CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Nickel

2.1.1 Chemistry and application of nickel

Nickel (Ni) is a chemical element located in the first transition series group VIII of the periodic table with atomic weight and atomic number of 58.71 and 28, respectively. An environmental nickel (Ni), occurred generally in soils and volcanic dust, is composed of five stable isotopes i.e. ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and ^{64}Ni which ^{58}Ni (68.27%) is the most abundant. For physical properties, nickel is a silvery-white and slight golden lustrous metal with melting point at 1453 °C. Moreover, the useful properties of Ni are relatively low thermal and electrical conductivities, high resistance to corrosion and oxidation, excellent strength and toughness at elevated temperatures, magnetic capability, and comfortable alloy formation with several metals [4].

Because of unique physical and chemical properties, metallic nickel and its intermetallic compound are highly significant in the modern industry. The major use of nickel is the preparation of alloys in many fields [5] such as

- Stainless steel

- Rechargeable batteries

- Coinage

- Magnets

- Electric guitar strings

- Microphone capsules

- Special alloys

- Foundry products

- Plating products

- Catalysts and other chemicals

2.1.2 Nickel in gold plating solutions [6]

Acid gold plating solutions were initially developed for the fabrication of electronics, particularly for edge contact areas in printed circuit boards. Since then, acid gold plating solutions have been widely used in jewelry applications because of the high corrosion resistances of the deposits and the uniform brightness of coatings. The acid gold electrolytes containing nickel or iron were used for co-depositing gold-iron or gold-nickel on the substrate. However, gold-nickel solution is more attractive than gold-iron solution because of greater properties in hardness of the coatings and good resistance to corrosion of the costume jewelry. For the electroplating procedure, nickel is initially established as a barrier layer on the substrate material followed by the deposition of gold on top of nickel barrier.
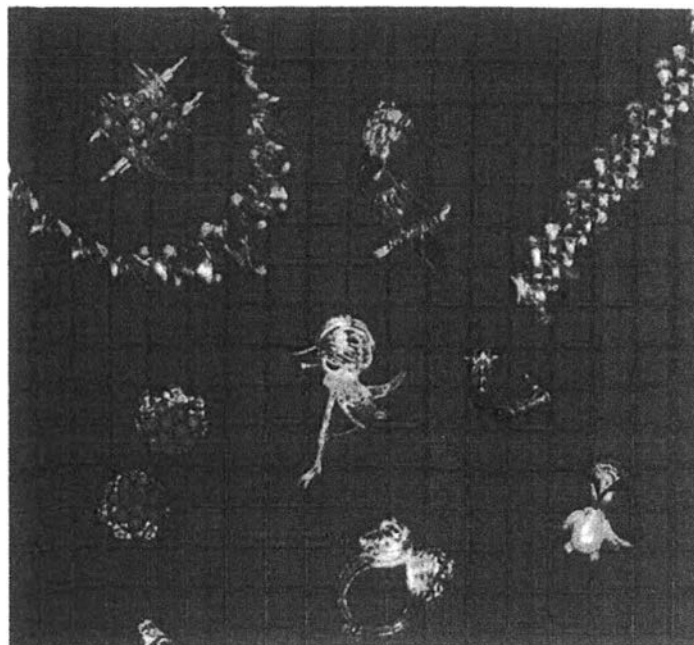
Figure 2.1 Gold-plated costume jewelry (5 μm gold-cobalt on nickel-plated tin alloy).

2.1.3   Environmental exposure

According to the high popularity in the use of nickel in a wide range of industrial production, the high consumption of nickel-containing products unsurprisingly leads to a high tendency of environmental pollution. Nickel might be released via ambient air, water, and soil to the environmental zone [7]. Surely, it can then contaminate in fruits, vegetables, food and drinking water, linking to the increase of human illness and hospitalization. The safe intake of Ni level should be controlled in food (0.1–0.3 mg Ni/day), drinking water (less than 0.02 mg Ni/day) and ambient air (0.0001–0.0007 mg Ni/day) [8]. In jewelry, the European Union (EU) established the upper limit of nickel released to be 0.2 mg Ni/cm^2/week. Furthermore, the maximum limits of nickel in environmental sample have been established by the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) to be 0.07 and 0.04 ppm, respectively [9].

2.1.4 Health effect

One of the most human health risk from the exposure to nickel is an allergic contact dermatitis. The contact dermatitis is the effect of allergic reaction to nickel that general people or worker are exposed via dermal contact with airborne nickel, liquid nickel solution, or nickel-containing metal items such as jewelry and prosthetic devices [1].

Jewelry allergy is a common cause of allergic contact dermatitis. Most jewelry allergy is originated by nickel metal in the manufacturing and productions of precious metal alloys. After human body is contacted with the jewelry which releases the excess nickel level, eczema (an inflammation of the skin) is then occurred. The common sites of jewelry allergy are the earlobes, the fingers, and the neck which is possibly results from wearing the earrings, rings, and necklaces, respectively. The affected contact areas cause intense irritation and may become acute dermatitis (red and blistered skin) or chronic dermatitis (dry, thickened and pigmented skin).
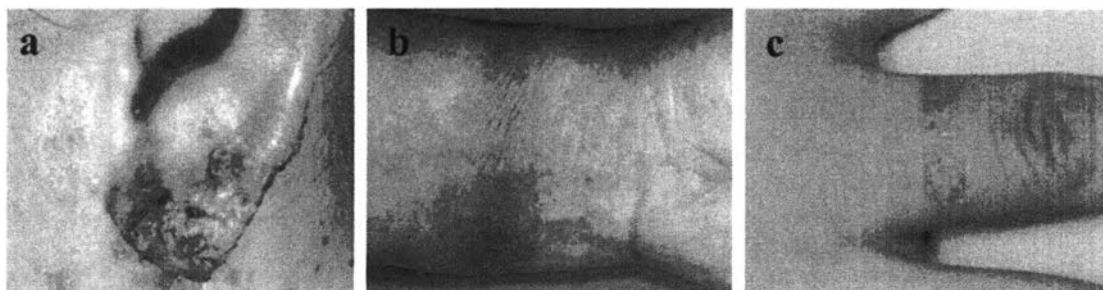

Figure 2.2 Jewelry allergy; (a) infected earring reaction, (b) watch strap reaction and (c) wedding ring dermatitis [10].

Moreover, the serious health effects from exposure to particulate nickel in air including chronic bronchitis, lung cancer, and nasal sinus cancer, have appeared in patients who have breathed dust containing certain nickel compounds while working in nickel refineries or nickel processing plants.
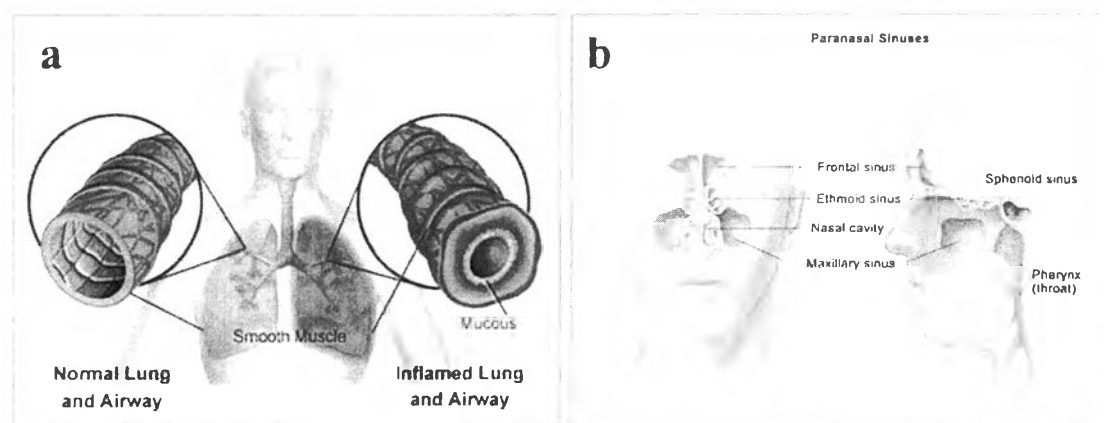

Figure 2.3 Health effect from exposure to particulate nickel; (a) chronic bronchitis and (b) cancer of nasal cavity [11, 12].

Lung and nasal sinus cancers occur in people, received insoluble nickel compounds at upper level than 10 mg nickel/m^3. From the recent histopathology information [13], it indicated that aerosols of water-soluble nickel compounds, generated in nickel electro-refining plants (e.g., from Ni(II) sulfate), are carcinogenic to the human respiratory system as well.

In addition, there are many reports from U.S. Department of Health and Human Services found that metallic nickel may reasonably lead to be a human carcinogen. Similarly, the International Agency for Research on Cancer (IARC) classified metallic nickel (nickel powder) in group 2B and nickel compounds (NiSO$_4$, NiCl$_2$, NiCO$_3$ and NiNO$_3$) in group 1 as a possible carcinogenic to humans. The United States

Environmental Protection Agency (EPA) has also classified nickel refinery dust and nickel subsulfide in Group A to be a human carcinogen.

2.1.5 Conventional method for nickel (Ni(II)) determination [14]

According to the serious health risk obtained from the human exposure to nickel, the development of an alternative analytical approach with real-time detection and portability for prompt reporting the results of nickel monitoring in the environmental and industrial areas is considerably important.

The most common techniques used to determine nickel in food, biological, and environmental matrices are atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and electrochemical methods. Although all of these techniques offer highly selective, sensitive and accurate quantification of metals, they are high operation cost, time-consuming, and in need of sophisticated equipments.

2.2 Colorimetric method [15, 16]

Colorimetry is one of analytical method for the quantification of analyte of interest by measuring the relative absorption of light (usually visible) relating to a known concentration of the analyte. The theory of colorimetry involves the measurement of the amount of absorbed or emitted light by a colored sample, monitored by naked human eye or a spectrophotometer. The amount of light absorbed is called absorbance which is a function of the colored solute concentration. The colorimetric procedure is illustrated in Figure 2.4.
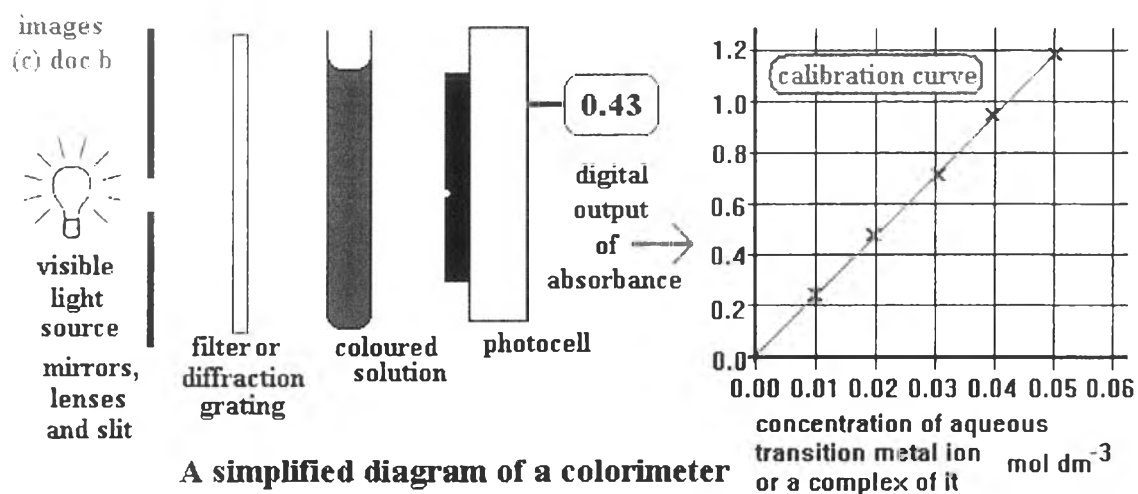
Figure 2.4 A simplified diagram of colorimeter [17].

Previously, standard commercial pigments and dyes have been widely used as a colorimetric reagent to react with a target analyte; however, the low molar absorptivity (ε) of the pigments and dyes involved in the narrow range of their visible wavelength. In recent years, nanoparticles (NPs) have been extensively used instead of pigments and dyes due to higher ε value. Additionally, scattered and absorbed light of NPs is simultaneously measured at the same time, distinguishing to the pigments which can only detect either scattered light or absorbed light. As the NPs colors are related to their size and shape, sensitive optical changes can be achieved without requiring complicated chemical reaction. If the dimension of the nanoparticles is adjusted by increasing or decreasing within a few nm, changes in color of solution can be accomplished [18].

2.3   Nanoparticles [19, 20]

Nanotechnology is a rapid growing science of engineering method in which fully functioning devices are manufactured at the molecular scale, generating and exploiting particles in nanometers level (1 nm = 1 billionth of a meter). There are many definitions for nanotechnology as follows:

- Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 - 100 nanometer range.

- Creating and using novel structures, devices and systems containing with properties and functions because of their small and/or intermediate size.

- Ability to control or manipulate size in the atomic scale.

Figure 2.5 shows various sizes of matter or material in the range of millimeter (mm) to nanometer (nm). A normal diameter of a human hair is 80,000 nm, and a virus size is around 100 nm. A nanometer-sized particle is smaller than a living cell which can be observed under microscopes. The prefix 'nano' is originated from the Greek word for dwarf, meaning one billionth. A nanometer (nm) is one thousand millionth of a meter, 10^9. Therefore, the theoretical size of nanomaterial should be within 100 nm and down to a few nanometers.

Small world

NANOMETRES IN CONTEXT
DIAMETERS

Tennis Ball
65mm

Sugar cube
10mm

Grain of sand
1mm

Human hair
0.08mm

Red blood cell
5,000nm

Typical
bacterum
1,000nm

Typical virus
100nm

Carbon
nanotube
10nm

Quantum dots
5nm

DNA strand
1nm

Carbon atom
0.07nm

100,000,000nm
(100mm)

10,000,000nm
(10mm)

1,000,000nm
(1mm)

100,000nm
(0.1mm)

10,000nm
(0.01mm)

1,000nm
(100mm)

100nm

10nm

1nm

0.1nm

PATENTS ON NANOMATERIALS
NUMBER OF PATENTS

2,000

1,500

1,000

500

0
1990 92 94 96 98 00 02 04 06

A model
of a carbon
nanotube

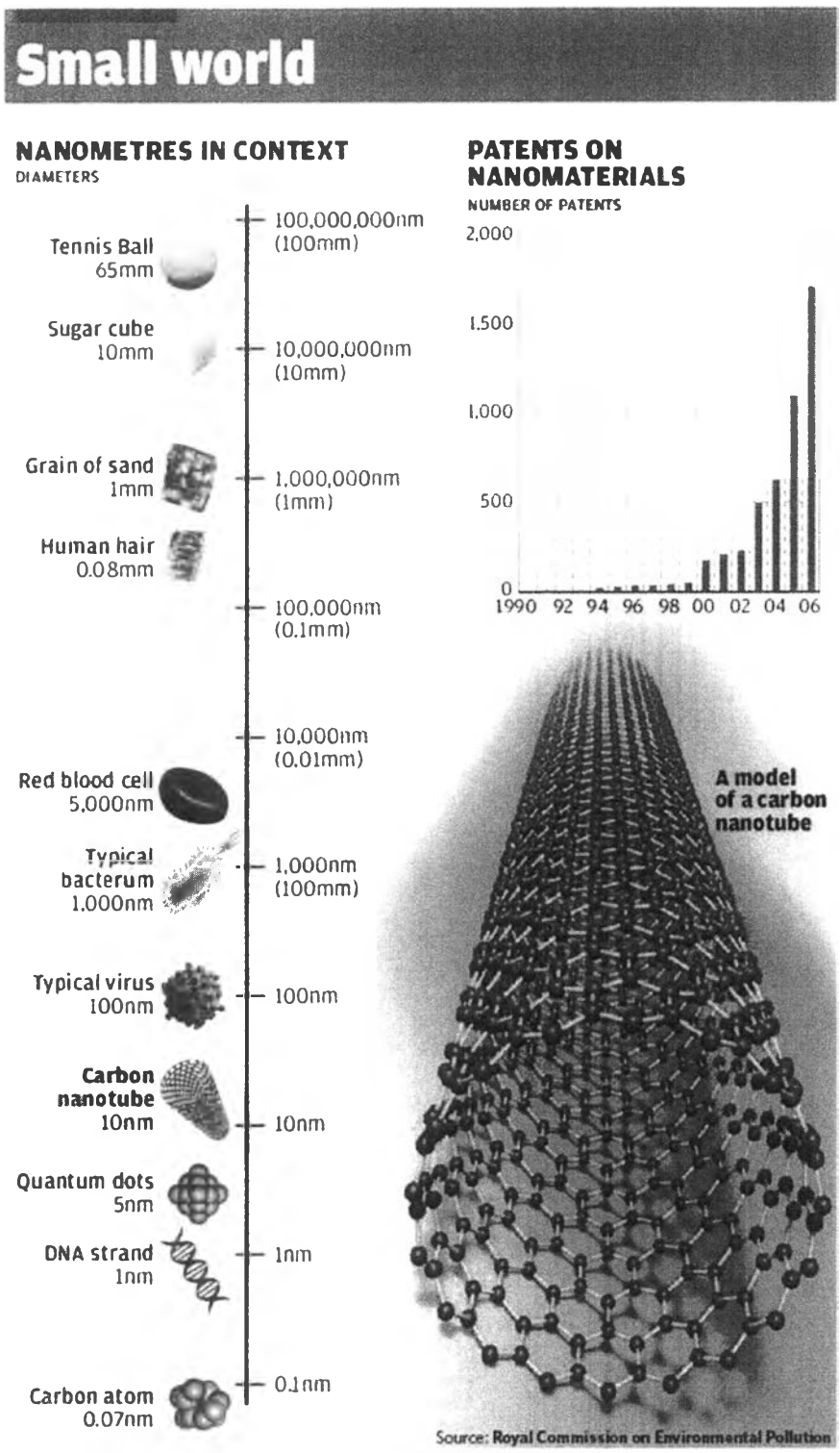Source: **Royal Commission on Environmental Pollution**

Figure 2.5 A comparative overview of the sizes of well-known items and nanoscale particles [21].

Various nanoparticles (NPs) are generally classified on the basis of their dimensionality, morphology, composition, uniformity, and agglomeration, as shown in Figure 2.6.
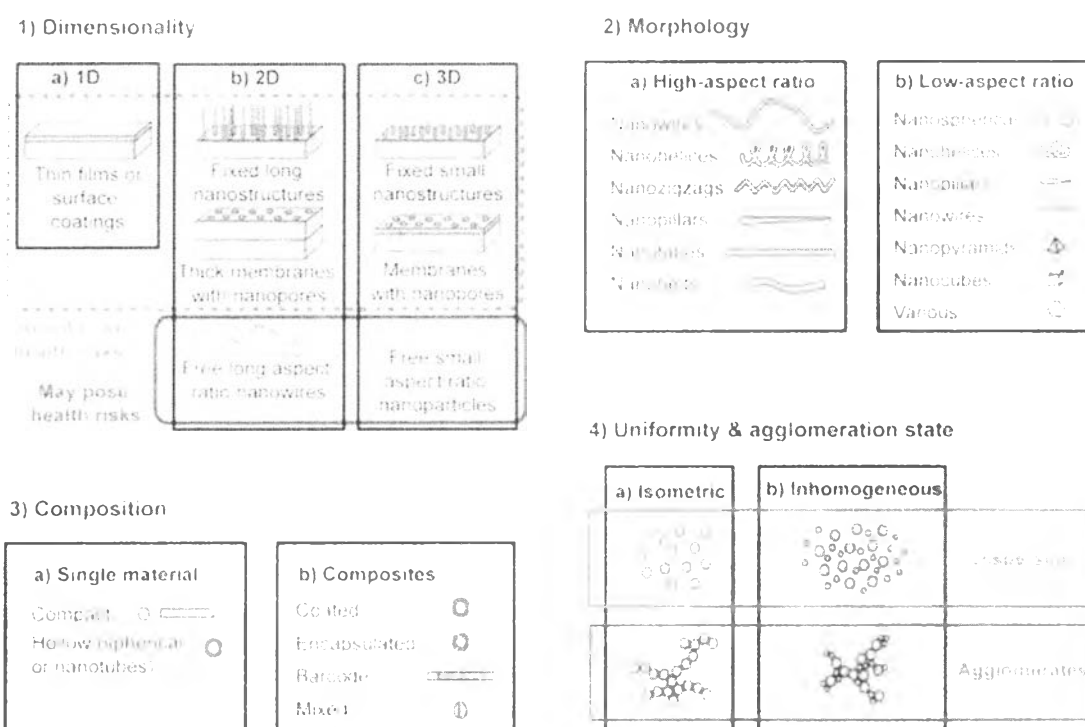

Figure 2.6 Classification of nanostructured materials from the point of view of nanostructure dimensions, morphology, composition, uniformity and agglomeration state [22].

NPs are currently made from a very wide variety of materials and chemicals such as titanium, zinc, aluminium, iron oxides, and silicate nanoparticles. Another nanoparticles, popularly used in recent years, is pure metal nanoparticles. The advantageous and outstanding properties of pure metal nanoparticles includes ease of synthesis, high capability of mass production, and very large reactive surface area that can bind to substance easily. In order to improve the hardness, long-lasting

stability and selectivity of pure metal nanoparticles, the coating or mixing with solid

composite at low temperature is needed [23]. Because of their properties, NPs have

been introduced as a forefront of research in enormous applications (Table 2.1). The

synthesis of NPs especially gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs)

have been broadly developed to generate the desired size, shape, and adsorption of

NPs. The optical property and adsorption of UV-vis light are different, depending on

the size of NPs. Therefore, metal nanoparticles have attracted increasing attention in

application to colorimetric sensor because of their simplicity, high sensitivity, low cost,

rapidity, and adequate miniaturization of the sensing devices.

Table 2.1 The properties and general applications of AuNPs and AgNPs [24].

Nanoparticles	Gold (AuNPs)	Silver (AgNPs)
Structures and properties	• Optical properties depending on size and shape. • Surface plasmon band (SPB) tuned by changes in nanoparticle size, shape and surface functionalities. • Oscillation frequency influenced by dielectric constant of surrounding materials and types of solvent used. • Electromagnetic properties influenced by degree of dispersion and proximity of AuNPs. • Colors highly depending on interparticle distance (interparticle plasmon	• Properties dependent on size, shape, synthesis method and differences in dielectric environment. • Good conductivity. • Chemical stability. • Antibacterial and antimicrobial activities. • Highest efficiency of plasmon excitation over all three metals (Ag, Au and Cu) – plasmon resonances within visible spectrum • Highest SERS signal enhancement among other metal nanoparticles.

	coupling) due to individual spherical AuNPs aggregation.	

Common methods of synthesis	• Bottom up (chemical)
	  - Nanosphere lithography
	  - Citrate reduction method
	  - Seeding technique
	  - Two-phase reaction
	• Top down (physical)
	  - Photolithography
	  - Electron beam lithography
		• Bottom up (chemical)
		  - Lee-Meisel method
		  - Borohydride, citrate, ascorbate, and elemental hydrogen reduction
		• Top down (physical)
		  - Microwave irradiation
		  - Photo-reduction
		  - Microemulsion
		• Biological
		  - Enzymatic reduction
		  - Non-enzymatic reduction

General applications	• Homogenous and heterogeneous catalysis • Biosensors • Drug and protein delivery • SERS • Anti-counterfeiting	• Excellent catalyst • Antimicrobial products • Colorimetric sensor • Enhanced Infrared absorption spectroscopy • SERS • Anti-counterfeiting

2.3.1 Localized surface plasmon resonance (LSPR) [25, 26]

The distinctive optical characteristics of metal nanoparticles correlate with the collective oscillations of conduction electrons surrounding metal nanoparticles. This oscillation results in a strong plasmon band, known as localized surface plasmon resonance (LSPR). LSPR spectral position and properties (i.e.

extinction) can be changed by varying the elemental material type, particle shape, and size. Spectral properties of several nanoparticles between ultraviolet (UV) and near-IR wavelengths are shown in Figure 2.7.
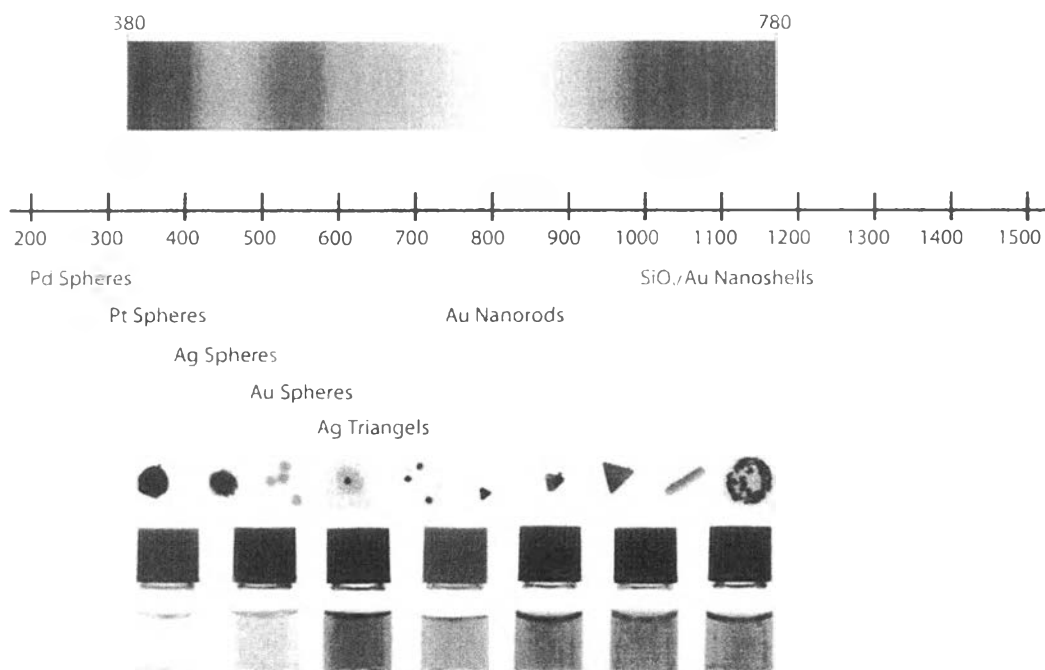

Figure 2.7 A wide range in the electromagnetic spectrum obtained from various colloidal nanoparticles of different material, dimension, and shape cover. Pd: Palladium, Pt: Platinum, Ag: Silver, Au: Gold, SiOx: Silicon oxide [27].

Consequently, analytical applications using metal nanoparticles is based on the LSPR principle of nanostructures assembly which can easily observe by naked-eye. The understanding in the optical LSPR behavior before and after aggregation process of nanoparticle is needed. Indeed, superior abilities of modern nanotechnology in the different shapes and sizes of metallic nanoparticles have been extremely attractive in numerous technical applications [25].

2.3.2   Silver nanoparticles

Among colorimetric sensors, silver nanoparticles (AgNPs) have been used as an alternative colorimetric sensor because it is low cost material with higher extinction coefficients compared with gold nanoparticles and copper nanoparticles (approximately 100 fold). The high extinction coefficients leads to the improvement of visibility based on the difference in optical brightness and the increase of sensitivity when using absorption spectrophotometry [28].

Various AgNPs shapes have been synthesized as shown in the Figure 2.8 such as sphere, plate, cube, triangle, wire. Configurations of wire and rod depend on the synthesis method and different stabilizers [29].
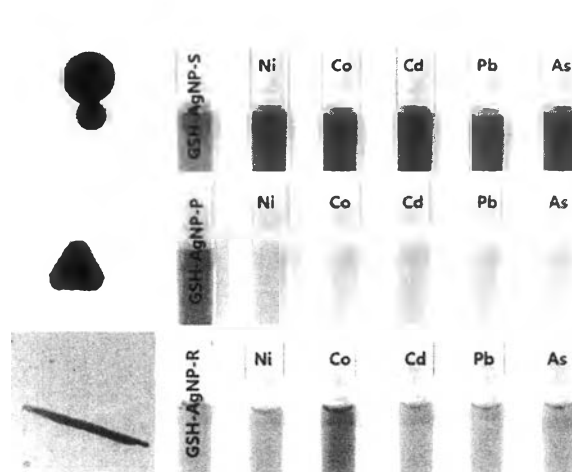

Figure 2.8 Selectivity of scattering plasmonic optical properties from various colloidal AgNPs shapes (sphere, triangle and rod, respectively).

Distinguishing to other AgNPs shapes, silver nanoplates (AgNPls), which is a kind of AgNPs with platelet configuration, exhibit broader range of absorption and scattering properties in both visible and near-IR regions of the spectrum which can improve the optical properties of AgNPs and enhance the sensitivity in order to use as

a sensor. As shown in Figure 2.9, the optical resonance of AgNPls can be altered within wavelengths of 550 nm-1300 nm via changing AgNPls diameter and thickness. Furthermore, nanoplates (NPls) have been applied in many techniques such as surface-enhanced raman scattering (SERS), photovoltaics, molecular detection, and photothermal cancer therapies [3].
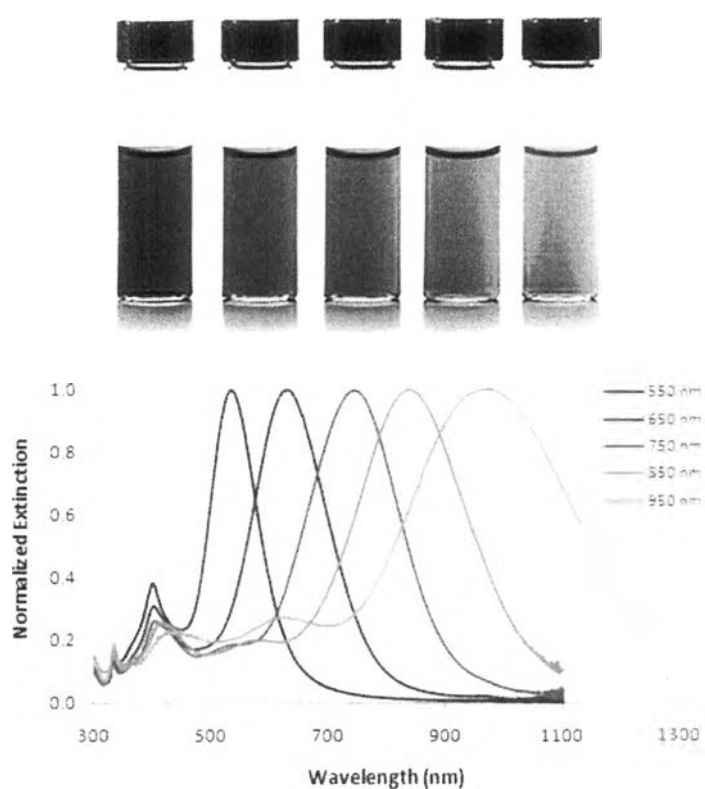

Figure 2.9 Absorbance spectra of various AgNPl sizes.

2.3.3 Modified surface of nanoparticles (NPs) [30]

In general, a strategic development of metal nanoparticles based colorimetric assay is the surface modification. Ligand-modified surface of AgNPs have been increasingly explored for selective and sensitive detection of analytes of interest. This utility can be extended through noncovalent assembly methods, possessing the

ability to regulate spacing and structure in the resulting nanocomposite systems. Directed self-assembly of nanometer-sized building blocks using noncovalent interactions (e.g., hydrogen bonding, acid-base proton transfer, and electrostatic forces) has been demonstrated as an effective way to create tailored nanomaterials. There are many assembly strategies for modification surface of NPs, for example:

- Biologically programmed nanoparticle assembly

  - Antigen – antibody

  - Proteins and oligonucleotides

- Organic ligand modified nanoparticle building blocks

  - Thiols and their derivatives

  - Amines and their derivatives

  - Fullerenes

- Self-assembly generated by inorganic ligands

  - Sulfide coordination

  - Electrostatic self-assembly on silica substrates

- Surfactant-mediated nanoparticle aggregates

  - Monomeric surfactant

  - Micelles

=   Reverse micelle

● Polymers as architectures of nanoscale assemblies

2.4   Ultraviolet-visible spectrophotometry [31]

UV-vis spectrophotometry is routinely used in analytical chemistry for the quantitative determination of the transmittance or reflectance of a target analyte as a function of wavelengths in the range of 200 nm to 700 nm. The spectroscopic result is the absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state of the target compound or material. The principle behind absorbance spectroscopy is Beer-Lambert Law which the equation is described below. For a single wavelength, A is absorbance (unitless, usually seen as arb. units or arbitrary units), ε is the molar absorptivity of the analyte compound or molecule in solution ($M^{-1}cm^{-1}$), b is the path length of the cuvette or sample holder (usually 1 cm), and c is the analyte concentration (M).

$$A = \varepsilon bc \qquad \text{(Beer-Lambert Law)}$$

The absorption spectrum of a compound is one of the most beneficial physical properties in terms of qualitative and quantitative analysis. Within the range of visible wavelength, color of the solution and absorption properties are associated due to the complementary colors. As shown in Figure 2.10 and Table 2.2, if the color of solution is green/blue, the absorption of red color is occurred and located in the UV-vis spectra at 610 - 750 nm.
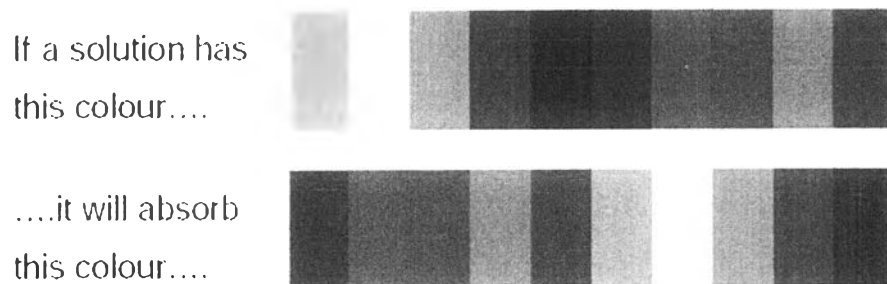
If a solution has
this colour....

....it will absorb
this colour....

Figure 2.10 Complementary colors.

Table 2.2 Complementary colors data [17].

The wavelength (nm) of the observed transmitted color of the solution	The observed transmitted color of the solution	The complementary colour of the solution i.e. the color of the filter
400-435	violet	yellowish-green
435-480	blue	yellow
480-490	greenish-blue	orange
490-500	bluish-green	red
500-560	green	purple
560-580	yellowish-green	violet
580-595	yellow	blue
595-610	orange	greenish-blue
610-750	red	bluish-green

UV-vis spectrophotometers are normally classified into two types including a single-beam spectrophotometer and a double-beam spectrophotometer. The common components of UV-vis spectrophotometer are light source, monochromator, sample compartment, and detector.
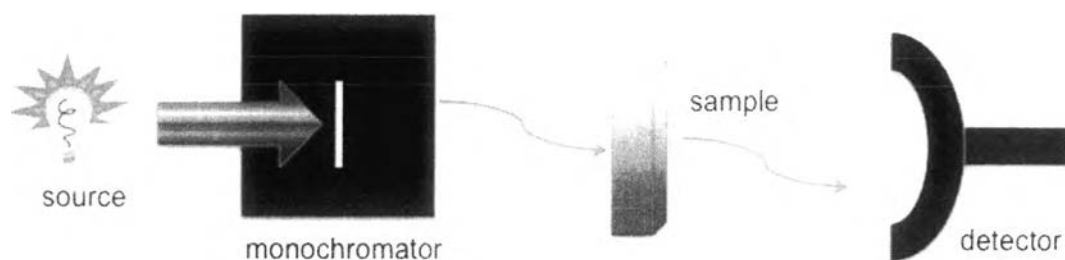
Figure 2.11 Components of a single-beam UV-vis spectrophotometer [32].

There are 2 types of light source in the UV-vis spectrophotometer. The light source for the detection in ultraviolet region is typically a deuterium lamp generating the light with the wavelength between 185 nm to 375 nm. For visible region, a tungsten filament source is usually used because it is very bright and emits light over the entire visible region and some wavelengths of near infrared region.
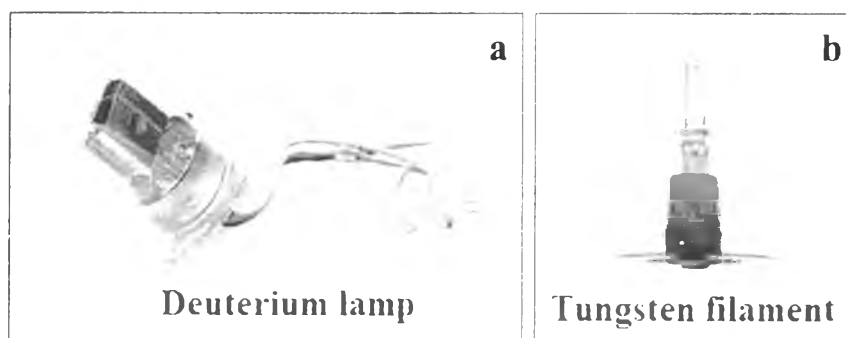

Figure 2.12 Light sources; (a) deuterium lamp, (b) tungsten filament [33].

The second component of UV-vis spectrophotometer is monochromator. The function of a monochromator is to produce a beam of monochromatic (single wavelength) radiation by separating the narrow band of wavelengths from visible and ultraviolet sources. The essential components consists of (1) entrance slit, (2) collimating device (to produce parallel light), (3) a wavelength selection or dispersing system, (4) a focusing lens or mirror and (5) an exit slit. In addition, the dispersing

element are conventionally divided into 2 types comprising of diffraction grating and prism.

For the principle operation of dispersive system, the process is shown in the Figure 2.13. The entrance slit is where light enters the monochromator from the source. The beam passed through a dispersing element to spatially separate the light into its component wavelength. For visible light, a beam of white light is dispersed into rainbow colors. The narrow band of the spectrum is selected by passing through the exit slit. After that, he monochromatic light from this exit slit passed onto the sample compartment.
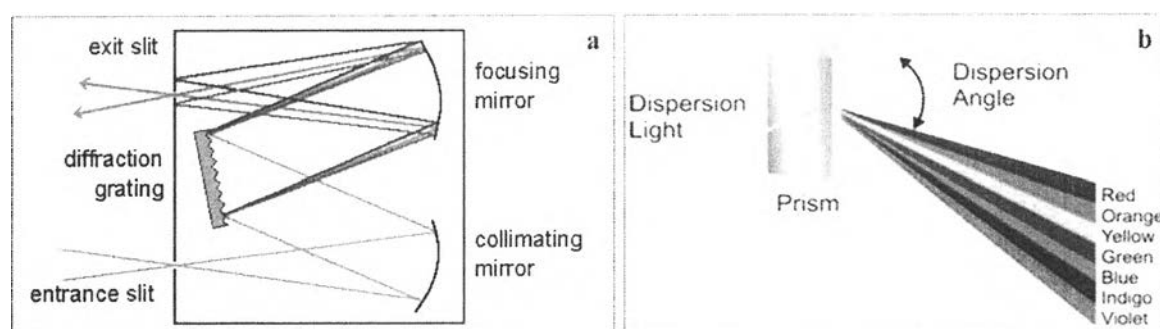

Figure 2.13 The dispersive system; (a) diffraction grating [34], (b) prism [35].

The sample compartment is a sample holder which the monochromatic light passes through. The sample compartment is an enclosure with a lid which can be opened and closed in order to insert and remove the cuvette. In general, cuvettes are made of glass or quartz, depending on the wavelength range of interest.

Usually, photomultiplier tubes or photodiodes are used as detectors in UV-vis spectrophotometers. After light passing through the sample, the signal can be generated, amplified and shown on the screen of the spectrophotometer.
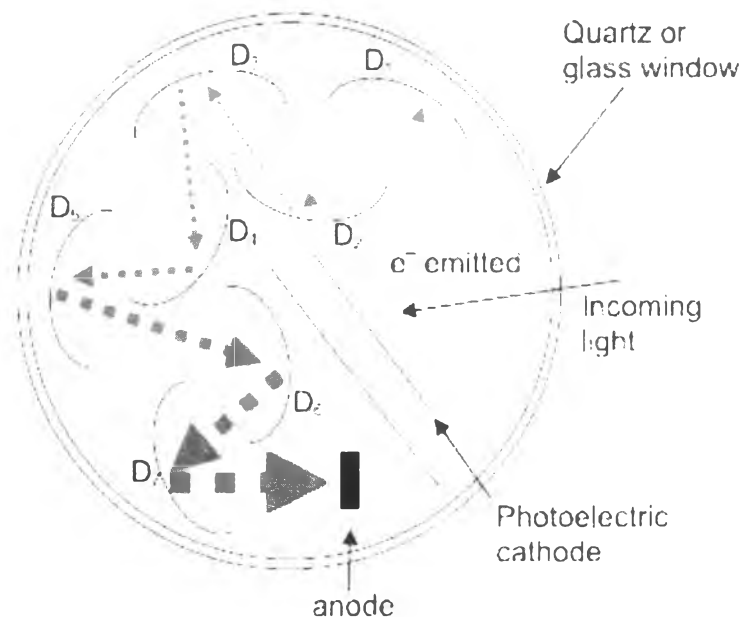
Figure 2.14 The photomultiplier tube consists of a photocathode, an anode, and dynodes [36].

For a double-beam spectrophotometer, its components is similar to a single-beam spectrophotometer as shown in Figure 2.15. However, a double-beam spectrophotometer can instantaneously measure two beams of light passing through two sample compartments, containing the blank and the sample solution. A double-beam spectrophotometer shows an advantage over single-beam spectrophotometer which can reduce operation time and increases accuracy due to measurement of blank and sample at the same time.
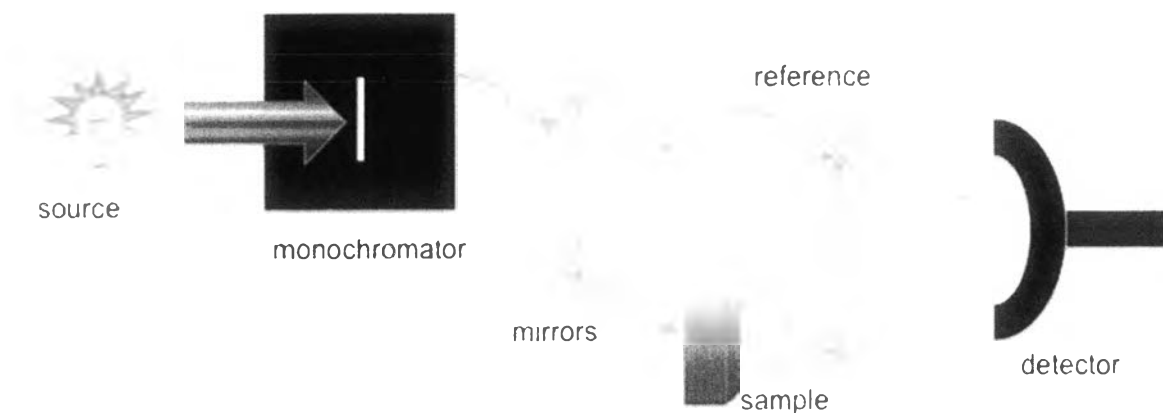
Figure 2.15 The diagram of a double-beam spectrophotometer [32].

2.5 Literature survey

2.5.1 Conventional methods for Ni(II) detection

There are many analytical methods for the determination of Ni(II) including high performance liquid chromatography (HPLC), atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and electrochemical methods as illustrated below.

In 2006, Aouarram et al. [37] demonstrated the use of a permeation liquid membrane system for the preconcentration and separation of nickel in natural and sea waters and subsequent determination by atomic absorption spectroscopy. 2-Hydroxybenzaldehyde N-ethylthiosemi-carbazone (2-HBET) in toluene is used as the active component of the liquid membrane. A detection limit of this approach was found to be 0.012 µg L^{-1} for nickel detection. This methods provide a simplicity and economy and enables the elimination of matrix interferences in waters.

In 2010, Cacho et al. [38] developed a new analytical methodology for the direct identification and quantification of nickel complexes in extracts of non-accumulator plants for investigation of the mechanism involved in the nickel provision for endosymbiotic bacterial cells. The normal phase liquid chromatography methodology was performed for fast and sensitive separation of nickel-organic complexes, and has been applied to the detection and quantification of various nickel complexes in pea nodule cytosolic extracts. Results indicated that nickel citrate and nickel malate accounts was found for 99% of nickel present in pea nodule cytoplasm fraction.

In 2011, Baysal and Akman [39] presented direct determination of copper and nickel in hair samples by solid sampling AAS. After optimization of parameters, the average recoveries of copper in two different certified reference hair samples were 105.7 and 97.6%. Moreover, the recoveries of nickel in the both certified reference hair samples were in 95.2 and 96.4%. The limits of detection (3σ, N=10) for copper and nickel were 22 ng/g and 35 ng/g, respectively. Finally, this method was successfully applied for the determination of copper and nickel concentrations in the hairs of different persons.

In the same year, Segura et al. [40] used a bismuth film electrode (BiFE) for Ni(II) determination by AdSV in the presence of 1-nitroso-2-napthol (NN). Under optimal condition, the calibration curve of nickel detection was in the range of 10.0–70.0 μg L^{-1} with detection limit of 0.1 μg L^{-1}.

Piankova et al. [41] presented a used carbon screen-printed electrodes (CSPE) as substrate for bismuth nanoparticles immobilization. Under the optimal

condition, direct current (DC) voltammetric stripping response is directly proportional to the Ni concentration in the range from 0.85×10^{-8} to 8.48×10^{-8} M with the detection limit is 3.2 nM.

In 2012, Dobrowolski and Otto [42] developed a novel method using dimethylglyoxime-impregnated activated carbon (DMGC) for preconcentration and simultaneous determination of Ni(II) and Co(II) ions in the reference plant materials coupled with the carbon slurry sampling graphite furnace atomic absorption spectrometry technique (GFAAS). The detection limits for nickel and cobalt were 0.02 and 0.001 mg/g, and quantification limits were 0.06 and 0.004, respectively. This method has been successfully tested by the analysis of certified reference materials and real sample as well.

In the same year, Neodo et al. [43] presented an electrochemical methodology for Ni(II) detection which is suitable for an acidic solution environment without the use of chelating agents. The nickel-ion quantification was achieved in solutions with pH values ranging from 8 to 4 using a bare boron-doped diamond electrode. For analytical performance of this method, limit of detection of 26.1 μM and linearity of Ni(II) determination within 10 to 500 μM were reported.

In 2013, Nurak et al. [44] developed a novel fabrication of paper-based devices by a spraying method with lacquer coupled electrochemical detection for nickel determination. In this work, a new method for fabricated paper- based using acrylic lacquer to create a hydrophobic area was presented. Cu-enhancer solution was employed to increase sensitivity of nickel detection using anodic stripping voltammetry. The result shows that the portable electrochemical paper-based devices

was successfully developed and applied to determine nickel in wastewater of a jewelry factory.

In the same year, Gomez-Nieto et al. [45] reported the simultaneous and direct determination of nickel and iron in plants and lichens using high-resolution continuum source graphite furnace atomic absorption spectrometry. The metal level can be measured directly without any pretreatment step. The limits of detection were 25 mg kg^{-1} and 0.40 mg kg^{-1} for iron and nickel detection, respectively. The proposed method was used to determine both metals in different bioindicator samples with successful results.

In the same year, Martin-Cameán et al [46] reported to optimization and validation of a sample preparation procedure to determine cobalt (Co), chromium (Cr), copper (Cu), and nickel (Ni) in oral mucosa cells obtained from patients with and without orthodontic appliances, coupled with the extraction and digestion of the samples and quantification of the elements by inductively coupled plasma mass spectrometry (ICP-MS). Limits of detection were found to be 0.10, 0.38, 0.49 and 0.67 ng mL^{-1} for Co, Cr, Cu, and Ni, respectively.

From previous studies, these conventional methods for Ni(II) detection offered highly selective, sensitive and accurate quantification of nickel. However, these methods are rather expensive, complicated and time-consuming. Therefore, the colorimetric methods have been extensively used for metal detection recently.

2.5.2   Colorimetric methods for Ni(II) detection

In 2010, Zamora et al. [47] successfully used a digital imaging for determination of the nickel content of metallic meteorites by using reaction between nickel and dimethylglyoxime. This method served as a fairly simple, inexpensive and can be applied to current, straightforward, robust, cost-effective instrumentation.

In 2011, Wang et al. [48] presented a novel coumarin Schiff base compound (L) prepared from 7-diethylaminocoumarin-3-aldehyde and 3-amino-7-hydroxycoumarin as a chemoselective Ni(II) sensor. With the addition of Ni(II) to CH_3CN solution of L resulted in a rapid color change from yellow to red. Moreover, other common alkali- metal ions, alkaline earth metal ions, transition- metal ions and rare earth metal ions showed the negligible spectral change. Therefore, this advantage of method exhibited a selective Ni(II) over other metals.

In the same year, Abebe et al. [49] designed a novel turn-on fluorescein-based chemosensors for highly sensitive and selective detection of Co(II) and Ni(II) in both detection modes of absorption and emission. The binding with both ions is reversible, as indicated by the bleaching of the color when the metal is extracted with EDTA.

In the same year, Jiang et al. [50] reported a new coumarin based colorimetric sensor for selective detection of nickel. An electron-donating hydroxyl group and an electron-withdrawing pyridyl moiety in the structure of coumarin derivative was designed and used as a new colorimetric chemosensor for Ni(II) ion. Remarkably, the chemosensor exhibited 200 nm bathochromic shift upon the addition

of Ni(II) ion, allowing the selective detection of Ni(II) ion by the naked eye over a great number of environmental interfering ions including other alkali metal and alkaline earth metal cations. By the "naked eye", this sensor served the detection limit of Ni^{2+} ion as low as 0.5 μM.

In 2012, Aksuner et al. [51] described a new optical sensor membrane for the determination of Ni(II) based on the immobilization of the fluorescent thiazolo-triazol derivative in PVC matrix. This optode provides a wide linear range of 1.0×10^{-9} – 4.4×10^{-3}M for Ni(II) ions with the detection limit of 8.5×10^{-10} M. The optode membrane showed a very good selectivity, good durability, short response time towards the detection of Ni(II) ion and good results for applications in direct determination of Ni(II) in real samples.

In 2013, Fegade et al. [52] have designed and synthesized malonohydrazide based fluorescent probe (7E, 8E) –N1′, N3′-bis (1-(2-hydroxyphenyl) ethylidene) malonohydrazide (receptor 5) for selective detection of Ni(II). The fluorescence spectra of receptor 5 have shown distinct enhancement with the addition of Ni(II) ion over other surveyed cations. This proposed method was used to measure Ni(II) in various fields such as biological and environmental samples.

In the same year, Goswami et al. [53] designed and synthesized a new quinoxaline based receptor (HQNM), which exhibited a remarkable color change from colorless to yellow upon specific binding with nickel. In this work, the receptor showed specific selectivity toward nickel over possible interfering cations. Thus, a significant bathochromic shift in UV–vis spectrum with a sharp yellow color was observed which is suitable for the selective detection of nickel ion.

From previous studies, it can be conducted that the colorimetric assay is widely used for detection of Ni(II) owing to good selectivity and high sensitivity. However, the previous colorimetric sensorsstill required complicated synthesis procedure and need of hazardous and expensive chemicals. Therefore, the colorimetric assay based on metal nanoparticles have attracted increasing attention because of their simplicity, outstandingly prompt measurement, high sensitivity, and adequate miniaturization of the sensing devices.

2.5.3 Metal nanoparticles-based colorimetric methods for Ni(II) detection

In 2009, Li et al. [54] reported the synthesis of glutathione-stabilized silver nanoparticles (GSH-AgNPs) in water media for colorimetric assay of Ni(II). In the presence of N(II), the yellow GSH-AgNPs solution turns to a deep orange color, accompanying the red shifting of surface plasmon absorption band. The sensor exhibited the selectivity and sensitivity toward other representative transition-metal ions.

In 2011, Krpetic et al. [55] investigated the colorimetric detection of AuNPs for trace detection of Ni(II). The modification using covalently attached nitrilotriacetic acid moieties along with the l-carnosine dipeptide on the nanoparticle surface for a rapid and selective detection of Ni(II) ions was accomplished. This systematic study demonstrates that significantly lower detection limits can be achieved by varying core sizes of gold nanoparticles.

In 2012, Shang et al. [56] developed a colorimetric assay based on silver nanoparticles (NAC-AgNPs) capped with N-acetyl-L-cysteine ($C_5H_9NO_3S$, NAC). The

sensor showed high selectivity towards Ni(II) over other cations under specified conditions. In the presence of Ni(II), rapid aggregation of NAC-AgNPs was induced along with color change from yellow to deep orange with linear range from 2 to 48 µM and a detection limit of 0.23 µM.

In 2013, Azzam et al. [57] synthesized the nanostructure of dithiol surfactants with gold nanoparticles (AuNPs). This sensor exhibited good performance for Ni(II) and Zn(II) ions detection.

Based on these previous studies, the nanoparticles-based colorimetric assay has been widely studied and used for the detection of Ni(II) because of simplicity, good selectivity and high sensitivity. Therefore, the aim of this work is to develop a novel colorimetric assay using GSH and Cys modified AgNPls for selective detection of Ni(II) and to use this proposed method to measure Ni(II) in the jewelry industrial sample.