



Investigating the extrinsic size effect of palladium and gold spherical nanoparticles



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ABSTRACT

In many optical applications, knowing the variations of the plasmonic resonance wavelengths of a special kind of nanoparticles in terms of their size before the experiment began, can assist the users in selection of an appropriate preparation method for the optimum functionality. In this work, in order to show the role of the preparation method on the mean size and the size distribution of nanoparticles, two different chemical bottom-up and physical top-down methods were used for the synthesis of palladium and gold nanoparticles. Chemical reduction of metal salt and laser ablation in liquid media methods were respectively used for preparation of palladium and gold nanoparticles. It is shown that the chemical bottom-up method results in the formation of smaller particles with narrower size distribution. Optical properties and plasmonic resonance absorption of the prepared nanoparticles were investigated by UV–vis spectroscopy and their size distribution were determined by transmission electron microscopy (TEM) images. Using the measured size distribution of nanoparticles, their optical extinctions are modelled using the Mie theory of scattering. A comprehensive study on the extrinsic size effect of palladium and gold nanoparticles is performed and the dipolar and the quadrupolar Mie resonances in these nanoparticles are investigated in details. The reported results can be used for selecting the preparation method of these nanoparticles and for choosing the appropriate laser wavelength to excite stronger or weaker Mie resonances for specific applications.

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1. Introduction

Nanoparticles (NPs) can be made of different types of materials such as metals, metal oxides, silicates and ceramics. Although there are NPs made of other types of materials, for example material based on composite samples or polymeric semiconductors, but nowadays, materials in the first category have wide applications and have been the subject of numerous studies. Generally speaking, NPs show new properties, such as optical, morphological and etc., compared with their bulk samples [1,2]. Typically, metal and metal oxide NPs are spherical in shape and are prepared with appropriate physical characteristics for specific needs [3,4]. The high surface to volume ratio of NPs is the main factor accounting for their widespread use as catalysts and also in structures such as electrodes. Using the same characteristic of NPs causes significant interaction between them and the host materials in nanocomposites and

induce special properties such as increased optical, nonlinear optical [5] and electrical [6] properties.

As it is well-known, there are two basic methods for preparation of NPs: top-down and bottom-up methods [7]. In the top-down synthesis method, one starts with a bulk sample and by reducing its dimensions reaches a product with nanoscale dimensions [8]. A process that is mostly done using the physical techniques and hence there is little control over the preparation procedure and NPs with wide size distributions are often prepared [9]. In the bottom-up synthesis method, first the required building blocks are prepared and then by their aggregation, NPs are formed [10]. The bottom-up preparation of NPs is mostly achieved using chemical and biological techniques [11]. The used method for preparation of NPs affect their size distribution, surface defects and morphology. Compared with physical methods, chemical methods have better control over size distribution, shape and surface defects of the prepared NPs. NPs that are prepared by chemical methods often have narrower size distributions with less surface defects [12]. The three major chemical methods that are in common use for preparation of metal NPs are chemical reduction of metal salts, thermal

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and photochemical decomposition of metal complexes and electrochemical reduction of metal salts [13]. Chemical reduction of metal salts is the most important and the most common chemical method for synthesis of metal NPs. In this method, by using a suitable reduction agent, NPs are prepared from the solution containing the desired metal salt [14]. Furthermore, some of the main physical methods that are typically used for preparation of NPs include etching through the masks [15], ball milling [16], application of severe plastic deformation [17] and laser ablation [18] and pulsed laser deposition [19] methods.

The most interesting feature of metal NPs is their optical properties that depend on their size [20], shape [21] and the surrounding medium [22]. Optical properties of metal nanostructures are interesting and complex as a result of excitation of surface plasmons by electromagnetic waves. The surface plasmon excitation in metal NPs leads to the optical properties which are difficult to achieve in other materials. This property leads to a wide range of applications for these NPs [23] in fields such as biological imaging and fabrication of nano-antennas and solar cells. Typically, the localized surface plasmon frequency of metals locates in the visible or near-ultraviolet spectral regions [24–27]. The plasmonic properties of metal nanostructures have been the subject of intensive empirical and theoretical studies. For instance, plasmonic properties of palladium (Pd) nanodisk arrays are already studied over large size and spectral ranges [28]. In addition, the reported frequency of plasmon resonance peaks for 50-nm Pd nanocubes is reported to be at around 400 nm [29]. For spherical Pd NPs around 10 nm in size has not been any response in the frequency range between 300 and 1500 nm [30]. Recently developed methods for preparation of the triangular and hexagonal Pd nanoplates allowed demonstrating the shift of the surface plasmon resonance peaks from 225 nm to 530 nm [31,32]. The frequency peak of surface plasmon resonance for gold (Au) NPs around 15 nm in size and Au nanocubes with side lengths of 44 nm have been measured to be around 538 nm and 527, respectively [33]. The surface plasmon peaks of Au nanorods are relatively sharp in the longitudinal direction and peak frequency for longitudinal sizes of 40, 55 and 74 nm is measured to be at 653, 728, 846 nm, respectively [34]. The surface plasmon peak of Au nanobranched in the longitudinal direction for longitudinal size of 80 nm have also been reported to be at 1141 nm [34]. Pronounced surface plasmon peaks at ~530 nm are commonly observed for Au spherical NPs [28].

It should be noted that the mentioned plasmonic peaks are reported for specific kinds of nanostructures with their own characteristic sizes and there is no comprehensive study on variation of this feature with size of spherical NPs. Precise theoretical study of the relationship between localized surface plasmon resonance frequency and size of NPs is only available for simple geometries such as spherical NPs. The Mie theory of scattering yields exact solutions for spherical NPs and can be readily used to study the interaction of light with these types of NPs [35]. It is also possible to investigate the surface plasmon resonance frequency of the non-spherical metal NPs using approximate methods such as quasi-static approximation, discrete dipole approximation and finite difference time domain method [36]. There are two different kinds of NPs size effects: intrinsic effects that concern specific changes in volume and surface properties of materials and extrinsic effects, which are size-dependent responses to external fields [37]. In investigating the intrinsic optical effects one particularly focuses on the question of how the optical properties vary as a function of NPs size and geometry. On the contrary, extrinsic size effects deal with the collective electronic or lattice excitations in NPs which are known as the Mie resonances. The electronic and the lattice excitations are dominant in metal and dielectric NPs, respectively. A number of studies have been reported so far in which the extrinsic

size effect of NPs have been investigated. The effect of NPs size on their extinction and the Mie resonances wavelength has been studied for Pd nanocubes [30] and Au [38], Ag [39] and ZnO [40] NPs.

In this paper, effect of the preparation method on mean size and size distribution of metal NPs is investigated. Laser ablation in liquid media and chemical reduction of metal salt methods were respectively used for preparation of Au and Pd NPs. Au and Pd NPs have been selected based on the fact that their plasmonic resonance behavior are quite dramatic [37] and fairly weak [30], respectively. In this way, it would be possible to check the validity of the Mie theory modelling in two different extreme cases. Preparation of these NPs with the two different methods makes also possible to model the extrinsic size effects for their two different mean sizes and size distributions. Optical properties and plasmonic resonance absorption of the prepared NPs were investigated by UV–vis spectroscopy. Using the measured size distributions and the Mie theory, the optical absorption spectra of NPs were calculated and compared with the empirically measured ones. A comprehensive study of the extrinsic size effects of Au and Pd NPs is presented and their dipole and quadrupole excitations are investigated.

2. Preparation of NPs

As mentioned in the previous section, the most common bottom-up method for preparation of metal NPs is the chemical reduction method of metal salts. Laser ablation of metals in liquid media is also a simple and widely used physical method for top-down preparation of NPs. In this work, Pd and Au NPs were prepared by chemical reduction of metal salts and laser ablation in water, respectively. In the following, the preparation methods will be described in more details.

2.1. Preparation of Pd NPs

In order to prepare the Pd NPs, first 178.0 mg PdCl₂ salt was dissolved in 12 mL HCl (0.2 M) and 500 mL deionized water to form H₂PdCl₄ (2 mM) aqueous solution. The formed solution stirred for 3 h and then 30 mL of the stirred solution was added to 40 mL deionized water, 133.4 mg PVP and 8 drops of HCl (1 M). The formed mixture is heated at 120° C. 28 mL ethanol was added to the H₂PdCl₄ as a reducing agent and then stirred for 3 h to get a dark brown solution. In this way, H₂PdCl₄ (as solvent and reducing agent) decreased by ethanol. Consequently, Pd NPs were formed and subsequently were stabilized by PVP.

2.2. Preparation of Au NPs

Au NPs were prepared by ablating a golden plate in deionized water with a Nd:YAG pulsed laser at 1064 nm wavelength. The pure golden plate (~99.99%) was placed at the bottom of a glass cell filled with 10 mL of deionized water. The laser repetition rate, energy and pulse duration were 10 Hz, 85 mJ and 30 ns, respectively. The laser beam was focused to a spot size of ~1 mm by an $f = 20$ cm convex lens. In order to prevent from crater formation on the surface, the plate was rotated during ablation with a constant rotation speed (10 rpm). Laser ablation lasted for 20 min until the color of water changed from colorless to purple.

3. Absorption modelling by Mie theory of scattering

In the Mie theory, diffraction from spherical NPs is exactly calculated using the Maxwell's equations with convenient boundary conditions in spherical coordinates. This theory can be used to

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