Preparation and characterization of polymeric thin films containing gold nanoshells via electrostatic layer-by-layer self-assembly

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ABSTRACT

As an initial step in the development of surfaces for collecting thermal energy, gold shell/silica core particles (~200 nm in diameter with shells ~25 nm thick) were synthesized and incorporated into organic polymeric thin films. The morphologies of these nanoshells were characterized with scanning and transmission electron microscopy. Powder X-ray diffraction demonstrated that the gold layers were highly crystalline. Thin films containing the gold nanoshells and polyethyleneimine were generated using dip-coating techniques based on electrostatic layer-by-layer self-assembly methods. Scanning electron microscopy was used to image the resultant composite films, which contained uniformly distributed gold nanoshells with limited aggregation. The optical properties were analyzed by absorption spectroscopy, revealing broad extinctions ranging from the visible to the near-IR spectral regions. X-ray photoelectron spectroscopy spectra were also obtained to determine the elements present and the oxidation states of these elements.

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1. Introduction

Metal nanoparticles (NPs) derived from noble metals have drawn wide interest because of their unique and tunable optical properties and their efficient photo-thermal effects [1]. The most notable optical feature of these NPs is their surface plasmon resonance (SPR), which arises from an interaction between an electromagnetic wave and the conduction electrons present in the metal. Under the irradiation of light, electrons near the surface of the metal NPs are driven by the light wave's electric field to oscillate collectively when the frequency of the optical excitation matches their natural frequency, a process that also leads to a maximum of energy absorption [2,3]. The peak position of the SPR band for metal nanoparticles varies with the particle size, shape, and composition, along with the refractive index of the surrounding medium [4–8]. Studies of this enhanced absorption of light have included investigations of heat generation by metal NPs under illumination, an associated physical property [9,10]. Because the absorption of incident photons is greatest when the light produces a resonance response, the conversion of photon energy into heat energy, as well as the heat transfer from the NPs to the surrounding matrix, can be maximized for a metal NP system through prudent NP design. The heating effect is especially strong for metal NPs because they have a high optical quantum yield (i.e., they are poor emitters of light). Analyses of this heating effect have included efforts to measure the temperature on the surface of gold nanoparticles (AuNPs) when they are optically excited [9,10].

One effort to modify the wavelength at which an NP system absorbs light has been through the development of shell/core metal nanoparticles called "nanoshells" [5,7,11,12]. Gold nanoshells (AuNSs) consist of a spherical dielectric core, such as silica or polystyrene, surrounded by a thin gold shell. Most metal NPs that exhibit SPR behavior generally adsorb or scatter light over the ultraviolet and visible regions of the electromagnetic spectrum. In contrast, the SPR of AuNSs can be tuned to a wider range of frequencies than typical AuNPs, ranging from the ultraviolet to the near-infrared regions of the electromagnetic spectrum. AuNSs having SPRs in the near infrared region are well suited for hyperthermia applications in biological systems because biological fluids and tissue are transparent over this range of the electromagnetic spectrum. Apart from their optical properties, AuNSs are biologically inert and their surfaces can be readily functionalized with selective biomolecular linkers for the purpose of targeting them to specific sites of interest [13]. Some potential applications that have been explored that rely on their optical and thermal properties include biological imaging and detection, drug delivery, and the photothermal treatment of various diseases, such as cancer [14–18]. The most common synthetic approach for producing AuNSs has been the "seeded-growth" method [5,11]. This route involves the synthesis of silica NPs and the functionalization of their surface with terminal amine groups to facilitate the attachment of much smaller colloidal gold particles, which then serve as seeds to template the subsequent growth of a polycrystalline gold shell in a controlled manner.

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The utilization of nanoshells in device architectures has also been pursued [19,20]. In particular, an assembled layer of nanoparticles to generate thin-film structures has many promising applications, including the incorporation of functional layers in optoelectronic devices, the development of efficient electrodes for fuel cells, and the improvement of biosensor performance [21–26]. Zhang et al. have reported the fabrication of multilayered AuNP thin films on aminosilane-functionalized quartz substrates [25]. These researchers showed that the use of layer-by-layer (LBL) assembly with poly(allylamine hydrochloride) afforded tightly packed AuNPs; however, the NPs began to agglomerate and form large clusters with an increase in the number of assembled layers. Separately, Shao-Horn and co-workers reported the fabrication of composite thin films composed of AuNPs and multiwalled carbon nanotubes using electrostatic LBL assembly [22]. These researchers fabricated thin films by the assembly of positively charged 2-aminoethanethiol-stabilized AuNPs together with negatively charged carboxylic acid functionalized-multiwalled carbon nanotubes on an organosilane-modified ITO electrode.

In this manuscript, we describe a process for the fabrication of polymeric thin films containing AuNSs. These composite materials are being developed for use in solar-thermal collectors [27], a project which complements separate efforts that target the use of AuNSs for plasmon-enhanced dye-sensitized solar cells [28]. In the present study, in order to optimize light exposure for these surface-bound metal particles, AuNSs dispersed within polyethyleneimine (PEI) films were prepared via electrostatic layer-by-layer assembly using simple dip-coating techniques. Specifically, a thin film of water-soluble PEI was adsorbed onto a glass microscope slide, and then negatively charged AuNSs were absorbed electrostatically from aqueous solution onto the positively charged surface. The process could be repeatedly cycled to increase the thickness of the film in a controlled manner. The use of PEI was particularly effective for particle dispersion because the polymer readily absorbed on the substrate and allowed only limited aggregation of the nanoshells.

2. Experimental section

2.1. Synthesis of silica nanoparticles and functionalization of the surface

Ammonia (3.0 mL, 30% NH_3 as NH_4OH assay) was added to ethanol (50 mL). The mixture was stirred vigorously, and 1.5 mL of tetraethyl orthosilicate (TEOS) was added dropwise. Over the course of 30 min, the solution changed from clear to opaque white. An excess of (3-aminopropyl)trimethoxysilane (APTMS, ~0.5 mL) was then added to the vigorously stirred silica nanoparticle solution. The mixture was stirred for 2 h, and then gently refluxed for an additional 1 h to enhance covalent bonding of the APTMS groups to the silica nanoparticle surface. The APTMS-coated silica nanoparticles were isolated by centrifuging the mixture and then redispersing in ethanol.
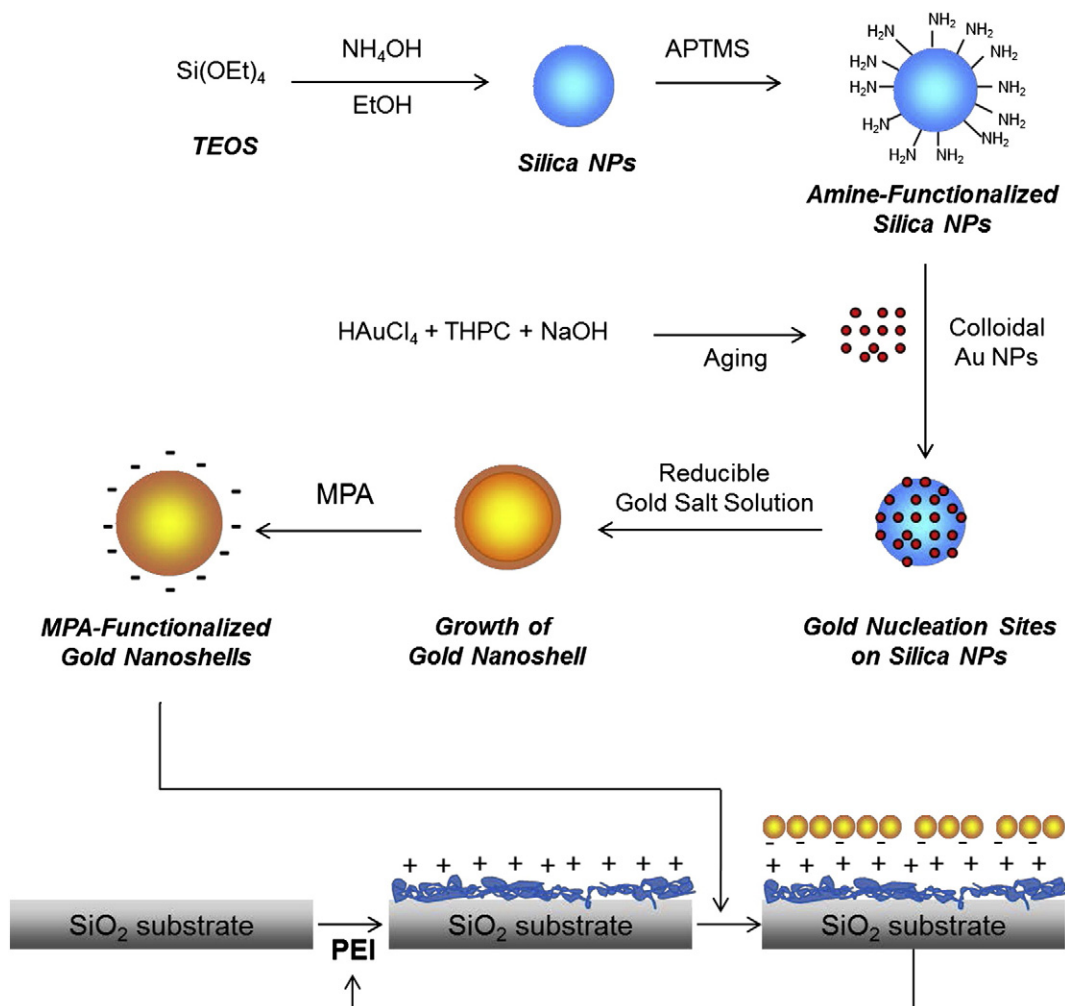
Scheme 1. Preparation of gold nanoshells; acronyms are defined in the Experimental section.