



In situ formation of silver nanoparticle layer by supramolecule-directed assembly

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ABSTRACT

We report an in situ synthesis route for preparation of a layer of AgNPs (silver nanoparticles) on the silicon surface by employing an immobilized supramolecular layer as a directing agent. The AgNPs were immobilized and stabilized by a calix[7]hydroquinone monolayer which in turn was immobilized on the silicon surface by covalent layer-by-layer assembly. The calix[7]hydroquinone moiety served as a nano-reactor, container and template in the in situ synthesis process. AgNPs were formed by reduction of Ag ions by the hydroquinone form of the calix[7]arene. The AgNPs were obtained as plate-shaped particles with a diameter of about 10 nm and a height of less than 2 nm, and were stabilized and wrapped by calix[7]arene molecules. By repeated application of the redox properties of calix[7]arene, the size of the AgNPs can be adjusted continuously up to islands of 100 nm or larger. The process of in situ synthesis under controlled conditions, together with calibrated variation of particle size has the potential to serve as building blocks for electronic nano-devices. A significant advantage derived by this method of formation and assembly is its surfactant-free nature that enables access to the active surface of the nanoparticle.

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1. Introduction

Supramolecular structures can be found extensively in nature and living cells [1], and they play significant roles in physical and natural systems. Taking a cue from nature, supramolecular assembly is also an important bottom-up method to fabricate nanostructures with high resolution. The concept of nano-devices is widely explored by this method, such as molecular switches [2] and nano-machines [3]. However, these pseudo nano-devices are far from real devices with applicable functions due to their rudimentary structure and difficulty in operation. They are usually synthesized in solutions, so that separation of product is needed after each reaction which is often tedious. Furthermore the resulting systems are dispersed in solution and are difficult to be assembled with other systems. To address this issue, one simple method is to incorporate supramolecules into multilayer structures through LbL (layer-by-layer) assembly [4]. Through the combination of LbL and supramolecular techniques, molecules can be immobilized on solid surfaces so that the devices can be structured in conjunction with synthesis, and also, the separation of the product in each step becomes facile.

In particular, the supramolecules can be aligned on the surface in a prescribed manner, facilitating further assembly. By this method, nano-sensors [5], supramolecular n/p-heterojunctions [6] and microcapsules for drug delivery [7] have been investigated.

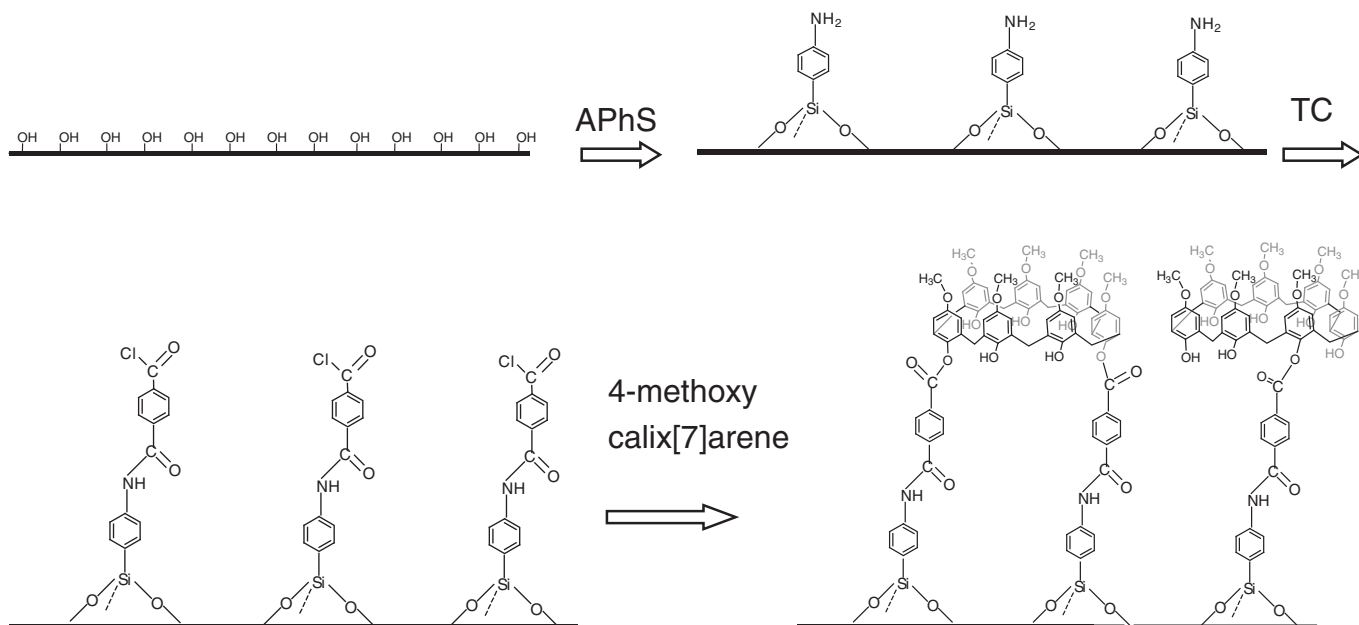
The calix[n]arene–metal complex [8] is an important supramolecular system in which ‘n’ represents the number of phenol units in one calixarene molecule. Their properties, such as cation recognition [8], ion transport and redox properties [9], can be finely tuned by modifying the upper and lower rims of calix[n]arene or changing the number of the phenol units. Calix[n]arene has shown potential applications when incorporated into multilayer films by LbL assembly, such as rare metal enrichment [10], ion selective sensor [11–13], colorimetric chemosensor [14], ion channel [15] and selective ion transportation [10]. In situ synthesis of nanoparticles [16–18] is another interesting application of LbL assembly, because formation of nanoparticles on the surface is an important aspect of nano-fabrication. Furthermore, combined with LbL assembly, in situ synthesis techniques can facilitate formation of nanoparticles on the surface of devices with different shapes, which may not be achievable by conventional methods of synthesis. In particular, calix[n]arene with reducing properties is a good candidate for in situ synthesis of metal nanoparticles as well as nanowires [19], since they can capture metal ions from dilute solutions through the formation of multiple cation– π interactions [8]. By this method, Gao et al. [20] incorporated aminocalix[4]arene into multilayer layer films by electrostatic LbL assembly and synthesized AgNPs (nanoparticles) in situ with a diameter of about 6 nm. However, stable multilayer structures are desired for fabrication of nanodevice building

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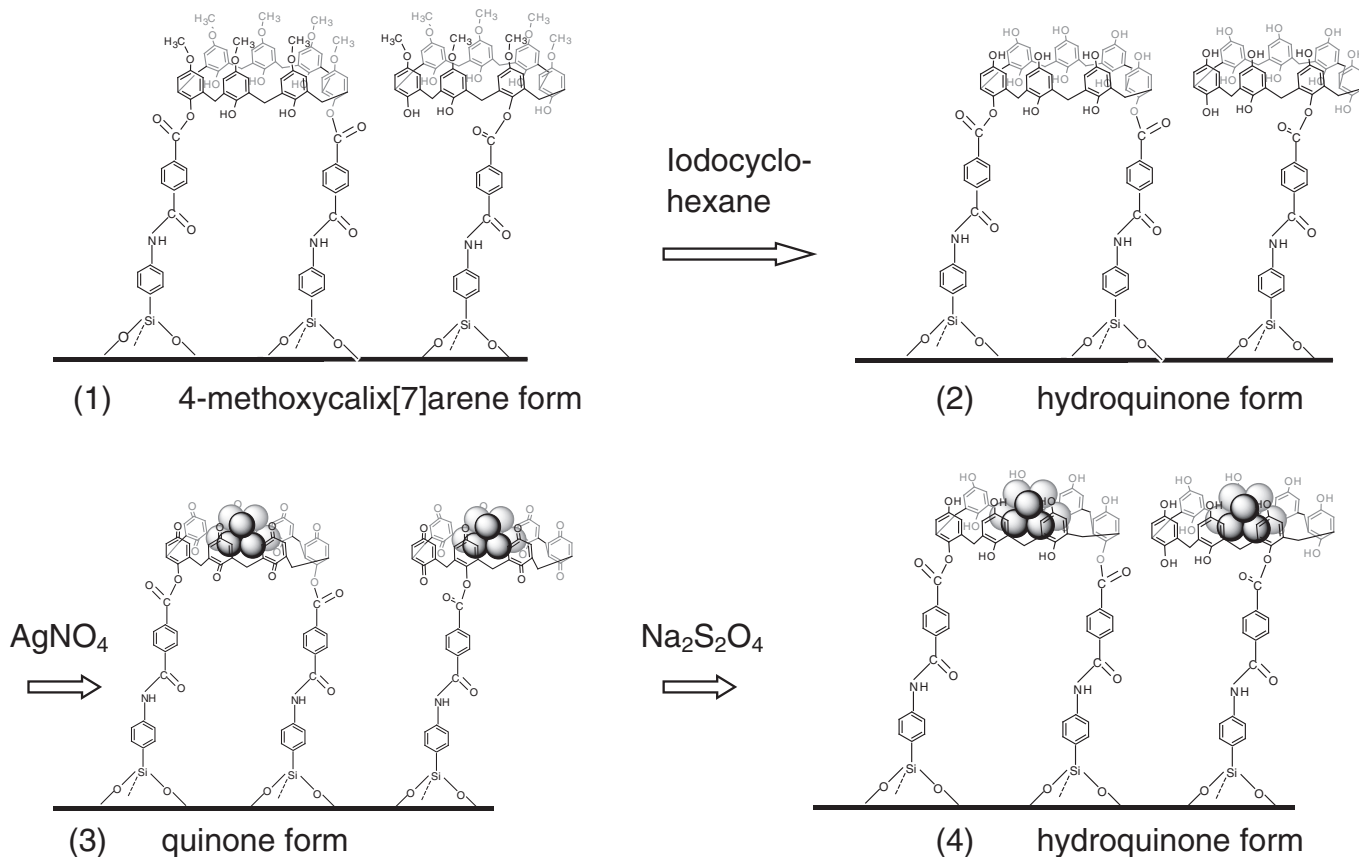
Scheme 1. Immobilization of 4-methoxycalix[7]arene on SiOH surface.

blocks, and most of the electrostatic multilayer structures are not stable in polar solvents [21,22] and salt solutions [23], and therefore have limited application for further assembly manipulation.

Covalent LbL assembly is a simple method to fabricate stable multilayer structures which could endure many harsh conditions including high temperature, polar solvents and ultrasonic environments [24]. Combination of covalent LbL and supramolecular assembly techniques

may provide a solid and versatile method to fabricate nano-structures that could endure many assembly steps. However, little work has been done to explore the feasibility and efficiency of such a combination of techniques.

By covalently immobilizing calixarene on a surface and using it as a template to synthesize and shape NPs, the robustness and stability afforded by the immobilized, reactive matrix can be exploited to



Scheme 2. In-situ synthesis of silver nanoparticles.

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