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Nanoparticle layer deposition for highly controlled multilayer formation based on high-coverage monolayers of nanoparticles

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ABSTRACT

This paper establishes a strategy for chemical deposition of functionalized nanoparticles onto solid substrates in a layer-by-layer process based on self-limiting surface chemical reactions leading to *complete* monolayer formation within the multilayer system without any additional intermediate layers — nanoparticle layer deposition (NPLD). This approach is fundamentally different from previously established traditional layer-by-layer deposition techniques and is conceptually more similar to well-known atomic and molecular layer deposition processes. The NPLD approach uses efficient chemical functionalization of the solid substrate material and complementary functionalization of nanoparticles to produce a nearly 100% coverage of these nanoparticles with the use of "click chemistry". Following this initial deposition, a second complete monolayer of nanoparticles is deposited using a copper-catalyzed "click reaction" with the azide-terminated silica nanoparticles of a different size. This layer-by-layer growth is demonstrated to produce stable covalently-bound multilayers of nearly perfect structure over macroscopic solid substrates. The formation of stable covalent bonds is confirmed spectroscopically and the stability of the multilayers produced is tested by sonication in a variety of common solvents. The 1-, 2- and 3-layer structures are interrogated by electron microscopy and atomic force microscopy and the thickness of the multilayers formed is fully consistent with that expected for highly efficient monolayer formation with each cycle of growth. This approach can be extended to include a variety of materials deposited in a predesigned sequence on different substrates with a highly conformal filling.

1. Introduction

Layered structures have been a target of intense research for many decades. For example, the ability to produce exceptional conformal filling over the high aspect ratio features needed in microelectronics has been based on the formation of targeted strong chemical bonds in the course of atomic layer deposition (ALD) (see reviews [1,2] and multiple references therein) and the need for high-level control at the slightly larger scale for applications such as photoresist formation or metalorganic layer growth has been realized in molecular layer deposition (MLD) [3–6] processes. Both approaches utilize surface-limited reactions to form a layer of one atom to several atoms thick that are perfectly suitable for a wide variety of applications. The main advantage of both methods is in atomic- and molecular-level precision for the multilayers created. One of the main disadvantages is that the growth rate and the size of the building elements are very limited.

At the same time, layered materials with structural fragments of nanometers to tens of nanometers in size are needed for applications such as spintronics, specifically tunnel magnetoresistance [7], heterogeneous catalysis [8], magnetic materials [9], solar energy conversion with photoelectrochemical cells [10,11] and many more. The formation of such films and materials using lithography or ALD and MLD methods is a very complex and expensive task.

Here we report the formation of multilayer systems based on *nearly complete monolayers* of nanoparticles covalently bound to a solid support in a self-limited surface process that utilizes "click chemistry" based on a reaction between azide and alkyne functionalities to form a triazole ring according to a general scheme shown in Fig. 1. It is appropriate to term this approach as nanoparticle layer deposition (NPLD), in analogy to ALD and MLD.

Conceptually, similar approaches have been envisioned for a number of systems [12,13], including covalent [14] or guest-host interactions [15]; however, achievement of a nanoparticle multilayer system in which each single layer is comprised of a *complete* monolayer has so far remained elusive.

On the other hand, high coverage can sometimes indeed be achieved by more traditional and well established approaches to layer-by-layer growth [16]. It should be emphasized that the process described here is fundamentally different from what is commonly referred to as layer-by-layer (LBL), where polymer layers [17,18], polyelectrolytes [19], nanoparticle-incorporated materials [20–22], and supramolecular thin films [23] are deposited based on a continuous polymer film

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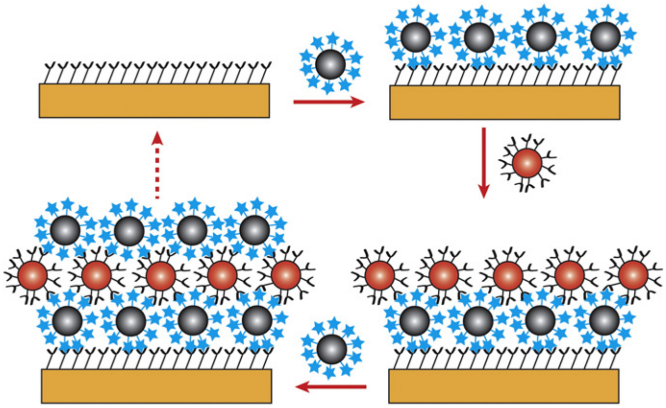

Fig. 1. Basic scheme of nanoparticle layer deposition. After modifying the surface with azide functionality, a layer of complementary alkyne functionalized nanoparticles is deposited on the surface. This surface is now the basis for the second layer of nanoparticle deposition. Each layer can be used as a starting point for the complementary functionalized layer.

formed by a variety of deposition methods. Although useful in various applications, these approaches often involve polymers or fibers as alternate layers, which not only determine the properties of a resulting composite multilayer but also suggest that conformal filling with such processes is very difficult.

The proposed NPLD strategy takes advantage of the traditional LBL techniques but employs the approach that is rooted more in ALD and MLD. An excellent review of the recent achievements in all of these methods [16] compares recent developments in LBL techniques to advances in ALD or MLD.

The general approach described here can be utilized to form continuous layers consisting of nanoparticles of nanometers to microns in size, made of a variety of materials, and constructed in a variety of shapes. Most importantly, compared to other currently used techniques for construction of relatively thick layers, the proposed process should lead to conformal filling of intricate features, as well as flat surfaces.

In order to demonstrate the feasibility of such an approach, the complete monolayer-by-complete monolayer formation was performed using silica particles of different sizes with very narrow size distribution, so that the completion and quality of the layers could be monitored straightforwardly with microscopic analytical techniques. The chemistry was followed where appropriate with infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) to confirm *covalent* bonding.

The *interlayer* bonding described here is based on the application of a copper-catalyzed “click reaction” between azide and alkyne functional groups to form the triazole ring in a cycloaddition process. Although a number of coupling processes are available for similar strategies, this high-yield “click reaction” is extremely selective [24,25]. Furthermore, the triazole ring formed is highly stable against subsequent interactions [24]. Thus, this reaction has been applied in a variety of different fields, for example in drug delivery [24,26,27], polymer, and material science [28–31], making it universally acceptable for a wide range of applications. In fact, in an approach similar to MLD, Such et al. have employed this “click reaction” to create a layered film of covalently-bound polymers [25].

From a perspective of designing 3-dimensional materials with predesigned properties in a controlled fashion, continued efforts have been reported for the synthesis and characterization of cluster-assembled materials which can be tailored to exhibit collective properties unlike those of their individual components [32,33]. Functionalized nanoparticles can be assembled together to form composite materials including the assemblies of inorganic nonmagnetic nanoparticles [13,31,34,35] and magnetic nanoparticles that were recently explored [36–39]. For monolayer formation, Toulemon et al. reported that magnetic iron oxide nanoparticles could be assembled on solid substrates through “click chemistry” to form a *single* layer [39] and Kinge et al. have demonstrated the use of this “click reaction” to attach a layer of magnetic nanoparticles to a surface in pre-determined patterns through microcontact printing [37]. Upadhyay et al. have used this reaction to build layers of functionalized metallic nanoparticles starting with an alkyne-terminated solid substrate and demonstrated the possibility of multilayer formation and general applicability of this approach to a set of substrates and nanoparticles [13]. This last publication targeted the use of multilayer systems for electrocatalytic applications and proposed a well-conceived roadmap for building such multilayers. The synthesized structures performed well in the processes; however, only limited coverages were achieved most of the time both for monolayers and for multilayers, with parts of the surface covered with nearly close-packed monolayers and at the same time some empty or low-coverage areas. In addition, controlling the completion of a monolayer without depositing additional layers seems to be difficult. To overcome these issues, a modified surface preparation procedure based on a sonication-assisted reaction rather than self-assembly followed by chemical modification, is offered in this work. Carefully selected chemical pathways for modification of the nanoparticle surfaces, the use of nanoparticles of different sizes to confirm the formation of complete monolayers within the multilayer system and to rule out simultaneous deposition of multiple layers in a single step, and spectroscopic confirmation of the covalent bonding of the nanoparticles are presented.

It should be pointed out that the properties of multilayered materials and individual layers can be altered by ALD-like reactions between preassembled nanoparticles and small chemical compounds during the deposition process [40]. This observation and previous experience in surface modification of solid substrates with buckyballs [41], biomolecules [42,43], and nanoparticles [42] can be expanded for surface functionalization of silica nanoparticles and their deposition on a gold-coated substrate in a layer-by-layer manner. Again, it should be emphasized that this is not a process of self-assembly but rather a chemically-driven self-limiting process. Thus, the formation of the first stable layer with high coverage is the first task. Then, this very high-coverage layer is used as a platform for nanoparticle layer deposition of silica nanoparticles of different sizes in a second *complete* monolayer to form a continuous stable layered film. Thus, the proposed NPLD process relies on a chemical property of a single nanoparticle as a building block for producing multilayered structures based on completion of each monolayer within them.

2. Experimental details

2.1. Sample preparation

Prefabricated gold substrates (1000 Å gold thickness on silicon wafer support with titanium adhesion layer, Sigma Aldrich) were cleaned by immersing the substrate into piranha solution (1:3 (by volume) hydrogen peroxide (30%, Fisher Scientific):concentrated sulfuric acid (98%, Fisher Scientific)) for 5 min followed by immersion in ultrapure water (18 MΩ cm, Quantum EX, EMD Millipore) for 5 min. The substrate was then washed with HCl (37%, Fisher Scientific), water, ethanol (200 proof, Decon Laboratories, Inc.) and then dried under a flow of nitrogen gas. The clean Au substrate was immersed in a 1 mM solution of 11-azido-undecanethiol (96%, Krackeler Scientific, Inc. or synthesized following a previously established procedure [44]) in ethanol for 24–36 h in the dark to produce the azide-terminated monolayer on Au substrate. The surface was then washed with ethanol, methylene chloride (99.9%, Fisher Scientific), and water, and dried under a flow of nitrogen gas. A titration experiment to react surface azide was performed by immersing the gold substrate into 4:1 methanol:water (by volume) with ~15 mM 5-hexynoic acid (97%, Sigma-Aldrich) in methanol (99.9%, Fisher Scientific). Catalytic amounts of copper sulfate pentahydrate (>99%, Fisher Scientific) and sodium ascorbate (>99%, Fisher Scientific) were added to the solution and the mixture was sonicated for 24 h,