The surface-plasmon-resonance effect of nanogold/silver and its analytical applications

Aihui Liang, Qingye Liu, Guiqing Wen, Zhiliang Jiang

Gold and silver nanoparticles (Au/AgNPs) are widely used in analytical chemistry, and their intense colors have inspired artists and fascinated scientists.

This review describes the absorption and Rayleigh-scattering effects of the surface-plasmon resonance (SPR) of Au/AgNPs. Specifically, the color associated with Au/AgNPs is utilized for immunoassay and aptamer assays. SPR-Rayleigh scattering is used for nanoanalysis, when combined with immune, aptamer and nanocatalysis reactions.

Keywords: Absorption; Aptamer assay; Gold nanoparticle (AuNP); Immune reaction; Immunoassay; Nanoanalysis; Nanocatalysis; Rayleigh scattering; Silver nanoparticle (AgNP); Surface-plasmon resonance (SPR)

Abbreviations: AD, Adenosine; AgssDNA, Nanosilver-ssDNA; APOA1, Apolipoprotein A1; APOB, Apolipoprotein B; AptAu, Aptamer-modified nanogold; C3, Complement component 3; CC, Cancerous cell; dsDNA, Double-stranded DNA; DP, Dopamine; DS, Diethylstilbestrol; Fb, Fibrinogen; FD, Formaldehyde; GICA, Gold immunochromatography assay; HB, Hepatitis B; HBsAg, Hepatitis B virus surface antigen; HEV, Hepatitis E virus; hCG, Human chorionic gonadotrophin; INGRS, Immunonanogold resonance scattering; INGC-GERS, Immunonanogold catalytic gold-enhanced resonance scattering; INGC-SERS, Immunonanogold catalytic silver-enhanced resonance scattering; LA-β, lactamase; LSPR, Localized surface-plasmon resonance; LOD, Limit of detection; MA, Melamine; Malb, Microalbumin; NG, Nanogold; NS, Nanosilver; NTA, 3-nitro-1H-1,2,4-triazole; OTA, Ochratoxin A; PA, Prealbumin; PC, Prostate cancer; R, Radius; RRS, Resonance Rayleigh scattering; RS, Resonance scattering; ssDNA, Single -stranded DNA; SPR, Surface-plasmon resonance; TNT, Trinitrotoluene; TM, Thrombin

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1. Introduction

Nanoscience and nanotechnology are recent revolutionary developments of science and technology that are evolving at a very fast pace. They penetrate all areas of physical and chemical sciences, biological sciences, health sciences, and other interdisciplinary fields [1,2]. Particles with sizes in the range 1–100 nm are called nanoparticles (NPs) that are a number of atoms or molecules bonded together and are intermediate in size between individual atoms and aggregates large enough to be called bulk material. NPs are divided into metallic, non-metallic, semiconductor and organic NPs, which have high surface-to-volume ratio, quantum-size effect and electro-dynamic interactions. Metallic NPs, good representatives of NPs, possess unique optical, electronic, chemical, and magnetic properties that are strikingly different from those of the individual atoms and their bulk counterparts [3,4]. Both gold and silver, ancient noble metals, have NPs that show novel colors and have received considerable attention from researchers [5].

The intense absorption and scattering of light from noble-metal NPs are the source of the beautiful colors in stained glass windows and have attracted the interest of many scientists. Although scientists have known that the characteristic hues of these noble-metal-NP suspensions arise from their strong interaction with light, the advent of NP optics has allowed deep understanding of the relationship between material properties (e.g., composition, size, shape, and local dielectric environment) and the observed color of a metal suspension. An understanding of the optical properties of noble-metal NPs, especially gold and silver, is of both fundamental and practical significance [6–14].

In this review, we summarize the surface plasmon resonance (SPR) absorption

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and SPR-Rayleigh-scattering effects of the two ancient noble-metal NPs, and their spectral analysis. Although similar to the title, the SPR sensor and imaging using gold NPs (AuNPs), the surface-enhanced Raman scattering detection and imaging techniques have been reported [14], but are not reviewed in this article.

2. Surface-plasmon-resonance effect

Noble-metal elements, including copper, silver and gold, exhibit metal shine due to free electrons. When the light electromagnetic wave shines on a metal, it is resonant with free electrons on the surface. And the resonant free electrons, as the source of an electromagnetic wave, produce the wave that is transmitted to the metal exterior (i.e. reflected light). The reflection efficiency of silver is 97%, but it is not in color. The white color is also called silver white. Gold yellow is the mixture of metal shine and yellow color that absorbs the wave apart from green light, while strongly reflecting visible light in the green to red light region. Thus, the naked eye sees the color of gold as yellow. AuNPs and silver NPs (AgNPs) exhibit strong visible absorption bands that differ from the color of the bulk metals [15–22]. These absorption bands result when the incident photon frequency is resonant with the collective oscillation of the conduction free electrons and is known as the localized surface plasmon resonance (SPR). SPR excitation results in wavelength-selective absorption with extremely large molar extinction coefficients of approximately 3×10^{11}/M/cm [23], resonance Rayleigh scattering (RRS) [24–28] with an efficiency equivalent to that of 10^6 fluorophors, and the enhanced local electromagnetic fields near the surface of the NP, which are responsible for the intense signals observed in all surface-enhanced spectroscopies [29,30].

SPR light absorption and SPR light scattering coexist in the SPR process of NPs. Fig. 1 shows surface-plasmon oscillation [31,32]. The electric field of an incoming light wave induces polarization of the free electrons with respect to the much heavier ionic core of a spherical NP. The positive charges in the NP are assumed to be immobile and the negative charges (i.e. free electrons) move under the influence of external fields. Displacement of the negative charges from the positive ones therefore occurs when the metallic NP is placed in an electric field. There results a net charge difference at the NP boundaries. This, in turn, gives rise to a linear force to restore the system. As a consequence, a dipolar oscillation of the electrons is created, and is known as the surface-plasmon oscillation. The collective oscillation of the electrons is also sometimes denoted as the dipole-particle plasmon resonance to differ from plasmon excitations that occur in bulk-metal surfaces. SPR is the coherent excitation of all the free electrons within the conduction band, leading to an in-phase oscillation [33]. Please note that plasmons also exist in the bulk and at the surface of large chunks of material [34,35]. However, because of a mismatch between the plasmon-dispersion relation and that of the photon, the plasmons cannot be excited by ordinary plane-wavelength light. The speciality of NPs is that momentum conservation is no longer required and the plasmons can be excited by ordinary light. In small clusters, the surface and the bulk plasmon are coupled, and the charge density varies everywhere in the particle [36–38]. Multi-polar resonances exist for individual NPs and can be excited. The only difference between multi-polar plasmons and dipolar plasmons is the shape of the surface charge

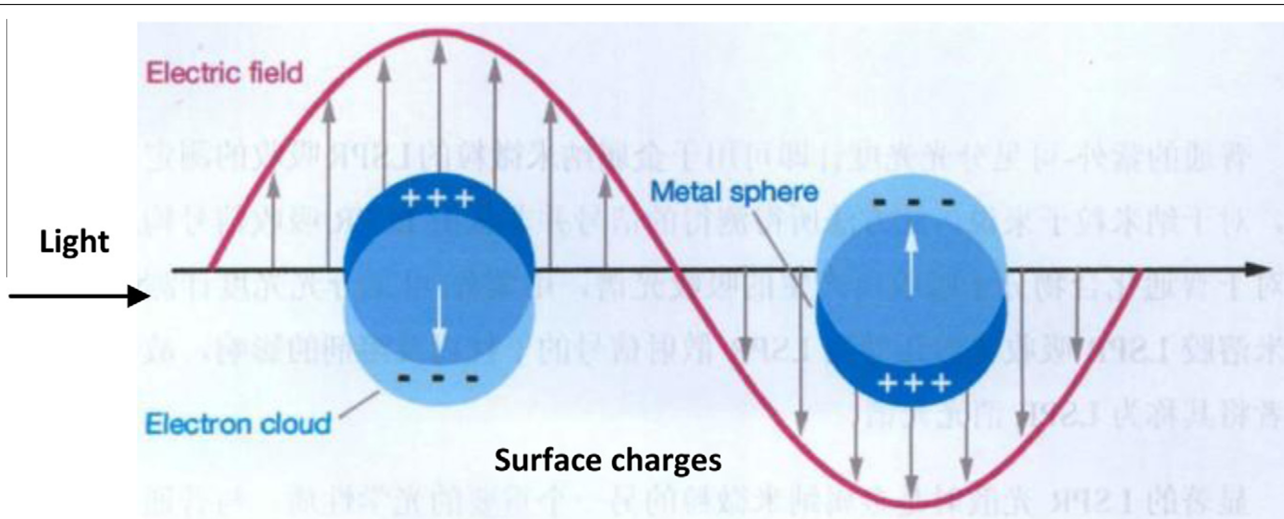

Figure 1. Surface-plasmon resonance (SPR) of spherical nanometal particle [31,32]. A dipole is induced and oscillates in phase with the electric field of the incoming light.