Advances in Colloid and Interface Science 225 (2015) 37–52

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Historical perspective

Mycofabrication of common plasmonic colloids, theoretical considerations, mechanism and potential applications

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ARTICLE INFO

Available online 17 August 2015

Keywords:
Plasmonic nanoparticles
Optical properties
Biomedical applications
Fungal synthesis
Mechanism of biosynthesis

ABSTRACT

A coupling of the plasmon on the surface of metal nanoparticles with an incident photon enhances a broad range of useful optical phenomena, such as resonant light scattering (RLS), surface plasmon resonance (SPR) or Raman scattering. Due to these unique optical properties plasmonic nanostructures of different sizes and shapes have gained increasing popularity in areas such as cancer diagnosis, photothermal therapy as well as the imaging of living cells, detection of pathogens, biomolecules, metal ions, and the catalysis of various reactions in wet chemistry. This article reviews the current trends in the synthesis of plasmonic nanoparticles, particularly gold (AuNPs) and silver (AgNPs), using fungi as well as the proposed mechanisms for their mycofabrication. We provide an overview of the theoretical concepts of plasmonic nanoparticles which are sensitive electromagnetic responses that determine these nanoparticles applications.

Contents

1. Introduction

Nanotechnology is at the cutting edge of research in all areas of science, engineering and technology. At its core are nanoscale materials and nanoparticles (NPs) in particular, composing differently shaped structures in the sizes ranging from 1 nm to 100 nm in 2 or 3 dimensions [1].

The difference in nanomaterials' properties in comparison to their bulk counterparts arises from their small size and high surface-to-volume ratio. This results in materials exhibiting entirely different qualities on the nano-level in terms of density, resistivity, magnetisation and the dielectric constant [2].

The use of nanosized substances stretches hundreds, or even thousands of years back. Gold nanoparticles (AuNPs) were used by

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http://dx.doi.org/10.1016/j.cis.2015.08.003
0001-8686/

craftsmen to produce a ruby red colour. Roman artisans mixed gold chloride into molten glass to produce red coloured pottery. One of the most famous examples of this technique is the Lycurgus Cup, one of a class of Roman vessels known as cage cups or diatreta, which contains both gold and silver nanoparticles [3].

The very first scientific study of nanomaterials was conducted by Michael Faraday in 1857. In his pioneering work, "Experimental Relations of Gold (and Other Metals) to Light", he explains the origin of the colour in the red glaze and glass [4].

The unique optical, electronic, and catalytic properties of plasmonic nanoparticles are greatly influenced by their size, shape, and crystal structure. These properties give nanomaterials exponentially increasing potential for application in such areas as electronics, photonics, catalysis, information storage, chemical and biological sensing, imaging, environmental remediation, drug delivery and biological labelling [5–9].

2. Theoretical considerations and application of plasmonic nanoparticles

Both silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) are most commonly used plasmonic nanostructures. They derive their valuable qualities, not only from their small size which dictates their difference to the bulk counterparts, but also from the unique property of strong optical extinctions. This arises from an electrodynamic phenomenon known as free electron gas plasmons that can propagate on the surface and in the bulk of the metal. Surface plasmons can be categorized into two types: surface plasmon polaritons, which propagate along metal surfaces in a waveguide-like fashion until released at some distance from their point of origin and localised surface plasmon resonances (LSPR), in which incident light is absorbed or scattered by the oscillating electric dipoles within a metal nanoparticle [10].

2.1. Phenomenon of localised surface plasmon resonance (LSPR)

The LSPR dipole oscillations, Fig. 1, are much stronger for plasmonic nanoparticles, noble metals like Au and Ag, than other metals. The intensity of the dipole oscillations and their wavelength depend on factors affecting the electron charge density on the surface of the particle such as the metal type, particle size, shape, structure, composition and the dielectric constant of the surrounding medium [11].

In the simplified case of metal nanospheres with a radius (R) that is much smaller than the incident photon, the plasmon response is dipolar in nature and the strength and frequency of the resonance is related to the total number of electrons in the oscillating dipole defined by the particle volume, or R^3, the complex dielectric function $\varepsilon(\omega)$ of the metal the particle made of, and the dielectric constant of the local medium ε_m. The plasmonic response is directly measureable by optical extinction (C_{ext}) and can be quite intense.

The resonance condition leading to maximum polarization in Eq. (1) below is $|\varepsilon(\omega) + 2\varepsilon_m| = 0$, requiring $\varepsilon(\omega)$ to be negative. However, the complex dielectric function must be divided into real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ components in order to remove the phase-dependent term from the equation; resonance is thus achieved when $\varepsilon_1(\omega) = -2\varepsilon_m$ and $\varepsilon_1(\omega) \ll 1$. The dielectric function is negative when ω is below some threshold frequency ω_p, known also as the plasma frequency [12]

For spherical particles smaller than 20 nm, the extinction cross-section C_{ext} particles can be calculated using Mie theory the formulations of which are derived from Maxwell's equations [13]:

$$\mathbf{C_{ext}} = \frac{24\pi^2 \boldsymbol{R}^3 \boldsymbol{\varepsilon_m}^{3/2}}{\boldsymbol{\lambda}} \frac{\boldsymbol{\varepsilon_2}}{(\boldsymbol{\varepsilon_1} + 2\boldsymbol{\varepsilon_m})^2 + \boldsymbol{\varepsilon_2^2}}. \quad (1)$$

The dielectric constant of the surrounding medium ε_m is related to the refractive index of the medium by $\varepsilon_m = (n_m)^2$. The real part of the dielectric constant $\varepsilon_1(\omega)$ of the metal determines the LSPR position and the imagery part $\varepsilon_2(\omega)$ determines the bandwidth. AuNPs, AgNPs and CuNPs possess strong LSPR bands in the visible region, in comparison to other metal nanoparticles that have broad and weak bands in the UV region [4,14]. In some sources, the LSPR is described in terms of extinction efficiency Q_{ext}, which is defined as the ratio of C_{ext} to geometrical cross-section area, πr^2 in the case of spheres [13].

The LSPR band of plasmonic nanoparticles with sizes smaller than 10 nm is dampened due to the phase changes resulting from the increased rate of electron-surface collisions compared to larger particles [15]. Increasing particle size causes a red shift of the SPR wavelength and an increase in the absorption intensity. Further increase in the size of plasmonic nanoparticles results in the broadening of plasmonic peak and development of the longitudinal plasmonic absorption. A significant band broadening of the colloids with particles larger than 100 nm can be explained by dominant contributions from higher order electron oscillations [16].

2.2. Optical properties of plasmonic nanoparticles

In the localised plasmon resonances an incident light is absorbed or scattered by the oscillating electric dipoles within a metal nanoparticle. A coupling of the plasmon on the surface of metal nanoparticles with an incident photon enhances a broad range of useful optical phenomena, such as resonant light scattering (RLS), surface plasmon resonance (SPR) or Raman scattering, all of which have great potential for applications in ultrasensitive chemical and bimolecular detection and analysis [12].

The total light extinction of electromagnetic waves after passing through matter results from the absorption and scattering processes. Due to the SPR oscillation, the light absorption and scattering are greatly enhanced, 5–6 orders of magnitude more than the most strongly absorbing organic dye molecules and the emissions of the most strongly emitting fluorescent molecules [17].

The surface plasmon absorption, scattering and total extinction efficiencies are generally studied by using Mie theory [11]. The optical absorption and scattering are dependent on the size of the nanoparticles. For a 20 nm AuNP, the total extinction is mostly contributed by absorption, Fig. 2(a) [17]. With the size increase to 40 nm, the scattering

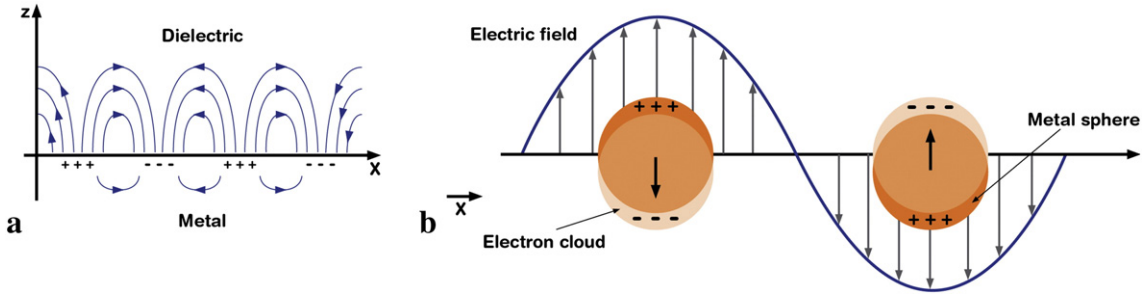

Fig. 1. Incident light upon the surface of plasmonic metals generates propagating surface plasmons in bulk metals (a) and localised (standing) plasmon resonances in nanostructured plasmonic materials (b).