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New aspects of gold nanorod formation via seed-mediated method

Monique G.A. da Silva, Ábner M. Nunes, Simoni M.P. Meneghetti, Mario R. Meneghetti *

Grupo de Catálise e Reatividade Química–GCaR, Instituto de Química e Biotecnologia da Universidade Federal de Alagoas, Av. Lourival de Melo Mota, s/n CEP 57072-970, Maceió, AL, Brazil

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ABSTRACT

Gold nanorods (AuNRs) were obtained via a wet chemistry technique, in aqueous medium, employing crystallisation seeds. The kinetics of formation, the aspect ratio, and the selectivity of the particles were evaluated according to the parameters of synthesis: the growth-driving agent, seed, and gold precursor concentrations. In 2–4 h, the rod particles attained the expected size and shape under kinetic control, and were stable for at least 2 days. In order to obtain good quality AuNRs in good yields, without enrichment, we suggest keeping the growth-driving agent/gold molar ratio, the Au^{I}/seed ratio, and the concentration of the reagents in the final solution within specific ranges. For example, even if good molar ratios between the reagents are maintained, relatively highly concentrated reaction solutions lead to AuNRs with lower aspect ratios. The main properties of the prepared colloidal systems and the nanoparticles were evaluated by UV–vis spectroscopy and transmission electron microscopy, respectively.

1. Introduction

For centuries, the search for new materials with precise characteristics and applications has been one of the most important stimulants of technological development [1]. In general, to fabricate the most simple or complex device or object, it is essential to search for materials that exhibit the desired physico-chemical properties for the aspired application. But can a particular material, with identical chemical composition and structural arrangement, display different properties? The answer is yes, but this largely depends on the dimensions of the material itself or the dimensions of the components [2,3].

Outstanding properties can arise when materials are in the nanometric scale, but this is not only due to dimensional features, like the surface/volume ratio (very high for nanostructures), but it also depends on the form, environment, and organisation of the particles that comprise the nanostructured material. Indeed, these features are consequence of a "nano-effect", and most of them are associated with quantum-like laws [4,5].

Metal particles, like Au, Ag, and Cu, are known to absorb specific wavelengths of the visible spectrum when they possess nanometric dimensions. This singular absorption is due to the collective resonant oscillation of the electrons of the conducting band promoted by the electric field of the incident light at the particle surface [6,7]. This effect is called surface plasmon resonance (SPR), and was first elucidated by Mie in 1908 [8,9]. For that reason, for example, the optical properties of gold nanoparticles (AuNPs) can be significantly modified if their dimensions are in the range of 1 to 100 nm [10,11]. Indeed, with precise synthesis control, it is possible to prepare colloidal solutions of AuNPs with different colours [12].

Spherical AuNPs typically display one absorption band in the visible or near-infrared spectrum, and just one range of these electromagnetic radiations can induce the expected SPR (Fig. 1). On the other hand, anisotropic nanoparticles display different absorption bands since different SPR energies are generated [6]. Nanorods and

* Corresponding author.
E-mail address: mrm@qui.ufal.br (M.R. Meneghetti).

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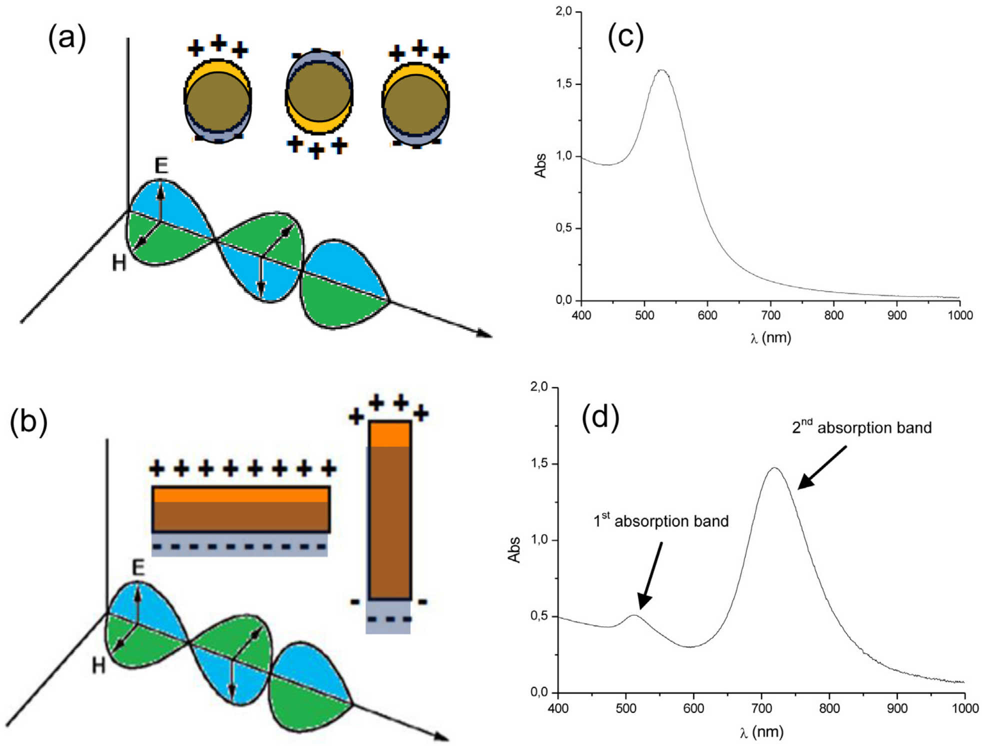

Fig. 1. (a) Illustration showing the single surface plasmon resonance on a spherical (a) and rod-like (b) gold nanoparticles, generated due to the interaction of the particle with the electromagnetic field of the incident light. (c) and (d) are an illustration of the respective typical outline UV–vis absorption spectrum expected for those colloidal solutions.

nanowires, for example, display two typical absorption bands; one related to the longitudinal, and the other to the transversal SPR (Fig. 1) [13].

It is worth noting that one can profit from the optical features of AuNP-based structured systems and use relatively simple UV–vis(-NIR) spectroscopy to evaluate and follow the synthetic procedures and the characteristics of the final product [14,15].

This great versatility of colloidal systems of AuNPs, in terms of optical properties, continues to attract the attention of several research groups. New synthetic strategies to obtain specific AuNPs in high yields, for precise applications [16,17], are frequently observed in the modern literature [10,18,19]. In addition to studies in the field of photonics [20] and optics [6,21], applications of AuNPs can also be found in areas like catalysis [22], sensors [23], medical diagnosis [24,25], and tumour treatment [26,27].

Metal nanoparticles can be prepared on the bases of physical and chemical methods, following two main approaches: (i) bottom-up or (ii) top-down methodologies. Nanoparticles obtained via the top-down approach are based on physical methods, and are normally generated from larger particles. Sputtering [18,28,29], sonolysis [30], and nanolithography [31,32] are examples of techniques based on this practice. On the other hand, methods based on "wet chemistry" follow, in general, the bottom-up approach. In this latter case, nanoparticles are frequently prepared from molecular metal precursors that, after specific chemical transformations, generate very reactive "solvated" metal atoms that soon interact to each other via metal–metal bonds until they reach the size and shape of the desired metal nanoparticle. These nanoparticles remain, in many cases, dispersed in the liquid matrix, like colloidal solutions [33,34].

Of all the possible metal nanoparticle shapes that can be generated, the spherical ones are the most thermodynamically stable, since, with this shape, the lowest surface potential is achieved, and, for this reason, the particles are easier to obtain. However, depending on the concentration of the metal source in the solution and/or the presence of particular chemical compounds (growth-driving agents), other forms of nanoparticles can be obtained [35,36]. Indeed, there are a series of studies that report on the preparation of nanoparticles of several different forms, i.e. tetrahedral [37], cubic [38], prismatic [39], cylindrical [40], star-like [41], hollow [42], disk [43], etc. [44].

Several research groups have focused on anisotropic nanoparticle synthesis, especially because of their optical properties, which are closely related to the presence of different surface plasmons [45]. The most common strategies used to control the shape and size of anisotropic nanoparticles are based on wet chemistry methodologies [46–50].

Among the range of shapes possible for AuNP, rod-like particles are particularly well studied. In particular, many