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# Amorphous nanoshell formed through random growth and related plasmonic behaviors

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## ABSTRACT

The optical properties of gold nanoshell formed through random growth process were numerically investigated by employing finite-difference time-domain method. The growth process can be divided approximately into four stages according to the optical spectra and 3D morphology. The incomplete nanoshell with surface coverage ratio ($R$) around 70% was found to form surface 'hot spots' with high field enhancement, which are useful for surface enhanced Raman scattering. Additionally, high Purcell factor and quantum efficiency at the core center for the nanoshells with $R\sim 90\%$ are suitable for encapsulated fluorescent probe that can exploit the high surface plasmonic enhancement effect.

## 1. Introduction

Metallic nanoshells, consisting of a spherical dielectric core homogeneously coated with a concentric nanoscale metallic shell, have currently received wide attention mainly because of its highly tunable plasmonic properties [1,2]. By varying the relative dimensions of the core and shell, nanoshells can be designed and fabricated with plasmon resonances from visible to infrared regions of the spectrum [3–5], showing their potentials in widespread applications, such as biomolecular sensing [6,7], surface-enhanced Raman scattering (SERS) [8–10], controlled drug delivery [11], biological imaging [12], and photothermal cancer therapy [13,14]. The synthesis of gold nanoshells usually involves gradual deposition of small gold colloids onto the surfaces of dielectric cores grown by the Stöber method [15]. The gold particles then grow and coalesce, from isolated islands to incomplete rough coating, finally form a continuous complete shell covering the dielectric core [3,4,16,17]. During shell growth, evolution of the extinction properties has been experimentally observed, showing that the resonant peak which firstly remains at ~520 nm resulting from gold colloid, undergoes a tendency of red shift, then at later time of a dramatic blue shift to nanoshell resonance [3,8,18–20]. To understand the evolution behaviors of optical resonance, a few theoretical models have been proposed to simulate the formation process [19–23]. For example, through analyzing plasmon modes of a series of spheres and hemispheres, Preston et al. studied optical spectra of incomplete nanoshell during growth qualitatively [20]. Moreover, in order to quantitatively simulate growth process for all coverage possibilities, Lin et al. assumed that metal nanoparticles are uniformly distributed on the silica surface for simplicity [22]. While Pena-Rodriguez et al. proposed that the deposition process was artificially divided into two stages, and in the initial stage overlapping between metal particles were not allowed [23]. Although these models have addressed partially the evolution behaviors of optical properties such as extinction spectrum and near-field enhancement, the growth process is not yet modeled well. For instance, during a realistic nanoshell growth, the adsorption of metal seed particles, the growth and coalescence of metal islands, all should be a random way.

On the other hand, the researchers just recently are aware of the distinct properties of amorphous nanoshell and the related potential applications. Oubre et al. simulated the optical spectra of nanoshells with surface defects using finite-difference time-domain (FDTD) method, finding a red shift of plasmon resonance along with the increasing surface roughness [24,25]. This red shift, resulting from strengthened interparticle plasmon coupling which can be explained by plasmon hybridization theory [26–29], leads to the generation of numerous 'hot spots' for intense localized field [23,25]. The appearance of near-field electromagnetic enhancement in the incomplete nanoshell structure makes it desirable for

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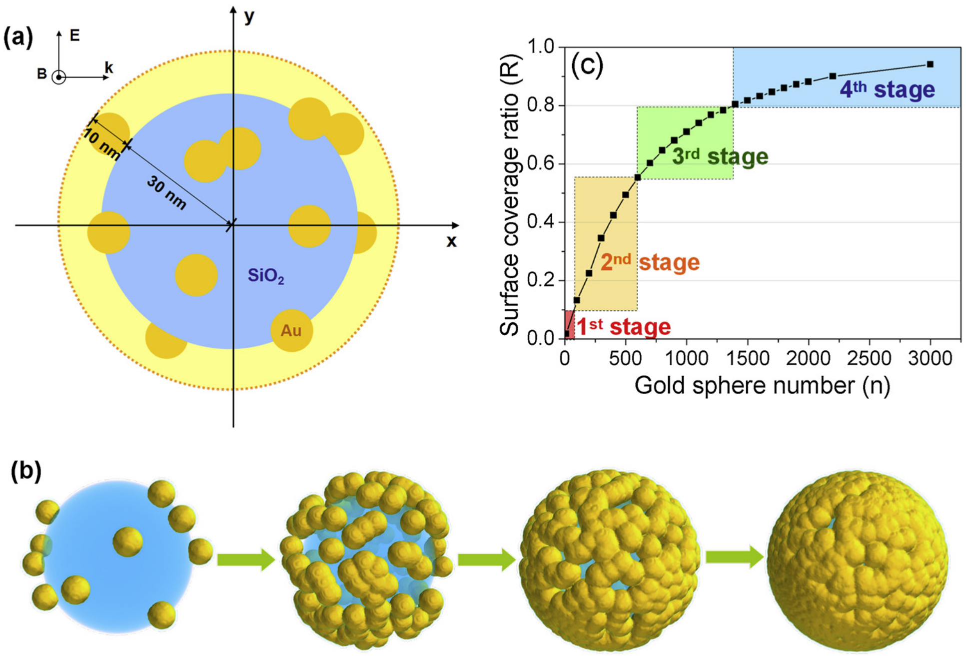

**Figure 1.** (a) 2D schematic illustration of nanoshell random growth model. 30-nm-radius silica core is surrounded by several 10-nm-diameter gold nanospheres randomly distributed on the silica surface. (b) Calculated surface coverage ratio ($R$) as a function of gold sphere number.

SERS applications [9,30], and several methods has been used to introduce more defects on gold nanoshell so as to lead high SERS, surface enhanced fluorescence (SEF) enhancement and versatility [31–33]. To understand and optimize the performance, the growth process should be modeled and investigated through a systematic theoretic model, and it is necessary to make a clear relation between the growth of nanoshells and the corresponding plasmonic behaviors.

Here, we develop a random model to simulate the nanoshell growth in which many gold nanoparticles are attached randomly onto the surface of a silica core. The optical properties of the random growth nanoshell with all possible coverage conditions are

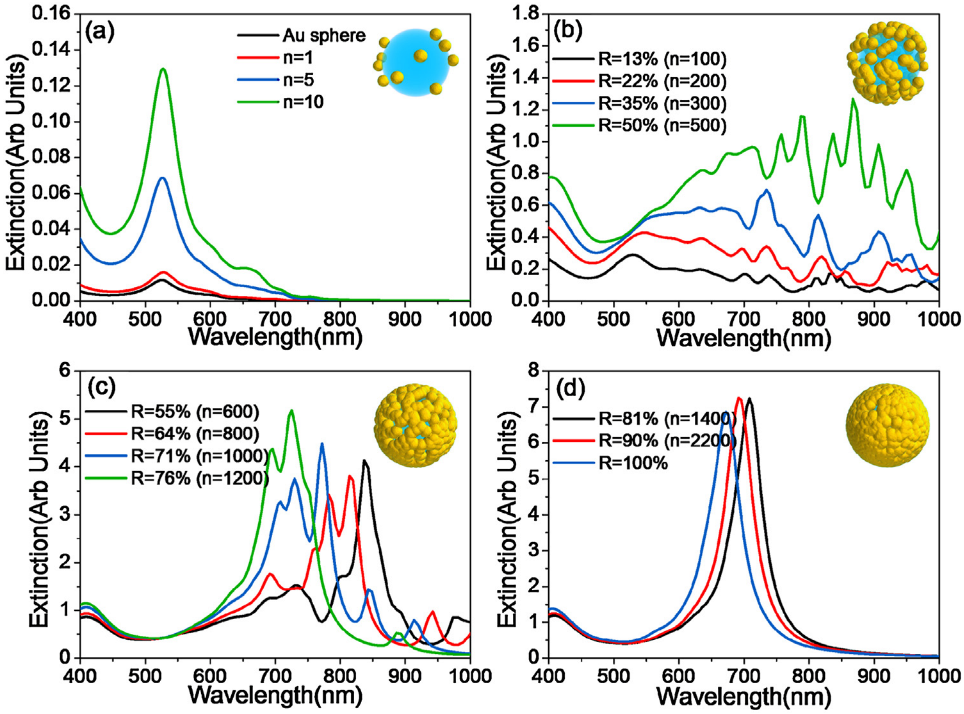

**Figure 2.** Optical extinction spectra of incomplete nanoshell with different surface coverage ratio during growth. The evolution process is approximately divided into four stages. (a) 1st stage ($0 < R < 10\%$): separated gold spheres; (b) 2nd stage ($10\% < R < 55\%$): spheres gradually coalesce into various isolated gold islands; (c) 3rd stage ($55\% < R < 80\%$): a connected but incomplete coating; (d) 4th stage ($R > 80\%$): nearly complete nanoshell with only a few pinholes. Then nanostructures is illuminated by planar Gaussian light source as depicted in Figure 1a.