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An anisotropic propagation technique for synthesizing hyperbranched polyvillic gold nanoparticles

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ABSTRACT

Of late, many synthesis processes have been studied to develop irregular nano-morphologies of gold nanostructures for biomedical applications in order to increase the efficacy of nanoparticle theranostics, tune the plasmonic absorbance spectra, and increase the sensitivity of biomolecule detection through surface enhanced Raman spectroscopy. Here we report, a novel, non-seed mediated versatile single pot synthesis method capable of producing hyperbranched gold "nano-polyvilli" with more than 50–90 branching nanowires propagating from a single origin within each structure. The technique was capable of achieving precise tuning of the branch propagation where the branching could be controlled by varying the duration of incubation, temperature, and hydrogen ion concentration.

1 Introduction

Gold nanomaterials have been extensively studied for biomedical applications owing to their unique physical and chemical properties as well as the ease of manipulation, modification, and biocompatibility [1–10]. These nanomaterials possess unique optical properties because of surface plasmon oscillations of free electrons. Such optical properties have been utilized for various biomedical applications including photothermal ablative therapies [7, 11], near infra-red (NIR) imaging [9, 12], as well as gene and therapeutic delivery [3, 13]. The absorbance maxima of gold nanoparticles depends on their size and shape because of the surface plasmon resonance (SPR) effect [9, 14, 15]. Spherical nano-gold shows a shift in the absorbance maxima towards the infra-red (IR) region of electro-magnetic radiations with an increase in the particle

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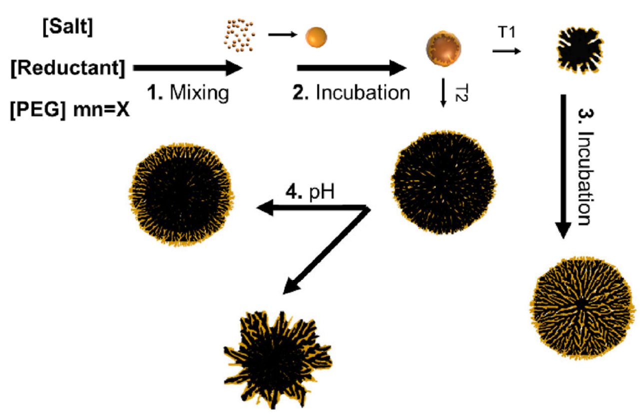
size [16–18], thus making the near-infrared region (NIR) an interesting window for tissue imaging due to the low tissue absorbance in that range. Hence, the application of gold nanomaterials offers promising platforms for achieving this goal. The manipulation of the spectra is possible through size tuning; however, as particles approach larger sizes, they no longer exhibit plasmonic effects and lose the advantages of the "nano" dimension. Therefore, by manipulating the aspect ratio and circularity index of nano-gold, the effective size of the nanoparticle system is maintained while inducing a shift of the absorbance maxima towards the NIR. Of late, various irregular morphologies of Au nanoparticles have been reported, e.g., stars [9, 19], cages [10, 11], cones [20], rods [12], and prisms [21]. All these morphologies result in the wavelength tuning of the signature SPR peak. These irregular shapes, in addition to the SPR absorbance shift, have larger surface area to volume ratio as compared to that of the conventional spherical nanoparticles, and can thus bind more drug molecules [22–26], act as sensitive contrast agents [27–29], present greater amount of targeting ligands [30–33], and have a greater extent of cellular interactions [34–37]. Branched and dendritic morphologies are enticing because of their broad surface area, which is comparable to that of snowflakes, neurons, and villi and microvilli of the intestine. Branching in gold nanostructures also results in a spectral shift towards the IR range as well as the signal enhancement for Raman spectroscopy because of the SPR effect. These branches, which act as "nano-antennae", are responsible for the signal enhancement of the optical energy into the sub-diffraction volumes [9]. As the absorbance maxima for nano-gold increases towards the IR range, the applicable penetrative depths for the NIR imaging and photothermal ablative therapies improve further. Therefore, a controlled synthesis of stable hyperbranched dendritic nanostructures would result in a highly efficacious drug and contrast agent delivery vehicle in addition to providing a superior sensing surface through plasmonics and surface enhanced Raman spectroscopy (SERS). Thus far, the most successful attempts for high branching nanodendrons have been through lithography [14], which seems to be not very practical for large scale developments [38–40]. Seed mediated synthesis of gold nanostars having up to eight branches [9, 41–43] has been reported; however, the technique is limited by the size of the seeding particles and low number of branching arms. The other known approaches include the synthesis through interfacial reactions [44], which are limited due to the constrained directional growth at the interfacial plane. A clear unmet synthetic need is a technique with supreme control over the sprouting growth addressing all the issues mentioned above. This work develops a novel, non-seed mediated single pot synthesis method for producing hyperbranched gold "nano-polyvilli" (NPV) with precise tuning of branch propagation by controlling the incubation duration, temperature, and hydrogen ion concentration (Scheme 1).

2 Results and discussion

2.1 Three-dimensional (3D) anisotropic growth crystallization

In diffusion limited non-equilibrium systems, the spontaneous emergence of branched, dendritic, and complex structures evolves, as is seen in corrosion [45], bacterial growth [46, 47], and the solidification of crystals [48–50]. The simplest alternative to these



Scheme 1 Branching growth propagation control scheme. Artistic renditions of branch tuning pathway. Within this synthetic pathway branched growth can be controlled through the mixing of the reaction constituents (1), primary incubation conditions (2) where the growth is initiated, an optional secondary incubation (3) where higher ordered branching can be achieved, and finally pH manipulation (4). These artistic renditions were created using a model for snowflake growth (in the Electronic Supplementary Material (ESM)).