduction", *Mater. Chem. Phys.*, 2008, Vol. 108, 45.
- [83] Ludovico Cademartin, Geoffrey A. Ozin, "Concepts of Nanochemistry", 2009, Wiley-VCH.
- [84] J. T. G. Overbeek, J. W. Goodwin, "Colloidal Dispersions", 1983, Springer.
- [85] T. Cosgrove, "Colloid Science: Principles Methods and Applications", 2<sup>nd</sup> Edition, 2010, Wiley-Blackwell, Oxford.
- [86] R. J. Hunter, "Foundations of Colloid Science", 1<sup>st</sup> Edition, 1987, Oxford University Press, Oxford.
- [87] J. Israelachvili, "Intermolecular and Surface Forces", 2<sup>nd</sup> Edition, 1991, Academic Press Limited, London.
- [88] A. C. Pierre, "Introduction to Sol Gel Processing", 1998, Kluwer, Norwell, MA.
- [89] J. Polte, "Fundamental Growth Principles of Colloidal Metal Nanoparticles a new perspective", *CrystEngComm*, 2015, Vol. 17, 6809-6830.
- [90] G.D. Parfitt, "Dispersion of Powders in Liquids with Special Reference to Pigments", 1981, Applied Science, London, 1.
- [91] C.J. Brinker and G.W. Scherer, "Sol Gel Science: The Physics and Chemistry of Sol Gel Processing", 1990, Academic Press, San Diego, CA.
- [92] P. C. Hiemenz, R. Rajagopalan, "Principles of Colloid and Surface Chemistry, 3<sup>rd</sup> Edition", 1997, Marcel Dekker, New York.
- [93] B. V. Derjaguin, L. Landau, "Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes", *Acta Physicochim*, URSS, 1941, Vol. 14, 633.

- [94] E. J. W. Verwey, J. T. G. Overbeek, "Theory of the Stability of Lyophobic Colloids", 1948, Elsevier, Amsterdam.
- [95] A. W. Adamson, "Physical Chemistry of Surfaces", Chapter 5, 1990, Wiley, New York.
- [96] M. Smoluchowski, "Zur kinestichen Theorie der Brownschen Molekularbewegung und der Suspensionen", Ann. Phys., 1906, Vol. 21, 756-780.
- [97] E. Hückel, "Die Karaphorese der Kugel", *Phys. Z.*, 1924, Vol. 25, 204-210.
- [98] D. C. Henry, "The Cataphoresis of Suspended Particles. I. The equation of Cataphoresis", Proc. Roy. Soc. London, A, 1931, Vol. 133, 106.
- [99] C. Pfeiffer, C. Rehbock, D. Hühn, C. Carrillo-Carrion, D. J. de Aberasturi, V. Merk, S. Barcikowski, W. J. Parak, "Interaction of Colloidal Nanoparticles with their local environment: the (ionic) nanoenvironment around nanoparticles is different from bulk and determines the physic-chemical properties of the nanoparticles", J. R. Soc. Interface, 2013, 11:20130931.
- [100] T. Kim, C. Lee, S. Joo, K. Lee, "Kinetics of gold nanoparticle aggregation: Experiments and modelling", *Journal of Colloid and Interface Science*, 2008, Vol. 318, 238-243.
- [101] E. J. W. Vervey, J. H. de Boer, "Surface Oxide Films", *Recueil Des Travaux Chimiques Des Pays-Bas*, 1936, Vol. 55, 675-687.
- [102] F. Hofmeister, "Zur Lehre von der Wirkung der Salze Zweite Mittheilung", Arch. Exp. Pathol. Pharm., 1888, 24, 247-260.
- [103] C. Rehbock, V. Merk, L. Gamrad, R. Streubel, S. Barcikowski, "Size Control of Laser-fabricated surfactant-free gold nanoparticles with highly diluted electrolytes and their subsequent bioconjugation", *Phys. Chem. Chem. Phys.*, 2013, Vol. 15, 3057-3067.

- [104] V. Amendola, M. Meneghetti, "Laser ablation Synthesis in Solution and Size Manipulation of Noble Metal Nanoparticles", *Phys. Chem. Chem. Phys.*, 2009, Vol. 11, 3805-3821.
- [105] G. A. Parks, "The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems", *Chem. Rev.*, 1965, Vol. 65, 177-198.
- [106] D. W. Thompson, I. R. Collins, "Electrical-properties of the Gold Aqueous Solution Interface", J. Colloid Interface. Sci., 1992, Vol. 152, 197-204.
- [107] J. P. Sylvestre, S. Poulin, A. V. Kabashin, E. Sacher, M. Meunier, J. H. T. Luong, "Surface Chemistry of Gold Nanoparticles Produced by Laser Ablation in Aqueous Media", J. Phys. Chem. B., 2004, Vol. 108, 16864.
- [108] S. Petersen, A. Barchanski, U. Taylor, S. Klein, D. Rath, S. Barcikowski, "Penetrating-conjugated Gold Nanoparticles – Design of Cell Penetrating Nanomarkers by Femtosecond Laser Ablation", J. Phys. Chem. C., 2011, Vol. 115, 5152-5159.
- [109] G. Charron, D. Hühn, A. Perrier, L. Cordier, C. J. Pickett, T. Nann, W. J. Parak, "On The Use of pH Titration to Quantitatively Characterise Colloidal Nanoparticles", *Langmuir*, 2012, Vol. 28, 15141-15149.
- [110] S. H. Brewer, W. R. Glomm, M. C. Johnson, M. K. Knag, S. Franzen, "Probing BSA Binding to Citrate-Coated Gold Nanoparticles and Surfaces", *Langmuir*, 2005, 21:20, 9303-9307.
- [111] F. Zhang, Z. Ali, F. Amin, A. Feltz, M. Oheim, W. J. Parak, "Ion and pH sensing with Colloidal Nanoparticles: Influence on surface charge and colloidal properties", *ChemPhysChem.*, 2010, Vol. 11, 730-735.
- [112] J. Kunze, I. Burgess, R. Nichols, C. Buess-Herman, J. Lipkowski, "Electrochemical evaluation of citrate adsorption on Au(111) and the stability of citrate-reduced gold colloids", *Journal of Electroanalytical Chemistry*, 2007, Vol. 599, 147-159.

- [113] N. E. Hoskin, "Solution to the Poisson-Boltzmann equation for the potential distribution in double layer of a single spherical colloidal particle", *Trans. Faraday Soc.*, 1953, Vol. 49, 1471-1477.
- [114] S. L. Brenner, R. E. Roberts, "Variational Solution of Poisson-Boltzmann equation for a spherical colloidal particle", J. Phys. Chem., 1973, Vol. 77, 2367-2370.
- [115] L. R. White, "Approximate Analytic Solution of The Poisson-Boltzmann equation for a Spherical Colloidal Particle", J. Chem. Soc. Faraday Trans. II, 1977, Vol. 73, 577-596.
- [116] C. N. Patra, "Molecular Solvent Model of Spherical Electric Double Layers: A Systematic Study by Monte Carlo Simulations and Density Functional Theory", J. Phys. Chem. B, 2009, Vol. 113, 13980-13987.
- [117] C. N. Patra, "Structure of Spherical Electric Double Layers Containing Mixed Electrolytes: a Systematic study by Monte Carlo Simulations and Density Functional Theory", J. Phys. Chem. B, 2010, Vol. 114, 10550-10557.
- [118] D. V. Talapin, A. L. Rogach, M. Haase, and H. Weller, "Evolution of an Ensemble of Nanoparticles in a Colloidal Solution: Theoretical Study", J. Phys. Chem. B, 2001, Vol. 105, 12278-12285.
- [119] T. Itakura, T. Torigoe, K. Esumi, "Preparation and Characterisation of Ultrafine Metal Particles in Ethanol by UV irradiation Using a Photoinitiator", *Langmuir*, 1995, Vol. 11, 4129-4134.
- [120] K. Esumi, K. Matsuhisa, K. Torigoe, "Preparation of Rodlike Gold Particles by UV Irradiation using Cationic Micelles as a Template", *Langmuir*, 1995, Vol. 11, 3285-3287.
- [121] A. Henglein, "Radiolytic preparation of Ultrafine colloidal gold particles in aqueous media", *Langmuir*, 1999, Vol. 15, 6738-6744.

- [122] A. Henglein, D. Meisel, "Radiolytic control of the size of colloidal gold nanoparticles", *Langmuir*, 1998, Vol. 14, 7392-7396.
- [123] A. Pal, "Photoinitiated gold sol generation in aqueous Triton X-100 and its analytical application for spectrophotometric determination of gold", *Talanta*, 1998, Vol. 46, 583-587.
- [124] A. Pal, "Photochemical formation of gold nanoparticles in aqueous Triton X-100 and its applications in SERS Spectroscopy", *Curr. Sci.*, 1998, Vol. 74, 14-16.
- [125] T. K. Sau, A. Pal, N. R. Jana, Z. L. Wang, T. Pal, "Size controlled synthesis of gold nanoparticles using photochemically prepared seed particles", J. *Nanopar. Res.*, 2001, Vol. 3, 257-261.
- [126] G. Schmid, "Clusters and Colloids metals in the embryonic state", *Chem. Rev.*, 1992, Vol. 92, 1709-1727.
- [127] K. Mallick, Z. L. Wang, T. Pal, "Seed-mediated successive growth of Gold particles accomplished by UV irradiation: a Photochemical approach for sizecontrolled synthesis", *Journal of Photochemistry and Photobiology A: Chemistry*, 2001, Vol. 140, 75-80.
- [128] M. Anbar, "The reactions of hydrated electrons with inorganic compounds", *Quart. Revs.*, 1968, Vol. 4, 578-598.
- [129] N. Basco, G. A. Kenney, D. C. Walker, "Formation and photodissociation of hydrated electron dimmers", J. Chem. Soc. D: Chem. Comm., 1969, Vol. 16, 917-918.
- [130] J. W. Boyle, J. A. Ghormley, C. J. Hochanadel, J. F. Riley, "Production of hydrated electrons by flash photolysis of liquid water with light in the first continuum", *J. Phys. Chem.*, 1969, Vol. 73(9), 2886-2890.

- [131] A. Pal, S. K. Ghosh, K. Esumi, T. Pal, "Reversible Generation of Gold Nanoparticle aggregates with changeable Interparticle Interactions by UV Photoactivation", *Langmuir*, 2004, Vol. 20, 575-578.
- [132] S. A. Dong, S. X. Wang, Y. K. Pan, "The New Progress on Material Science and Engineering", 2003, Beijing Publishing.
- [133] S. A. Dong, S. P. Zhou, "Photochemical synthesis of colloidal gold nanoparticles", *Material Science and Engineering B*, 2007, Vol. 140, 153-159.
- [134] S. Yang, T. Zhang, L. Zhang, S. Wang, Z. Yang, B. Ding, "Continuous synthesis of Gold Nanoparticles and Nanoplates with controlled size and shape under UV irradiation", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2007, Vol. 296, 37-44.
- [135] B. Ding, S. Yang, Y. Wang, Q. Wang, R. Zhang, "UV Irradiation Induced Formation of Au Nanoparticles at Room Temperature: The case of pH Values", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2007, Vol. 301, 174-183.
- [136] J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot, A. Plech, "Turkevich Method for Gold Nanoparticle Synthesis Revisited", J. Phys. Chem. B, 2006, Vol. 110 (32), 15700.
- [137] M. A. Uppal, A. Kafizas. M. B. Ewing, I. P. Parkin, "The effect of initiation method on the size, monodispersity and shape of gold nanoparticles formed by the Turkevich Method", *New J. Chem.*, 2010, Vol. 34, 2906-2914.
- [138] E. Gachard, H. Remita, J. Khatouri, B. Keita, L. Nadjo, J. Belloni,
   "Radiation-induced and chemical formation of gold clusters", *New J. Chem.*, 1998, Vol. 22, 1257-1265.
- [139] J. Belloni, M. Mostafavi, H. Remita, J. L. Marignier, M. O. Delcourt, "Radiation-induced synthesis of mono- and multi-metallic clusters and nanocolloids", *New J. Chem.*, 1998, Vol. 22, 1239-1255.

- [140] K. D. N. Vo, C. Kowandy, L. Dupont, X. Coqueret, N. Q. Hien, "Radiation synthesis of chitosan stabilised gold nanoparticles comparison between e<sup>-</sup> beam and γ irradiation", *Radiation Physics and Chemistry*, 2014, Vol. 94, 84.
- [141] N. Hanžić, T. Jurkin, A. Maksimović, M. Gotić, "The synthesis of gold nanoparticles by a citrate-radiolytical method", *Radiation Physics and Chemistry*, 2015, Vol. 106, 77-82.
- [142] U. Kreibig, M. Vollmer, "Optical properties of metal clusters", Springer series in material science 25, 1995, Springer-Verlag, New York.
- [143] G. Mie, "Beiträge zur Optik trüber Medien", Ann. Phys., 1908, Vol. 25, 377.
- [144] U. Kreibig, P. Zacharias, "Surface plasma resonances in small spherical silver and gold particles", *Zeitschrift für Physik*, 1970, Vol. 231, 128.
- [145] F. L. Pedrotti, L. S. Pedrotti, L. M. Pedrotti, "Introduction to Optics", 3<sup>rd</sup> edition, 2007, Pearson Addison Wesley, San Francisco.
- [146] C. F. Bohren, D. R. Huffman, "Absorption and scattering of light by small particles", 1983, Wiley, New York.
- [147] U. Kreibig, B. Schmitz, H. D. Breuer, "Separation of plasmon-polariton modes of small metal particles", *Phys. Rev. B*, 1987, Vol. 36, 5027.
- [148] X. Huang, P. K. Jain, I. H. El-Sayed, M. A. El-Sayed, "Gold nanoparticles: interesting optical properties and recent applications in cancer diagnostics and therapy", *Nanomedicine* (Lond.), 2007, Vol. 2(5), 681.
- [149] X. Huang, M. A. El-Sayed, "Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy", *Journal of Advanced Research*, 2010, Vol. 1 (1), 13-28.
- [150] J. Turkevich, G. Garton, P. C. Stevenson, "The color of colloidal gold", *Journal of Colloid Science*, 1954, Vol. 9 (1), 26–35.

- [151] A. V. Gaikwad, P. Verschuren, E. Eiser, G. J. Rothenberg, "A Simple Method for Measuring the Size of Metal Nanoclusters in Solution", *J. Phys. Chem. B*, 2006, Vol. 110 (35), 17437-17443.
- [152] P. N. Njoki, I. S. Lim, D. Mott, H. Park, B. Khan, S. Mishra, R. Sujakumar, J. Luo, C. J. Zhong, "Size correlation of optical and spectroscopic properties for gold nanoparticles", *J. Phys. Chem. C*, 2007, Vol. 111, 14664-14669.
- [153] D. P. Sprunken, H. Omi, K. Furukawa, H. Nakashima, I. Sychugov, Y. Kobayashi, K. Torimitsu, "Influence of the Local Environment on Determining Aspect-Ratio Distributions of Gold Nanorods in Solution Using Gans Theory", J. Phys. Chem. C, 2007, Vol. 111, 14299-14306.
- [154] K. S. Lee, M. A. El-Sayed, "Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition", J. Phys. Chem. B, 2006, Vol. 110, 19220-19225.
- [155] K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, "The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment", J. Phys. Chem. B, 2003, Vol. 107, 668-677.
- [156] H. Hovel, S. Fritz, A. Hilger, U. Kreibig, M. Vollmer, "Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping", *Phys. Rev. B*, 1993, Vol. 48, 18178-18188.
- [157] T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Spirkl, J. Feldmann, "Surface-Plasmon Resonances in Single Metallic Nanoparticles", *Phys. Rev. Lett.*, 1998, Vol. 80, 4249-4252.
- [158] P. K. Jain, M. A. El-Sayed, "Universal Scaling of Plasmon Coupling in Metal Nanostructures: Extension from Particle Pairs to Nanoshells", *Nano Lett.* 2007, Vol. 7, 2854-2858.
- [159] T. J. Normal Jr., C. D. Grant, D. Magana, J. Z. Zhang, J. Liu, D. Cao, F. Bridges, A. van Buuren, "Near-Infrared Absorption of Gold Nanoparticle Aggregates", J. Phys. Chem. B, 2002, Vol. 106, 7005-7012.

- [160] V. Amendola, M. Meneghetti, "Size Evaluation of Gold Nanoparticles by UV-vis Spectroscopy", J. Phys. Chem. C, 2009, Vol. 113, 4277-4285.
- [161] X. Liu, M. Atwater, J. Wang, Q. Huo, "Extinction Coefficient of Gold Nanoparticles with Different Sizes and Different Capping Ligands", *Colloids* and Surfaces B: Biointerfaces, 2007, Vol. 58, 3-7.
- [162] W. Haiss, N. T. K. Thanh, J. Aveyard, D. G. Fernig, "Determination of Size and Concentration of Gold Nanoparticles from UV-Vis Spectra", Anal. Chem., 2007, Vol. 79, 4215-4221
- [163] G. Yin, S. Y. Wang, M. Xu, L. Y. Chen, "Theoretical Calculation of the Optical Properties of Gold Nanoparticles", *Journal of the Korean Physical Society*, 2006, Vol. 49 (5), 2108-2111.
- [164] M. Alsawafta ,M. Wahbeh, V. V. Truong, "Simulated Optical Properties of Gold Nanocubes and Nanobars by Discrete Dipole Approximation", *Journal* of Nanomaterials, 2012, Article ID 283230.
- [165] Chris D. Geddes, "Reviews in Plasmonics 2010", 2012. Springer-Verlag, New York.
- [166] J. E. Hansen, L. D. Travis, "Light scattering in planetary atmospheres", *Space Science Reviews*, 1974, Vol. 16, 527.
- [167] S. W. Chu, T. Y. Su, R. Oketani, Y. T. Huang, H. Y. Wu, Y. Yonemaru, M. Yamanaka, H. Lee, G. Y. Zhuo, M. Y. Lee, S. Kawata, K. Fujita, "Measurement of a Saturated Emission of Optical Radiation from Gold Nanoparticles: Application to an Ultrahigh Resolution Microscope", *Phys. Rev. Lett.*, 2014, Vol. 112, 017402.
- [168] H. Lee, K. Y. Li, Y. T. Huang, P. T. Shen, G. Deka, R. Oketani, Y. Yonemaru, M. Yamanaka, K. Fujita, S. W. Chu, "Measurement of Scattering Nonlinearities from a Single Plasmonic Nanoparticle", *J. Vis. Exp.*, 2016, Vol. 107, e53338, doi:10.3791/53338.

- [169] G. Schmid, "Large Clusters and Colloidal Metal in the Embryonic State", *Chem. Rev.*, 1992, Vol. 92 (8), 1709.
- [170] P. Ramasamy, S. Guha, E. S. Shibu, T. S. Sreeprasad, S. Bag, A. Banerjee, and T. Pradeep, "Size tuning of Au nanoparticles formed by electron beam irradiation of Au25 quantum clusters anchored within and outside of dipeptide nanotubes", *J. Mater. Chem.*, 2009, Vol. 19, 8456-8462.
- [171] Y. Chen, Y. Huang, N. Liu, J. Su, L. Li, Y. Gao, "Fabrication of nanoscale Ga balls via a Coulomb explosion of microscale silica-covered Ga balls by TEM electron-beam irradiation", *Scientific Reports*, 2015, Vol. 5, No. 11313.
- [172] A. Einstein, "Theorie Der Opaleszenz von Homogenen Flüssigkeitsgemischen in der Nähe des Kritischen Zustandes", Annalen der Physik, 1910, Vol. 33, 1275.
- [173] B. Chu, "Laser Light Scattering", 2<sup>nd</sup> Ed., 1991, Academic Press, New York.
- [174] R. Pecora, "Dynamic Light Scattering Applications of Photon Correlation Spectroscopy", 1985, Plenum Press, New York.
- [175] Particle Size Analysis Photon Correlation Spectroscopy, ISO document, ISO 13321:1996, Part 8, 1996
- [176] W. Tscharnuter, "Photon Correlation Spectroscopy in Particle Sizing, Encyclopedia of Analytical Chemistry", 2000, John Wiley & Sons Limited, Chichester.
- [177] R. J. Glauber, "Coherent and Incoherent States of the Radiation Field", Phys. Rev. 1963, Vol. 131, 2766.
- [178] A. J. F. Siegert, "On the Fluctuations in Signals Returned by Many Independently Moving Scatterers", *Rad. Lab. Rep.* 465, 1943, Massachusetts Institute of Technology, Boston.

- [179] N. C. Ford, "Theory and Practice of Photon Correlation Spectroscopy, in Measurement of Suspended Particles by Quasi-elastic Light Scattering", 1983 Wiley-Interscience, New York.
- [180] N. Ostrowsky, D. Sornett, P. Parker, E. R. Pike, "Exponential Sampling Method for Light-scattering Polydispersity", *Opt. Acta*, 1980, Vol. 27, 83.
- [181] S. W. Provencher, "A Constrained Regularization Method for Inverting Data Represented by Linear Algebraic or Integral Equations", *Computer Physics Communications*, 1982, Vol. 27, 213.
- [182] S. W. Provencher, "CONTIN: A General Purpose Constrained Regularization Program for Inverting Noisy Linear Algebraic and Integral Equations", *Computer Physics Communications*, 1982, Vol. 27, 229.
- [183] B. Weiner, W. Tscharnuter, A. Banerjee, "Developing Fiber Optic Probes for Noninvasive Particle Size Measurements in Concentrated Suspensions using DLS", 1996, Brookhaven Corp. Internal Memorandum.
- [184] W. van Megen, S. M. Underwood, "Dynamic Light Scattering Study of Glasses of Hard Colloid Spheres", *Phys. Rev. E*, 1993, Vol. 47 (1), 248.
- [185] R. D. Neuman, M. A. Jones, N. F. Zhou, "Photon Correlation Spectroscopy Applied to Hydrometallurgical Solvent Extraction Systems", *Coll. Surf.*, 1990, Vol. 46, 45.
- [186] R. Radünz, D. Rings, K. Kroy, F. Cichos, "Hot Brownian Particles and Photothermal Correlation Spectroscopy", J. Phys. Chem. A Lett., 2009, Vol. 113, 1674.
- [187] P. M. R. Paulo, A. Gaiduk, F. Kulzer, S. F. G. Krens, H. P. Spaink, T. Schmidt, M. Orrit, "Photothermal Correlation Spectroscopy of Gold Nanoparticles in Solution", *J. Phys. Chem. C*, 2009, Vol. 113, 11451.

- [188] B. Khlebtsov, N. Khlebtsov, "On the Measurement of Gold Nanoparticle Sizes by the Dynamic Light Scattering method", *Colloid J.*, 2011, Vol. 73 (1), 118.
- [189] M. Gadogbe, S. M. Ansar, G. He, W. E. Collier, J. Rodriguez, D. Liu, I. W. Chu, D. Zhang, "Determination of Colloidal Gold Nanoparticle Surface Areas, Concentrations, and Sizes through Quantitative Ligand Adsorption", Anal. Bioanal. Chem., 2013, Vol. 405, 413.
- [190] Hong Du, "Mie-scattering Calculation", Appl. Optics, 2004, Vol. 43(9), 1951.
- [191] P. Laven, "Simulation of Rainbows, Coronas, and Glories by use of Mie Theory", Appl. Opt., 2003, Vol. 42 (3), 436-444.
- [192] J. A. Lock, P. Laven, "Mie scattering in the time domain. Part I & II. The role of surface waves and diffraction", *Journal of Optical Society of America A*, 2011, Vol. 28 (6), 1086-1106.
- [193] J. A. Lock, P. Laven, "Understanding Light Scattering by a Coated Sphere. Part 1: Theoretical Considerations", *Journal of Optical Society of America A*, 2012, Vol. 29 (8), 1489-1497.
- [194] J. A. Lock, P. Laven, "Understanding Light Scattering by a Coated Sphere. Part 2: Time Domain Analysis", *Journal of Optical Society of America A*, 2012, Vol. 29 (8), 1498-1507.
- [195] P. B. Johnson, R. W. Christy, "Optical Constants of the Noble Metals", *Phys. Rev.* B, 1972, 6, 4370-4380.
- [196] P. Schiebener, J. Straub, J. M. H. Levelt Sengers, and J.S. Gallagher, "Refractive index of water and steam as function of wavelength, temperature and density", J. Phys. Chem. Ref. Data 19, 1990, 677.
- [197] D. Segelstein, "The complex refractive index of water" M.S. Thesis, 1981, Univ. Missouri, United States.

- [198] C. J. Sansonetti, J. Reader, "Spectrum and energy levels of singly-ionized mercury (Hg II)", *Phys. Scr.*, 2001, Vol. 63, 219–242.
- [199] E. C. Benck, J. E. Lawler, and J. T. Dakin, "Lifetimes, branching ratios, and absolute transition probabilities in Hg I", J. Opt. Soc. Am. B, 1989, Vol. 6, 11–22.
- [200] BLB datasheet, Osram GmBH, 2016
- [201] D. C. Morton, "Atomic data for resonance absorption lines II. Wavelengths longward of the Lyman limit for heavy elements", *Astrophys. J., Suppl. Ser.* 2000, Vol. 130, 403–436; Erratum: 2001, Vol. 132, 411.
- [202] G. M. Hale, M. R. Querry, "Optical constants of water in the 200nm to 200μm wavelength region," *Applied Optics*, 1973, Vol. 12, 555-563.
- [203] S. Boonsuya, W. Chachai, S. Tancharakorn, "Photon flux density of Siam Photon Source in soft X-ray wavelengths", *Thai J. Phys.*, 2010, Vol. 5, 152.
- [204] S. Soontaranon, S. Rugmai, "Small Angle X-ray Scattering at Siam Photon Laboratory", *Chinese J. Phys.*, 2012, Vol. 50 (2), 204-210.
- [205] I. J. Breßler, J. Kohlbrecherb, A. F. Thunemanna, "SASfit: a tool for smallangle scattering data analysis using a library of analytical expressions", J. *Appl. Cryst.*, 2015, Vol. 48, 1587–1598.
- [206] S. Rahman, "Size and Concentration Analysis of Gold Nanoparticles With Ultraviolet-Visible Spectroscopy", Undergraduate Journal of Mathematical Modeling: One + Two, 2016, Vol. 7 (1), Article 2.
- [207] D. Paramelle, A. Sadovoy, S. Gorelik, P. Free, J. Hobleya and D. G. Fernig, "A rapid method to estimate the concentration of citrate capped silver nanoparticles from UV-visible light spectra", *Analyst*, 2014, Vol. 139, 4855.
- [208] Jing Shang and Xiaohu Gao, "Nanoparticle Counting: Towards Accurate Determination of the Molar Concentration", *Chem Soc Rev.*, 2014, Vol. 43 (21), 7267–7278.

- [209] J. Zheng, C. Zhou, M. X. Yu, J. B. Liu, "Different sized luminescent gold nanoparticles", *Nanoscale*, 2012, Vol. 14, 4073.
- [210] M. A. Yurkin, D. de Kanter, A. G. Hoekstra, "Accuracy of the discrete dipole approximation for simulation of optical properties of gold nanoparticles", J. *Nanophoton.*, 2010, Vol. 4 (1), 041585.
- [211] Xi-bin Xu, Zao Yi, Xi-bo Li, Yu-ying Wang, Xing Geng, Jiang-shan Luo, Bing-chi Luo, You-gen Yi, and Yong-jian Tang, "Discrete Dipole Approximation Simulation of the Surface Plasmon Resonance of Core/Shell Nanostructure and the Study of Resonance Cavity Effect", *J. Phys. Chem. C*, 2012, Vol. 116 (45), 24046–24053.
- [212] Gang Yin, Song-You Wang, Ming Xu and Liang-Yao Chen, "Theoretical Calculation of the Optical Properties of Gold Nanoparticles", *Journal of the Korean Physical Society*, 2006, Vol. 49 (5), 2108-2111.
- [213] M. Alsawafta, M. Wahbeh, and Vo-Van Truong, "Simulated Optical Properties of Gold Nanocubes and Nanobars by Discrete Dipole Approximation", *Journal of Nanomaterials*, 2012, Article ID 283230 (9).
- [214] V. A. Bogatyrev, L. A. Dykman, B. N. Khlebtsov, N. G. Khlebtsov, "Measurement of Mean Size and Evaluation of Polydispersity of Gold Nanoparticles from Spectra of Optical Absorption and Scattering", *Optics & Spectroscopy*, 2004, Vol. 96 (1), 128.
- [215] E. L. Crow, K. Shimizu, "Lognormal Distributions: Theory and Applications", 1987, CRC Press, 15.
- [216] S. V. Jenkins, Haiou Qu, T. Mudalige, T. M. Ingle, Rongrong Wang, Feng Wang, P. C. Howard, Jingyi Chen, Yongbin Zhang, "Rapid determination of plasmonic nanoparticle agglomeration status in blood", *Biomaterials*, 2015, Vol. 51, 226–237.

- [217] Rose M. Cooper, "Behavior of Gold Nanoparticles in Physiological Environment and the Role of Agglomeration and Fractal Dimension", Master Thesis, 2015, Wright State University, United States.
- [218] A. N. Bashkatov , E. A. Genina, "Water refractive index in dependence on temperature and wavelength: a simple approximation", 394 Proc. of SPIE Vol. 5068, Saratov Fall Meeting 2002: Optical Technologies in Biophysics and Medicine IV, 2003
- [219] T. Hendel, M. Wuithschick, F. Kettemann, A. Birnbaum, K. Rademann, and J. Polte, "In Situ Determination of Colloidal Gold Concentrations with UV–Vis Spectroscopy: Limitations and Perspectives", *Anal. Chem.*, 2014, Vol. 86 (22), 11115–11124.
- [220] M. S. Affandi, N. Bidin, M. Abdullah, M. S. Abd. Aziz, M. Al-Azawi, W. Negroho, "In situ measurement of gold nanoparticle production", J. Nanophotonics, 2015, Vol. 9, 093089-1.
- [221] R. D. Murley, "Mie Theory of Light Scattering—Limitations on Accuracy of Approximate Methods of Computation", J. Phys. Chem., 1960, Vol. 64 (1), 161–162.
- [222] M. Quinten, "Limitations of Mie's Theory Size and Quantum Size Effects in Very Small Nanoparticles", Optical Properties of Nanoparticle Systems: Mie and beyond, 2011, Wiley-VCH Verlag.
- [223] J. Tuoriniemi, Ann-Cathrin J. H. Johnsson, J. P. Holmberg, S. Gustafsson, J. A Gallego-Urrea1, E. Olsson, J. B. C. Pettersson, and M. Hassellöv, "Intermethod comparison of the particle size distributions of colloidal silica nanoparticles", Science and Technology of Advanced Materials, 2014, Vol. 15 (3), 312.
- [224] H. C. van de Hulst, "Light scattering by small particles", 1981, John Dover Publications, New York.

- [225] H. E. Toma, V. M. Zamarion, S. H. Toma, K. Araki, "The Coordination Chemistry at Gold Nanoparticles", J. Braz. Chem. Soc., 2010, Vol. 21 (7) 1158-1176.
- [226] C. M. Hoo, N. Starostin, P. W. Martha, L. Mecartney, "A comparison of atomic force microscopy (AFM) and dynamic light scattering (DLS) methods to characterize nanoparticle size distributions", *J. Nanopart. Res.*, 2008, Vol. 10 (Suppl. 1): 89.
- [227] J. Tuoriniemi, Ann-Cathrin J. H. Johnsson, J. P. Holmberg, S. Gustafsson, J. A. Gallego-Urrea, E. Olsson, Jan B. C. Pettersson, M. Hassellöv, "Intermethod comparison of the particle size distributions of colloidal silica nanoparticles", *Science and Technology of Advanced Materials*, 2014, Vol. 15 (3), 035009.
- [228] A. R. Podaa, A. J. Bednara, A. J. Kennedya, A. Harmona, M. Hull, D. M. Mitranod, J. F. Ranvilled, J. Steevensa, "Characterization of silver nanoparticles using flow-field flow fractionation interfaced to inductively coupled plasma mass spectrometry", *Journal of Chromatography A*, 2011, Vol. 1218: 27, 4219-4225.
- [229] G. C. Bushnell, Y. D. Yan, D. Woodfield, J. Raper, R. Amal, "On Techniques for The Measurement of The Mass Fractal Dimension of Aggregates", *Adv. Colloid Interface Sci.*, 2002, Vol. 95 (1), 1.
- [230] G. Beaucage, H. K. Kammler, S. E. Pratsinis, "Particle Size Distributions From Small-angle Scattering Using Global Scattering Functions", J. App. Cryst., 2003, Vol. 37, 523.
- [231] C. Forbes, M. Evans, N. Hastings, B. Peacock, "Statistical Distributions", 4th Ed., 2011, John Wiley and Sons Inc., New York, pp. 131.
- [232] Z. Khan, T. Singh, J. I. Hussain, A. A. Hashmi, "Au(III)–CTAB reduction by ascorbic acid: Preparation and characterization of gold nanoparticles", *Colloids Surf. B: Biointerfaces*, 2013, Vol. 104, 11–17.

- [233] B. R. Pauw, "Everything SAXS: small-angle scattering pattern collection and correction", J. Phys.: Condense Matter, 2013, Vol. 25 (38), 383201.
- [234] C. Vonk, "On two methods of determination of particle size distribution functions by means of small-angle X-ray scattering," *Journal of Applied Crystallography*, 1976, Vol. 9 (6), 433–440.
- [235] O. Glatter, "Determination of particle-size distribution functions from smallangle scattering data by means of the indirect transformation method," *Journal of Applied Crystallography*, 1980, Vol. 13 (1), 7–11.
- [236] H. G. Krauthaeuser, W. Heitmann, A. Kops, and G. Nimtz, "Small-angle Xray scattering analysis of particle-size distributions of mesoscopic metallic systems with consideration of the particle form factor," *Journal of Applied Crystallography*, 1994, Vol. 27 (4), 558–562.
- [237] A. Agbabiaka, M. Wiltfong, and C. Park, "Small Angle X-Ray Scattering Technique for the Particle Size Distribution of Nonporous Nanoparticles", *Journal of Nanoparticles*, 2013, Article ID 640436.
- [238] K. R. Brown, M. J. Natan, "Hydroxylamine Seeding of Colloidal Au Nanoparticles in Solution and on Surfaces", *Langmuir*, 1998, Vol. 14 (4), 726-728.
- [239] M. Tran, R. DePenning, M. Turner, and S. Padalkar, "Effect of citrate ratio and temperature on gold nanoparticle size and morphology", *Materials Research Express*, 2016, Vol. 3, 105027.
- [240] Haibing Xia, Shuo Bai, Jürgen Hartman, and Dayang Wang, "Synthesis of Monodisperse Quasi-Spherical Gold Nanoparticles in Water via Silver(I)-Assisted Citrate Reduction", *Langmuir*, 2010, Vol. 26 (5), 3585-3589.
- [241] X. Liu, J. G. Worden, Q. Huo, J. P. Brennan, "Kinetic study of gold nanoparticle growth in solution by Brust-Schiffrin reaction", J. Nanosci. Nanotechnol., 2006, Vol. 6 (4), 1054-1059.

- [242] Y. Inoue, Y. Tsutamoto, D. Muko, K. Nanamura, T. Sawada, Y. Niidome, "Stepwise preparation of spherical gold nanoparticles passivated with cationic amphiphiles", *Analytical Sciences*, 2016, Vol. 32, 875.
- [243] Karolina Sokołowska, "Surface modification of gold nanoparticles and nanoclusters", MSc. Thesis, 2016, University of Jyväskylä, Finland.
- [244] L. Bentea, M. A. Watzky, and R. G. Finke, "Sigmoidal Nucleation and Growth Curves Across Nature Fit by the Finke–Watzky Model of Slow Continuous Nucleation and Autocatalytic Growth: Explicit Formulas for the Lag and Growth Times Plus Other Key Insights", J. Phys. Chem. C., 2017, Vol. 121 (9), 5302-5312.
- [245] M. R. Ivanov, H. R. Bednar, and A. J. Haes, "Investigations of the Mechanism of Gold Nanoparticle Stability and Surface Functionalization in Capillary Electrophoresis", ACS Nano, 2009, Vol. 3 (2), 386-394.
- [246] E. J. Devid, P. N. Martinho, M. V. Kamalakar, Ú. Prendergast, C. Kübel, T. Lemma, Jean-François Dayen, T. E. Keyes, B. Doudin, M. Ruben, and S. J. van der Molen, "The influence of molecular mobility on the properties of networks of gold nanoparticles and organic ligands", *Beilstein J. Nanotechnol.*, 2014, Vol. 5, 1664-1674.
- [247] P. Hirschle, T. Preiß, F. Auras, A. Pick, J. Völkner, D. Valdepérez, G. Witte, W. J. Parak, J. O. Rädlerb, and S. Wuttke, supplementary notes for "Exploration of MOF nanoparticle sizes using various physical characterization methods is what you measure what you get?", *CrystEngComm*, 2016, Vol. 18 (23), 4359-4368.
- [248] C. Zhang, L. Wang, F. Wu, N. Deng, "Quantitation of hydroxyl radicals from UV photolysis of Fe(III)-citrate complexes in aerobic water", *Environ. Sci. Pollut. Res. Int.*, 2006, Vol. 13 (3), 156-160.

- [249] J. M. Gorham, R. I. MacCuspie, K. L. Klein, D. H. Fairbrother, R. D. Holbrook, "UV-induced photochemical transformations of citrate-capped silver nanoparticle suspensions", J. Nanopart. Res., 2012, Vol. 14, 1139.
- [250] A. A. Moya, "Theory of the formation of the electric double layer at the ion exchange membrane-solution interface", *Phys. Chem. Chem. Phys.*, 2015, Vol. 17 (7), 5207-5218.
- [251] N. L. Johnson; S. Kotz; N. Balakrishnan, "Continuous Univariate Distributions, Volume 1", 1994, Chapter 16, New York: Wiley.
- [252] A. R. Poda, A. J. Kennedy, M. F. Cuddy, A. J. Bednar, "Investigations of UV photolysis of PVP-capped silver nanoparticles in the presence and absence of dissolved organic carbon", *J. Nanopar. Res.*, 2013, Vol. 15, 1673.
- [253] D. M. Black, C. M. Crittenden, J. S. Brodbelt, and R. L. Whetten, "Ultraviolet Photodissociation of Selected Gold Clusters: Ultraefficient Unstapling and Ligand Stripping of Au<sub>25</sub>(pMBA)<sub>18</sub> and Au<sub>36</sub>(pMBA)<sub>24</sub>", J. Phys. Chem. Lett., 2017, Vol. 8 (6), 1283-1289.
- [254] P. F. Dunn, "Measurement and Data Analysis for Engineering and Science", 2005, New York: McGraw–Hill.
- [255] M. Haahr, S. Haahr, "Random Noise Generator: Random strings set from 1 to 10000", retrieved from www.random.org, 13 October 2017.
- [256] R. Weichert, "In-situ Characterization of Nanoparticles by Polarized Light Scattering and Laser-Induced Incandescence", KONA Powder and Particle Journal, 1998, Vol. 16, 207-215.
- [257] A. Gogoi, G. A. Ahmed, A. Choudhury, "Nanoparticle Size Characterisation by Laser Light Scattering", *Ind. J. Phys.*, 2009, Vol. 83 (4), 473-477.
- [258] B. Santra, M. N. Shneider, R. Car, "In situ Characterization of Nanoparticles Using Rayleigh Scattering", *Scientific Reports*, 2017, Vol. 7, 40230.

### XIX List of Publications

- J. C. Chong, S. L. Lee, N. Bidin, "Characterisation of Photochemically Initiated Gold Nanoparticles Synthesized via Incoherent Ultraviolet Radiation", *Jurnal Teknologi*, 78(3-2), 165-170, 2016.
- J. C. Chong, N. Bidin, S. L. Lee, M. M. Sanagi, S. Rugmai, S. Soontaranon, "Optical Extinction Coefficients of Gold Nanoparticle Aggregates by Small Angle X-ray Scattering (SAXS)", *Journal of Physical Science*, 28 (1), 61-71, 2017.
- J. C. Chong, S. L. Lee, N. Bidin, "Technical Note: Optical Extinction Coefficient of Polydisperse Spherical Gold Nanoparticles in Water", *Malaysian Journal of Fundundamental and Applied Science*, 12 (4), 121-125, 2016.