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Photonics properties of gold and silver nanoparticles[*]

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Abstract

Gold and silver nanoparticles exhibit several interesting properties, and have been utilized in many applications. The examples of these applications are photothermal therapy, solar cell, sensing, and even as the active components in the commercially available consumer products such as detergents, cosmetics, and paints. For scientists, one of the most interesting properties of gold and silver nanoparticles are their photonics properties, which were created by the interaction of electromagnetic field (light) with the nanoparticle. This review was focused on the photonics properties of gold and silver nanoparticles, the applications that employed these properties, as well as the synthesis methods of gold and silver nanoparticles which could influence their photonics properties. Expectantly, the provided basic knowledge should promote the collaborative and multidisciplinary researches that utilize photonics properties of gold and silver nanoparticles.

Introduction

In the present, it is almost inevitable for human beings to encounter with noble metal nanoparticles (MNPs) in their daily life, especially, gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs). Several products have been claimed to consist of AuNPs and AgNPs. The examples of these products in Thailand are detergents, cosmetics, and paints. These products were claimed to show extra and useful properties arose from added AuNPs and AgNPs such as antibacterial, (Sharma, Yngard, and Lin, 2009: 83-96) and self-cleaning. (Anderson et al., 2016: 1500623) In addition to these capabilities, AuNPs and AgNPs also exhibit other interesting properties, particularly, their photonics (photons- related) properties which have potentials to be employed in many applications such as photothermal therapy, solar cell, and sensing. The synthetic methods of these AuNPs and AgNPs, and added chemical in the synthesis steps such as stabilizing agents, can greatly affect the photonics properties of these noble MNPs. Therefore, the aim of this review is to summarize and give the basic knowledge of AuNPs and AgNPs, which may inspire and benefit utilization of AuNPs and AgNPs in the

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[*] The aim of this review article is to give the basic knowledge of AuNPs and AgNPs and their photonics properties.

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multidisciplinary researches. In this review, the basic principle of synthetic methods of noble AuNPs and AgNPs, their photonics (photon-related) properties, and selected applications utilizing the photonics properties of these noble MNPs will be described.

Syntheses of AuNPs and AgNPs

In general, synthesis of noble MNPs occurs through chemical reaction (redox) in a solution phase, this method is known as “chemical reduction method”. Therefore, oxidizing and reducing agents are required in the MNPs syntheses. Commonly, oxidizing agents are the salts of noble metals (gold and silver). These salts are water soluble and serve as metallic-cations precursors (Au^{3+} and Ag^{+}), which will be reduced by the reducing agents to form the dispersed solid metals (oxidation state of zero) in the reaction mixture. The formation of a MNP starts with the nucleation of a small metallic seed (nucleus, 1-5 nm in diameters), which is caused by the reductions and accumulation of the metallic-cations precursor, then further reductions of additional metallic-cations lead to growth of the MNP nucleus, and eventually formation of the MNP. (Murphy et al., 2005: 13857-13870) The examples of common silver and gold salts used for AgNPs and AuNPs syntheses are silver nitrate, and chloroauric acid, respectively. The reducing power of a reducing agent plays an important role in formation of the noble MNPs and their properties. (Murphy et al., 2005: 13857-13870) In principle, use of a weak reducing agent results in slow reaction and small size of MNPs. On the other hand, use of strong reducing agent results in fast reaction and large size of MNPs due to the aggregation. Therefore, obtaining MNPs with desirable size should be straight forward. However, other factors can greatly affect the reaction. For example, if the reduction rate of Ag^{+} is too fast, the AgNPs can aggregate and precipitate (Murphy et al, 2005: 13857-70) or if the reduction rate of Ag^{+} is too slow, the AgNPs may be further oxidized by the dissolving oxygen and the dark Ag_2O will be formed. (Yin et al., 2002: 522-527) Therefore, appropriate synthesis condition is required to obtain the MNPs with desirable size and shape. The examples of common reducing agents for synthesis of MNPs are sodium citrate, (Li et al, 2014: 2498-2504) sodium borohydride, (Zhang et al., 2011: 18931-18939) hydrazine, (Patil et al., 2012: 15013) and formaldehyde (Zienkiewicz-Strzałka et al., 2013: 337-343). In addition to common chemical reducing agents, more environmental friendly reducing agents such as vegetable oil, (Kumar et al., 2008, 236-241) glucose, (Sharma, Yngard, and Lin, 2009: 83-96) and xyloglucan (Yeasmin et al., 2015:39992-39999) could also be used to synthesize MNPs with a slower reduction rate due to their weak reducing powers, therefore, in some studies uses of high temperature were required to increase the rate of reaction. (Kumar et al., 2008, 236-241; Meena, and Philip., 2013; 154-

160) Furthermore, stabilizing agents are usually added during the MNPs synthesis steps to prevent aggregation of the MNPs and help stabilizing the MNPs. These stabilizing agents could either be very high molecular weight macromolecules (surfactants) such as polyvinylpyrrolidone (PVP), (Zhang et al., 2011: 18931-18939) and polyvinyl alcohol (PVA), (Patil et al., 2012: 15013) or low to moderate molecular weight molecules such as cetyltrimethylammonium bromide (CTAB), (Busbee et al., 2003: 414-416) citrate, (Bastús et al., 2014: 2836-2846) and decanoate. (Dong et al., 2009: 6269-6275) These stabilizing agents can either be non-ionic such as PVP, and PVA or ionic such as CTAB, decanoate and citrate salts. The non-ionic and ionic stabilizing agents have been proposed to stabilize the MNPs with different mechanisms, the non-ionic stabilizing help prevent aggregation by capping and surrounding a MNP via self-assembly or entropic driven processes. On the other hand, the ionic stabilizing agents were proposed to bind to a MNP via electrostatic interaction. In some cases, specific stabilizing agents were selected in order to use MNPs in specific applications, especially, sensing applications. (Zhou et al., 2014: 106-111) In addition to controlling the size of the synthesized MNPs, controlling the shape of the synthesized MNPs is also in demand because of the specific and useful photonics properties arise from a specific shape of the MNPs. For instance, strong electromagnetic field enhancement, which is useful for sensing and solar cell applications, can be obtained from the MNPs, especially the elongated and sharp-edge MNPs. (Sanchez-Gaytan et al., 2012: 10318-10324) These elongated and sharp-edge MNPs are originated from heterogeneous growth of MNPs during the synthesized steps, this growth is commonly achieved by promote heterogeneous growth of the MNPs by addition of ionic and low molecular weight stabilizing agents. (Busbee et al., 2003: 414-416; Murphy et al., 2005: 13857-13870) Although, the mechanism was still unknown, it has been proposed that the ionic stabilizing agent were selectively bind to only some facets of the nucleation seed of MNP due to the different in electron densities caused by incomplete (heterogeneous) shape of the nucleation seed. Therefore, various size and shape of MNPs can be obtained by variation of synthesis condition such as reducing agents, temperatures, pH and stabilizing agents. (Dong et al., 2012: 1-9; Meena, and Philip, 2013: 154-160). For example, spherical AgNPs can be prepared by reduction of Ag^+ by coconut oil at boiling temperature. (Meena, and Philip, 2013: 154-160) or triangular prism NPs can be synthesized by reduction of Ag^+ by $NaBH_4$ in the presence of hydrogen peroxide and citrate. (Zhang et al., 2011: 18931-18939) In addition to variation of reducing agent, photo irradiation can also use to selectively synthesize NPs with selected size and shape. (Stamplecoskie, and Scaiano., 2010: 1825-1827) AuNPs with different

morphologies can be also synthesized such as branched (star-like) AuNPs, obtained by using hydroxyphenol as a reducing agent with controlled temperature (Lee, and Park, 2011: 2965-2971) or triangle AuNPs that can be produced by citrate reduction with controlled temperature. (Shankar, Bhargava, and Sastry, 2005, 1721-1727) The photonics properties of AuNPs and AgNPs are greatly influenced by their sizes and shapes, therefore, the MNPs synthesis methods are very important for utilization of their photonics properties. The influences of sizes and shapes of the MNPs on their photonics properties were described in the following section.

Photonics properties of AuNPs and AgNPs

The photonics properties of MNPs are mainly the consequent of the electromagnetic-induced phenomenon called "Localized Surface Plasmon Resonance, LSPR", which is originated from the coherent oscillations of the conductive electrons at the surfaces of MNPs upon excitation (illumination) of electromagnetic field (light). Illustration of LSPR of a MNP upon excitation of an electromagnetic filed (light) is shown in figure 1.

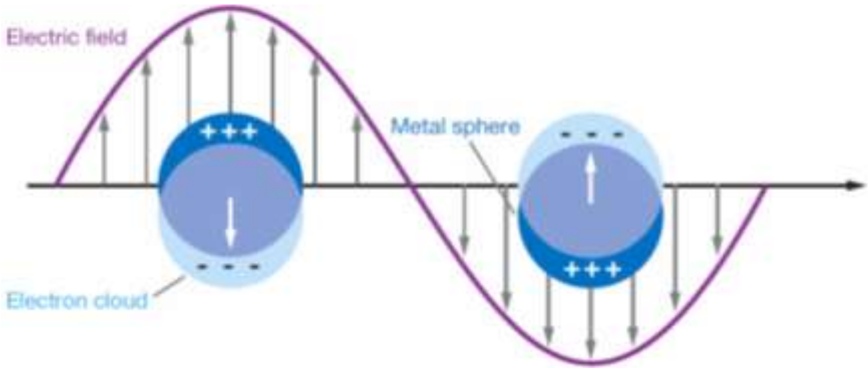


Figure 1. LSPR generation of a MNP. Electromagnetic illumination leads to coherent oscillations of electron cloud at the surface of a MNP. (Willets, and Van Duyne, 2007: 267-297)

LSPR is unique to metal type, shape, and size of MNPs. (Willets, and Van Duyne, 2007: 267-297) For AuNPs and AgNPs, their LSPR are mainly in visible wavelengths (400 – 700 nm), and can even be tuned to UV and near IR wavelength by controlling theirs sizes and shapes with specific synthesis conditions. For examples, the spherical AgNPs show LSPR at 410 nm, (Meena, and Philip, 2013: 154-160) while the triangular AgNPs exhibit broad SPR from 400 nm to near-IR with a peak at 710 nm. (Zhang et al., 2011: 18931-18939) These specific absorptions of the MNPs via their LSPRs are reflected as the different colors of MNPs in the solution phases as shown in figure 2.

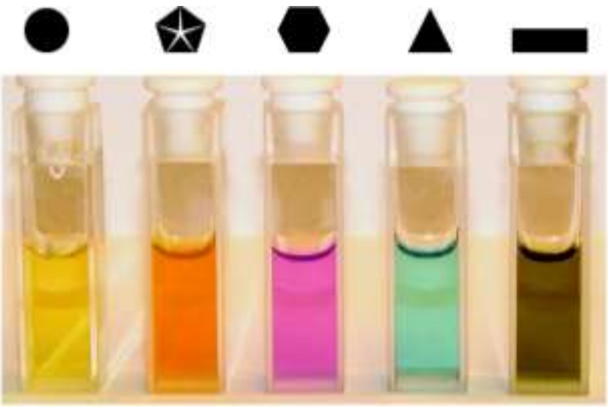
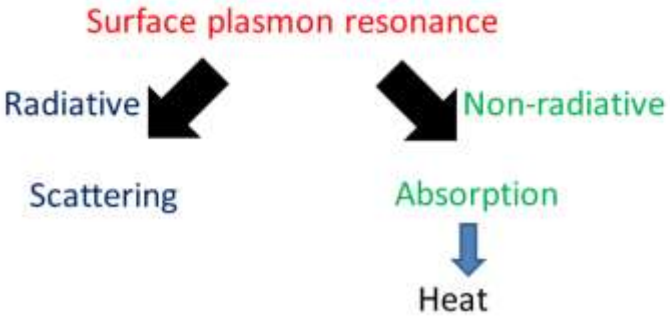


Figure 2. AgNPs solutions with different sizes and shapes, the shift of their LSPRs reflect as AgNPs solutions with different colors. The figure was adapted from Stamplecoskie and Scaiano., 2010: 1825-1827.

As discussed earlier, electromagnetic field illumination leads to LSPR of MNPs, which will eventually undergo dampening (in femtoseconds time scale) and release energy both via radiative and non-radiative pathways as a scattering and absorption, respectively. (Chang et al., 2012: 1936-1945) The simplified scheme to explain the energy damping of the LSPR is shown in figure 3. For the MNPs with size in order of ten of nanometers, they exhibit low emissive quantum yield and the absorption is dominant, therefore the absorbed energy is mostly transfer non-radiatively to the surrounding environment as heat, while for the larger MNPs, the scattering (emission) is dominant. (Chang et al., 2012: 1936-1945)

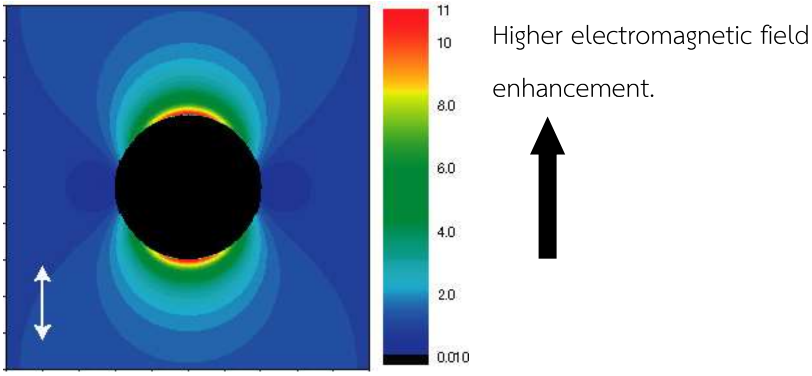
Figure 3. LSPR damping via radiative and non-radiative pathways.



Moreover, LSPR of MNPs are always accompanied by strong electromagnetic field enhancement up to tenth order of magnitudes in the vicinity of the MNPs surfaces as shown in figure 4, (Plech et al., 2006: 44-47; Grubisic et al., 2012: 4823-4829) this effect is known as “plasmon enhancement”. Many studies have been reported to utilize the plasmon enhancement of MNPs in spectroscopic and sensing applications. (Garcia-Leis et al., 2013: 7791-7795; Khatua et al., 2014: 4440-4449) Additionally, change in electric field (dielectric) of the surrounding environment can also shift LSPR of MNP. The examples are linking of organic molecules to MNP or changes of solvents resulted in shifting of the LSPR. (Mayer, and Hafner, 2011: 3828-57) This sensitive nature of LSPR to changes of electromagnetic field of the surrounding environment leads to use of MNPs-based in sensing applications. (Zhou et al., 2014: 106-111; Chen et al., 2014: 6843-6849) Due to their outstanding photonics properties, AuNPs and AgNPs have gained lots of attentions owing to their potentials to be utilized and applied in the multidisciplinary researches.

Figure 4. Distribution of the electromagnetic field in the vicinity of a spherical MNP upon light illumination. The field enhancement was very high at the area close to the surface of the MNP. The figure was adapted from Plech et al., 2006: 44-47.

Applications utilizing photonics properties of AuNPs and AgNPs



Higher electromagnetic field enhancement.

In this review, the applications utilizing photonics properties of AuNPs and AgNPs will be categorized into the following three groups, applications utilizing strong electromagnetic field enhancement in vicinity of the MNPs surface, sensing applications, and photothermal-related applications.

Applications utilizing plasmon enhancement of the AuNPs and AgNPs

The strong electromagnetic field enhancement, which occurs in parallel to LSPR upon electromagnetic field excitation, can be employed in many types of applications. The general idea is this field enhancement can transfer the absorbed energy non-radiatively to the acceptors (fluorescence molecules or electrons), which analogous to increasing energy input for the acceptors. For instance, in a solar cell system, this strong electromagnetic field enhancement transfer extra energy to the surrounded electrons around the surfaces of the MNPs, this extra energy results in larger populations of electrons that can move to excited state and consequently, more electricity is produced. (Salvador et al., 2012: 10024-10032; Zhang et al., 2013: 4505-4510) These energetic-enhanced electrons are known as “hot electrons". Another example, is utilizing the strong electromagnetic field generated by MNPs to increase emissive quantum yield of the fluorescence molecules that located close to the MNPs surface. In this case, the field enhancement upon electromagnetic field excitation of MNPs could transfer the energy to the fluorescence molecules which lead to larger number of excited electrons and resulted in increasing of fluorescence intensity up to 1000 folds, therefore higher emissive quantum yield was observed. (Khatua et al., 2014: 4440-4449) Similarly, Raman signal could also be enhanced up to 10^4 folds by the field enhancements of AuNPs and AgNPs, this spectroscopic technique is known as "Surface Enhanced Raman Scattering" (SERS). (Garcia-Leis et al., 2013: 7791-7795; Sanchez-Gaytan et al., 2012: 10318-10324) The required criteria for the non-radiative energy transfer from the MNPs to the fluorescence or other acceptors molecules is the absorption (LSPR) of the MNPs must overlap with the absorption of the fluorescence or other acceptor molecules, larger overlapping of the absorptions leads to higher emission intensities or higher efficiency of solar cell.

Sensing applications utilizing sensitive nature of LSPR to change of electromagnetic field of the surrounding environment

LSPR is sensitive to the change of electric field (dielectric) of the surrounding environment, this is due to the nature of the LSPR that originated from coherent oscillations of the conductive electrons at the surface of the MNPs, therefore additional electrical force from change of the electric field of their surrounding can affect the oscillations and results in shifting of LSPR. This effect is analogous to the fundamental frequency of a swing which makes the swing go higher but external force such as wind results in the lower swing position.The change of the electric field could be created by change of solvent, (Mayer, and Hafner, 2011: 3828-57) vicinity molecules, addition of molecules such as heavy metal ions (Zhou et al., 2014: 106-111; Chen et al., 2014: 6843-6849) or even attaching of two single MNPs via linker. (Park et al., 2008: 553-556) Therefore, sensing applications utilized monitoring the LSPRs of AuNPs or AgNPs are possible. For example, Hg^{2+} in aqueous samples could be detected by monitoring the change of LSPR wavelength of AuNPs that were attached to each another as a cluster via chemical linker, the addition of Hg^{2+} which exhibited higher affinity (Hard –Soft Acid-Base, HSAB principle) to the linker led to separation of the AuNPs cluster and change of the LSPR, which reflected as the color change. Similarly, AgNPs could also be used in heavy metal sensing applications. (Zhou et al., 2014: 106-111; Chen et al., 2014: 6843-6849)

Photothermal-related applications

Generation of heat is another aspect of the photonics properties of AuNPs and AgNPs. The generate heat can be used in medical-related applications such as photothermal imaging and photothermal cancer therapy (Gobin et al., 2007: 1929-1934; Huang et al., 2006: 2115-2120). The uses of photothermal-related of the AuNPs and AgNPs in living cell are usually operated by using the laser sources in near-Infrared (IR) wavelengths in order to minimize cell damaging. Furthermore, gold and silver have been shown to be compatible with living cell. (Shukla et al., 2005: 10644–10654; Pauksch et al., 2014:439-449) Additionally, the generated heat can also be used for energy-related applications, In direct sunlight illumination, solution of AuNPs with silica core could generate heat which could bring the solution to boiling temperature, (Neumann et al., 2013: 42-49) created steams which could be used in applications such as electricity generation and sterilization. The basic principle to maximize the heat generation from the AuNPs or AgNPs is matching of their LSPRs with the wavelength of the illumination source. For the solar-energy related applications, broader LSPR is desirable because the sunlight illumination profile is broad and range from ultraviolet (UV), visible to near-IR wavelengths.

Summary

AuNPs and AgNPs possess interesting photonics properties, these properties are depended on size and shape of the MNPs, therefore, are influenced and vice versa tunable by the synthetic methods. These photonics properties are occurred in parallel to LSPR of MNPs, which are caused by interaction of light with the MNPs. The applications that utilized these photonics properties of AuNPs and AgNPs can be categorized into three groups. The applications that utilized strong electromagnetic field enhancement and photothermal phenomena of the MNPs surface are most effective at the LSPR wavelengths of the MNPs. While the use of the AuNPs and AgNPs in sensing applications are relied on the sensitive nature of LSPR to change of electric field (dielectric) of the surrounding environment. The synthesis principle and photonic properties of the AuNPs and AgNPs that were described in this review should benefit and support the noble MNPs-integrating researches.

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