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Synthesis and characterization of extremely small gold nanoshells, and comparison of their photothermal conversion capacity with gold nanorods†

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The current methods for preparing gold nanoshells (AuNSs) produce shells with a diameter of approximately 40 nm or larger, with a relatively large polydispersity. However, AuNSs with smaller diameters and more monodispersity are better suited for biomedical applications. In this work, we present a modified method for the preparation of AuNSs, based on the use of sacrificial silver nanoparticles (AgNPs). We customized the Lee–Meisel method to prepare small and monodisperse AgNPs that were used as sacrificial nanoparticles to prepare extremely small monodispersed AuNSs with an average diameter from 17 to 25 ± 4 nm. We found that these AuNSs are faceted, and that the oxidized silver likely dissolves out of the nanoparticles through some of the facets on the AuNSs. This leads to a silver oxide plug on the surface of the AuNSs, which has not been reported before. The smaller AuNSs, prepared under the best conditions, absorb in the near infrared region (NIR) that is appropriate for applications, such as photothermal therapy or medical imaging. The AuNSs showed absorption peaks in the NIR similar to those of gold nanorods (AuNRs) but with better photothermal capacity. In addition, because of their negative charge, these AuNSs are more biocompatible than the positively charged AuNRs. The synthesis of small, monodisperse, stable and biocompatible nanoparticles, like the ones presented in this work, is of prime importance in biomedical applications.

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Introduction

Metallic nanoparticles have been studied for several decades because of their attractive physical and chemical properties inherent to their size, which makes them useful for various applications, such as catalysis, optics, information storage, biological and chemical sensing, surface Raman scattering, bionanomedicine, *etc*.[1] In particular, gold nanoparticles (AuNPs) have generated great interest because they are highly inert, and generally biocompatible. In addition, they have a good capacity to absorb light due to their strong surface plasmon resonance.[2] The synthesis of AuNPs is not new; Faraday described the production of colloidal gold by the reduction of chloroauric acid by phosphorus more than a century ago.[3] With the development of Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM), the shape and size of these nanoparticles have been determined. These observations have helped in the development of better synthesis methodologies to improve the physical characteristics of the nanoparticles, such as size and shape as well as better controlled optical properties. Nowadays, AuNPs have been synthesized with great control over size and shape such as nanospheres,[4] nanorods,[5] nanostars,[6] nanotubes,[7] nanocubes,[8] nanodisks,[9] nanowires,[10] hollow nanogolf gold balls[11] and nanoshells.[12–14] One of the main features of the nanoparticles is that their absorption peak depends on their size and shape, and for medical applications it is desirable to develop nanoparticles that absorb in the transparent window of biological tissues; the NIR, from 800 to 1200 nm.[15,16]

In recent years, gold nanoshells (AuNSs) and nanorods (AuNRs) have been studied extensively due to their strong surface plasmon absorption that helps them converting NIR radiation into heat, which is favourable for their use in photothermal therapies for cancer treatment,[17,18] photothermally triggered drug release,[19] and gene therapy.[20] In addition, their strong light scattering makes them good contrast agents for medical imaging.[21] *In vivo* experiments of injected AuNPs in the blood stream of mice with a cancerous tumour, show that these particles accumulate primarily in the tumour, showing

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